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Improving Indoor Air Quality (IAQ) Through Novel Wood-based Panel Modifications

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Improving Indoor Air Quality (IAQ) Through Novel Wood-based Panel Modifications

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Improving indoor air quality (IAQ) through novel wood-based panel modifications and the impacts on basidiomycete decay and mould colonisation

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Summary

Indoor air quality and the effects of airborne contamination on human health, have been of growing concern in recent years (Mitchell et al., 2007; Salthammer et al., 2003; Takeda et al., 2009). Following long exposure to pollution, individuals suffer from eye and respiratory discomfort, headaches and a feeling of lethargy linked to poor indoor air quality (Haghighat and De Bellis, 1998). Previously research has focused on primary particles, outdoor pollution penetrating inside buildings (WHO, 2010) and chemicals (Mitchell et al., 2007). More recently, research has begun to involve the relationship between a building's environment, its occupants' activities, the different sources of pollutants and means of mitigation.

This study was conducted to investigate the potential of improving IAQ by modifying Medium Density Fibre board (MDF) to become a multi-functional product that will actively absorb indoor air pollutants. The first aim was to determine if changing the refiner pressure of woodchip during MDF panel production would affect the atmospheric formaldehyde absorption capabilities of the MDF panel. The second was to determine if adding a scavenger of pollutants (physical modification) to the MDF panel structure would actively absorb formaldehyde and volatile organic compounds (VOC) from the atmosphere. Following on from this, modified MDF panels were produced on a pilot scale. These modified MDF panels underwent a series of rigorous tests to determine if the scavengers remain active to absorb formaldehyde and VOCs from the atmosphere, post production and the impacts on panel properties. The results revealed firstly that the modified MDF panels could absorb formaldehyde and secondly that the scavengers added to the panel, remained active and could absorb both formaldehyde and other tested VOC's. However, there were some implications to panel properties, namely mechanical.

An additional part of this thesis was the study of how the modifications affect the panels' susceptibility to fungal attack by both mould fungi and basidiomycete decay. The modified MDF panels were also exposed to VOCs to determine any relationship between the absorption of VOCs and on mould colonisation. The modifications were found to alter the dynamics of microbial growth and cultivation, as well as alter susceptibility differently with each of the modifications.

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List of Abbreviations

AC	Ash content
A	Area
AC	Activated carbon
ACF	Activated carbon fibres
ANOVA	Analysis of Variance
a_w	Water activity
B.E.T	Brunauer, Emmett and Teller theory
BD	Bulk density
BS-EN	British Standard - European commission standard
CF	CNSL and formaldehyde
CFU	Colony forming unit
CNSL	Cashew nut shell liquid
CTMP	Chemo-thermo-mechanical pulping
CT	Condensed tannins
DOAS	Differential optical absorption spectroscopy
DSC	Differential scanning calorimetry
DSI	Decay susceptibility Index
DVS	Dynamic vapour sorption
EMC	Equilibrium moisture content
EWP	Engineered wood panels
F	Formaldehyde
F/U	Formaldehyde urea ratio
F_i	Moisture content factor
FLEC	Field and Laboratory Emission Cell
FTIR	Fourier transform infrared absorption
$\dot{g}$	Water vapour flow rate
GC-FID	Gas chromatography flame ionisation
GC-MS	Gas chromatography - mess spectrum
GHG	Greenhouse gas
H	Hydrogen
HDI	Hexamethylene di-isocyanate resin
h_m	Convection mass transfer coefficient
HMw	Heavy molecular weight VOC
IAQ	Indoor air quality
IB	Internal bond strength
L	Limonene
L	Length
LIFS	Laser-induced fluorescence spectroscopy
MC	Moisture content
MCS	Multiple chemical sensitivity
MDF	Medium density fibre
MDF.H	MDF in humid conditions

MDFMR	Moisture resistant MDF F/U
MDI	Methylene Diphenyl di-isocyanate resin
MF	Melamine formaldehyde resin
MOE	Modulus of elasticity
MOR	Modulus of rupture
MSD	Modular screw device
M_t	Mass
MUF	Melamine Urea- formaldehyde resin
MVOC	Microbial volatile organic compounds
OCIA	Organic compound in indoor air'
OSB	Orientated strand board
PAN	Polyacrylonitrile
PF	Phenol formaldehyde
pMDI	Polymeric/phenol isocyanate resin
PLS	Partial Least Square regression
PVAc	Polyvinylacetate
RH	Relative humidity
SBS	Sick building syndrome
SPME	Solid phase micro-extraction
SVOC	Semi volatile organic compounds
T	Toluene
T	Thickness
TDI	Toluene di-isocyanate resin
TF	Tannin formaldehyde resin
TMP	Thermo-mechanical pulping
TS	Thickness swell
TVOC	Total volatile organic compounds
UF	Urea - formaldehyde resin
VAHs	Volatile aromatic hydrocarbons
VAS	Volatile aldehydes
VIP	Variance of importance
VOC	Volatile organic compound
VVOC	Very volatile organic compounds
$\underline{W}$	Water vapour permeance
W	Water
W	Width
W_{ac}	Water absorption coefficient
WHO	World health organisation
Z	Water vapour resistance
δ	Water vapour permeability factor

0 Introduction

The hazards associated with poor outdoor air quality are well documented around the world, contributing to 800,000 deaths a year (WHO, 2008). It is largely understood that the sources of pollution are attributed to many different processes, both anthropogenic and natural. Recognised sources include volcanic activity, burning of coal generating sulphur dioxide, which in turn causes air acidification and acid rain, particulate matter and nitrogen dioxide released from transport; pollution from industry and agricultural processes. Research with modern technologies also enabled the recognition of secondary sources of pollution, due to chemical, meteorological and photochemical reactions between pollutants in the atmosphere (Patkó et al., 2013; Weschler, 2004). Today, air pollution is a global problem that is tackled at a national and international scale.

But what of our indoor air quality? Indoor air is defined as non-industrial air such as that in dwellings, offices, schools and hospitals (Brown et al., 1994). Indoor air pollution is not a new phenomenon, it has been known for hundreds of years that burning of fuels and wood releases combustion by-products. However, over time, the spectrum of indoor contaminants has increased and changed with modernisation (Spengler and Sexton, 1983). In recent years, the somewhat overlooked problem of poor indoor air quality (IAQ) and the sources of pollution has caught the attention of the media, although this media coverage can be exaggerated and alarmist. One example is a published article from the American newspaper *Media Equalizer* titled 'Forget Ebola, your Sofa will kill you instead'. This is clearly an over-exaggeration but there is evidence that the build-up of pollutants to harmful levels indoors can be hazardous to human health.

The work described in this thesis includes a comprehensive literature review that includes the cause, sources and types of indoor air pollutants, influencing conditions, the effects on human health and methods of mitigation that are currently under investigation and in use. From evidence gathered in the literature review, two modifications will be selected that are suitable for multi-functionalising medium density fibreboard (MDF). The following section describes the three main aims and objectives of this thesis.

0.1 Intention of study

The overall arching aim of this study is to develop a modification that can be applied to an existing construction material generating a multi-functional material that actively absorbs indoor air pollutants, to improve indoor air quality. The chosen construction material is the popular medium density fibreboard (MDF) for which current production is 11.3 million m^3 in Europe (EPF, 2014). Its popularity is due to its relative cheapness and its uniformity that makes it easy to work with. Hence MDF is found throughout domestic and commercial buildings in both construction and furnishings. The three main objectives of this study and the proposed methods of modification are described below. Appendix A depicts the overall plan of this study and the experiments conducted.

0.1.1 Identifying modifications

Using evidence collected from the literature review, a mechanical modification will be investigated that can be applied to MDF panel production to improve indoor air quality. This involves experimentation of two separate modifications; physical and mechanical. The first aim is to determine if changing the refiner pressure of woodchip during MDF panel production will affect the atmospheric formaldehyde absorption capabilities of the MDF panel. The second aim is to determine if a physical modification of adding a scavenger of pollutants to the MDF panel structure will be able to actively absorb formaldehyde and volatile organic compounds (VOC) from the atmosphere.

0.1.2 Modifying Medium Density Fibreboard

Following on from the development of appropriate mechanical modification (refiner pressure) to the fibre and identification of useable formaldehyde and VOC scavengers, MDF panels will be produced on a pilot scale at the Biocomposites Centres' Bio-Refining Technology Transfer Centre (Mona, Anglesey, UK). These modified MDF panels will then undergo a series of methodical testing to determine if the scavengers remain active post production and are still able to actively absorb formaldehyde and VOCs from the atmosphere. As MDF is a contributor to the build-up of indoor air pollutants, the MDF emissions will also be analysed to determine if

the chosen modifications reduce or increase formaldehyde and VOC emissions from the MDF panel.

The primary purpose of an MDF panel is its use in construction and it is important that the modifications do not significantly impair the properties of the MDF panel. Therefore, the mechanical and hygric properties of the modified MDF panel will be investigated to determine if and how the modifications affect these properties.

0.1.3 Implications on microbiological activity

There are also requirements of wood-based materials such as MDF to have low levels of susceptibility to basidiomycete decay and mould growth and colonisation. Therefore an additional part of this thesis is the study of how the modifications affect the panels' susceptibility to basidiomycete decay, and mould colonisation and growth.

Indoor fungal growth is ubiquitous around the world and contamination of the indoor environment can cause serious structural and aesthetic damage but it can also be a significant contributor to poor indoor air quality. As part of this section of the study, the modifications to the MDF panel was evaluated for its implications on susceptibility to mould growth and colonisation. The modified MDF panels were also exposed to VOCs to determine any relationship between the absorption of VOCs and effects on mould colonisation.

1 Literature Review

1.1 Indoor air pollution

In an attempt to combat climate change, the UK government ambitiously aims to reduce its greenhouse gas (GHG) emissions by 80% by 2050. New legislation such as the Climate Change Act 2008, Energy Bill 2012 and the Building Regulations and associated technical guidance (Shrubsole et al., 2014) have been implemented, targeting GHG emission reductions in the building sector. Such new legislation, policies and incentives have generated a greater push for retrofitting old and new dwellings and public buildings to increase air tightness and energy efficiency (Knudsen, et al., 2002; Shrubsole et al., 2014; Spengler and Sexton, 1983; Weschler, 2004; Yu and Kim, 2010). It has been noted that total pollutant concentrations are heightened as a consequence of increased building tightness, resulting from reducing air exchange (Allen et al., 2016; Takagaki et al., 2000). According to the US environmental Protection Agency (EPA) indoor air can be 2-5 times more polluted than outdoor air (Allen et al., 2016; Wolkoff et al., 1997; Yrieix et al., 2010). It has been shown that the mean concentration of individual compounds in established buildings is generally below 50 μgm^{-3}, while total compound concentrations are substantially higher e.g. 1100 μgm^{-3} (Brown et al., 1994). It is this build-up of total chemical compound emissions that is now recognised as a potential hazard to human health (Yu and Kim, 2010), even if they are considered relatively chemically inert (Wolkoff et al., 1997). The scientific understanding of indoor air quality has increased in the past few decades. In previous studies, much of the work has been focused on primary particles, outdoor pollution penetrating inside buildings (WHO, 2010) and chemicals (Mitchell et al., 2007). More recently, research has begun to involve the relationship between a building's environment, its occupants' activities and the different sources of pollutants. Indoor air pollution takes many forms and is ubiquitous, although the types of pollution vary around the world. In developing countries, smoke from the combustion of solid fuels such as coal (Zhang and Smith, 2003), gases and particulate matter are the most common pollutants of indoor air and might be responsible for 1.6 million deaths a year (WHO, 2010).

In more modern countries and buildings, pollution is a complex mix of volatile organic compounds (VOCs). According to the EC Directive 1999, VOCs are compounds having, at 293.15 K (20^{o}C), a vapour pressure of 0.01 kPa or more, or having a corresponding volatility under particular conditions of use. The World Health Organisation (WHO) defines a VOC as any compound with a boiling point between 50-100°C and 240-260°C, corresponding to having saturation vapour pressures at 25^{o}C greater than 100 kPa. These VOCs include; alkanes, alcohols, branched cyclo-alkanes, halogenated compounds, ketones, aldehydes, esters, aromatic hydrocarbons and terpenes (Brown et al., 1994). Most compounds can be subdivided into volatile aromatic hydrocarbons (VAHs), volatile aldehydes (VAS) and semi-volatile compounds (SVOCs) (Yu and Kim, 2010). Often these VOCs are grouped for simplicity as total VOCs (TVOC) and the total quantity and composition of emissions vary with the type of building and its primary use. This information has helped to increase the level of concern regarding indoor pollution as most people spend between 70-80% of their time indoors (Brown et al., 1994; Yrieix et al., 2010) and the proportion of emissions that are inhaled, is greater when emissions occur indoors than outdoors (Nazaroff and Weschler, 2004).

Brown et al., 1994, pooled data from literature from a number of different countries and found that dwellings have higher TVOC concentrations than in established public buildings.

There are government initiatives in place to target this build-up of indoor pollution. In European countries such as Germany, Finland and France, there are environmental schemes in place to provide criteria for control of building environment quality and include certification limits for emissions from building materials (Yu and Kim, 2010). The UK government developed Building Regulations (England and Wales 2006 edition) which incorporated performance criteria for dwellings and other buildings to provide adequate ventilation and prevent the build-up of moisture, humidity and indoor pollutants to levels that could be harmful to human health (Yu and Kim, 2010).

There are a great number of sources of both VOCs and formaldehyde. VOCs occurring naturally in the environment are known as biogenic emissions. Vegetation,

for example, is known to release alcohols, aldehydes and ketones (Roffael, 2006). Natural materials also emit differing quantities of formaldehyde e.g. meat (2–20 $mgkg^{-1}$), fruit and vegetables (6.3-35 $mgkg^{-1}$) (Trézl et al., 1997) wood (0.04 $mgkg^{-1}$) (Mayer and Boehme, 1997) and even volcanoes are known to produce formaldehyde (WHO, 2010). It is also a product of human metabolism and can be detected in human breath at levels ranging from 1.2 to 72 ppb (Moser et al., 2005). Other sources of formaldehyde include: furniture, paints, varnishes, textiles, wallpapers, glues, detergents, disinfectants, shampoos, electronic equipment and cosmetics (WHO, 2010). VOCs have also been reported to be emitted from solvent thinners, furniture, air fresheners, pesticides, cleaning products, degreasers, cleaners, scented candles, cigarettes, lubricants and liquid fuels (Ghoshal and Manjare, 2002; Nazaroff and Weschler, 2004; Niedermayer et al; 2013; Petry et al., 2014). Emissions have also been recorded from construction materials, such as thermal and acoustic insulation materials commonly used to line the interior of ventilation systems and ducts (Haghighat and De Bellis, 1998), gypsum board, medium density fibreboard (MDF), solid wood, orientated strand board (OSB), flooring, carpets, tables, chairs and even cements (Brown et al., 1994; Kim, 2010; Makowski and Ohlmeyer, 2005; Ohlmeyer et al., 2008; Yu and Kim, 2011). It must be noted that only a proportion of VOCs found in products such as cleaning agents are considered a direct hazard to human health (Nazaroff and Weschler, 2004; Schripp et al., 2012). Common types of VOCs include benzene, toluene, cyclohexane, ethylbenzene, m,p-xylene, n-nonane and naphthalene (Reitzig et al., 1998; Wolkoff et al., 1997) and less common types include DMP (dimethyl phthalate), camphene, o-xylene and C_{12}-alkene. Many of these VOCs are malodorous and do not go unnoticed by occupants. Outdoor air pollutants are also often found in the indoor environment and in higher concentrations than outdoors (Brown et al., 1994).

1.1.1 Primary pollutants

Indoor air pollutants can be categorised according to their source, either primary or secondary. Primary sources range from fuel combustion from cooking, heating or smoking to synthetic materials and chemicals from various products and building products (Mitchell et al., 2007; Spengler and Sexton, 1983; Uhde and Salthammer,

2007). Primary emissions result from several mass transport processes (Haghighat and De Bellis, 1998) and their effects on a materials' emissions are complex, but can be considered in two main processes. The first is diffusion within the material, which can be a result of concentration, partial pressures, temperature and density gradients, all of which can vary with the product type, composition and properties (such as porosity, capillary structure and thickness) (Hun et al., 2010; Ohlmeyer et al., 2008; Wolkoff, 1998). Each compound has its own diffusion coefficient dependent upon its molecular weight, molecular volume and temperature and the material's characteristics (Haghighat and De Bellis, 1998). Volatile organic compounds that have low molecular weights will quickly decay and emit rapidly from their source and will escape the confines of a building within weeks or months (Markowicz and Larsson, 2014). Such VOCs are unbound to the materials. Other VOCs are emitted by slow decay processes such as aging and degradation of a material e.g. hydrolysis or sorption processes causing chemical reactions and are typically chemically bound between an absorbent and adsorbate, or can be physically bound by van der Waals or electrostatic forces (Markowicz and Larsson, 2014). These slow decaying VOCs last for longer periods of time inside buildings, as they are less reactive (Markowicz and Larsson, 2014).

The second emission process is via emissions from the materials' surface (Wolkoff et al., 1997). For a given air volume, there are far more surfaces indoors than outdoors, so surface reactions must exert a greater influence on chemical composition of indoor air compared to that outdoors (Weschler, 2004). Reactions occur between a material's surface and the air are influenced by mechanisms such as convection and evaporation (Hun et al., 2010). As long as there is a gradient between the two, surface emissions will occur. The amount of emissions is influenced by surface energies and characteristics, surface velocity, turbulence and properties of the air (Haghighat and De Bellis, 1998). It has been considered that reactions with indoor surfaces contribute to indoor pollution just as much as reactions in the gas phase (Weschler, 2004).

1.1.2 Secondary pollutants

Secondary pollutants are those that occur as a result of chemical reactions between primary pollutants (Patkó et al., 2013; Weschler, 2004), pollutants from outdoors, ozone (O_3) or UV-light (Kim, 2010; Knudsen, et al., 2002; Uhde and Salthammer, 2007; Wolkoff et al., 1997). For example, oxidation of VOCs often results in the formation of formaldehyde (WHO, 2010) and cleaning products that contain VOCs react with unsaturated organic compounds, producing secondary pollutants (Nazaroff and Weschler, 2004). Such chemical reactions are a major factor in the composition and concentration of indoor air pollution (Weschler, 2004). Often, these reactions are a major source of VOCs that are short lived and highly reactive (Weschler, 2004). It is these VOCs that add further complication in predicting future indoor air pollution.

Ozone (O_3) present inside buildings can be emitted from items such as photocopiers and printers, but the main source is the outdoor environment (Schripp et al., 2012). Ozone is a strong oxidising agent (Zhang and Smith, 2003) and can react freely with unsaturated chemical VOCs in indoor air (Knudsen et al., 2002). Ozone is highly reactive with indoor material surfaces (Knudsen, et al., 2002; Schripp et al., 2012) and readily oxidises terpenes naturally occurring in the air (Nazaroff and Weschler, 2004; Roffael, 2006; Schripp et al., 2012; Weschler, 2004) and often results in hydroxyl radical formation (Weschler, 2004). O_3 oxidation of C-C double bonds also results in simple aldehydes, including formaldehyde (Hun et al., 2010; Roffael, 2006; WHO, 2010; Wolkoff et al., 1997). It has been found that reactions between ozone and styrene and between ozone and limonene can produce up to 500 μgm^{-3} of formaldehyde (Conner, 1996). Ozone reactions are thought to dominate indoor chemistry and hence ozone is found in comparatively low concentrations indoors. However, some of the reactions can result in the formation of ultrafine particles (Hodgson et al., 2002) which can have adverse human health affects (Schripp et al., 2012) and form hydroxyl radicals (OH) and nitrate radical (NO_3) (Weschler, 2004). These radicals can then result in further chemical reactions with most organic compounds found in indoor air (Nazaroff and Weschler, 2004; Weschler, 2004). However, there are some discrepancies in some studies, due to the complexity of the topic. It has been shown that ozone will react with some compounds, but it has

also been shown not to react with other VOCs such as limonene (Knudsen et al., 2002).

Hydrolysis reactions provide another example resulting in secondary pollutants. Hydrolysis that occurs on material surfaces results from the surface moisture e.g. damp building materials (Weschler, 2004). This is a problem when it comes to esters, which are susceptible to hydrolysis (Uhde and Salthammer, 2007). Esters are present in the room as they are used in various products such as insecticides and pesticides. Dampness in buildings is suspected of facilitating hydrolysis of esters thus contributing to health problems associated with damp buildings (Weschler, 2004). Hydrolysis also results in aldehyde emissions, namely formaldehyde from different surfaces (Hun et al., 2010).

However, it is often hard to singularly describe a VOC as a primary emission or secondary emission (Uhde and Salthammer, 2007). Formaldehyde for example, is naturally ubiquitous in the atmosphere and can be generated through many chemical reactions.

1.2 Emissions from wood-based construction panels

1.2.1 Emissions from solid wood

Formaldehyde has become a main target for attention as a main indoor pollutant (Takagaki et al., 2000) as it is a suspected carcinogen and mutagen (Hodgson et al., 2002; Hun et al., 2010, 2010; Kim et al., 2006c; Salem and Böhm, 2013; Xu et al., 2010; Yu and Kim, 2011). It is known to occur in greater concentrations indoors than outdoors, especially in buildings with lower ventilation rates (Gullbrekken et al., 2015; Salthammer et al., 2010). According to the World Health Organisation (WHO), in non-industrial buildings, formaldehyde levels should be below 0.1 mgm^{-3} (Yu and Kim, 2011).

Formaldehyde is a ubiquitous pollutant (WHO, 2010; Xu et al., 2010) because it occurs naturally in the environment, even in marine environments, and is present and reversibly bound in all biological material, (Trézl et al., 1997; Salthammer et al., 2010). Solid wood also naturally releases formaldehyde (Salem and Böhm, 2013) with the quantity dependent on a number of factors e.g. wood species, see Table 1. All the 5 mentioned wood species emit a sufficient quantity of formaldehyde to be

detected by smell (0.1 – 0.5 ppm) and cause irritation to eyes, nose and throat 0.5 – 1 ppm (Salem and Böhm, 2013).

Table 1: Formaldehyde emissions (ppm) from solid wood species

Species	HCHO concentration (ppb)	Reference
Oak (*Quercus)*	9	(Meyer and Boehme, 1997; Roffael, 2006)
Spruce (*Picea)*	3	(Meyer and Boehme, 1997)
Douglas fir (*Pseudotsuga*)	4	(Meyer and Boehme, 1997; Salem and Böhm, 2013)
Pine (*Pinus*)	3	(Meyer and Boehme, 1997; Salem and Böhm, 2013)
Beech (*Fagus*)	2	(Meyer and Boehme, 1997; Roffael, 2006; Salem and Böhm, 2013)

Emissions also vary between softwood and hardwood (Roffael, 2006) and age of the wood (formaldehyde emissions increase with age) (Kim, 2010; Weigl et al., 2009). This is a result of the differences in quantities of the three main wood components; cellulose, hemicellulose and lignin, all of which do emit formaldehyde (Salem and Böhm, 2013). Hemicellulose contributes more to formaldehyde release than cellulose while lignin emits the most (Schäfer and Roffael, 2000). It has been shown that even the different sugars that make up hemicelluloses, emit different quantities of formaldehyde (Schäfer and Roffael, 2000).

Wood is also known to emit natural VOCs such as terpenes, isoprene (Costa et al., 2013a) and organic acids (Roffael, 2006) although in very small quantities, 0.3 mgm^{-3} TVOCs (Schripp et al., 2012). These terpenes, found in oleoresin, are essential components for defence against insect and fungi (Costa et al., 2013a). Hardwoods such as oak and beech are found to emit more organic acids than terpenes, whereas softwoods emit more terpenes and aldehydes compounds than organic acids (Costa et al., 2013a; Jiang et al., 2002; Kim, 2010; Roffael, 2006; Schripp et al., 2012). The organic extractives found naturally within softwood, such as organics fatty acids,

waxes, resins, phenolics and acids (Costa et al., 2013a; Salem and Böhm, 2013; Schäfer and Roffael, 2000) also contribute to VOC emissions (Jiang et al., 2002; Salem and Böhm, 2013), whereas inorganic extractives such as magnesium, calcium and potassium, do not (Schäfer and Roffael, 2000). However, although softwoods do emit many natural terpenes such as α-Pinene, β-Pinenes and 3-Carene these are considered non-harmful VOCs (Kim, 2010; Makowski and Ohlmeyer, 2005; Patkó et al., 2013; Roffael, 2006; Wolkoff et al., 2000). Therefore, the types and quantities of these VOCs depend highly upon species and thus should be considered on an individual wood species basis, rather than wood collectively. This release of formaldehyde and volatile organic compounds exists naturally in forest environments, continues throughout wood processing and ultimately in wood-based products (Roffael, 2006; Schäfer and Roffael, 2000).

Newly constructed buildings have higher emissions than in established dwellings, the source of which are from construction materials and building contents (Brown et al., 1994; Hun et al., 2010; Ohlmeyer et al., 2008; Schäfer and Roffael, 2000; Spengler and Sexton, 1983; Stachowiak-Wencek et al., 2011; Yu and Kim, 2011). It has been noted that some VOCs, namely formaldehyde are found in much higher concentrations in new and renovated dwellings (Kim et al., 2007; Kim, 2010). Sorption and diffusion of emissions from many building construction materials such as floorings, carpets, wood and gypsum boards have been greatly described in literature, but wood-based materials such as orientated strand board (OSB) have not received the same attention (Niedermayer et al., 2013). This is surprising as wood-based panels are very frequently used in construction of houses and are a common source of many VOCs (Makowski and Ohlmeyer, 2005). However, research in this area is increasing.

1.2.2 Emissions from Medium Density Fibreboard

To obtain a full understanding of these emissions and how they can be mitigated, the initial source of the compounds need to be identified.

The term “composite material” is used to encompass a variety of materials, which are made up of two or more constituent materials that often possess different physical or chemical properties. “Wood composites materials” include a number of

panel, moulded products and lumber/timber products, including laminated wood products. The most common amongst these are engineered wood panels (EWP), such as plywood, medium density fibreboard (MDF), orientated strand board (OSB) and particleboard. All EWP's can be modified and engineered to meet a variety of specifications, maintaining the wood's inherent properties and improving these properties through science and technology. Wood and wood-based composites are a major source of aldehydes and terpene hydrocarbons (Hodgson et al., 2002) and therefore have big influences on indoor air quality. For the purpose of this literature review, the focus will be on medium density fibre (MDF).

1.2.2.1 MDF Production

Medium Density Fibreboard (MDF) is a wood-based material, manufactured by bonding ligno-cellulosic fibres with synthetic binders under heat and pressure. The raw material primarily used are wood fibres, however further research and development is underway to look at other lingo-cellulosic sources, mostly agricultural waste such as bagasse. MDF was first developed from hardboard manufacturing in USA in 1965 (Thoeman et al., 2010) as an alternative to the wet-process fibreboards, which generate large quantities of polluted waste water. Another drive was to utilise wood waste from wood products industry such as softwood and plywood, which were previously burnt or sent to landfills. The first European MDF manufacture was built in the former German Democratic Republic at Ribnitz-Damgarten in 1973 (Thoeman et al., 2010). Today, MDF production now accounts for 20% of panel production in Europe (Rivela et al., 2006). MDF has a significant advantage over particleboard, in that it possesses a near uniform density through the panel, resulting in a panel with a homogenous core, which is especially suited to embossing, moulding and general machining and is more dimensionally stable. MDF is now a highly developed panel that has a number of end-use requirements from flooring, partition walls to decorative surface veneer. Previously MDF was classified by BSEN 1142 (1989) but provided only 2 grades of MDF and moisture resistant MDF (MDFMR). Today, there are now 6 recognised types of MDF, in accordance with BSEN 622 (Table 2).

Table 2: EN 622 MDF panel types

EN Type	Description	Environmental Conditions
MDF	General purpose	Dry
MDF.H-1	General purpose	Humid
MDF.H-2	General purpose	Humid
MDF.LA	Load bearing	Dry
MDF.HLS-1	Load bearing	Humid
MDF.HLS-2	Load bearing	Humid

The current production of MDF is an automated and linear process, consisting of several major steps. Figure 1 shows the main process stations of MDF production (Thoeman et al., 2010). This production process can be divided into 6 major steps; chipping, refining, dry blending, drying, forming, hot pressing and finish.

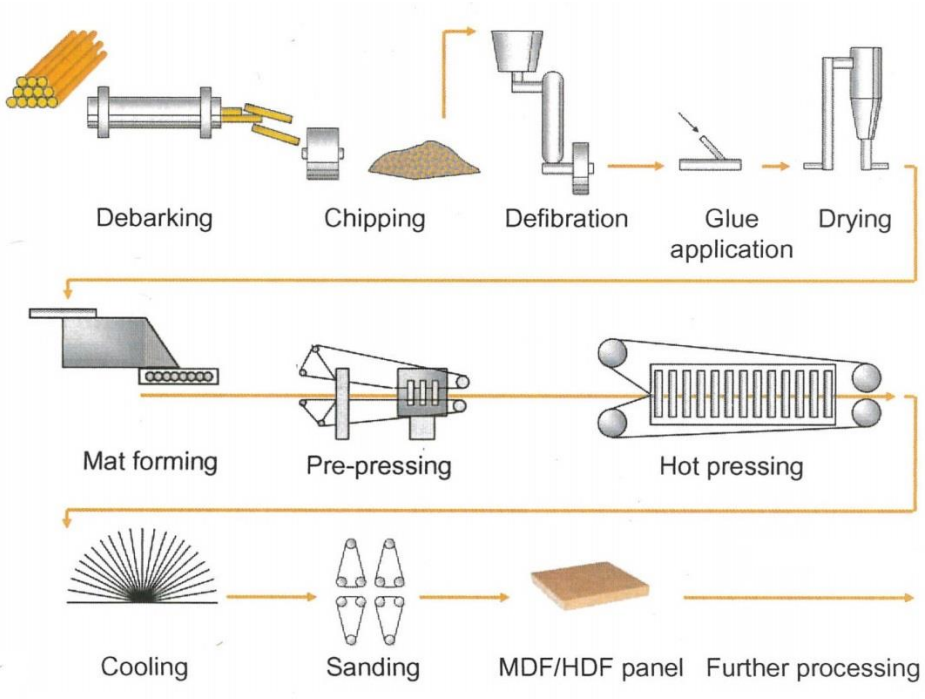


Figure 1: MDF Panel Production Process (Ansell, 2015)

During the chipping stage, solid de-barked wood, recycled or virgin wood, is chipped into relatively uniform particles. These chips are screened to remove any chips

smaller than 2mm and larger than 50mm and then washed. Washing of the chips is now considered a compulsory step to remove impurities such as bark and oils (Thoeman et al., 2010) . These now softened chips are used to generate a plug in the screw feeder, which helps to force out the free water in the wood chips. These wood chips are fed into the refiner digester, where the chips are squeezed and compressed and heated with steam to 6-10 bar pressure (87-145 pound force per surface inch (psi)). This generates an internal temperature of 175-190°C. The chips are fed between two rotating metal plates at approximately 1500 rpm, separating the fibres at the lignin binder by centrifugal force, reducing the chips to individual fibres.

The fibres are combined with resin (binder), wax and hardeners, catalysts and scavengers, depending on the production requirements. For MDF the most common resin used is urea-formaldehyde (UF). On an industrial scale the resin is applied to the fibres in the blow-line and wax is added just after the chips are refined. On smaller pilot scales, the resin is sprayed onto the fibres in a rotating dry blender. As the wet resinated fibre now has a moisture content (MC) of 40%, they are put through 'flash tube dryers' at high pressure with heated air at 260°C to get the fibres' MC reduced to 7-9%. The fibres are transported at 30 ms^{-1} to a cyclone, where the dry fibre is separated, ready for mat forming.

In industry pneumatically controlled sifters (classifiers) and filters remove any clumps of fibres and lay individual fibres without forming layers in the fibre mat. This is a continuous process on a conveyer belt, where the speed can be altered to accommodate the required final panel specified thickness (slower speed for thicker panel). This uniform mat has a very low density and requires a pre-press before final hot pressing. The pre-pressed mat is then pressed between two hot (180-210°C) metal plates, at a pressure of 0.5-5.0 MPa, to obtain the required density (496-801 kgm^{-3}) and thickness. MDF most commonly comes in three thickness; 12, 18 and 20mm.

Panels are cooled in ambient conditions and sanded on both sides of the panel to target thickness to ensure density uniformity. The MDF panels are usually then cut to commercial dimensions, 4ft by 8ft (1.2m by 2.4m) and offcuts can be hammer milled and recycled back into the industrial system

1.2.2.2 Formaldehyde based resin

Formaldehyde is produced on a global scale for a number of industrial processes such as preservatives, disinfectants and biocides (Salthammer et al., 2010). Formaldehyde is relatively easy to manufacture by oxidising methane or methanol in the presence of a catalyst and may also be called methanal or methyl aldehyde. The largest producers of formaldehyde are China (34%) United States of America(14%) and Germany (8%) (Salthammer et al., 2010).The annual production of 37% formaldehyde aqueous solution is approximately 18.14 million tonnes (20 million tons). This formaldehyde can be used in a number of industries including the production of cork, paper, in products to improve tear strength, coating materials, cosmetics and to improve bonding of rubber to tyre cords in the tyre industry (Conner, 1996); however, almost 70% of this production is used exclusively for the synthesis of formaldehyde based resins (Conner, 1996; Salthammer et al., 2010).

Adhesives used in wood-based composites are primarily amino resins. The name "amino resin" or "aminoplasts" encompasses any thermosetting synthetic resin, formed by polymerisation of amine with aldehydes. The most common use for formaldehyde, regarding the indoor environment, is the use in thermosetting resins. The most common amino resins used in wood-based panels production are: Urea-formaldehyde (UF), Melamine-urea-formaldehyde (MUF), Phenol-formaldehyde (PF) and Melamine-formaldehyde (MF). Although the chemistry and exact formulations of resins do vary depending on the manufacturer, the general chemistry remains constant. Below is a summary of the chemistry for UF, MUF, PF and MF resins.

Urea-formaldehyde (UF)

UF resin is the most commonly used resin for wood-based panels. It is cheap to produce, rapid curing and is very compatible with a number of additives (Salthammer et al., 2010). UF resins also provide some microbiological resistance as well as improve abrasion resistance (Conner, 1996). Approximately 1 million tonnes of UF resin is produced every year, with the majority of being used in particleboard production although 27% goes to MDF production (Conner, 1996).

UF resin is manufactured by heating urea (CH_4N_2O), derived from carbon dioxide (CO_2) and ammonia (NH_3), with formaldehyde (HCHO) to produce branched and linear polymers with a 3-dimensional structure that can be found in cured resin. Figure 2 shows the structure and reaction of urea and formaldehyde.

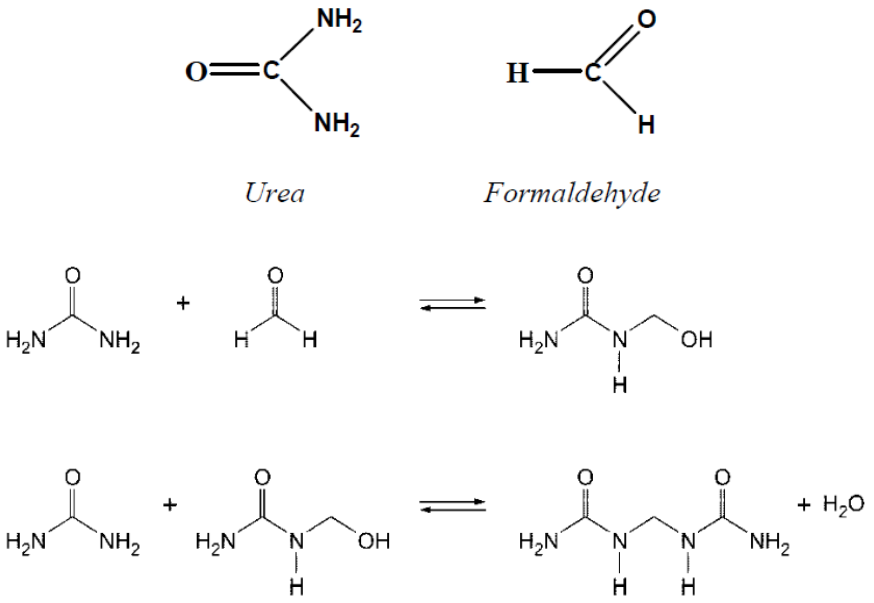


Figure 2: Urea and formaldehyde reaction

Note that this reaction is reversible and therefore wood-based panels bonded with UF resin can release significant amounts of formaldehyde throughout its service life. Synthesis of UF resins occurs in two stages. The first stage is to hydroxymethylolate by the addition of formaldehyde. This reaction is really a combination of a series of reactions that lead to the formation of mono-, di- and trimethylol ureas (Conner, 1996). These reactions can occur over the range of pH but on industrial scales occur between 8-9 pH. The second stage is the condensation of the methylolureas to low molecular weight polymers. This stage occurs at lower pH range, nearly acidic. Water is drawn out from the resin under a vacuum to achieve a desired solids content (usually 60-65% (Conner, 1996)). Further urea can be added after the second stage to reach the desired formaldehyde to urea ratio. Overall, the production of UF resins is relatively flexible and allows specific tailoring of the resin for desired gel times, tack, resin catalysts and viscosity.

The molar ratios of UF are very important to consider. Low F/U ratios increase shelf life and lower free formaldehyde emissions but have high viscosity and longer curing times and reduce panel strength and water resistance (Park et al., 2006).

Melamine-urea-formaldehyde (MUF)

MUF resin was developed as a compromise between UF and MF resin, as melamine is expensive and is very similar to UF resins (Salthammer et al., 2010). However, this loss of melamine, replaced by urea, does reduce the water resistance and strength properties of the final panel produced. Copolymers are formed with the addition of urea. This is achieved in two ways: first by simply mixing UF and MF resins or secondly by copolymerisation of urea and melamine during resin formation. The latter forms a resin with superior qualities. Generally the ratios of melamine and urea are 50:50 or 40:60.

Phenol-formaldehyde (PF)

PF resin is the most common of phenolic resins. There are two major types of phenols used to form PF; resol and novolacs (Pérez et al., 2007). PF resins are formed by the catalysed combination of phenols from petroleum and formaldehyde.

In resol formation, methylolation takes place on all the positions of the phenol ring to produce mono-, bi-, or tri-methylated structures. These structures bind together by methylene or ether links to form the resin structure. Resol based PF resins have high formaldehyde to phenol ratios, 1.8:1 to 2.0:1.

Novolacs are formed by the acid catalysis of the reaction. They are lacking in methylated groups, hence a hardener must be used as well as elevated temperatures to form a resin. The addition of the hardener releases formaldehyde, which aids the formation of methylene links between molecules.

Melamine-formaldehyde (MF)

MUF is manufactured in a similar fashion to UF resin but urea is replaced with melamine ($(C_3N_3)(NH_2)_3$). In the first stages of MF formation, the melamine is methylated to form methylol compounds. Unlike urea, the melamine is completely methylolated. Another important difference between MF and UF resin is that

condensation of MF can occur in alkaline, acidic and neutral conditions. The following stages of MF formation are the same as for UF resin; methylene and ether bridges form and the molecular weight rapidly increases. The final curing process renders the resin insoluble and infusible due to the reaction of ammonium and methylene groups. This results in a water-proof resin and produces a panel that can be used in humid environments and outside.

Table 3 summarises the advantages and disadvantages of these four resins. The main disadvantage of all these resins is the release of formaldehyde from the final pressed panel. There has been substantial research and development in reducing this emission of formaldehyde as well as replacing such resins with bio-based resins.

Table 3: Advantages and disadvantages of commercial resins

Resin type	Advantages	Disadvantages
Urea-formaldehyde (UF)	Inexpensive Use under a variety of curing conditions Fast reaction times Colourless	Water solubility High quantities of free HCHO
Melamine-urea-formaldehyde (MUF)	Compromise of strength and cost between UF and MF Hydrolysis resistance Cheaper than MF	Melamine is costly Increased curing time (Dunky, 1998)
Phenol-formaldehyde (PF)	Lower phenol to formaldehyde ratios Fast reaction time Very moisture resistant	Coloured Costly Reduced mechanical properties
Melamine-formaldehyde (MF)	Improved hydrolysis resistance (Dunky, 1998)	Costly Longer curing time

There is no legal limit on formaldehyde emissions worldwide but there are a number of international guideline values and recommendations for formaldehyde in the

indoor atmosphere. In 2004 European and British testing standards (BS EN) developed the E1 and E2 classification system for wood-based panels used in construction, based on their release of formaldehyde. In 2006, emission class E1 became obligatory for construction panel production in Europe (Schwab et al., 2014). Table 4 summarises the requirements of E1 and E2 boards in accordance to the European standard.

Table 4: Requirements of wood-based panels in accordance to BSEN standards

Country Standard	Test Method	Board Class	Limit value
Europe EN 13986	EN 717-1 EN 120	E1 -PB, MDF, OSB	≤ 0.1 ppm ≤ 8 mg/100g of oven dry board
	EN 717-1 EN 717-2	E1 - PLW	≤ 0.1 ppm ≤ 3.5 mg/(h.m^2)
	EN 717-1 EN 120	E2 - PB, MDF, OSB	> 0.1 ppm > 8 ≤ 30 mg/g (oven dry)
	EN 717-1 EN 717-2	E2 - - PLW	> 0.1 ppm > 3.5 ≤ 8.0 mg/(h.m^2)

1.2.3 Formaldehyde release from wood based panels

There is a vast array of the sources of formaldehyde in the indoor environment, from insulation material, carpets, cooking, computers, furniture, air cleaners, books and human metabolism (Curling et al., 2012; Salthammer et al., 2010; Uhde and Salthammer, 2007). However the greatest contributor to indoor formaldehyde concentrations is wood-based panels (WHO, 2010). Wood based products are notorious for their emissions of formaldehyde throughout their service life (Brown, 1999; Hun et al., 2010; Takagaki et al., 2000). MDF and chipboard are a significant source of formaldehyde (Hun et al., 2010; Lu et al., 2012; Salem et al., 2012). These products are popularly used in commercial buildings, public buildings, dwellings and schools (Yu and Kim, 2011) and are regularly used for cabinets, tables, shelving, furniture and for construction materials in wall components (Salem et al., 2012; Yu and Kim, 2011).

Formaldehyde based resins have superb bonding properties and are inexpensive (Kim et al., 2007) and are therefore greatly used for adhesives in wood-based panel manufacturing (Yu and Kim, 2011). The use of acid as a catalyst for UF synthesis and increased cure times increase the rate of hydrolysis and subsequently formaldehyde liberation (Conner, 1996).

However, the most significant disadvantage of these resins is the release of formaldehyde from the panels, called 'free formaldehyde'. Formaldehyde has been recorded to be emitted from wood-based materials at temperatures anywhere between 20-30^{o}C and 20-60% relative humidity (RH) (Yu and Kim, 2011). This free formaldehyde can be trapped within pores of the panel structure and is slowly released through diffusion processes. This release of formaldehyde is the largest source of indoor formaldehyde. Industrially produced panels do undergo an 'off gassing' period, where the panels are stored to allow for the emission of the unbound formaldehyde, before it is sold and used. The second largest source of indoor formaldehyde is through hydrolysis of aminomethylene linkages (Dunky, 1998) and polymer chains (Yu and Kim, 2011), breaking the weak bonds of formaldehyde with the material resulting in longer term emissions (Hun et al., 2010; Salem et al., 2012; Yu and Kim, 2011). For older materials bonded with formaldehyde based resins, hydrolysis of the C-N bond of the polymer structure causes the release of formaldehyde (Salem and Böhm, 2013; Salthammer et al., 2010). This process is exacerbated when a material is exposed to higher relative humidities, hence MDF panels bonded with UF resins are not desirable in areas of high RH such as bathrooms and kitchens (Yu and Kim, 2011).

Particleboard has been found to emit between 10-237 $\mu gm^{-2}h^{-1}$ (0.01 – 0.237 ppm) of formaldehyde (Hodgson et al., 2002) and MDF emits higher quantities, between 258-364 $\mu gm^{-2}h^{-1}$ (0.258 – 0.364 ppm) (Hodgson et al., 2002). This is primarily because MDF panels are produced using urea-formaldehyde (UF) resins (Xing et al., 2006b) and UF resin generates substantially higher formaldehyde emissions than any other resin bonded panel (Hodgson et al., 2002; Salem et al., 2012). In Europe, more than 90% of particle and fibreboards are bonded with urea formaldehyde (UF) resins (Schäfer and Roffael, 2000). There are however alternative synthetic resins available such as phenol-formaldehyde (PF), polymeric isocyanate (PMDI) and tannin

formaldehyde (TF) resins which emit lower levels of formaldehyde than UF resins. Phenol formaldehyde (PF) resin bound products such as plywood and hardboard emit significantly less <10 $\mu gm^{-2}h^{-1}$ (>0.01 ppm). However the problem of emissions is not solved as formaldehyde is still emitted throughout a products service life (Roffael, 2006).

Formaldehyde alone is hazardous in its natural state as it is highly reactive and can denature proteins and hydrocarbons (Xu et al., 2010) and will readily photo-oxidise in carbon dioxide (WHO, 2010). However, once in the indoor atmosphere it can additionally react with other chemical compounds in the indoor atmosphere and subsequently generate secondary pollutants (Patkó et al., 2013; Roffael, 2006) and its degradation can also lead to the formation of free radicals such as H (hydrogen) (Roffael, 2006). Formaldehyde also quickly reacts with hydroxyl radicals to give formic acid (WHO, 2010).

Formaldehyde raises major concerns over human health and environmental implications and there is exceptional research effort conducted to try to fully understand the mechanisms of its release from numerous wood based panels and how it can mitigated.

1.2.4 VOC emissions from wood-based panels

There are a number of factors that influence the VOCs emitted from wood-based products. As a result, different wood products have different VOC profiles.

1.2.4.1 Wood species

The VOCs emitted are dependent upon the wood species they are comprised of (Kim, 2010). For example, hardwood species such as ash and oak produce higher amounts of acetic acid and formic acid and less terpene compounds (Gabriel et al., 2015; Kim, 2010) but in contrast softwoods produce less organic acid and more terpenes (Kim, 2010). As a consequence, product's manufactured from hardwoods are expected to have lower VOC emissions than softwoods as softwood contains higher amounts of volatiles in softwoods (Jiang et al., 2002; Weigl et al., 2009). Baumann et al., (2000) found that emissions of aldehydes were reduced when MDF boards are made from hardwood species rather than softwood species such as pine.

1.2.4.2 Wood treatment

The emissions detected from wood-based panels are also influenced by how the wood is dried and treated prior to production. The length of time the wood is dried after logs have been harvested, debarked and cut can influence emissions. The longer the drying period, the fewer emissions observed in the final product (Beakler et al., 2005; Weigl et al., 2009). As the water evaporates from the material, the organic compounds are volatilised and are emitted from the surface of the material (Beakler et al., 2005). This does, however, create a temporary peak in formaldehyde emissions from solid wood as hydrolytic processes occur, leading to the formation of formaldehyde as the lignin and hemicelluloses degrade (Weigl et al., 2009).

1.2.4.3 Product production

The production procedure of a building material will influence its emissions profile. Different wood-based products may be processed in different ways but all are exposed to an extreme condition, such as heat or moisture or chemical in order to produce the product, and this will affect observed emissions. High temperatures of 200°C required to produce OSB degrades the wood, resulting in acetic acid, hexanal and aldehyde emissions (Uhde and Salthammer, 2007). Baumann et al., 2000 revealed that even when the same wood species, Southern pine, is used to produce MDF and particleboard, the emissions of aldehydes from MDF samples were much higher than aldehyde emissions from particleboard. But the study also showed that MDF made of different wood species, had lower emissions than particleboard.

The product specifications can also influence the total VOC emissions observed. Particleboard has been found to release TVOC concentration of 459-3477 μgm^{-3} (Stachowiak-Wencek et al., 2011) that varied with panel thickness. Panels of 15mm thickness were found to a have much higher TVOC emissions than panels of 8mm thick (Stachowiak-Wencek et al., 2011). This is due to the higher amount of raw material required to produce a thicker panel of the same density.

Surface treated wood-based materials also produce different compositions of emissions than untreated products, due to the different lacquers and oils used (Jensen et al., 2001). The Jensen et al., (2001) study showed that surface treated

wood-based products release more unsaturated aldehydes, esters and glycol ethers. It has also been noted in a number of studies that, laminated panel products such as melamine films or finish foils not only emit fewer VOCs (Hun et al., 2010; Schripp et al., 2012; Stachowiak-Wencek et al., 2011), but also that the profile of VOCs changes too. Stachowiak-Wencek et al., 2011 noted that the dominant groups of VOCs from particleboard were aldehydes, but when particleboards were finished with foils, the dominant group changed to ketones.

1.2.4.4 Product type

Baumann et al., (2000) evaluated VOCs emitted from particleboard and MDF and found different VOC profiles between the products. Particleboard mostly emits 20-22% monoterpenes and terpene hydrocarbons (Hodgson et al., 2002) and 27-32% aldehydes (Roffael, 2006). While, MDF releases fewer terpenes, showing that the MDF production process affects the emissions (Baumann et al., 2000; Gabriel et al., 2015). This release of terpenes is related to the wood species used to produce MDF and the differences in processes.

Orientated strand board (OSB) emit several VOCS but the dominant groups, like that found in particleboard, are terpenes and aldehydes (Jensen et al., 2001; Makowski and Ohlmeyer, 2005; Ohlmeyer et al., 2008; Stachowiak-Wencek et al., 2011), whereas plywood is reported to predominantly emit pentanal or hexanal (Hodgson et al., 2002). Jensen et al., 2001 conducted a study on emissions from wood and wood-based products, the results showed that OSB, produced using phenol glue, emitted significantly higher concentrations of aldehydes, compared to plywood, particleboard and MDF. Wood-based flooring, also emits a different VOC profile compared to wood-based products designed for construction. These VOCs include toluene, benzene and styrene (Kim, 2010) and these emissions vary with flooring treatment during production and whether it has a veneer or not. Often veneers add to the TVOC due to the formaldehyde based resin used to bind it to the wood surface (Kim, 2010). Kim, 2010 also found that engineered flooring such as plywood had lower formaldehyde compared to laminate flooring. However VOC emissions were higher for engineered flooring than laminate flooring.

It is highly important we understand the differences in VOC emissions from different wood-based products and that general statements about VOCs from such products, cannot be made (Baumann et al., 2000). There is evidence that different wood species and how they are processed and treated generate differences in the quantities and the types of VOCs released from products. Therefore, wood-based products should not be classified in one category when considering legislation and regulations which aim to reduce indoor pollution.

A difference in the combinations of factors results in different VOCs and these different chemical groups have different reactivity and therefore lifespan in the indoor environment. As stated before, some VOCs are longer lasting than others, while others that are highly reactive can result in other secondary emissions. For example, unsaturated compounds happily react with ozone (Weschler, 2004) while others with nitrogen oxides and in the presence of sunlight, form ozone (Ghoshal and Manjare, 2002). Some VOCs are more readily detected by humans than others. Aldehydes of heavy molecular weight, such as hexanal are commonly the source of unwanted odours at low concentrations (Hodgson et al., 2002). Due care must also be given when considering the composition of TVOCs, as some compounds are more harmful than others. Wood does contain and emit organic compounds such as α-Pinene, β-Pinenes and 3-Carene (Kim, 2010; Makowski and Ohlmeyer, 2005). Terpenes α-Pinene and β-Pinenes are considered as non-harmful VOCs (Kim, 2010) therefore materials' emissions hazards cannot be assessed based purely on TVOCs as some may not be harmful or a cause of illness.

1.2.5 Environmental parameters

There have been many studies that show that indoor environmental parameters influence a material's emissions rate and subsequently therefore, indoor air quality (Kim, 2010). The two main parameters that affect emissions are temperature and relative humidity (RH). The absorption and desorption mechanisms between a VOC and a materials surface can also be influenced by temperature and relative humidity as well as their physical and chemical properties (Markowicz and Larsson, 2014; Nazaroff and Weschler, 2004). Therefore, studies have been conducted investigating

a single material's emissions at different temperatures, relative humidities and ventilation rates.

1.2.5.1 Temperature

Emission rates tend to increase with increased temperature as elevated temperatures generally increase the rate at which indoor and material surface reactions occur, although there are some exceptions (Weschler, 2004; Wolkoff et al., 1997). It has been found that even from solid wood an increase in temperature results in more formaldehyde being liberated from the starch and lignin components (Salem and Böhm, 2013; Schäfer and Roffael, 2000). An increase in temperature from 23˚C to 40 ˚C increased formaldehyde emission rates over 5 times from particle boards (Pacheco-Torgal et al., 2012). Andersen et al., 1975 also reported similar findings and formaldehyde emission rates from chipboard doubled for every 7˚C temperature rise between 14-31 ˚C. Xiong and Zhang, (2010) evaluated the formaldehyde emissions from MDF. They noted that at room temperature, the MDF panels emitted far below the limit set by European standards, but as temperatures were increased, the increase in formaldehyde emission was exponential. Temperature acts as a catalyst for chemical reactions and for formaldehyde bound to materials provides the additional kinetic energy needed to overcome the binding forces (Pacheco-Torgal et al., 2012). However this type of formaldehyde emission is smaller than free formaldehyde emissions and emissions resulting from hydrolysis reactions (Pacheco-Torgal et al., 2012).

Temperature fluctuations alter the VOC profile, as observed with higher temperatures, less volatile compounds such as diterpene, can be emitted (Hun et al., 2010; Roffael, 2006). This is important when considering when to take samples from an environment as at lower temperatures some of these VOCs would not be detected. However, not all VOCs are affected by temperature increases (Pacheco-Torgal et al., 2012). Haghighat and De Bellis, (1998) conducted an experiment evaluating the VOC emissions from paints and varnishes, which revealed that with increasing temperature the TVOC emissions rates increased; however individual compounds did not always follow the same trend, with some showing higher emission rates at lower temperatures.

1.2.5.2 Relative Humidity (RH)

The studies of the influence of RH on VOC emissions are more complicated than for temperature and are largely dependent on the VOC in the material and the material in question (Wolkoff, 1998). However, studies such as that conducted by Markowicz and Larsson, (2014) and Netten et al., (1989) have found that increased relative humidity does increase emissions of formaldehyde, likely due to the fact that formaldehyde is highly hydrophilic and an increase in air moisture increases rates of hydrolysis. Andersen et al., (1975) reported that when chipboard is exposed to 30% RH and then to 70% RH the formaldehyde emissions double (Wolkoff, 1998).

Although it is still true that hydrolysis of VOCs does increase emissions, it is VOC specific. It has also been noted that, despite increased emissions of formaldehyde from materials, the diffusion coefficient shows little change despite the increased RH (Pacheco-Torgal et al., 2012). As water is polar and based on the "like for like" principle VOCs susceptible to hydrolysis are also polar compounds (Markowicz and Larsson, 2014). Therefore some non-polar organic compounds e.g. toluene behave differently to increased RH, with release rates not increasing with RH.

However, changes in RH can impact VOC emissions in unsuspected ways. Haghighat and De Bellis, 1998 found that emissions from painted surfaces, at the same temperature and different RH, increased at 35% RH but decreased again at 62% RH. Wolkoff, (1998) found that the VOC texanol emission profile was unaffected by different RH. Netten et al, (1989) also reported that different composite materials will respond differently to changes in RH, with wood based materials and ceiling tiles showing an increase and gypsum board, plaster, cement and terracotta brick exhibiting a decrease in formaldehyde emissions with increased RH. This highlights that different VOCs from different sources will respond to environmental conditions uniquely and specifically to the material and VOC relationship, with some increasing or decreasing emissions concentration rates or with negligible changes (Pacheco-Torgal et al., 2012). For example, Fang et al., (1999) experimented on TVOC emissions from building materials at 30%, 50% and 70% RH. The results obtained showed that TVOC emissions from floor varnish and wall paints correlated with

increasing RH, however TVOC emissions from carpet and PVC flooring, showed a negligible change in emissions.

To add to the complexity, RH has also been shown to affect secondary emissions in the indoor environment, namely through hydrolysis reactions and result in such VOCs as ammonia and butanol being emitted from flooring (Kim, 2010).

1.2.5.3 Ventilation

Unsurprisingly a lower ventilation rate increases concentrations of formaldehyde and VOCs (Conner, 1996; Nazaroff and Weschler, 2004). Low ventilation rates increase the accumulation of VOCs and formaldehyde in a building or in a single room. Without adequate ventilation gas phase reaction chemistry is promoted and therefore an increase in secondary pollutants occurs (Weschler, 2004). However, a reduced concentration in VOCs increases the difference in vapour pressures between the VOC source and the indoor atmosphere and this vapour difference drives evaporation from the VOC source and therefore increases its emission rates. However, in turn, as diffusion plays a key role in emissions from a material, if diffusion of a volatile compound to a materials' surface is slower than the rate of evaporation then the overall emission rate is reduced. As a result, the influence of ventilation and surface interactions and emissions is a very complex one and again can often be VOC specific.

Insulation of a building also influences indoor air quality and not in the least because it increases building tightness and reduces air exchange. Different types of insulation emit their own VOCs and formaldehyde. A heavily insulated building will also increase average house temperatures and relative humidity thereby increasing the impact of them on emissions. This is especially true during summer periods and can result in overheating of a building, especially in top floors of high-rise buildings (Shrubsole, 2015).

1.2.5.4 Other parameters

Building occupants

Another major influence on indoor air is the building occupants' daily activities, work routine, preferences for particular products and their frequency of use such as

cleaning, candles, smoking, cooking with gas or oil etc. The presence of pets can also affect air quality. Human occupants can also generate spatial variations of pollutants in different rooms as some are used more than others, used for different purposes and contain different, localised sources of VOCs (Nazaroff and Weschler, 2004).

VOC characteristics

The characteristics of individual or groups of VOCs will also influence indoor air quality. An example is glycol ester, which is released from aqueous cleaning products slowly over hours if not days after its application (Nazaroff and Weschler, 2004). Other VOCs, as mentioned before, can be more or less susceptible to environmental conditions and have different chemical reaction capabilities. VOCs of a low or moderate vapour pressure or high polarity may bind onto materials surfaces or into the bulk of a material, reducing peaks in concentrations of pollutants in an indoor environment (Nazaroff and Weschler, 2004). Some materials can also absorb VOCs released from other materials and desorb them at a later time (Haghighat and De Bellis, 1998; Markowicz and Larsson, 2014; Niedermayer et al., 2013) creating a buffering of pollutants.

Air velocity

One other environmental parameter that influences emissions is the air velocity across the surface of a material. This can occur on smaller scales, such as disturbances by an occupants' movement through a room, or by drafts and open windows. The air velocity across the surface of a material will affect what is called the convection mass transfer coefficient (h_m) of VOCs (Pacheco-Torgal et al., 2012). A higher air velocity can decrease the layer of still air adjacent to the material surface, increasing h_m and increase emissions from that material (Pacheco-Torgal et al., 2012). This affect is also influenced by the diffusion capabilities of the VOC in question. If diffusion is greater, then the influence of air velocity will be negligible (Pacheco-Torgal et al., 2012).However, for some VOCs, it can increase emissions through oxidative reactions (Wolkoff, 1998). It has also been stated that VOC emission rates from construction materials are only temporarily influenced by air

velocity, during the first few days after production but not to any great extent (Wolkoff, 1999).

1.3 Impacts on human health

Environment is often associated with the great outdoors but it does include indoor spaces and it is where we spend up to 90% of our time (Petry et al., 2014; Yrieix et al., 2010). Therefore consideration must be given to the air quality we breathe. In 2010 the *Daily Express* published an article entitled 'Cancer warning in house chemicals'. In the same year *The Guardian* published 'Why your sofa maybe harmful to your health'. In response to the growing public concern over indoor air quality, the Royal College of Physicians released a report 'Every breath we take: Lifelong impact of air pollution' in February 2016. The report highlights the difference in indoor and outdoor air pollution, the major sources, some of the methods of mitigation and most importantly, its effects on human health.

1.3.1 Sick Building Syndrome (SBS)

Multiple chemical sensitivity (MCS), is a disorder attributed to exposure to chemicals in the environment at low concentrations (Sari et al., 2004). A most commonly reported form of MCS and effect VOCs on human is known as 'sick building syndrome' (SBS) (Andersson et al., 1997; Sari et al., 2004). SBS is a multifactorial problem that includes a number of chemical, physical and psychological and biological factors (Brinke et al 1998) and is a collection of non-specific and variable symptoms, from dizziness, lack of concentration, nausea, depression, drowsiness, eye and respiratory tract irritation, bronchitis, cardiovascular problems even disturbances in memory (Allen et al., 2016; Brinke et al., 1998; Ghoshal and Manjare, 2002; Haghighat and De Bellis, 1998; Jensen et al., 2001; Niedermayer et al., 2013; Ohlmeyer et al., 2008; Petry et al., 2014; Stachowiak-Wencek et al., 2011; Zhang and Xu, 2003). It has also been suggested that a significant amount of respiratory illness and lung cancers maybe be a result of avoidable indoor air pollution (Haghighat and De Bellis, 1998). A survey conducted in office building in the United States of America and Europe showed that 20% or more of the occupants frequently experience SBS symptoms (Brinke et al., 1998).

There is much evidence that suggests VOCs are responsible for SBS. There have been suggested relationships between VOC and SBS since the 1990's but there is some confusion between the level of TVOCs to cause SBS (Brinke et al 1998). The toxic effects of poor indoor air quality are difficult to ascertain as there are so many different sources of pollutants and therefore many toxicants (Jensen et al., 2001). However, some individual VOCs and their exposure pathways have been thoroughly researched. For example, electrostatic equipment such as photocopiers emit ozone (O_3) and nitrogen oxide (NO) and it has been found that with increased exposure to such equipment, SBS prevalence also increases (Brinke et al., 1998; Wolkoff et al., 1997). In some instances, the 'lowest concentration of interest' (LCI), which defines the concentration of particular volatile substances present in indoor air, which at a continued exposure has no effect on human health or comfort (Jensen et al., 2001).of some VOCs have been determined. Essentially is a toxicology evaluation of individual substances in VOC emissions from selected materials, the higher the value,, the less toxic to human health. A few examples of VOC determined LCI values include; benzene 5µg m^{-3}, toluene 1900 5µg m^{-3}, α-pinene 1500 5µg m^{-3}, hexanal 8905µg m^{-3} and aliphatic hydrocarbons 6000 5µg m^{-3} (Jensen et al., 2001).

Epidemiological studies of airway irritation symptoms have shown that O_3 reacts with unsaturated VOCs (Wolkoff et al., 2000). People can be exposed to VOCs through a number of pathways such as volatilisation, inhalation of airborne droplets or suspension powders (such as those used in carpets cleaners) and inappropriate mixing of cleaning products, generating chemical reactions and/or release of toxic gases, namely chlorine gas (Nazaroff and Weschler, 2004) and those with cleaning jobs are at a considerably higher risk of inhalation exposure. There have been a number of cases whereby humans have suffered directly from VOCs from the use of cleaning products, suffering conditions such as asthma allergy and respiratory irritation (Nazaroff and Weschler, 2004). Not surprisingly, cases of SBS have often coincided with building renovations (Reitzig et al., 1998) due to the increased quantities of new materials, paints and varnishes etc. emitting VOCs. It is known that most oxidising agents are irritants and therefore play a role in the indoor air induced irritation to the eyes and throat (Wolkoff et al., 1997). Even at low levels, these very reactive compounds may be a cause of SBS.

It has also been suggested that due to confounding factors, SBS may present itself in different symptoms for individuals based on race, gender, smokers, immune responses as well as from other factors such as ventilation type, building age and exposure time (Brinke et al 1998).

With increasing cases of SBS and adverse effects of VOCs, products must meet a set criterion such as BSEN panel product formaldehyde emission standard, for end-users and professional users (Jensen et al., 2001). However, despite a growing awareness of poor indoor air quality and improved emission control strategies, especially those focused around formaldehyde, control strategies have reduced VOC emissions although this has not resulted in a decrease in SBS cases (Wolkoff et al., 1997). This suggests that SBS is also caused by secondary VOCs from chemical reactions taking place and the reaction products in indoor environments (Uhde and Salthammer, 2007; Wolkoff et al., 1997). It is suspected that increased levels of ozone (O_3) indoors and subsequent reactions with VOCs is the cause for the increased prevalence of SBS (Wolkoff et al., 1997). Sundell et al., 1993 also concluded that chemical reactions of some VOCs resulted in the formation of irritating VOCs, such as formaldehyde.

It is largely argued whether singular VOCs can be held responsible for the health problems associated with poor indoor air quality, or if non-volatile compounds can also be held accountable. Considering industrial buildings, workers are exposed to high concentrations of one or a few VOCs, whereas in domestic buildings the occupants are exposed to very low concentrations of a very high number of VOCs, so it has been suggested that it is the total volatile organic compounds (TVOCs) that are responsible for SBS (Brinke et al 1998). It has also been suggested that SBS is not a continuous reel of symptoms, but an overlap of allergic symptoms caused by different factors that contribute to SBS caused by different individual VOCs, combination of VOCs and individual responses to exposure (Wang et al., 2008).

If VOCs are not absolutely the cause of, they do contribute to poor indoor air quality (Markowicz and Larsson, 2014; Niedermayer et al., 2013; Stachowiak-Wencek et al., 2011) and more airtight constructions do cause the accumulation of these VOCs, individually or collectively, to harmful levels and provoke health problems (Niedermayer et al., 2013).

1.3.2 Formaldehyde and human health

Formaldehyde is also associated with SBS (Sahlberg et al., 2013) but has more defined limits than other VOCs as it is a prominent indoor pollutant with many known and well understood sources. However, there is some controversy over how toxic gaseous formaldehyde actually is and when individuals are most at risk. Formaldehyde is classed as an electrophile, which means it can react with nucleophilic biogenic compounds in the body (Salthammer et al., 2010) and its high solubility in causes rapid adsorption in the respiratory and gastrointestinal tract (Salthammer et al., 2010).

WHO, 2010 accumulated available research data and evaluated the effects of acute and short term exposure to formaldehyde. WHO has estimated the absolute odour threshold for formaldehyde is between 0.06-0.22 mgm^{-3}. On average, according to WHO, formaldehyde exposure concentrations are 0.03 – 0.06 mgm^{-3} in homes and work spaces (Sari et al., 2004), therefore in some homes, formaldehyde can be detected by humans through smell alone. No irritation can be found up to 0.37 mgm^{-3} (30ppm) of formaldehyde air loading however, loadings above 0.625 mgm^{-3} (50ppm), eyes and upper respiratory tract of humans become irritated (Arts et al., 2008; Weigl et al., 2009). Data collated by WHO, 2010 revealed that the effects of formaldehyde exposure are various and from its simple odorous nature, sensory irritation to the eyes and upper respiratory tract, asthma and eczema (skin becomes rough and itchy patches of inflamed skin and potentially blistered) but no definite evidence could be found that formaldehyde affects lung function or causes cancer. It is accepted that formaldehyde emissions between 0.5-1ppm result in the most common symptom of irritation of the eyes and the upper respiratory tract (Arts et al., 2008; Brinke et al., 1998; Kim et al., 2006b; Spengler and Sexton, 1983; Yu and Kim, 2011) as 98% of human exposure to formaldehyde occurs via inhalation of indoor air (WHO, 2010). There is evidence of a correlation between buildings of high formaldehyde concentrations and childhood asthma (Brown, 1999; Hun et al., 2010). This eye and respiratory irritation is caused by the chemosensory effect and the interaction with localised nerve endings, called sensory irritation (Arts et al., 2008), which naturally leads to reflex responses such as sneezing, vasodilation, rhinorrhea

(increase mucus in nasal passage), lacrimation (watery eyes) and changes to the rate and depth of breathing as part of instinct of self-protection (Arts et al., 2008; Sahlberg et al., 2013). Above 1.0 ppm, formaldehyde exposure results in extreme discomfort within 30 minutes (Patkó et al., 2013; Salem and Böhm, 2013). At these higher concentrations, formaldehyde will lead to more prominent reactions e.g, cytotoxic reactions such as redness and swelling in respiratory tract or itching of exposed areas (Arts et al., 2008; Jensen et al., 2001).

However, the human responses to formaldehyde show much natural variation. Norbäck et al, (1995) studied asthmatic symptoms and exposure to formaldehyde. The results revealed there was a greater relationship between formaldehyde concentrations and symptoms of breathlessness during the night compared to during the daytime. No conclusion could be arrived at for the cause of this but it was suggested it could be a result of the build-up for pollutant during the day or individuals are more susceptible to pollutants during sleep. The authors of formaldehyde studies have acknowledged that any results can be somewhat contradictory as not only is there variation in sensory symptoms between individuals but also results maybe be influence by participant bias, former experience and placebo effects (Arts et al., 2008) as well as odour detection ability between males and females and between adults and children (Sahlberg et al., 2013; Wang et al., 2008).

As it is a very common pollutant with potential health risks, the European Commission set an indoor air limit exposure to formaldehyde at 1 μgm^{-3} (0.8 ppb) (Arts et al., 2008), based on the threshold for nose and throat irritation. In the UK the Committee on the Medical Effects of Air Pollutants recommended a limit of 100 μgm^{-3} for indoor formaldehyde 2004 (Salthammer et al., 2010). However other European countries have different regulations, for example in France, the French Agency for Environmental and Occupational Health Safety set a limit of 10 μgm^{-3} for long term exposure and 50 μgm^{-3} for short term exposure. As a result of the intense research and development of regulations and improvements in manufacturing techniques, the exposure concentrations to formaldehyde are much lower than in previous decades. However, the problems regarding formaldehyde exposure are more akin to lower formaldehyde concentrations but for much longer periods of

time and some studies have shown a relationship between low formaldehyde concentration inhalation over long time periods for respiratory illnesses in humans (Salthammer et al., 2010; Sari et al., 2004).

The confounding problem faced by modern researchers and regulating and governing bodies lies in the fact that TVOCs encompass all known VOCs, SVOCs VVOCs and any secondary VOC produced from chemical reactions. Different compositions of TVOCs may cause greater, lower or different symptoms. As there is such a vast variety of VOCs found within buildings it is unrealistic if not impossible to fully understand the relationships and reactions between the VOCs and the effects they could have on human health.

1.4 Sampling VOCs and analysis

Due to the growing concern of the adverse effects of indoor pollution from formaldehyde and VOCs on human health, legislation and guideline values of concentration have sparked an increase in research into this field of science. Since the problem of indoor air pollution was first addressed in the 1970's, there has been a vast quantity of scientific research across the world, but not without its problems and areas of bias. This section briefly highlights some of the problems faced when sampling and analysing indoor air and VOCs.

There is naturally a vast amount of volatile organic compounds and it is impractical to study each individual compound and develop an emissions profile for all of them. Therefore, specific compounds such as formaldehyde are targeted or a material's emissions or a total VOC (TVOC) concentration is recorded. However, when comparing studies, this can become somewhat problematic as the results and analysed observations made are limited by the equipment, sampling techniques used, spatial and temporal variations and environmental factors (Markowicz and Larsson, 2014; Wolkoff et al., 1997). Taking air samples within buildings of TVOCs can also be influenced by particular compounds found in much higher concentrations than others and can mask true emission mechanisms taking place (Haghighat and De Bellis, 1998). Temporal and spatial variations can also affect TVOC measures as materials may buffer VOCs by temporarily absorbing compounds and desorbing them at a later time (Haghighat and De Bellis, 1998; Markowicz and

Larsson, 2014; Niedermayer et al., 2013). Materials such as nylon and olefin fibre carpets will absorb more non-polar compounds while materials such as gypsum board absorb polar compounds (Hun et al., 2010; Markowicz and Larsson, 2014). The air sampling location is very important. It is not always suitable to take an air sample or reading from the centre of a room as there could be localised emissions from particular materials (Nazaroff and Weschler, 2004) and therefore the TVOC reading is not truly representative of a real life scenario. The air sampling period is also important, as some VOC concentrations can be time dependant (Brown et al., 1994). For example if the occupants are cooking or the position of the sun relative to the window. There could also be 'inter-zonal' transport of VOCs in buildings, due to ventilation, draughts and occupant movements, whereby the VOC in question could be brought in from elsewhere and increasing exposure to some VOCs that would otherwise go unexposed (Nazaroff and Weschler, 2004). Another problem is that TVOC samplings also incorporate natural VOCs some of which are harmless and unless the TVOCs are broken down into their individual compounds, the term TVOCs can be misleading for studies considering the impacts on human health (Kim, 2010). All of the above mentioned can cause readings of VOCs to be false or only tell part of the story.

Environmental chambers are a good technique for determining TVOC concentrations and were first introduced in the 1980's and have now been standardised in Europe in ISO 16000 (Kim et al., 2007). However the main limitation of these is mainly their cost and time consumption (Kim et al., 2007). Other in-situ techniques include differential optical absorption spectroscopy (DOAS), Field and Laboratory Emission Cell (FLEC), Fourier transform infrared absorption (FTIR) and laser-induced fluorescence spectroscopy (LIFS). The FLEC method is a popular method due to its high sensitivity and has also become part of a standardised method ISO 16000 in Europe (Kim et al., 2007). These test methods have a number of benefits but they are costly and the sensitivity is strongly affected by RH and therefore not always suitable for routine tests (Salthammer et al., 2010). When comparing such in-situ studies, one has to ensure that certain aspects have been addressed as so many internal (material type, age, composition) and external (ventilation, temperature, RH, time) factors can influence TVOC measurements. All of these variables can be

influenced by the building itself and the buildings' primary purpose, be it a school, for domestic or public purpose (Brown et al., 1994). For true comparisons of a buildings total emissions, all of these factors should be the same and this is of course can be hard to achieve.

There are also limitations with other analytical equipment such as Gas chromatography–mass spectrometry (GC-MS). This is a common method used to identify if particular VOCs are present rather than just determining TVOC. However, this equipment also has its limitations. Apart from the cost it is also limited by its internal library of compounds. There can also be some subjective error, as the GC-MS can reveal a significant number of peaks and some at lower peak areas may be rejected from the final analysis or masked by more concentrated compounds (Kim et al., 2007). This creates a level of uncertainty when analysing GC-MS results (Yrieix et al., 2010). Other compounds that have particularly high reactivity may not be sampled or may be destroyed during the analysis procedure (Weschler, 2004). There are a number of compounds that are undetectable with modern analytical equipment or are decomposed, e.g. when exposed to high temperatures in a chromatographic column or are short-lived (Weschler, 2004). Indeed, modern sampling methods and specific environments can mean that some compounds are never detected unless analysed with specialised equipment and specific regimes. However, there has been significant research conducted looking at specific materials and products.

It remains, despite some difficulties, important to continue conducting research and analysing VOCs of potentially hazardous characteristics and how they impact indoor air quality to develop suitable remediation measures. If individual, groups or particular sources of VOCs can be identified and then steps can be taken to replace sources and/or mitigate their emissions, such as removing formaldehyde in binders and resins. The identification of particular VOCs can also indicate that other mechanisms are taking place. For example the identification of 1-octen-3-ol indicates the presence of moulds (Markowicz and Larsson, 2014), which also affect on indoor air quality.

1.5 Efforts to reduce emissions

Work on assessing the human health effects of poor indoor air has lagged behind the assessment of health effects of outdoor pollution for a number of reasons. This is largely because the study of outdoor air pollution was at higher levels of pollution from coal smoke and photochemical smog (WHO, 2010). But also because it is more feasible to monitor outdoor pollution on a large enough scale to develop standards and regulations than indoor pollution (WHO, 2010).

1.5.1 Control measures

Assessing the human health risks of indoor air pollution is quite difficult and far more complicated owing to the multitudinal sources of pollutants as well as the types of pollutants: chemical, particles and biological materials. Difficulties also arise into investigating how they interact with their environment. However, despite the difficulties there have been some significant research studies and regulations developed to combat the issue of poor indoor air quality. The reduction of emissions can be tackled at four different levels: occupants, architects and developers, manufacturers and government.

1.5.1.1 Occupants

Many VOCs are emitted from products such as cleaning agents, e.g. Terpenes, such as limonene are very commonly used as a fragrance in many different household products such as solvents, candles, odorants, cleaning agents and essential oils (Wolkoff et al., 2000). Residential occupants can proactively alter the VOC profile of indoor air by reducing the quantity of use of such items or by ensuring they are used and maintained correctly (Spengler and Sexton, 1983).

1.5.1.2 Architects and Developers

Architects and developers should consider indoor air quality in building design and consider appropriate ventilation systems for the building in question.

Ventilation

Adequate ventilation appropriate to the building design can significantly reduce the concentration of VOCs to harmless levels (Kim et al., 2006c) by creating air exchange to dilute and remove pollutants such as smoke (Spengler and Sexton, 1983). Ventilation helps to maintain indoor RH at a level that restricts microbiological activity, and thus reduce emissions of fungal VOCs and mycotoxins which have been shown to increase with increasing moisture content of a substrate (Nielsen, 2003; Viegas et al., 2015)**.** Recent studies have shown that environmental factors also influence the sorption capacity of materials and the ventilation rate is a key factor (Deng et al., 2012). Ventilation can be classed as natural, mechanical or a combination of both and the correct system must be applied specifically to the design of the building. An incorrect ventilation system can in itself aid indoor pollution and have adverse effect on human health (WHO, 2009). However, ventilation systems need to be suitably designed and correctly installed in the building it is intended for and adequately maintained and used.

Substitute materials

Developers should try to eliminate, contain or reduce highly pollutant emitting materials and products wherever possible (Spengler and Sexton, 1983). Substitution of highly emitting materials for materials with lower emissions is an obvious way to reduce indoor pollution. However, substitute materials must have the same or better property characteristics as the originals. Hence, there has been a lot of research on current product emissions profiles and property characteristics of alternative materials. There have been advances in reducing emissions from existing products, such as using odourless paints, carpet glues and replacing conventional oils for turpentine oils, which contain fewer compounds that would otherwise be emitted into the indoor environment (Reitzig et al., 1998). Such advances require the developers and architects to have knowledge of and be willing to use such alternatives, regardless of other factors such as cost.

Architects and developers should also consider using materials that can be multifunctional and actively absorb formaldehyde and VOCs from the indoor environment. Niedermayer et al., (2013) conducted an experiment on 25 different

materials commonly currently used in construction and found that MDF, OSB, particleboard, 3 layer boards, gypsum, plasterboards, sealants, insulation materials will absorb indoor air pollutants. Interestingly, the capabilities of wood-based construction materials to absorb VOCs showed distinct differences despite being produced with the same or similar constituent parts. MDF panels had the strongest absorption of pollutants such as hexanal, butyl acetate, p-xylene and α-pinene and showed the lowest release of absorbed VOCs whereas solid wood plywood board absorbed the least pollutants and OSB desorbed the most VOCs after absorption. The results also revealed differences in the types of VOCs absorbed; OSB, although it absorbed lower concentrations of VOCs than MDF, had a stronger absorption of hexanal. The data acquired revealed that some of these materials have high absorption capacities and will strongly bind compounds, which are then less likely to be desorbed by the material. Uncoated gypsum and other materials such as paper, perlite-based ceiling tiles, cork wall coverings, wheat board and clays have shown an ability to absorb ozone present in indoor air (Tittarelli et al., 2015). Cementitious materials, although solid, are “breathing materials” that can absorb and adsorb many compounds (Tittarelli et al., 2015). Hoang et al., (2009) found that 10 common green building materials will remove ozone from the atmosphere. These materials include wheat board, ceramic tiles, coated and uncoated bamboo. The results showed that uncoated and unpigmented materials showed a better capacity to remove ozone. Pearlite ceiling tiles absorbed the most. However, it must be remembered that these construction materials are also sources of emissions. It has been studied that gypsum dry walling also has the potential to absorb VOCs and quickly after the initial exposure to VOCs (short lag time) and will slowly decay the VOCs and release them after exposure. Hence, the gypsum dry walling acts as a buffer. However, with increasing RH emission rates increase (Markowicz and Larsson, 2014).

In attempts to increase sustainability and reduce waste, recycling wood products into new wood-based products has become popular and has obvious benefits. However, recycled wood products are large contributors to indoor VOC concentrations due to their contamination with resins and waxes (Costa et al.,

2013a). Therefore using virgin wood to produce wood-based products can help reduce indoor emissions.

Developers must be cautious in their choice of materials and ensure that the sequestering characteristics of the chosen materials outweigh their own emissions overall (Niedermayer et al., 2013). A balance has to be struck between the choices of low emitting products, aesthetics, economics, sustainability, influence on human health and mechanical properties in order to reach the desired "green building" that is safe and sound.

1.5.1.3 Manufacturers

Manufacturers of products and materials should ultimately test their products for emissions and any links to human health, certify and label products that are potential sources of air pollutants (Spengler and Sexton, 1983). Where possible, manufacturers should collaborate with research institutes and conduct research into alternative compositions and methods of production. This will ultimately assist in developing and producing a building product that can be efficiently produced and reduce or absorb indoor pollutants (Wolkoff, 2003). During the last decade, there has been strong scientific active research into developing building products with lower VOC and formaldehyde emissions (Wolkoff, 2003).

Product modifications

As formaldehyde has received a great deal of attention as a possible carcinogenic compound, formaldehyde emissions from wood-based panels have declined significantly between 1970 and 2005 (Roffael, 2006). Even with extensive efforts to reduce formaldehyde emissions, formaldehyde will always be present in the indoor environment, simply because it is emitted from natural materials such as wood. Therefore although "zero emission" wood-based panels are not achievable (Meyer and Boehme, 1997; Roffael, 2006; Weigl et al., 2009), there are simple measures that can be implemented to reduce natural emissions of formaldehyde and VOCs.

Prior to processing

There some very simple and economic measures to reduce natural emissions of formaldehyde and VOCs such as drying and storing the wood for longer periods of time before processing (Roffael, 2006; Salem and Böhm, 2013). This increases the time allowed for natural emissions to diffuse from green wood which would other be in the finished product. Emissions from pine greenwood decrease by 50% after 14 days' worth of storage (Roffael, 2006).

The composition of the wood-based panels produced also makes a difference to the emissions profile; furnish ratios used in production, such as particle board made with more beech has lower formaldehyde emissions than those consisting of more pine particles (Salem and Böhm, 2013). For particleboard, emissions can be reduced by simply reducing the area/volume ratio, i.e. increase wood particle size. As this will reduce diffusion less formaldehyde is released and rates are reduced (Salem and Böhm, 2013). Wood-based panels produced using pine wood species have been shown to emit higher amounts of TVOCs than alternative wood species such as poplar (Costa et al., 2013a). The size of the wood particles also makes a large difference to formaldehyde emissions. Finer wood particles have a greater surface area and therefore more formaldehyde emissions than larger wood chips. However, the quantity of formaldehyde released from wood is negligible compared to concentrations emitted from resin bonded wood based panels and VOC emissions such as pinenes are harmless to human health (Salem and Böhm, 2013). Therefore modifications made prior to processing may help but do not make a large enough contribution to reducing emissions.

Production process

It has been shown that the formaldehyde emissions from wood-based panels is governed by moisture content as well chemical processes (Boruszewski et al., 2011). The moisture content of the raw materials used to produce wood-based panels will affect the quantity of free formaldehyde emitted. A moisture content increase from 0% to just 4% MC resulted in a 6-fold increase in formaldehyde emissions (Boruszewski et al., 2011). Therefore a very simple method of reducing to formaldehyde emissions is to ensure the raw material is as dry as possible. As oven

drying of wood chips can be very costly, other simple measures can be used to ensure that the MC of the wood chip is reduced. Wood chip stored in piles will have a higher MC towards the middle and lower on the edges, therefore wood chip piles can be turned over or mixed to ensure even moisture migration and drying (Boruszewski et al., 2011).

Gabriel et al., (2015) showed that how the fibre for MDF boards is prepared influences its VOC emissions. Fibre for MDF can be produce from wood using thermo-mechanical pulping (TMP) or chemo-thermo-mechanical pulping (CTMP). CTMP is the same process as TMP but a chemical pulping agent such as sodium sulphite is also used. Gabriel et al., (2015) studied the use of hardwoods and softwood produced through TMP and CTMP and evaluated the different emissions from the final MDF product. The results revealed that increasing use of hardwoods and fewer softwoods in either process, reduced the emissions of terpenes and aldehydes. However, some emissions, showed a more complex relationship between wood species and pulping method. Acetic acid emissions were found to also increase with increasing use of hardwood but only using TMP process and CTMP process showed no significant change in acetic acid emissions. It was suggested that the use of chemical sodium sulphite acted as a buffer to acetic acid and subsequently decrease its emissions. This study revealed that fibre processing can expectantly influence different kinds of emissions from wood panels and that different wood species under different process emanate varying VOCs.

It has also been noted that, during wood-based panel production, longer press times and higher temperatures can reduce formaldehyde emissions from the final board product (Hun et al., 2010) However, such techniques such as drying and running board pressing schedules are costly, both in time and money.

Surface treatments

Different surface treatments can be applied to wood-based construction and insulation products to reduce types of VOC and formaldehyde emissions. Surface treatments aimed specifically at reducing formaldehyde can be physical or chemical.

Surface coatings

Physical surface treatments (placing a coating on the top surface of the panel) on construction panels include lacquer, paints and laminate surfaces can reduce emissions (Hun et al., 2010; Kim et al., 2006a; Schripp et al., 2012). It has been found that veneers and vinyl are very effective barriers for formaldehyde and other aldehydes emissions (Hodgson et al., 2002; Salem et al., 2012; Salem and Böhm, 2013). Low pressure melamine veneers can reduce formaldehyde emissions, compared to plane HDF (Kim, 2010). The impregnation of melamine-formaldehyde resin creates a coating which prevents emissions as it is less permeable (Kim, 2010). Wood-based panels can also be treated with wax scavengers of urea designed as a wood finish. Composite boards can be also treated with ammonia gas or ammonia salts (Kim et al., 2006a; Salthammer et al., 2010). However, this can in the long term result in additional emissions as the glues and solvents or non-cured components age and emit VOCs. It has been found that lacquered beech boards emitted significantly higher TVOCs than un-lacquered (Schripp et al., 2012). This shows that the TVOCs emitted result from the type of lacquers used and bonding surface (i.e. the type of board and its components). This has in turn helped fuel the desire to manufacture 'eco-friendly products' with the use of 'green lacquers', however even these so called 'eco-friendly' products such as lacquers based on linseed oil emit VOCs. Schripp et al., 2012 found that eco-lacquers emitted the greatest quantity of TVOCs, as they contain higher amounts of alkanes compared to OSB boards, floorings and exotic hardwood species. Wood based and engineered flooring products are known to emit many VOCs such as toluene, benzene and styrene. Different types of veneer can produce almost unique emissions profiles. Therefore developers and architects should understand these differences and specify and apply the correct coated products in a building.

Photocatalytic coatings

Another more promising surface treatment is the use of a photocatalytic coating. Combined with the right physical treatment, photocatalytic coatings can absorb external VOCs and formaldehyde from the indoor air as well as reduce product emissions. Photocatalytic air purification works through oxidation processes.

Molecular water absorbed on the photocatalyst will react with the positive gap generated from the UV activation. From this reaction, hydroxyl groups such as OH^+ are generated, which in turn oxidise the indoor air pollutants. Therefore photocatalytic oxidation reactions and success of removing indoor air pollutants are governed by the production of these hydroxyl radicals (Mo et al., 2009a). As such, in the absence of water vapour the ability to degrade such compounds such as acetone and toluene is significantly reduced (Mo et al., 2009a). Photocatalytic oxidation uses nano-semiconductor catalysts, activated by UV-light to convert organic compounds into its benign constituents such as water and carbon dioxide (Mo et al., 2009a). However, there is some evidence that certain reactions result in other compounds, contributing to secondary pollutants. For example, in the presence of ozone, titanium oxide (TiO_2) reacts with styrene to produce formaldehyde (Salthammer et al., 2010). Semi-conductor photocatalysts include zinc oxide (ZnO), zirconium dioxide (ZrO_2), tin dioxide (SnO_3), iron oxide (Fe_2O_3) and tungsten oxide (WO_3) (Hoffmann et al., 1995). The most commonly used is TiO_2 as it is relatively inexpensive and chemically stable (Mo et al., 2009a) and has use in numerous applications such as detoxification of waste water and VOC-polluted soil and in advances in improving surface hydroscopicity (Hashimoto et al., 2005). These photocatalysts have been studied in different preparations, which can be divided into gas-phase or liquid-phase (Mo et al., 2009a). One example of the liquid phase is water-in-oil micro-emulsions, where the nanoparticles are dispersed throughout the emulsion. These emulsions are thermodynamically stable and control a micro-environment on its surface where the chemical reactions may occur (Mo et al., 2009a). Another example is the use of TiO_2 as a coating or a film over another product or materials such as steel (Mo et al., 2009a; Yu et al., 2003). TiO_2 has also been found to have additional desired properties as an antibacterial agent (Yu et al., 2003). Salthammer and Fuhrmann, (2007) found that the addition of TiO_2 in indoor paints works as a catalyst, degrading nitrogen dioxide and formaldehyde. However, they also found that there was no degradation of other VOCs and carbon monoxide. This highlights that under various conditions and treatments, TiO_2 is not always a suitable modification to improve indoor air quality, although this does reveal potential for TiO_2 to be used as a scavenger for target VOC pollutants.

However, as the effectiveness of these catalyst's rely upon the formation of hydroxyl groups which oxidise the pollutants, the absence of water vapour results in a significantly reduced ability to degrade VOC such as acetone and toluene (Mo et al., 2009a). Excessive water vapour on the catalyst surface however, inhibits reaction sites and essentially outcompete pollutants, therefore reducing catalytic reactions with pollutants (Mo et al., 2009a). Temperature can also affect the efficiency of the photocatalytic oxidation reactions and adsorption abilities. It has been noted that the effect of temperature is different according to the VOC under investigation. Such as acetaldehyde and toluene have a decreasing reaction rate with photocatalysts, with increasing temperatures whereas compounds of ethylene reactions increase with increasing temperatures (Mo et al., 2009a). Therefore, there is room for further research and development into photocatalytic coatings.

Substrate treatment

Another, novel surface treatment is cold plasma pre-treatment of wood product. (H. Zhang et al., 2013) studied the effects of plasma pre-treatment of plywood and MDF and how it influenced formaldehyde emissions. Over the past decades plasma treatment has become more commercialised as it can improve surface properties without affecting bulk properties. It can improve surface wettability, increase surface adhesion or water resistance. A benefit of this treatment is that it is relatively inexpensive (Zhang et al., 2013). In the study conducted by (H. Zhang et al., 2013), cold air and ammonia plasma were used to pre-treat poplar veneer sheets for plywood and different F/U molar ratios of UF resin.

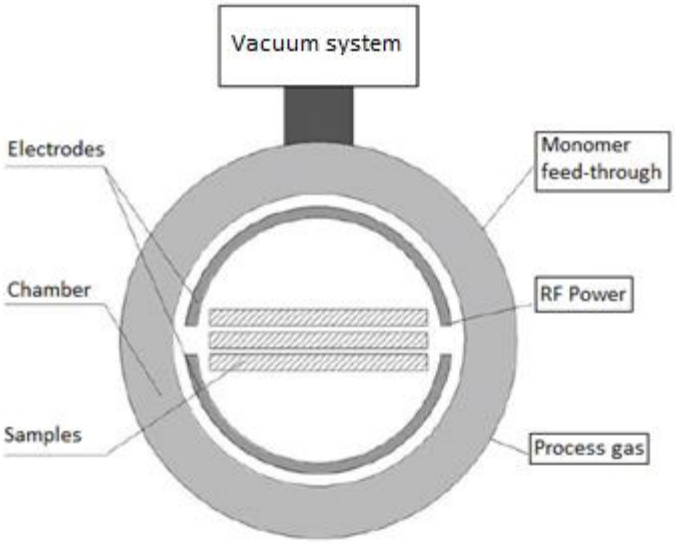


Figure 3: A schematic diagram of RF plasma system ((H. Zhang et al., 2013)

The composite raw materials were placed in a vacuum chamber (fig 3) between electrodes at a pressure of 160-200 Pa. A steady flow rate of air was passed over the samples and a radio frequency magnetron sputtering unit was used to produce cold plasma. The composite samples were exposed for 3 minutes, after which the materials were used to produce plywood and MDF panels. Increasing the F/U ratio increased formaldehyde emissions and pre-treatment with cold plasma and plasma with ammonia decreased emissions significantly. The greatest benefit of using such a method and technique is that the mechanical properties of panels produced are not impaired (H. Zhang et al., 2013).

Another substrate treatment is the use of urea as a pre-treatment. Hematabadi et al., (2012) used urea on a straw substrate intended for particleboard productions, at 5%, 10% and 15% concentrations. The results obtained by Hematabadi et al., (2012) revealed that with over 10% urea concentration, the mechanical properties of the panel were improved and the free formaldehyde emissions were reduced. It would appear that urea treatment of a substrate would reduce emissions, as the urea was able to penetrate the straw particles and still be able to react with the formaldehyde and thus increase bonding strength. It is possible that this form of substrate treatment could be applied to other materials that would otherwise not meet current EN standards.

Resin modification

When considering wood based panels, the major sources of emissions are the binders, resins, waxes or other additives added during production. Formaldehyde emissions result from unreacted formaldehyde escaping the material, condensation reactions between methylol groups and hydrolytic degradation of cured resin (Tohmura et al., 2000). The most effective method of reducing formaldehyde emissions during and after production is to address these three key factors by modifying or replacing the resin or binder used during production.

Chemical modification

How a resin is produced can influence formaldehyde emissions from the final product. It has been shown that UF resin produced at higher pH has a greater amount of methylol groups than those produced in more acidic conditions (Tohmura et al., 2000). This is because methylene linkages between urea and formaldehyde is lower in alkaline conditions and therefore formaldehyde emissions are higher (Tohmura et al., 2000). It has also be shown that an acidic catalyst in the resin will reduce formaldehyde emissions as the resin becomes more stable (Tohmura et al., 2000).

The most common method of reducing emissions from construction products is to replace formaldehyde resins with alternatives such as isocyanate based adhesives. These include; Methylene Diphenyl di-isocyanate (MDI), polymeric MDI (pMDI), toluene di-isocyanate (TDI) and hexamethylene di-isocyanate (HDI). Other chemicals include urea, ammonia, ammonium chloride, resorcinol, and peroxides although some are not as effective as others and can be expensive (Boran et al., 2012; Kim et al., 2006a).

In wood bonding, Isocyanate groups react with hydroxyl groups that are present in the wood components, such as cellulose, hemicellulose and lignin, to form urethane bonds (-O-C(O)-NH-) (Rowell, 1984). A good alternative to formaldehyde based resins is pMDI (phenol MDI), as it releases no free formaldehyde very quickly cures and forms chemical bonds by reacting hydrogen atoms and water. MDI is manufactured from aniline, formaldehyde and phosgene. It is unique in that it reacts with both the moisture in the material and the hydroxyl groups of the material

(Papadopoulos et al., 2002). The adhesive properties result from the covalent bonded urethane bridges, which are formed with the terminal hydroxyl groups of the cellulose molecules in the wood. This chemical bond is very strong and moisture resistant. Despite the fact that such resins are more costly than UF, the quantities of resin required to produce excellent bonding qualities are less (by dry weight) and therefore MDI is commonly used for MDF and particleboard production.

However, Jiang et al., (2002) investigated VOC emissions from hot pressing particle board using UF, PF and pMDI resins and showed that the use of isocyanate resins in wood-based panel production does not prevent all emissions. They found that the use of pMDI resulted in emissions of acetic acid and heavy molecular weight VOCs (HMw VOCs). However, when using isocyanates it has been proven that VOC and formaldehyde emissions are significantly less than emissions from panels bonded with UF, PF and MUF (Pratelli et al., 2013). Pratelli et al., (2013) studied the emissions from hardwood composites and found that VOC emissions, especially terpenes and lignin-polyphenols, decreased as the MDI penetrated into the cell walls of wood components although it was also concluded that MDI did not appear to affect emissions of formaldehyde from the wood. This could have been due to the high reactivity of isocyanate resins with water molecules, resulting in hydrolysis (Jiang et al., 2002). The reduced availability of water hindered the occurrence of hydrolysis reactions and therefore reduced emission rates (Jiang et al., 2002). Other specific VOC emissions, such as methanol, are reduced with the use of isocyanate resins. Methanol contains one hydroxyl group which readily reacts with isocyanate resins, therefore methanol emissions from wood-based products are markedly reduced compared to other conventional resins (Jiang et al., 2002).

The emissions of VOCs and formaldehyde from isocyanate resins are much lower than amino based resins and once cured exposure levels in indoor environments are low. Despite this and their higher bonding properties, the use of isocyanate resins is limited, due to its toxic nature. Emissions from such resins are most dangerous when in gas state (Wirts *et al* 2003). Isocyanates react with water and if breathed in, it will solidify in the lungs. These factors increase the need for more environmentally friendly and sustainable resin modifications to be developed to mitigate VOC and formaldehyde emissions.

Another alternative is to use organic compounds such as amines. Amines such as propylamine, methylamine, ethylamine and cyclopentylamine have been evaluated as potential scavengers of formaldehyde in UF resin (Boran et al., 2012) with all found to be successful in reducing formaldehyde emissions from MDF panels produced with the modified UF resin. Cyclopentylamine was the most effective formaldehyde scavenger due its cyclic structure. Although all amines reduced the formaldehyde emissions, ethylamine reduced modulus of elasticity below the control MDF panel and Cyclopentylamine, exceeding 0.8% ratio, reduced the modulus of elasticity below the control. However, regarding internal bond strength, all amine additions improved MDF properties. This shows that not all amines are equally suitable for formaldehyde scavengers in panel products as they affect its mechanical properties individually.

Polyurethane (PUR) adhesives are widely used in indoor environments, but such adhesives emit isocyanates, which react with amines to form polyurea compounds and emit monomers (Wirts et al., 2003). These emissions are strongest in their liquid state, before the adhesive has hardened. However, a study conducted by Wirts et al., (2003) revealed that if room temperatures exceed 40°C, totally emissions increase significantly. For some additives, if excess is added during production process, the panel properties will be adversely affected (Boran et al., 2011). This shows that any users of adhesives must ensure that it is suitable for its intended purpose and research studies must investigate emissions profiles across a range of environmental parameters.

Molar ratio

Another chemical modification to resin is to alter the ratios of formaldehyde to other compounds in a resin such as MF (melamine formaldehyde), UF (urea formaldehyde) or PF (phenol formaldehyde) resins (Park et al., 2006; Tohmura et al., 2000). It has been well documented that altering the ratio of formaldehyde in UF and PF resin will reduce formaldehyde emissions (Astarloa Aierbe et al., 2000; Kim et al., 2006a; Park et al., 2008; Zorba et al., 2008) although it does also affect the properties, such as strength, of the wood based panel properties. Myers, (1984) reported that formaldehyde emissions from particleboard decrease rapidly from F/U

2.0 to 1.0 and that to meet E1 emissions class, the optimal ratio should be below 1.2 (fig 4).

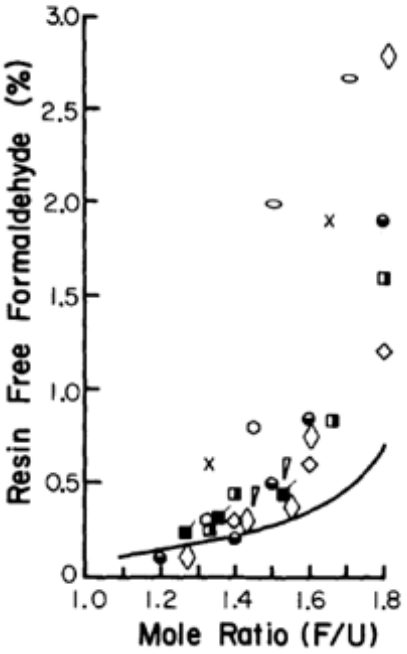


Figure 4: Effect of molar ratio on resin free formaldehyde content (Myers, 1984)

However, simply altering resin ratios may not be a suitable solution to reducing formaldehyde emissions on its own. Que et al., (2007) studied the influences of mole ratios of F/U (0.97 to 1.27) on the mechanical and physical properties of particleboard. It was concluded that lowering F/U ratio decreased thickness swell and the mechanical properties of the panel. Que et al., (2007) also noted that the deterioration in mechanical and physical properties could be overcome by using larger quantities of resin although this would increase the cost of production and product. Park et al., (2006) investigated the effect of the F/U molar ratio on thermal curing behaviour of UF resins, and the associated properties of particleboard bonded with them using DSC. The results showed that thermal curing reactivity of UF resin decreased with decreasing F/U mole ratio, as gel time increased. This could be due to a reduced availability of formaldehyde at lower F/U ratios. This is undesirable as it would increase production time, energy consumption and cost. Park et al, (2008) also looked at the influence of F/U ratio and melamine content on

the hydrolytic stability of MUF resins. The results revealed that higher F/U ratios and melamine contents resulted in more branched structures within the resin, which subsequently increased the resin's susceptibility to hydrolysis in acid conditions. This is important as curing reactions are reversible under acid hydrolysis, resulting in formaldehyde release from the panels (Dunky, 1998).

Natural modification

As chemical resins and those derived from fossil fuels are known sources for VOC and formaldehyde emissions, there are some advances in adhesive technology using natural and renewable sources that can be used instead. Agricultural, and protein wastes such as soybean, casein and blood are a good source for naturally derived adhesives (Guezguez et al., 2013). Protein based adhesives have been researched since the early 20th century but inexpensive petroleum based adhesives displaced protein adhesives (Pizzi and Mittal, 2003). However, the most popular and most researched protein based alternative is cashew nut shell liquid (CNSL). CNSL has been shown to be easily polymerised using formaldehyde to form a curing resin adhesive (Bisanda et al., 2003). Kim, 2010b experimented with a resin hybrid of CNSL and formaldehyde (CF) and CF combined with polyvinylacetate (PVAc) to replace UF resin. Results showed that emissions were lowest with CF resins though the addition of PVAc increased them slightly but still satisfied European standard E_o grade panels for formaldehyde.

Soybean is readily available and inexpensive. Renewable waste from the soybean oil industry contains between 35-55% proteins and shows potential as an adhesive (Liu and Li, 2007; Pizzi and Mittal, 2003). Gueguez *et al* (2013) describes the use of soy based adhesives as a substitute for synthetic MUF resin. The results showed that using 100% soy reduced emissions from 3.05 HCHO/mgm^{-2} h^{-1} to 0.13 HCHO/mgm^{-2}h^{-1}. It was concluded that soybean could be combined with MUF to prevent the release of free formaldehyde. Lorenz et al., 1999 investigated the influence of soy proteins combined with UF resin that had been modified differently on formaldehyde emissions. The modifications of soy investigated were: soy protein, soy flour, casein, dispersed soy protein and hydrolysed soy protein. The results showed that all modifications reduced formaldehyde emissions with increasing cure

temperature and percentage of soy solids added to resin. However, soy based resin produced an adhesive that retains its water solubility after curing and drying. The soy protein had to be modified itself through heat, exposing more functional groups such as acid amino groups, which have better potential to react with phenolic adhesives. The final panel product produced with soy and PF adhesive had higher mechanical properties and better cross linking structure and therefore fewer free formaldehyde emissions. However this process is energy, time and cost consuming and soybean proteins have other drawbacks. To give an example soybean flour is treated in an alkaline solution, which breaks down internal hydrogen bonds of the coiled protein molecules, opening the polar structure for adhesion to wood (Pizzi and Mittal, 2003). This results in a reddish brown stain on wood surface, which may not be desirable. This highlights the additional complications in designing and implementing modifications that reduce emissions from a product. It is not a case of one size fits all.

Another viable source of bio-waste is the waste whey protein from cheese making. Although it can be utilised as a food ingredient, more than 30% of the annual waste is disposed of in landfill (Wang et al., 2011). Whey proteins are compact globular proteins with low molecular weight, rich in free hydroxyl groups and amino groups (Wang et al., 2011). These functional groups mean that the whey protein will readily react with aldehyde groups (-CHO) and isocyano groups (-NCO), therefore it seems suitable to use as a formaldehyde scavenger. Work conducted by Wang et al., (2011) on whey protein based adhesives revealed that these free amino groups crosslinked with formaldehyde in UF and PF resins immediately when mixing. The resin became incredibly viscous due to agglomeration with PF resin. The same was found to be true of p-MDI, glyoxal and glutaraldehyde resins and formaldehyde emissions from modified UF resins were greater than without the whey protein. However, when combined with phenol-formaldehyde oligomer adhesive, the resin was stable and the plywood boards emitted much lower quantities of formaldehyde (Wang et al., 2011).

Kim et al., (2006a) evaluated different bio-based scavenger: tannin powder such as *Acacia mearnsii*, wheat flour, rice husk flour and charcoal in melamine formaldehyde (MF) resin to reduce free formaldehyde emissions. The results revealed that the bio-

scavengers, except rice husk flour reduced the levels of formaldehyde emitted from engineered flooring boards. Tannin powder and wheat flour contain many hydroxyl groups, making them good scavengers, reducing emissions by 20%. However, charcoal was the best formaldehyde scavenger used in MF resin, reducing emissions by 40%. Its high porosity with numerous minute holes provides a huge surface area improving its absorbency. However, charcoal MF floor boards had much lower strength properties. This is due to the inorganic content of the charcoal that hampers the crosslinking between polymers and functional groups. The poor absorbency of the rice husk flour was concluded to be a result of its very high ash content (96%) due to high amounts of silica. The presence of so much silica disrupted any reaction between formaldehyde and its hydroxyl groups.

Both of the afore mentioned studies show the complex reactivity of one protein source with different adhesives and that further research is required to determine their effectiveness in formaldehyde and VOC adsorption. Some waste sources should not necessarily be disregarded as a potential scavenger if it does not combine well with one adhesive. More research should be conducted to understand its chemistry and potentially find its perfect partner adhesive.

Tannins and extractives

Another natural modification is to use tannin extractives from different organic sources to replace synthetic resins and petroleum derived phenolic compounds (Bisanda et al., 2003; Kim, 2009a). Tannins have a number of applications but they are customarily used in converting animal hide into leather in inks, textiles and as corrosion inhibitors (Bisanda et al., 2003). The use of phenolic type compounds found in tannins is not new and has been around since the 1970's (Ping et al., 2012) and as such there has been much research in this area. Pine bark tannins were used in exterior particleboard on an industrial scale for almost a decade during the 1990's (Valenzuela et al., 2012) and condensed tannins extracted from bark from plants such as hemlock, wattle and pine were heavily studied in the 1980's (Rowell, 1984).

In recent years, increasing attention has been paid to the utilisation of natural tannins in resin to reduce VOC and formaldehyde emissions from wood-based panels. Tannins contain phenolic rings that are important for adhesion as these rings

provide the reactive sites for condensation with formaldehyde (Lee and Lan, 2006). Figure 5 shows an example of polyphenolic found in tannins.

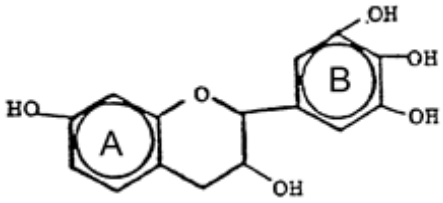


Figure 5: Example of polyphenolic found in tannins

Chemically, tannins are complex phenolic compounds of high molecular weight divided into two main categories; Hydrolysable tannins (HT), which are soluble in water, easily hydrolysed and therefore easy to react with other compounds and condensed tannins (CT), which have the most complex chemical structures made of flavonoid units (Bisanda et al., 2003). Generally these are carbon to carbon bonds that cannot be easily broken by hydrolysis (Bisanda et al., 2003). Phenolic tannins have proven very useful when applied to synthetic resins, as the cross linking between hydroxyl groups and phenolic rings are very strong. The improved bonding therefore decreases the emissions from wood-based panels (Weigl et al., 2009). Tannins can be blended with UF, MF resins as well and MDI, the latter forming better adhesives (Bisanda et al., 2003). Tannins have been shown to produce better resin blends with high moisture resistance (Bisanda et al., 2003), even exterior grade particleboard adhesives can be achieved from a combination of tannins with MDI (Rowell, 1984).

Although CNSL has good absorption and fast curing properties, it is expensive, whereas tannin extractives are readily available, renewable and cheaper (Bisanda et al., 2003; Kim, 2009a). Wood bark has been found to contain high quantities of soluble extractives that are polyphenolic in nature (Roffael et al., 2000). On average, 10-15% of a log consists of bark, which is removed during log processing. The utilisation of bark in the wood industry is relatively poor due its low qualities and limited market applications. However, if this bark can be utilised as an organic source of polyphenolic compounds to replace petroleum sources, then it will add substantial value to an otherwise waste product. Roffael et al., (2000) reported that

a water extraction of tree bark revealed that 60-80% of extractives are comprised of phenolic tannin polymers, with the rest being monomeric compounds such as pectin and sugars. Popular tree species for tannin extract include; oak (*Quercus*), wattle (*Acacia*), maple (*Acer*), birch (*Betula*), willow (*Salix*) and pine (*Pine*), mimosa bark, Quebracho (Bisanda et al., 2003; Kim, 2009a; Pizzi et al., 1994).

Boran et al., (2012) evaluated the use of extracted oak (*Quercus alba*) tannin as a formaldehyde scavenger, to lower the free formaldehyde emissions from medium density fibreboard, produced with urea formaldehyde resin. The results obtained showed that the formaldehyde release was reduced with increasing concentration of tannin extract in the UF resin. The free formaldehyde released decreased by 27.89% by just using a rate of 15% UF resins and 1% tannin solution because formaldehyde can easily react with the tannin resorcinolic A-ring and methylene bridges. The use of pine bark tannins to reduce formaldehyde emissions from MDF and particleboards was also explored by Valenzuela et al., (2012). The data revealed that formaldehyde emissions reduced enough to satisfy E1 emission class standard without impairing panel mechanical properties. The initial work was carried out produced panels with pine tannin and pMDI hybrid resins, with a later study without the pMDI was conducted. The panels produced that showed good results for both emissions and strength, revealing that pine bark tannin is an adequate adhesive without the use of synthetic resins. However, the excessive use of tannin extracts in resin solution can result in reduced mechanical properties, especially in MDF due to changes in the fibre structure (Boran et al., 2012) but also because the tannins can be 'too reactive' with formaldehyde. Tannins from coniferous tree species, such as pine, have higher amounts of resorcinolic type flavonoids. The main disadvantage of using tannins it that they have considerably faster reaction rates with all the formaldehyde, leading to much higher degrees of polymerisation thus reducing the mechanical strength properties of the final wood-based product (Boran et al., 2012).

Bisanda et al., (2003) also developed a new blend of HT tannin and cashew nut shell liquid (CNSL) with an emulsifier, to produce panels using coffee-husks particles and compared them to the performance of UF and PF resins. Results of differential scanning calorimetry (DSC) revealed that hydrolysed tannins had the lowest endothermic point at 120^{o}C, compared to UF and PF resin. Therefore, hydrolysed

tannins were shown to release less free formaldehyde than both PF and UF resin. This is important as at higher temperatures the more frequent breaking of methylene linkages in cured resin's polymer structure, the more formaldehyde and moisture vapour is released. It was also found that curing was faster with tannin resins than PF or UF resin. Mechanical tests of coffee-husk boards were also conducted on UF and tannin based panels and it was found that the boards had better modulus of elasticity (MOE), modulus of rupture (MOR) and water resistance than boards made with commercial resins.

Engineered flooring is a known large source of formaldehyde and VOC emissions due to it being constructed of a number of layers glued together, usually with a formaldehyde based resin (Kim, 2009a). Kim, (2009a) evaluated *Acacia mearnsii* tree tannin in UF resin to reduce TVOC and formaldehyde emissions from engineered flooring (plywood) bonded with fancy veneer. The results showed that tannin adhesive gave an excellent adhesive performance, good moisture resistance with trends of lower formaldehyde emissions, compared to UF resin. Without the veneer on the plywood, formaldehyde emissions were lower than 1.5 mgL^{-1} of E_1 grade European standard. However, the results also showed an increase in TVOCs emission but not necessarily toxic VOCs. This is a good example of where it is important to understand what types of VOCs are emitted and not simply accept the term TVOC. The addition of the tannin increased the TVOCs as the tannins do emit VOCs. However, these are natural and harmless to humans.

Further studies have also evaluated other natural sources other than tree bark for phenolic tannins. Extractives found in wood have also acted as scavengers to formaldehyde and reduce emissions from bonded wood panels (Schäfer and Roffael, 2000). Pizzi et al., (1994) investigated the possibility of using tannins extracted from pine (*Pinus radiate*) and Pecan nut (*Carya illinoinensis*) pith (fig 6). It was found that these materials contain the tannins procyanidin/prodelphinidin.

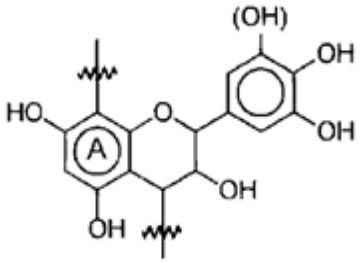


Fig 6a: Pine and pecan nut tannin

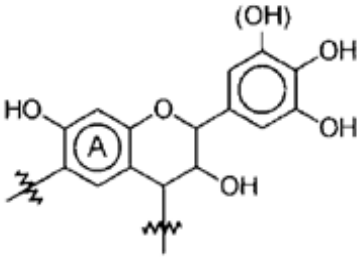


Fig 6b: Mimosa and quebracho tannin

Figure 6: Natural tannins and extractives

Procyanidin/prodelphinidin polymeric tannins the pine and pecan nut tannins are able to react faster with formaldehyde than commercially used mimosa and quebracho tannins (Roffael *et al*, 2000). Pizzi et al., (1994) used different resin formulations of paraformaldehyde, urea, pine and pecan nut tannins to produce particleboard, suitable for exterior use. It was concluded that pine and pecan nut tannins were a suitable renewable alternative to synthetic resins as it was demonstrated that these tannins provided a rapid curing of resin (saving time and energy) and that formaldehyde emissions were lower, passing E1 class emission standards.

Agricultural wastes, often poorly utilised, have also been considered as a source of tannins. Grape pomace is a solid waste from the grape juice and wine making industry, consisting of skins, stems and seed, which retain high levels of extractives (Ping et al., 2012). Ping et al., (2012) extracted grape pomace tannins using different aqueous solutions and combined the extracted tannins with pMDI and produced particleboards. Results revealed that tannins extracted in a solution of NA_2CO_3 gave the best performance, producing panels that met interior grade particleboard. More

importantly, the formaldehyde emissions were less than the European standards requirements of 6.5 mg $(100g)^{-1}$ of panel.

However, extraction of tannins and excessive use of tannins is not without its drawbacks. Different sources of tannins can yield tannins of varying reactivity and impair their reliability of use. Bisanda et al., (2003) also evaluated the use of tannins in different forms; powder, solid and hydrolysed. The results obtained showed that the curing behaviour of solid and powder tannin forms were very similar but hydrolysed tannin has better thermal stability. Ping et al., (2012) also found that the method of extraction can impact their performance in terms of formaldehyde emissions and mechanical strength. The economics and aesthetics of using tannins must also be considered to determine its success of use and performance, as different tannin sources, have different resin properties (Bisanda et al., 2003).

Absorbing Scavengers

As there as so many VOCs polluting indoor air, it is impractical to prevent emissions from all sources within a building and production streams completely (Salem and Böhm, 2013). It is questionable whether formaldehyde concentrations lower than 20 μgm^{-3} could be permanently maintained in normal living environments (Salthammer et al., 2010) as it is present in an abundant variety of sources in nature. As the emission sources of all VOCs cannot be eliminated, other approaches have been sought. One such method is the use of particular additives, termed 'scavengers', to actively absorb formaldehyde and VOCs from the indoor atmosphere. A huge advantage of wood-based panels, construction boards and cementitious materials is that they can easily be combined with adsorbents such as fillers or scavengers to enhance their sorption capabilities (Tittarelli et al., 2015). A material's absorption capacity is not easily determined as the capacity is determined its by physical properties and by the VOC physical and chemical properties (Deng et al., 2012).

Inorganic scavengers

Urea is a very common chemical added to materials used to absorb free formaldehyde emitted from formaldehyde based products such as particleboard and medium density fibreboard (MDF). However, it has been noted that excess use of

urea will reduce the mechanical properties of the final panel produced (Johnsson et al., 2014). Costa et al., (2013) compared the use of urea and sodium metabisulphite ($Na_2S_2O_5$) scavengers in particleboard produced from pine (*Pinus pinaster* Ait) and poplar (*Populus* spp.), and the effects on TVOC emissions. The study revealed that TVOC emissions from poplar particleboard were 25% less than pine particleboard. The addition of urea scavenger to the particleboards was not used to influence TVOC emissions in either type of particleboard, whereas the sodium metabisulphite reduced TVOC emissions by 40% but only in particleboard produced from pine. The reduction of TVOC emissions observed in poplar particleboard was negligible however, formaldehyde emissions were significantly reduced. This study showed that sodium metabisulphite is an excellent scavenger of aldehydes but is only very successful in softwood based panels.

Pozzolanic materials are a collection of materials that are comprised of reactive silicates and alumino silicates. A characteristic of such materials is that they are poorly crystallised materials that are rich in silicon dioxide (SiO_2) and aluminium oxide (Al_2O_3) with a porous form. Natural pozzolans are defined as either raw or calcined natural materials that have pozzolanic properties, such as pumicite, opaline chert and shales, tuffs and some diatomaceous earths. Artificial or man-made pozzolanic materials are commonly used in cements. Volcanic minerals added to exterior cladding and concrete panels to maintain permeability as volcanic minerals are rich in silicium (Gedikoglu et al., 2012). Kim, (2009b) investigated the use of pozzolanic materials in construction material MDF, to absorb formaldehyde. The pozzolanic material was 70µm in diameter and was loaded with 1, 3, 5 and 10% of UF resin. The results showed that the scavenger did not affect panel density or moisture content at either concentration. Unlike other organic additives added to panels, such as silica, that have adverse effects on mechanical properties, pozzolans seemed to have no effect on modulus of rupture (MOR), modulus of elasticity (MOE) and internal bond (IB) strength. Most importantly, formaldehyde emissions were reduced with increasing pozzolan concentrations. Total VOC emissions were also investigated and due to its rough and irregular surface and high surface area, TVOCs were also reduced. Another advantage of highly porous materials is that they can help to control humidity levels in indoor climates, without adding to energy costs

due to their hygroscopic abilities (Tittarelli et al., 2015). Pozzolanic materials can also be added to mortars and grouting (Gedikoglu et al., 2012). Zeolite materials with pozzolanic properties can be used to produce lightweight aggregates in concrete to increase sorption capabilities when used indoors. It can also act as an antibacterial agent (Das et al., 2004; Tittarelli et al., 2015). Tittarelli et al., (2015) studied the zeolites added to mortars and evaluated the sorption and moisture buffering properties. It was found that with the addition of zeolites, the mortars adsorption capabilities increased by 50% and the moisture buffering ability was three times greater than that of cement mortars. However, care must be given to the type of volcanic pozzolan material used as some such as natural montmorillonite (a clay) is rich in sodium and calcium, which strongly hydrates in the presence of water (Gedikoglu et al., 2012). This can lead to subsequent hydrolysis of compounds in a material leading to the release of volatile organic compounds.

Mesoporous silicas also have a very high surface area, open pore structure, uniform pore size and have been previously used as absorbents for environmentally hazardous chemicals, reaction catalysts and as chemical sensors (Kosuge et al., 2007). Thus there have been studies into the potential use of silicas as absorbers of VOCs. It has been stated that mesoporous silicas have a high natural affinity to benzene and for light hydrocabons (Kosuge et al., 2007). Such organic materials require further study in their applications in composite reinforcement, absorption characteristics and other industrial applications (Kosuge et al., 2007).

Nanoclays have also been evaluated for their adsorption capabilities. Nanoclays are already used as fillers to modify thermosetting resin for wood-based composite (Lei et al., 2008). Ashori and Nourbakhsh, (2009) studied the effects of layered silicate based nano-clay at different resin loadings (wt %) to reinforce MDF panels. The results showed that there is a significant improvement in bending strength and IB, with up to 6% loading of nano-clay. The addition of nano-clay also reduced thickness swell. Lei et al., (2008), also found that the addition of Na^{+}-montmorillonite (NaMMT) nanoclay, even in very small quantities, improved resin bonding properties and thus, panels mechanical properties. More importantly, it has been found that certain nano-clays will also reduce formaldehyde emissions. Nano-SiO_2 (silicone dioxide) combined with UF resin has been found to reduce formaldehyde emissions

from particleboard, plywood and MDF (Lin et al., 2006). Even at high F/U molar ratios the silicone-dioxide addition significantly reduced formaldehyde emissions in all three wood-based panels. This research opens up the potential of using nano-clays, especially alongside other additives and modifications to reduce formaldehyde and VOC emissions. There is scope for research into the use of nano-clay's to improve indoor air quality.

Graphite, a carbon nano-material, has also been investigated for its potential to absorb formaldehyde and VOCs. Graphite consists of one-atom thick sheet of carbon and these sheets are bonded in layers held by weak van der Waals forces. Since these are relatively weak, they allow a variety of molecules and ions to interlace between the graphite layers. Lee and Kim, (2012) tested four different types of graphite materials: natural graphite, expanded graphite, hammer mill graphite and fluid mill graphite. The absorption capabilities of each were examined using a thermal extractor for VOCs and 20L small chamber for formaldehyde. The results showed that all types of graphite were suitable for absorbing VOCs and formaldehyde. The highest absorption properties were observed in the hammer mill type graphite. These result from the porous structure and relatively large surface area. However, natural graphite was found to be the best at absorbing VOCs.

Organic

There has been considerable interest in utilising the vast swathes of agricultural wastes as an alternative use to burning or landfill (Bisanda et al., 2003). A main constituent of lignocellulosic material is cellulose, which is known to be a highly absorbent material (Tittarelli et al., 2015). There has been substantial research into the use of agricultural wastes as pollutant absorbers in many different forms.

Lignocellulosic waste

Buyuksari et al., (2010) and Ayrilmis et al., (2009) both looked into the use of stone pine (*Pinus pinea*) cones. In Turkey alone, stone pine forests cover 54,000 ha, yielding 3500 tonne of stone pine cones. Buyuksari et al., (2010) produced particleboards from pine (*Pinus negra*) and beech (*Fagus orientalis*) with fresh stone pine cones, added at levels of 10,20,30,40 and 50%. Results showed that despite a

reduction in MOE, MOR and IB mechanical properties, the MOE and MOR values of panels containing up to 30% pine cone, met the requirements for general purpose particleboard. Formaldehyde emissions decreased with increased cone addition, with 50% cone addition emitting the lowest concentrations at 1.99mg/100g compared to 2.48mg/100g for the 0% addition controls. Buyuksari et al., (2010) concluded that the high phenolic extractive content in the cones was responsible for absorbing the formaldehyde. Ayrilmis et al., (2009) also found that the addition of stone pine cone to particleboard slightly reduced the MOR, MOE and IB properties but increased thickness swell and water resistance. It was concluded that waste stone pine cone acts as a good scavenger to reduce formaldehyde emissions. Another advantage to using this agricultural waste is that *Pine pinea* is a widely consumed edible seed and, if used industrially, there would be no extra expense in collecting and drying the cones. Ayrilmis *et al* (2009) also found that the addition of Stone pine cone to particleboard slightly reduced MOR, MOE and IB properties but increased thickness swell and water resistance. It was concluded that waste Stone pine cone acts as a good scavenger to reduce formaldehyde emissions. Another advantage in using this agricultural waste is that *Pine pinea* is a widely consumed edible seed and, if used industrially, there would be no extra expense in collecting and drying the cones.

Edible nuts are grown and cultivated in a variety of climates around the world on different scales. They are globally popular and diverse in their origins, flavour, health benefits, harvesting methods and end use and can be divided into ground nuts and tree nuts. This enormous production of nuts every year generates a considerable amount of lignocellulosic waste. Table 5 summarises the cultivation, annual seed and waste production and uses of 6 globally popular edible nuts.

Table 5 Six major edible nuts, their source and annual production

Nut	Key points	Sourced	Annual production	Current use	Waste
Almonds (*Prunus dulcis*)	Ranked 1st in tree nut production[1].	Grown worldwide. North America, California greatest producer[4] (>637,000 tonnes/year)[3]	2.09 million tonnes[2]	Food source, mostly sold without shell.	0.7-1.5 million tonnes waste per year and has little industrial value[2]
Walnut (*Juglans regia*)	Ranked 2nd most popular tree nut[7].	17 major producers[5]. China largest producer (410,000 tonnes /year)[7], North America the 2nd (300,000 tonnes/year)[21] and Iran is the 3rd (150,000 tonnes/year)[5]	1.48 million tonnes[5]	Food source, oils and secondary oils[6]. Sold in and out of shell	Multitudinous uses from dye in cosmetics, used in insecticides, fillers, asphalt, glues[6] and improving tyre grip[5]
Pistachio (*Pistacia vera*)	11 species of pistachio but only *P. vera* is grown on commercial scale [6]	Grown mainly in Iran, Turkey and North America. Iran alone producing (>250,000 tonnes/year)[10,11]	489,000 tonnes[9]	Popular food source and antioxidant properties[8]. Sold in and out of shell	Little industrial value, sent to landfill or burnt[24] and small use in mordant[6] and colouring and glues[25]
Coconut	Salt tolerant	Indonesia is the leading	5.5 million tones[21]	Food, non-food	Husk used for rope and

(*Cocos nucifera*)	requiring constant supply of ground water[6], hence grown in coastal tropics	producer, followed by Philippines, India and Sri Lanka[21]. Malaysia alone requires 151,00ha of land for production[12]		products, cosmetics and oils.	matts and core can be used as peat substitute[23]. 13.6 – 18.14 million tonnes husk waste per annum[22]
Peanut or ground nut (*Arachis hypogaea*)	Most commercially important ground nut[13]. Ranked 2nd largest source of vegetable oil[6].	Grown worldwide. China 1st in production accounting for 40% of global production[14] (14.5 tonnes/year), followed by India (23%) [16].	32.22 million tonnes (including shell)[15]	Food source and vegetable oil. Sold in and out of shell	Largely sold in shell or sent to landfill
Sunflower seeds (*Helianthus annus*)	Ranked 3rd in oil production[19]	Grown worldwide. North Americaalone produces 1.72 million tonnes/year[19]	27 million tonnes[17](Almost exclusively cultivated for oil[18])	Food and oil. Sold largely in shell but also out of shell	Small value, sent to landfill or used as low grade roughage for livestock[19],

Data derived from: (Roux et al., 2001)[1], (Pirayesh and Khazaeian, 2012)[2], (Jayasena, 2016)[3], (Esfahlan et al., 2010)[4], (Malhotra, 2008)[5], (Wickens G E, 1995)[6], (Sze-Tao and Sathe, 2000)[7], (Gentile et al., 2007)[8], (Kahyaoglu, 2008)[9], (Kashaninejad et al., 2006)[10], (Razavi et al., 2007)[11], (Tan et al., 2008)[12], (Venkatachalam and Sathe, 2006)[13] (Diop et al., 2004)[14]. (Zhang et al., 2012)[15], (G. Zhang et al., 2013)[16], (Li et al., 2011)[17], (Hameed, 2008)[18], (Kamireddy et al., 2014)[19], (Sathe et al., 2009)[20], (Anirudhan and Sreekumari, 2011)[21], (van Dam et al., 2004)[22], (Konduru et al., 1999)[23], (Tavakoli Foroushani et al., 2016)[24], (Fadavi et al., 2013)

This enormous production of nuts every year generates a considerable amount of biowaste. Coconut production alone yields between 13.6-18.14 million tonnes of husk waste each year (van Dam et al., 2004). In Malaysia alone 151 000 ha of land is planted for coconut cultivation (2001) and each year 5280 Kg of husk waste is produced per hectare (Tan et al., 2008). Some of the biowaste produced does have a use however, shells such as the almond shell (Pirayesh and Khazaeian, 2012), sunflower seed (el-Halwany, 2013; Kamireddy et al., 2014) and pistachio nut shell (Tavakoli Foroushani et al., 2016) are considered to have little industrial value and are often sent into landfill or burnt as biofuel. Almond production annually produces 0.7-1.5 million tonnes of waste shell (Pirayesh and Khazaeian, 2012), which has little commercial or industrial value. However, lignocellulosic biowaste can be quite versatile in its use. Due to its extremely high lignin content, fibrous quality and shape, coconut has multiple uses (Mothé and Miranda, 2009; van Dam et al., 2004) for example door mats, matting, rope and cordage (van Dam et al., 2004; Wickens G E, 1995). Walnut shells can be dried, crushed into powder for dye, in make ups and refined for insecticides, fillers in plastics, asphalt roofing, glues or abrasive material in cleaning jet aircraft engines (Wickens G E, 1995). Pistachio nut shells can be used as a mordant (fixate of fabric dye) (Wickens G E, 1995) and crushed for colours, pesticides, glues, mineral oils and pulp production (Fadavi et al., 2013). Sunflower seed shells have little commercial value and become a disposal problem due to their low bulk density (Hameed, 2008) Onsite storage and transport becomes costly and impractical (Kamireddy et al., 2014). Often, this waste is used as low food grade roughage for livestock, bedding or composted (Kamireddy et al., 2014). Although sometimes burnt, it is not considered suitable for production as a biofuel in the form of pellets or briquettes as the shell contains a high silicon content. It also has a higher nitrogen content than wood and produces high quantities of pollutants when burnt, such as nitrogen oxides (Cosereanu et al., 2014).

Research has been conducted into more suitable uses such as a substrate for cultivating the edible fungus *Pleurotus ostreatus,* as they contain high amounts of protein, lipids and carbohydrates (Curvetto et al., 2002) and for particleboard production (Cosereanu et al., 2014; Gertjejansen et al., 1972). Waste shells from

nuts such as almond, pistachio, walnut and hazelnut have been used as bio-absorbents to treat contaminated water (Hameed, 2008; Kazemipour et al., 2008; Oguntimein, 2015). Pirayesh et al., (2013) studied the use of walnut and almond shells in particleboard, bonded with UF resin. The results revealed that with increasing shell concentration, formaldehyde emissions decreased and improved thickness swelling and water resistance, but the mechanical properties decreased. Walnut shell also contains high amounts of polar hydroxyl groups which are responsible for hydrogen bonds. These bonds affect adhesion and therefore, is partly responsible for lack of good adhesion between wood and shell (Pirayesh et al., 2013). Waste peanut and pistachio nut shells have also shown potential use as a bio-absorbent of pollutants such as heavy metals and dyes in aqueous solutions (Johns et al., 1998; Tavakoli Foroushani et al., 2016; Witek-Krowiak et al., 2011; Xu and Liu, 2008) although the shells do require a chemical activation. Research has also shown that coconut shells are suitable for binderless panel production (van Dam et al., 2004), which is of interest to the ecological and economical aspects.

However, not all lignocellulosic wastes have been found to be successful in reducing emissions and maintaining wood-based panel strength and mechanical properties.

Nemli and Çolakoğlu, (2005) looked into the use of mimosa bark added to black locust wood chips to produce particleboard. Previous work by Nemli et al., (2004) evaluated soaking wood chips for particleboard in mimosa bark extract solution, in the hope of reducing formaldehyde emissions. The treatment did prove effective in reducing formaldehyde emissions although at the cost of significantly reduce mechanical properties. The study by Nemli and Çolakoğlu, (2005) built upon this study of raw mimosa bark and found that, with a maximum addition of 6.25% to particleboard core did not affect the mechanical properties nor formaldehyde emissions. To reduce formaldehyde emissions from the particleboard, over 12% mimosa bark was required, however although again this significantly reduced the mechanical properties. It was concluded that further research was required to determine the most appropriate use of mimosa bark in reducing wood-based panel emissions.

Activated Carbons

Many organic materials have been studied for their potential as a source of activated carbons to remove pollutants from polluted water and atmosphere. Activated carbon fibres (ACFs) have shown great potential as formaldehyde and VOC scavengers (Rong et al., 2002a; Seo et al., 2009). Activated carbons have been used as adsorbents in various fields such as solvent recovery, petroleum refining, chemical processes and waste water treatment (Das et al., 2004; Mohamad Nor et al., 2013; Tanada et al., 1999). They have also been used in gas phase applications such as gas separation, catalysts, storage, purification and deodorisation of air (Mohamad Nor et al., 2013; Tanada et al., 1999). Activated carbons are characterised by their strong adsorption capacity due to their large internal surface area, porosity and high degree of surface reactivity (Mohamad Nor et al., 2013; Tanada et al., 1999; Tseng et al., 2015).

Mohamad Nor et al., (2013) conducted a review on activated carbons derived from lignocellulosic waste materials. The study was concluded that under appropriate activation conditions common pollutants, namely sulphur dioxide (SO_2), nitrogen dioxide (NO_2), hydrogen sulphide (H_2S) and other VOCs. It was concluded that with the large surface areas and high pore volumes generated with lignocellulosic activated carbons, they could be used as effective pollutant absorbers, with the added benefit of agricultural waste removal. Other agricultural wastes such as nut shells have shown their potential use as activated carbon for absorbing pollutants. Activated carbon produced from: walnut can be used as absorbent copper ions (Kim et al., 2001), hazelnut, apricot stone and almond can absorb heavy metals from waste water (Kazemipour et al., 2008), pistachio nut can remove organic compounds from air and water (Mohamad Nor et al., 2013; Tavakoli Foroushani et al., 2016), coconut waste can remove methylene blue in aqueous solutions (Tan et al., 2008), sunflower seed shell and peanut shells can act as an absorbent of CO_2 (Deng et al., 2015; el-Halwany, 2013) . The use of nut shell waste for use as an activated carbon has been well documented and shows huge potential as an effective absorber.

A study conducted by Boonamnuayvitaya et al., (2004) found that activated carbon from coffee residues absorbed formaldehyde in formalin due to the nitrogen

present on the carbon surface (Song et al., 2007). Kato et al., (2005) evaluated the adsorptive capabilities of moisture of activated charcoals produced from different materials. It was found that carbonised wood (*Quercus phillyraeoides*) charcoal and bamboo charcoal had different adsorption characteristics to activated charcoals. Activated charcoal moisture uptake was significantly greater than carbonised wood charcoal or bamboo charcoal. This high uptake of moisture could increase the number of VOC hydrolysing reactions if used as a VOC absorber. Bamboo charcoal was found to adsorb much higher amounts of formaldehyde than the other charcoal evaluated, due to its greater pore distribution and composition. This study highlighted that activated charcoal produced from different materials exhibit different pore structures and composition thus affecting is adsorption capabilities.

Activated carbons can also be derived from synthetic and inorganic materials. It has been found that porous carbons from polyacrylonitrile (PAN) have high formaldehyde adsorption capabilities as they have an abundance of nitrogen functionalities on the surface (Song et al., 2007). An experiment conducted by Song et al., 2007 showed that the pore structure, especially surface chemical composition, does influence adsorption capacity and PAN based AFCs showed the greatest ability to absorb formaldehyde due to its high quantities of nitrogen containing groups such as pyrrolic nitrogen and pyridinic nitrogen. Tseng et al., (2015) also suggested that activated carbons derived from synthetic materials could be produced with specific absorption characteristics by modifying the synthetic material during its production prior to carbonisation. Amine rich activated carbons produced from melamine formaldehyde and phenol formaldehyde resins could be specifically carbonised with nitrogen and carbon for adsorption specifically for carbons dioxide (CO_2) (Tseng et al., 2015). The study conducted by Tseng et al., (2015) showed that highly porous activated carbon could be produced with melamine modified phenol formaldehyde resin for CO_2 adsorption.

There are many advantages of using ACFs to absorb indoor pollutants. Its small diameter and porosity result in faster adsorption of VOCs compared to other commercially available absorbents such as zeolites and silica gels (Das et al., 2004). The structure of activated carbons gives it a more concentrated pore distribution, which give it a huge surface (Huang et al., 2007; Rong et al., 2002a). But if activated

carbons are exposed to high temperatures and the VOCs can be desorbed enabling the activated carbon to be reused (Das et al., 2004). How ACFs are prepared and what they are made from can influence the adsorption capabilities. ACFs activated by water or CO_2 are hydrophobic and therefore are only suitable for polar and polarisable molecules (Rong et al., 2002a). However, this can only be beneficial if certain VOCs are targeted. Rong et al., 2002 study showed that rayon based ACFs activated by air are good absorbers of formaldehyde due to the increased hydrogen bonding and increased surface area and total pore volume.

Activated carbons have also been added into existing construction materials. Kumar et al., (2013) explored the use of cheap activated charcoal as a filler resin for MDF panels. The activated charcoal was ground into a fine powder and mixed directly into UF resin and added in 3 concentrations, 0.2%, 0.5% and 1.04%. The results of using charcoal as a filler showed that filler increases cure times and mechanical strength properties increase. Additionally it is a cheap alternative to other fillers. The results also showed that the activation energy required was reduced with increasing the activated charcoal filler, thus requiring less energy in production the of activated carbons. More importantly, formaldehyde emissions decreased due to improved cross-linking in the resin, consequently improving mechanical properties. Seo et al., 2009 evaluated the absorption abilities of gypsum board made from activated carbon. The results showed that increasing proportion of activated carbon decreased VOC concentrations from gypsum board.

Activated carbons have also been added into cements. Cements are porous alkaline materials rich in calcium hydroxide ($Ca(OH)_2$) and calcium silicate hydrates (C-S-H) (Krou et al., 2015). Cements are characterised by high specific surface area and have previously been shown to adsorb nitrogen dioxide (NO_2) under ambient conditions (Krou et al., 2015). ACF can be added to cements to help remove ozone and NO_2 (Tittarelli et al., 2015). Krou et al., (2015) also evaluated the use of activated carbon in cement paste. The results obtained revealed that the activated carbon was able to significantly absorb toluene from the atmosphere. However, the activated carbon in hardened cement was unable to effectively absorb acetaldehyde, especially in the presence of CO_2 and high relative humidity. This

reveals that under certain conditions activated carbon is ineffective at absorbing some VOCs.

ACFs act as excellent sinks for air pollutants, however they do not break up or re-release pollutants, therefore adsorption saturation is quickly reached and the effectiveness of ACFs declines (Huang et al., 2007). There has been some research investigating how activated carbons can be improved to increase their service life and decrease desorption. (Tanada et al., (1999) studied the modification of activated carbon surface properties for selective adsorption and reactivity to formaldehyde. The study treated activated carbon with concentrated nitic acid and sulphuric acid for 24 hours, then reduced it down to iron powder and distilled in hydrochloric acid for 30 minutes and 60 minutes. The aim of this treatment was to increase the amino groups available on the activated carbon and subsequently increase formaldehyde adsorption. The results revealed that the treatment did increase the amount of amino groups and with increasing reaction times from 30 to 60 minutes, more amino groups were available and subsequently, greater amounts of formaldehyde could absorbed onto the activated carbon. Kazemipour et al., (2008) evaluated the effects of the length of carbonisation time and change in temperature on the effectiveness of activated carbons derived from various nut shell wastes. The results revealed that increasing or decreasing carbonisation time of the shells had no effect on the absorption properties but increasing temperature increased absorption properties. It was also noted that different carbonised waste shells were better at adsorbing some pollutants in waste water than others. Almond AC shell was found to be the best absorber of copper, hazelnut AC absorbed the greatest amount of cadmium, walnut AC absorbed the most zinc and pistachio AC the least of all pollutants. The difference observed is due to the waste shells individual composition. Hazelnut have a high carbon content, whereas walnut has a lower carbon and hydrogen content (Kazemipour et al., 2008). Such studies are important as they highlight that activated carbons derived from different sources will have varying adsorption properties. Therefore, when dealing with particular pollutants the correct activated carbon must be used to ensure maximum efficiency of adsorption.

Another lignocellulosic waste is pulp and paper sludge. The most common disposal method for waste paper sludge is landfilling, incineration and soil remediation (Migneault et al., 2011). However, as with most wastes, alternative disposal methods are being investigated for paper sludge due to costs, stricter regulations and public opposition (Migneault et al., 2011). Solid residue from the paper industry is what remains after cleaning waste water processes and largely consists of short cellulose fibres and inorganic components such as calcium carbonate (Ahmadi and Al-Khaja, 2001; Kim et al., 2009; Migneault et al., 2011). Migneault et al., (2011) investigated the use of waste paper sludge as a formaldehyde scavenger in MDF panels. The results revealed that formaldehyde emissions from the MDF panels, containing the sludge were reduced by 60% compared to unmodified MDF panels, without compromising internal bond strength. The reduction of formaldehyde emissions is due to the high nitrogen content of the waste sludge due to the high presence of proteins, which contain amine and amide groups that react and bind to the formaldehyde (Migneault et al., 2011).

Protein Wastes

Other sources of organic materials are also being studied for their potential use as formaldehyde absorbents. Organic, protein based materials such as sheep wool has been ear-marked for such studies. Wool fibre contains many amino groups and it is these amino groups than enable the wool fibres to absorb and bind to formaldehyde (Middlebrook, 1949). Wool has a molecular structure and a unique physical and chemical composition that make it an effective, natural absorber of formaldehyde (Huang et al., 2007; Salthammer et al., 2010). Wool has also been known to break up organic contaminants into harmless compounds to humans (Huang et al., 2007). Wool fibres are able to absorb formaldehyde in two ways; physi-sorption whereby the formaldehyde is sorbed into micro pores of the fibre structure and chemi-sorption where the formaldehyde forms a stable bond to the wool (Curling et al., 2012). However, under certain environmental conditions, such as high relative humidity, this captured formaldehyde can be re-released into the atmosphere, acting as a buffer rather than a permanent sink (Curling et al., 2012).

Chitosan has also shown potential as an effective absorber of pollutants (Du et al., 2009; Dutkiewicz, 1983; Mcafee et al., 2001; Monier, 2012). Monier, (2012) found that chitosan, chemically modified with 2-thioglyceraldehyde cross-linked with formaldehyde, in a resin form, which could then be used to absorb toxic metal ions mercuric ion (Hg^{2+}), copper ion (Cu^{2+}) and zinc ion (Zn^{2+}) from aqueous solutions. Miretzky and Cirelli, (2010) also noted the capacity of chitosan to absorb mercury in water due to its composition of amino and hydroxyl groups.

However, despite the vast array of research and development into reducing formaldehyde and VOC emissions, the advancement of such technologies relies upon industries and manufacturers willingness to take on such modifications to products and possibly modify productions processes at a cost.

1.5.1.4 Government and Organisations

On a larger scale, Governments should ensure compliance to building and ventilation regulations, sponsor research, establish mandatory guidelines, code and performance standards of buildings and materials. Governments should also provide adequate information to local governments and advise on public safety, construction materials and practices and available monitoring equipment (Spengler and Sexton, 1983). Many European and national activities have been ongoing to develop guidelines for emissions and indoor air quality.

The world Health Organisation (WHO) published the WHO Guidelines for Indoor Air Quality: Selected Pollutants. This document presents guidelines for 9 chemicals (benzene, carbon monoxide, formaldehyde, naphthalene, nitrogen dioxide, polycyclic aromatic hydrocarbons, radon, trichloroethylene and tetrachloroethylene) commonly present in indoor air that pose a risk to human health (WHO, 2010). However, the guidelines developed have been based on the toxicological and epidemiological data available, but there are other chemical compounds found within the indoor environment that can pose as a risk to human health.

In contrast to focusing on individual compounds, the European Commission published the EU Directive 2008/50/EC on ambient air quality and clean air for

Europe. This directive recognises the need to minimise emissions of hazardous pollutants, the effects on human health and the need to revise previous Directives to incorporate the latest in research findings. However, this directive focuses on outdoor air pollution. Table 6 lists four EU Directives that do consider VOCs and the need for mitigation procedures.

Table 6: European Directives

Directive	**Title**
2010/31/EU	The energy performance of buildings
2004/42/CE	Limitation of emissions of volatile organic compounds due to the use of organic solvents in certain paints and varnishes and vehicle refinishing products and amending Directive 1999/13/EC
2001/81/EC	National emission ceilings for certain atmospheric pollutants
1999/13/EC	Limitation of emissions of ***volatile organic compounds*** due to the use of ***organic*** solvents in certain activities and installations
2004/42/EC	Limitation of emissions of ***volatile organic compounds***
2016/1332/EU	Establishing the ecological criteria for the award of the EU Ecolabel for furniture (notified under document C (2016) 4778) (Text with EEA relevance)
94/63/EC	Control of volatile organic compound (***VOC***) emissions resulting from the storage of petrol and its distribution from terminals to service stations

The European directive 210/31/EU on the energy performance of buildings is particularly important as it outlines the requirements for new, existing and majorly renovated buildings to obtain the Energy Performance Certificate. Most importantly, it includes a list of criteria other than energy efficiency that the building must meet, including indoor climate conditions, indoor air quality and ventilation. The EU Environment and Health Action Plan 2004-2010 was developed with the World Health Organisation and considered indoor air quality. It brought about the end of smoking in indoor public spaces, highlighted the of multitude

sources of pollutants affecting air quality ranging from combustion to furniture to humans and emphasising a call for research on the impact of construction materials on human health. Governments and organisations should provide further research funding on materials VOC adsorption and emission properties and the physical, chemical and environmental factors that influence these in order to develop adequate and appropriate guidelines and standard methods (Wolkoff, 1998)

Some countries have passed laws to control the release of formaldehyde by developing standards for limiting its emissions from wood-based products, a main source for formaldehyde. Table 7 shows the current standards used in Europe, Australia and New Zealand, United States of America and Japan (Salem and Böhm, 2013). In Europe, this regulation is called the E1-Emissions class and is based on a number of European testing standards, which require the formaldehyde emission of a product be less than 0.1 mg m^{-3}.

A new concept called 'organic compound in indoor air' (OCIA) has been developed that considered individual compounds and includes biological organic compounds, non-proteins and non-glucans (provided they are in gaseous form) in the indoor environment and how they influence air quality (Wolkoff, 2003). One major improvement of OCIA is that its definition of what causes poor indoor air quality is it is broader than compounds defined by WHO (1989).

Table 7: Eight Current formaldehyde emissions standards for wood-based panels around the world (Salem and Böhm, 2013)

Country	Standard	Test Method	Board Class	Limit value
Europe	EN 13986	EN 717-1 EN 120	E1 -PB, MDF, OSB	≤ 0.1 ppm ≤ 8 mg/100g of oven dry board
		EN 717-1 EN 717-2	E1 - PLW	≤ 0.1 ppm ≤ 3.5 mg/(h.m^2)
		EN 717-1 EN 120	E2 - PB, MDF, OSB	> 0.1 ppm > 8 ≤ 30 mg/g (oven dry)
		EN 717-1 EN 717-2	E2 - - PLW	> 0.1 ppm > 3.5 ≤ 8.0 mg/(h.m^2)0.1 ppm
Australia & New Zealand	AS/NZS 1859-1 & 2	AS/NZS 4266.16 (desiccator)	E0 - PB, MDF	≤ 0.5 mg/L
			E1 - PB	≤ 1.5 mg/L
			E1 - MDF	≤ 1.0 mg/L
			E2 - PB, MDF	≤ 4.5 mg/L
USA	ANSI A 208.1 & 2	ASTM E1333 (large chamber)	PB	≤ 0.18 or 0.09 ppm
			MDF	≤ 0.21 or 0.11 ppm
Japan	JIS A 5908 & 5905	JIS A 1460 (desiccator)	F**	≤ 1.5 mg/L
			F***/"E0"	≤ 0.5 mg/L
			F****/"SE0"	≤ 0.3 mg/L

Labelling schemes are voluntary but have contributed to the development of low emission products (Yrieix et al., 2010). Some European member states have established mandatory requirements on VOC emissions from building products. Germany launched the AgBB (Ausschuss zur gesundheitlichen Bewertung von

Bauprodukten) scheme in the aim to control potential indoor emissions sources such as flooring (Allen et al., 2016; Makowski and Ohlmeyer, 2005; Roffael, 2006; Yrieix et al., 2010). Its main task is to develop a uniform health-related assessment scheme for products that potentially emit VOC that maybe harmful to human health. However, the testing involved evaluates a single product under chamber conditions, often, in real-world scenarios, the emission profile witnessed are quite different due to VOC to VOC and VOC to materials reactions (Uhde and Salthammer, 2007).

Such labelling schemes aid developers and designers in selecting appropriate construction and insulation materials and encourage manufacturers to produce low emitting products. Other labelling schemes include the Indoor Climate Labelling Scheme in Denmark and Norway based on odour or airway irritation thresholds, the B&Q Paint policy Scheme in United Kingdom which labels products with the percentage VOC emission, the Finnish Labelling Scheme with different categories (M1-M3) based on emissions of formaldehyde, ammonia, TVOC and carcinogenic compounds and the German Association of Wallcovering Manufacturers that limits formaldehyde air emissions to $<60\mu/m^3$ from building products and limits heavy metals (Wolkoff, 2003). In the majority of schemes, the only parameter measured and reported is the TVOC and no specific VOC is targeted (Wolkoff, 2003). This has its advantages as it reducing the concentration of TVOCs in the indoor environment. However, this should be used with caution as it can mask some more hazardous VOC which may remain at high concentrations and only less volatile VOCs concentrations decrease (Wolkoff, 2003).

1.6 Mycology

During the service life of buildings, bio based construction materials could be at risk of biodeterioration. Wood and wood based materials are particularly vulnerable to microbiological attack resulting in biodegradation. Biodegradation of materials consists of three major stages: biodeterioration, biofragmentation and assimilation (Falkiewicz-Dulik et al., 2015). The term “biodeterioration” is applied differently to biodegradable and durable materials. Biodeterioration of durable polymeric materials, for example, that have a long service life, may only affect the materials’

surface. In contrast, for biodegradable materials with a shorter service life, biodeterioration results in fragmentation of the material (Falkiewicz-Dulik et al., 2015). In both cases the biodeterioration may be due to similar biotic and abiotic processes. Therefore, when considering new novel materials the effects and consequences of all forms of biodeterioration must be taken into consideration. The most common form of biodeterioration results from biotic processes from microorganisms. Saprophytic organisms such as mould and decay fungi are the main agents responsible for the decomposition and recycling of dead organic matter and as such, are important organisms in nutrient cycles.

The classification of all living organisms is organised into the taxonomic system separated into; kingdoms, phylum, class, order, family, genus and species. Fungi make up one entire kingdom. Today, over 100,000 species have been identified and described although it is estimated that there are over 5 million species in existence that have not been officially classified (Viegas et al., 2015). There has been a growing recognition that there is a biological aspect to poor indoor air quality and consideration must be given to its involvement of microbiological activity of moulds and fungi (Petry et al., 2014; Viegas et al., 2015; WHO, 2009; Wolkoff, 2003). Microbial pollution involves hundreds of species of fungi and moulds that are able to colonise and grow on indoor surfaces.

Microorganisms can be transported into and around buildings on the surface of new materials, clothing, pets and can penetrate buildings though active or passive ventilation (WHO, 2009). Subsequently, fungal spores are found in every building on every surface and if conditions are adequate, the spores will readily germinate and grow on practically any surface. Moulds will readily colonise lignocellulosic materials but can also attack synthetic floor coverings, airplane fuels, oils, glues, paints and textiles (Pasanen et al., 1992; Schmidt, 2006). The presence of the multitude of fungi and mould species in indoor environments is largely attributed to excess moisture, dampness, lack of appropriate heating, inadequate ventilation and the enormous array of ‘edible’ materials within one building (WHO, 2009).

Microbiology growth within buildings has two major effects on the building and its occupants. The first is that fungal species (decay fungi) will degrade the substrate they have colonised and subsequently reduce the properties of the material and in

severe cases lead to structural failures (Singh et al., 2010). The most common and most destructive wood decaying fungus in buildings is *Serpula lacrymans,* which can grow very quickly, spreading throughout a building from one timber to another causing devastating effects (WHO, 2009). The second impact of fungi and moulds species is that they will also emit spores, cells fragments and volatile organic compounds that will pollute the indoor air and affect human health (Segers et al., 2016; WHO, 2009). Asthmatic and allergic individuals are particularly at risk, as fungi and moulds can activate the immune system (Nielsen, 2003; Segers et al., 2016). This is an added complication for individuals that are immune suppressed (Tudge, 2002).

1.7 Fungal Structures

Fungi are one of the 6 taxonomic kingdoms of which there are two major phylum groups: Ascomycota and Basidiomycota (Falkiewicz-Dulik et al., 2015). Ascomycota phylum contains over 60,000 classified species, however it is expected to be well over 1 million but only 5% of species have been classified so far (Falkiewicz-Dulik et al., 2015). Order Ascomycotina is a distinct group of fungi that are often identified by their more unusual structures. and consists of moulds, filamentous ascomycetes and true yeasts (Tudge, 2002). Basidiomycota are fungi that inhabit dead wood habitats and there are at least 30,000 known species to date (Falkiewicz-Dulik et al., 2015). Basidiomycetes contain the typical mushroom-shaped fungi, with gills pores and a central stem (Phillips, 2006). The basidiomycetes are particularly efficient at decaying wood matter, especially degradation of lignin (Falkiewicz-Dulik et al., 2015; Tudge, 2002). For the purpose of this study, the literature will focus on saprotrophic fungi that obtain their nutrients from dead and decaying organic matter.

1.7.1 Hyphae

The type of hyphae is characteristic of groups of fungi. In Ascomycetes and basidiomycetes groups, the fungi form septate hyphae. These hyphae are segmented into individual compartments with perforations allowing the movement of cytoplasm and organelles from one segment of hyphae to the next (Viegas et al.,

2015). The structure of the septa is characteristic of specific groups of fungi and can be used for species identification. The growth of the hyphae or elongation of cell occurs at the tip of the hyphae where the fungal cell wall material is deposited. This type of growth is referred to as 'apical growth' and results in hyphae that are uniform in diameter and if unconstrained, will form a circular colony of indeterminate length (Viegas et al., 2015). The small structure of the hyphae is what enables the hyphae to penetrate wood cell walls and aids in its survival in dry conditions.

As hyphae grow they will branch behind the growing tip (apical) to form a large network of hyphae. These hyphae can be spread thinly or clumped together to form mycelium.

1.7.2 Spores

A fungal spore is a reproductive single cellular body, with a thin wall that lacks an embryo.

Asexual spores are formed from hyphae and produced in large numbers. These spores are characteristically very small and suited for aerial dispersion, by insects or arthropods. These spores may also have slightly thicker walls to protect them from environmental extremes. Asexual spores are produced on the typical fruiting body of fungi and most commonly produced during autumnal conditions. A spore will germinate wherever it lands when environmental conditions are favourable and produce hyphae and eventually branch to form mycelium. At this stage, they are named 'monokaryotic' as they contain only one nuclei. Unique to ascomycetes and basidiomycetes, the hyphae fuse and exchange nuclei beomcing 'dikaryotic'.

Ascomycota are characterised by the production of sexual spores in sac like structures called the ascus (plural asci). Within the ascus, the asco-spores can be loose (naked) or encased within the ascus in a protective tightly-woven hyphal tissue called the ascocarp or ascoma (Viegas et al., 2015). The structural morphology of the sporangia is important for identifying ascomycete species. Asexual reproduction of ascomycetes is by the formation of branching structures called conidiophores, which bare conidia in which multinucleate spores are produced.

Basidiomycetes are characterised by their basidiomata, the fruiting body or the mushroom we are all most familiar with. During sexual reproduction these basidiomata support the basidia. From these basidia, basidio-spores are produced externally on fine extensions of the basidium. Figure 7 depicts the sexual spore production and life cycle of basidiomycetes.

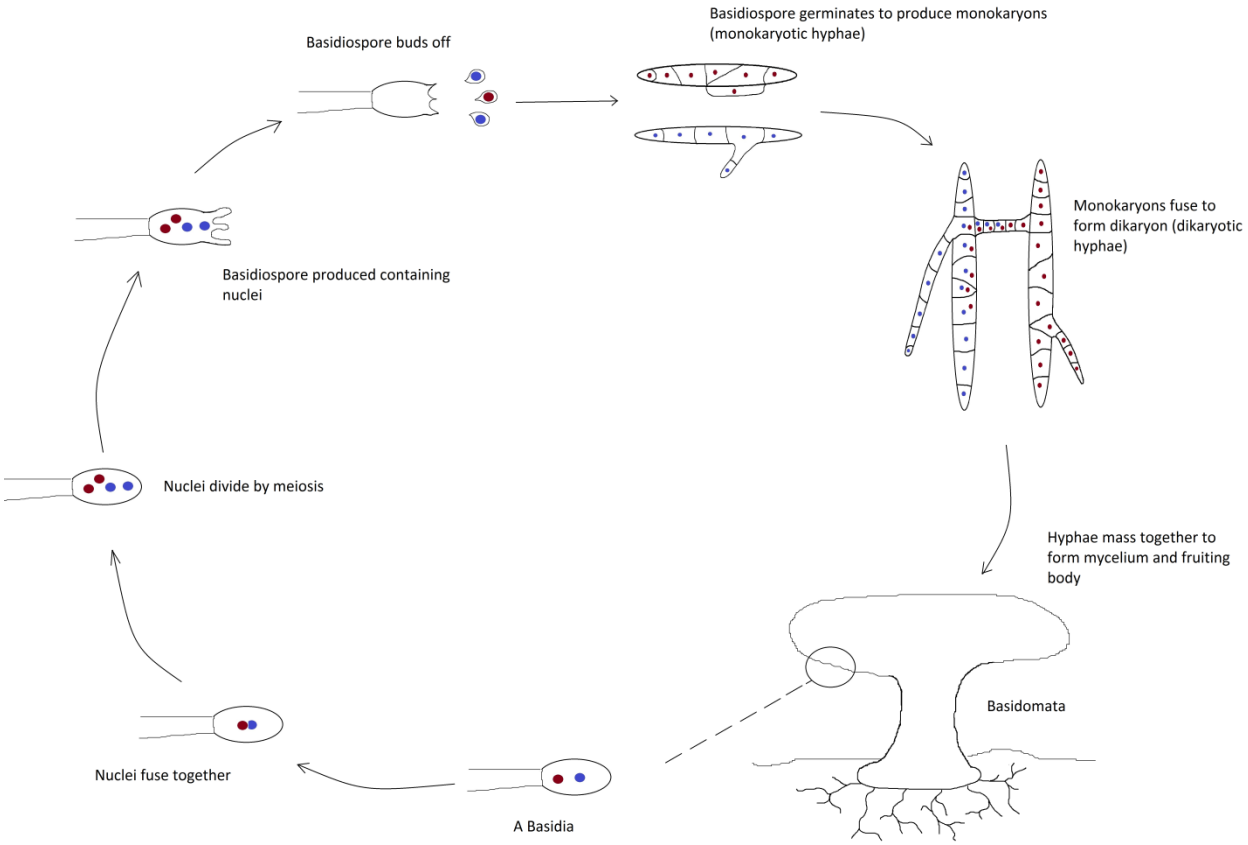


Figure 7: Basidiomycete sexual spore production

1.8 Growth conditions

The ability to attack a wide variety of materials is enabled by the variety of physiological responses demonstrated by mould fungi with regards to temperature, water activity, relative humidity and pH (Schmidt, 2006).

1.8.1 Oxygen

The vast majority of fungal species require oxygen to survive. Oxygen is used for oxidative metabolism to generate energy (Viegas et al., 2015). However for

biosynthesis of sterols and unsaturated fatty acids, oxygen is not required and most fungi can survive in anaerobic and anaerobic conditions (Viegas et al., 2015). The survival of fungi in anaerobic conditions depends on the fungal species (Scheffer, 1986) and some are better adapted to endure anaerobic conditions than others.

1.8.2 Temperature

Temperatures affect the rate of chemicals reactions. Increasing temperatures increased reaction rates and to some extent, microbial respiration and wood breakdown. Fungi can be classified into temperature classes. Mesophilic fungi are the most common, experiencing optimal growth at temperatures between 15-35°C (Viegas et al., 2015). Few species such as *Mortierella minutissima can survive and grow well at temperatures at 15*°C or below, these species are called Psychrotrophs (Robinson, 2001; Trytek and Fiedurek, 2005). Thermophilic fungi are fungi such as *Thermoascus aurantiacus* that can survive temperatures over 50°C and extreme thermophiles can withstand temperatures in excess of 60°C (Kalogeris et al., 2003; Maheshwari et al., 2000). When outside optimal growing temperatures fungal species become dormant or inactive and are only killed when temperatures exceed a species limitations and are maintained for long periods of time (Viegas et al., 2015). Concerning indoor environments, most fungi are mesophiles and their ability to withstand short periods of either high or low extremes becomes more important. On some wood surfaces such as building cladding, surface temperatures can reach extreme temperatures (70°C) during the summer season. Therefore the ability of a fungal species to survive such conditions for short lengths of time is important.

The spores of fungi can also survive exposure to extremes of temperature when dry. This ability is referred to as thermostability and is found widely among fungi (Viegas et al., 2015). Fungi that function in arid conditions such as *Trichocomaceae* and *Byssochlamys* are highly heat resistant and their ascospores can withstand temperatures of 120°C (Viegas et al., 2015).

Most fungi and moulds are content to grow at a range between 10-35°C and buildings support these ideal temperatures for mould and fungal growth (Singh et al., 2010). Therefore when considering indoor conditions, temperature is not

considered a limiting factor for growth but it can effect growth rates and the production of certain allergens and metabolites (WHO, 2009).

1.8.3 Water

All living organisms require water to survive as all life is comprised of water. Moisture availability is a critical factor for fungal and mould growth (Nielsen, 2003; Schmidt, 2007; van Laarhoven et al., 2015; WHO, 2009). Therefore, growth is predominantly controlled by moisture and thus species like moulds are most commonly found in areas of high humidity such as bathrooms and kitchens (Nielsen et al., 2004; Pasanen et al., 1992; Schmidt, 2006). Water is vital for fungal growth as water is the medium in which biological reactions occur, inside and outside of the fungi cells. The water also carries enzymes and other degradative agents to the substrate cell wall. The substrate's higher moisture content results in earlier colonisation and higher hyphal extension rates (growth rate) of fungi (van Laarhoven et al., 2015).

Concerning wood and wood-based materials, a moisture content of 20% or less can be considered as a general limit below which decay cannot occur, although there will be exceptions (Rowell, 2012). However distribution of water in wood is not uniform and fungi can infect a piece of wood. For most decay species, free water is required and the 20% figure is just below fibre saturation point of most wood species. Thus this figure should be taken as indicative only. Water in wood exists as bound or hygrscopic water within the cell wall due to hydrogen bonding of hydroxyl groups in cellulose and hemicelluloses (Schmidt, 2007). It also exists as free or capillary water in liquid form in the cell lumen and other holes such as pits in the wood tissue (Schmidt, 2007). Natural fibres are hygroscopic because their cell walls contain high amounts of water sorption sites (hydroxyl groups) and can expand to accommodate the water (Xie et al., 2010). This expansion creates space whereby reactions can take place, within the cell wall. The moisture content, free water, also influences the types and activity of any fungi present on or in the wood (Rowell, 2012). When a wood cell is saturated with water the amount of free water in the cell lumen can increase so much that fungal growth is inhibited. The amount of free water in the cell lumen influences diffusive gaseous exchange within the wood and

with the outside. Fungi respire, consuming oxygen as they grow and accumulate carbon dioxide. This build-up of carbon dioxide can occur at a much faster rate if the wood cell is saturated, as oxygen diffusion is much slower in water than air. Essentially the wood is too wet for optimal growth (Rowell, 2012). Although oxygen levels are reduced not all fungi species die but become dormant or inactive and will resume functional growth as the wood dries.

In the context of wood lumen saturation, density must also be considered as wood species have varying density. Wood species of high density have inherently lower lumen space and the effect of water filling the lumen is more pronounced at lower moisture contents. Therefore, some wood species can have a fibre saturation point at above 20%.

1.8.3.1 Moisture

Fungal and mould species that grow on any given substrate is dependent on the water activity (liquid water) of the substrate and their individual moisture requirements. Water activity (a_w) is a measure of the available water and is defined as the ratio of vapour pressure above a substrate relative to that above pure water measured at the same temperature and pressure (WHO, 2009). Fungal protoplasm has a a_w of its own and for fungi to be able to absorb water, the substrate must have a greater a_w than itself as water moves from high a_w to low a_w (van Laarhoven et al., 2015). Fungi and moulds can be categorised based on their water requirements. Primary colonisers require very little available water to colonise and grow, less than 0.8 a_w (Nielsen, 2003). Primary colonisers include species such as; *Aspergillus versicolor* (Górny, 2004), *Paecilomyces variotii* (Górny, 2004) and *Penicillium rubens* (WHO, 2009). Fungal species that can survive very dry conditions and a water activity as low as 0.6, are classed as xerophyilic organisms (Viegas et al., 2015). Secondary colonisers (phylloplane fungi) will grow at a a_w 0.8-0.9 such as *Cladosporium sphaerospermum* (Górny, 2004) and *Alternaria alternata* (Šegvić Klarić et al., 2007). Tertiary colonisers require the highest a_w of at least 0.9 for spores to germinate and start any mycelial growth (WHO, 2009). Tertiary colonisers include *Chaetomium globosum* (Šegvić Klarić et al., 2007) and *Trichoderma virens* (Górny, 2004). The presence of tertiary colonisers within buildings indicates a

serious condensation problem or repeated water damage, whereas primary colonisers are quite common on surfaces in areas of high humidity (WHO, 2009). Condensation problems within buildings arise from poor ventilation or water damage or leaks or ground water intrusion (Schmidt, 2006; WHO, 2009). Inorganic materials, comprised of trace amounts of organic materials can support growth if water activity is high enough (a_w 0.9-0.95) (Nielsen, 2003). Therefore, house dampness is a significant contributor to the presence of fungal growth, spores, fragments and subsequent allergens, mycotoxin and metabolite production (WHO, 2009). However, xerophilic moulds are also common in indoor environments but can often be overlooked especially using detection techniques that use high a_w isolation media (Viegas et al., 2015).

1.8.3.2 Relative Humidity (RH)

When considering the indoor environment and moisture availability, the relative humidity (water vapour) becomes a separate limiting factor for fungal growth (van Laarhoven et al., 2015). Relative humidity can be higher on colder, internal surfaces than the average of the room RH (WHO, 2009). When a porous material is exposed to vapour, water will penetrate into the pores via and adsorption and capillary condensation (van Laarhoven et al., 2015). Therefore a material will experience changes in its surface moisture content and affect fungal colonisation and growth. The optimal RH for fungal growth has been disputed in many studies. It is considered that the optimal range of relative humidity is between 70-90% for fungal growth on building materials (A. L. Pasanen et al., 2000). According to the World Health Organisation, RH should be maintained below 75% RH to limit fungal growth (WHO, 2009). Some studies report that RH as low as 65% RH is enough to encourage mould growth in the built environment (Singh et al., 2010). However, in real life scenarios RH and temperature on surfaces and in building structures change all the time, thus mould formation is a time-dependant process (WHO, 2009). Therefore a single limit value is inadequate for modelling fungal growth on indoor materials and to truly describe fungal growth and formation, dynamic models are needed to account for the effects of fluctuating RH and temperature, over a period of time (WHO, 2009). It is agreed that for most fungal species the

critical RH for fungal growth on wood and wood-based materials is between 75-80% RH and increasing RH results in an increase of metabolic activity of fungal cells, increasing growth and establishment (Segers et al., 2016; WHO, 2009).

As the relative humidity of an indoor environment can vary drastically during the year, day and between days, fungi and mould species have adapted to withstand changing conditions (Segers et al., 2016). As such, fungi and specifically of interest, mould species respond differently to changes in RH. Therefore it is vital to understand how species of fungi respond to changes in water availability if we hope to minimise and prevent growth and subsequent air pollution. Some mould species can survive for extended periods of time at low RH and resume healthy growth once conditions are favourable again (Segers et al., 2016). The conidia of *Aspergillus fumigatus* have been reported to survive a year, dormant, in dry conditions and still achieve full germination once conditions became more favourable (Lamarre et al., 2008).

The speed at which the relative humidity of an environment changes can also affect mould growth and survival rates at less than favourable conditions. Species such as *Talaromyces* and *Neosartorya* have been found to survive better when harshly dried to very low RH than when dried in ambient air (Wyatt et al., 2015). Segers et al., (2016) studied humidity dynamics on mould species *Cladosporium halotolerans, Aspergillus niger* and *Penicillium rubens.* It was reported that *A. niger* was able to grow at a lower a_w of 0.8 at 25°C than *C. halotolerans* and *P. rubens* (Segers et al., 2016). The mould species were then removed from conditions of 96% RH to conditions of 33% RH for one week. The results revealed that *C. halotolerans* was able to survive at lower RH and *A. niger* was not, despite its ability to grow at a lower a_w. Another example is the relationship between *Penicillium chrysogenum* and *Cladosporium sphaerospermum.* It has been shown that *C. sphaerospermum* is known to out-compete *P. chrysogenum* on various plasterboards materials, paints and plaster under variable water activity (a_w). However the relationship reversed when a_w is constant (Nielsen, 2003)

The survival of moulds is also dependant on how well their cells can withstand the sudden influx of moisture once RH conditions are more favourable again (Segers et al., 2016). Without adequate rigid structure, the cell walls may burst and fragment.

Segers et al., (2016) study also revealed that *C. halotolerans* had a more rigid cell wall structure due its composition. The *C. halotolerans* cell wall contains the pigment melanin, which is absent in other species such as *P. rubens*. The formation of enlarged cells with strengthened pigmented cell walls in the centre of a colony and the formation of hyphal bundles aid in preventing rupture during sudden humidity changes (Segers et al., 2016). This ability of *C. halotolerans* to cope with sudden dynamic changes in humidity is an ecological trait of this type of fungus. *C. halotolerans* is a phylloplane fungi (fungi that grow on leaves) and these fungi have evolved to endure highly dynamic changes in temperature, dew formation, sunlight and precipitation. As such, phylloplane fungi can restore growth a few minutes after rehydration following a drying period for up to 3 weeks (Segers et al., 2016). Other phylloplane fungi species include; *Alternaria, Aureobasidium, Phoma* and *Ulocladium* (Nielsen, 2003). The melanin in the cell walls provide protection from UV radiation but as UV radiation is less of a concern in indoor environments, the pigment acts more to prevent bursting and protection against reactive molecules (Segers et al., 2016).

The importance of this study shows that fungal species behave differently in dynamic moisture conditions and that calculations of a_w is not always enough to predict the responses of moulds to humidity changes. However, on a material surface, temperature, moisture content and ventilation can combine to generate micro-climates with a very high a_w in a room of low RH (Nielsen, 2003). Therefore, predictions must encompass both moisture content and relative humidity.

1.8.4 Nutrients

Unlike plant life, fungi use organic matter as their carbon source breaking the substrate down and assimilating carbohydrates (Viegas et al., 2015). Fungi and moulds are well evolved to derive their required nutrients from a diverse range of substrates from animal matter, plants, house dust, oils, paints, paper products, fabrics and construction materials. Therefore nutrients are not considered a limiting factor for indoor fungal growth (WHO, 2009). Where they get their nutrients from depends on the species of fungi; Saprophytic fungi obtain their nutrients from dead organic matter and parasitic fungi obtain nutrients by feeding on other living

organisms (usually plants) thus causing diseases. Moulds derive nutrition from wood by breaking down the storage compounds like starch into simple sugars, from the parenchyma cells. Decay fungi are readily capable of solubilising structural polysaccharides components of the cell walls. Decay fungi then absorb soluble carbohydrates utilising them to breakdown insoluble carbohydrates such as starches, cellulose and hemicelluloses and complex hydrocarbons such as lignin (Viegas et al., 2015).

Fungi also require mineral nutrients such as nitrogen, potassium, magnesium, copper and zinc. Such minerals are found in relatively low quantities in wood but they may be supplied by the surrounding environment or symbiotically from other living-organisms. Soluble nitrogen is the major limiting mineral for decay fungi. Nitrogen is present in proteins of wood, which, with sugars, are stored in the parenchyma cells. Fungal mycelium has a high nitrogen content compared to wood and nitrogen availability plays an important role in the growth of wood inhabiting fungi and their in their competitiveness. Some fungi are capable of actively conserving and recycling their cellular nitrogen. It should be also noted that high concentrations of some minerals e.g. copper and zinc, are toxic to fungi and thus have been used as the active ingredients in some wood preservatives.

1.8.5 pH

For the vast majority of fungal species, the optimal pH range for maximum growth and sporulation is between 5.5 and 6.5 (Viegas et al., 2015). The hydrogen environment of fungi is difficult to study because fungi change the pH of their environment as they grow because they produce acid, lowering substrate pH (Viegas et al., 2015). Wood decay fungi that cause brown rot, produce large amounts of oxalic acid and acidify their environment as they grow (Schmidt, 2007) with the oxalic acid acting as a catalysts for the hydrolytic breakdown of wood polysaccharides, breaking down hemicellulose and amorphous cellulose (Schmidt, 2007). Nonetheless, pH is an important factor as it influences mineral availability, enzyme activity, germination and membrane function (Magan and Lacey, 1984).

1.8.6 Light

Light is important to all life as an environmental signal for development and physiological changes. Although overall light does not play a major role in metabolism or growth of fungi it does have a number of effects on fungi (Viegas et al., 2015). Electrical signals related to wavelength and intensity, have been detected in response to light excitation of the fungus *Phycomyces blakesleeanus* (Mogus and Wolken, 1974). Light can also have morphological effects on basidiomycete fungi at a molecular level and stimulate the development of reproductive structures of other species such as *Aspergillus nidulans* (Velmurugan et al., 2010). In some fungi, some secondary metabolites are regulated by blue light by inhibiting mycotoxin production (Häggblom and Unestam, 1979). Light can also slightly alter the type and structure of morphology of pigments within fungal cells produced for protection from UV radiation (Cohen, 1967). Different wavelengths (colours) of light can affect the growth of different fungi species and to a varying extent. Velmurugan et al., (2010) reported that red light increased biomass production of 5 different fungal species and green and yellow light showed the least increase in biomass production. The study also revealed that blue light had an impact on only 2 of the 5 fungi in increasing biomass. This shows that different light conditions and wavelengths can influence fungi growth in different ways but light is not a limiting factor for fungi growth.

1.9 Wood decay and degradation

Wood decay fungi are considered to be the most economically important wood inhabiting fungi due to the destructive threat they pose (Schmidt, 2007). It was estimated in 1977 in the UK alone wood decaying fungi damaged £3 million worth of timber structures per week! (Schmidt, 2007). In the northern hemisphere, coniferous soft woods are the main source of interior structural timber and wood based products (Schmidt, 2007).

1.9.1 The nature of wood

Wood is a natural material found within the trunk of a tree and is responsible for the conduction of mineral solutions and crown support. The wood of the trunk can

be distinguished from the pith by the presence of growth rings, which extend the entire length of a tree. Figure 8 depicts the main components of a tree stem.

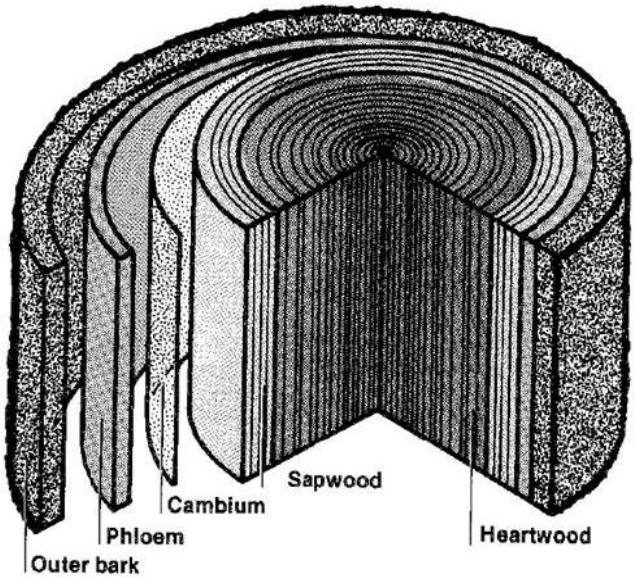


Figure 8: The main parts of a tree stem (Haygreen and Bowyer, 1982)

The growth rings are evident because of the wood produced in the early growing season are characteristically different from wood produced later (Desch and Dinwoodie, 1996). Earlywood is characteristically softer and more porous as the cells produced have thinner cell walls, large lumens and radial diameter. Latewood is the opposite, thicker cell walls and reduced lumen size result in denser wood (Haygreen and Bowyer, 1982). Figure 9 shows an illustration of a wood segment showing the principle structure.

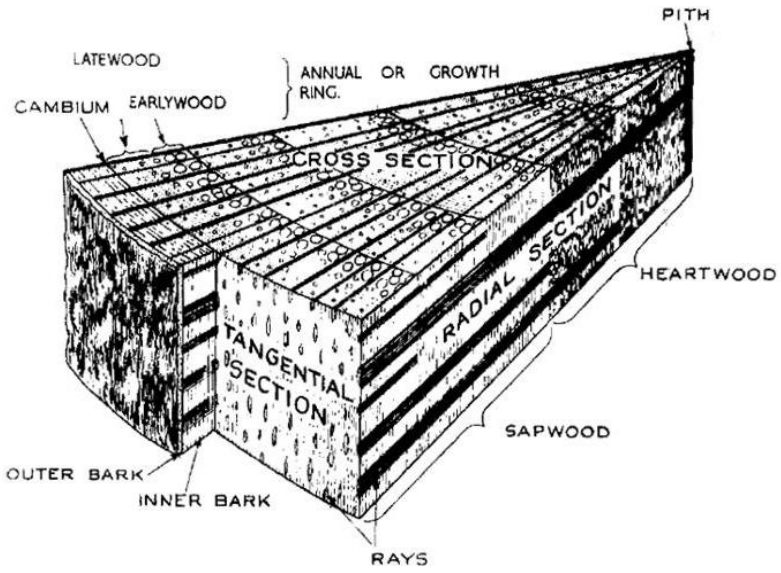


Figure 9: Principle wood structure (Desch and Dinwoodie, 1996)

The cross section of a tree trunk can be separated into heartwood, sapwood and inner and outer bark. The sapwood comprises of the outer ring of the trunk which is physiologically active, whereas the heartwood is physiologically inactive (Desch and Dinwoodie, 1996). As new growth layers form on the outside, the heartwood extends to include former sapwood cells (Desch and Dinwoodie, 1996). As the cells die, the moisture content falls and small quantities of extractives are deposited. This results in decreased permeability, increased acidity and durability, and the wood appears darker in colour (Desch and Dinwoodie, 1996).

Tree species can be categorised as softwood and hardwoods. For the purpose of this study, only softwoods are described.

1.9.1.1 Cellular Structure

The cambium comprises of two cell types; fusiform initials and ray initials. Fusiform initials are long thin cells, which divide into new cambial initials or xylem and phloem cells. Ray initials are shorter and divide into parenchyma cells (Haygreen and Bowyer, 1982). Once cell differentiation has occurred, it assumes one or more of three basic functions; support, conduction, and storage (Table 8). Support and conduction cells constitute 80% of wood volume (Desch and Dinwoodie, 1996). The structure and composition of these cells can be used to categorise tree species into

softwoods and hardwoods. Softwood species are characterised by consisting of 2 major types of cell that perform all 3 functions, whereas hardwoods have 4 types cells (Desch and Dinwoodie, 1996). These cells are tightly packed and linked by pits. Pits are areas where the cell wall has been modified to aid in conduction. Pits are normally perfectly matched to adjacent cell pits hence they exist in pairs (Haygreen and Bowyer, 1982).

Table 8: Wood cells and their functions

Function	Cells	Presence	Description
Support	Tracheids	Soft and hardwood	Vertically arranged, 100x diameter in length (H) and hollow
	Fibres	Hardwood	Thick walled, small lumen
Conduction	Tracheids	Soft and hardwood	Thin, needle shape
	Vessels	Hardwood	Thin walled, large lumen large diameter
Storage	Parenchyma	Soft and hardwood	Horizontally arranged, thin cell wall

For the purpose of this study only softwoods are described, as wood-based products are predominantly produced from softwood tree species pine, spruce and fir.

1.9.1.2 Softwood Structure

The xylem (wood) of softwoods is relatively simple and uniform. Softwood comprises of 5 wood cells, but only 2-3 occur in significant numbers, hence softwoods are similar in appearance (Haygreen and Bowyer, 1982).

Tracheids

Tracheids in softwoods make up 90-95% wood volume and are primarily used for conduction (Haygreen and Bowyer, 1982). These cells are hollow, needle shaped, approximately 2.5-5 mm in length (Desch and Dinwoodie, 1996). Newly formed

tracheids from the cambium have larger radial diameter and thinner cell walls. Latewood tracheids function as support cells because the cell wall is thicker with smaller lumens. In some species such as Pines, Douglas fir and Larch, the transition from thin to thick cell wall is abrupt (Haygreen and Bowyer, 1982). In true firs and hemlock, boundaries between early and latewood are harder to define because the transition is gradual.

Bordered pits

Tracheids are also identified by the presence of bordered pits. Bordered pits are conical depressions in the secondary wall, approximately 15-20µm in diameter (Desch and Dinwoodie, 1996). Figure 10 depicts the 3 types of pit pairs observed in wood (Haygreen and Bowyer, 1982). During pit development, primary and secondary walls are modified to form a ridged border and in the centre is a thickened membrane, called a torus. This torus is held in place by margo strands and can respond to differences in liquid pressure in adjacent cells, moving towards the cell of the lower pressure.

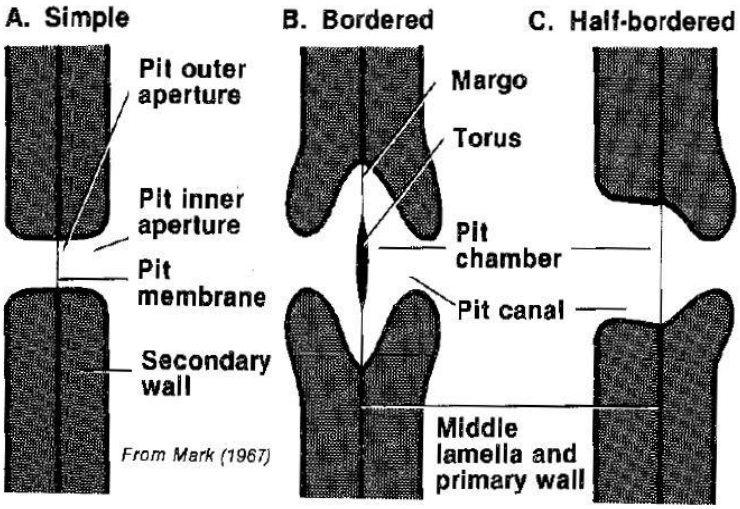


Figure 10 Types of pits pairs (Haygreen and Bowyer, 1982)

During drying, the water meniscus pulls the torus two one side. This phenomenon is called “pit aspiration” and is irreversible, decreasing wood permeability (Desch and Dinwoodie, 1996). Bordered pits are predominantly found on the radial wall of

earlywood tracheids (Desch and Dinwoodie, 1996). As the latewood tracheids main function is for support rather than conduction, latewood tracheids have fewer and smaller pits (Haygreen and Bowyer, 1982).

Rays, Ray Tracheids and Parenchyma

Food stored within the xylem is stored in an unsuitable state and requires a living cell to convert the food, ready for use (Desch and Dinwoodie, 1996). Thus parenchyma cells, unlike tracheids retain their protoplasm and live for many years. Parenchyma cells are also connected by pits to allow the movement of food. These pits are simpler and lack a torus and a border. In softwoods, there are two types of parenchyma; ray parenchyma and wood parenchyma. Ray parenchyma form narrow horizontal bands, radiating out from the medulla (pith) to the bark (Desch and Dinwoodie, 1996). Throughout the wood, these appear in parallel layers between tracheids. In most softwood species, the ray layer is only 1 cell wide (uniseriate) but in others, rays are 2 cells wide (biseriate) (Haygreen and Bowyer, 1982).

Rays also consist of ray tracheids. These are physiologically inactive and are structurally similar to longitudinal tracheids, with bordered pits (Desch and Dinwoodie, 1996). These cells are found on the edges of rays and are known as heterogeneous rays. Homogeneous rays only consist of either parenchyma or ray tracheids.

Resin canals

Softwoods, though not all, can be identified by their resinous nature, smell and tackiness when cut. Species such as pines, furs and larch have resin canals that are lined with epithelial cells, which secret resin (Desch and Dinwoodie, 1996). Resin canals are commonly found horizontally within rays and when this occurs rays are called fusiform rays (Desch and Dinwoodie, 1996). When a tree is wounded, resin can be produced, even if the species lack resin canals.

1.9.2 Chemistry of Wood

Wood comprises of 2 major components: lignin 18-35% and carbohydrate, principally made up of 50% carbon, 6% hydrogen and 44% oxygen and trace ions (Rowell, 1984). The carbohydrate portion of the wood can be divided into cellulose and hemicellulose. Wood does contain extraneous elements (organics and inorganics) but at the very most account for 4-10% dry weight (Rowell, 1984). The chemical composition of wood varies with wood type, part of tree, species and silviculture (climate, local pollution, geographical location etc.). It is the differences in how these basic building blocks are bonded that produce the variety of physical and mechanical performances of wood.

1.9.2.1 Cellulose

Cellulose, a polymer of anhydroglucose units, is a major building block of wood, accounting for 40-50% wood dry mass (Desch and Dinwoodie, 1996). Glucose produced from photosynthesis is transported to the apical meristems and cambial zone, where it is chemically modified (Desch and Dinwoodie, 1996). A water molecule from each glucose unit is removed producing an anhrydride of glucose (Haygreen and Bowyer, 1982). There are two forms of glucose, α-type and β-type. The chemical type of glucose depends upon the position of –OH on carbon 1, relative to the chemical ring (Desch and Dinwoodie, 1996). It should be noted that these –OH groups, that give rise to the hydrogen bonds, are highly hydrophilic. Anhydrides are linked together by β-type chemical bonds, which cannot be digested by humans and most animals. Anhydrides of glucose lie parallel to each other in a particular pattern to form crystal, which is repeated to form the "unit cell". As many as 8000 glucose are bonded to form one chain (Desch and Dinwoodie, 1996). 10,000 chains equate to 5µm of wood (Rowell, 1984).

Within the wood, cellulose exists in layers of parallel chains held together by intermolecular hydrogen bonds (Rowell, 1984). Cellulose that forms into a crystalline structure (crystallite) is known as cellulose 1 (Desch and Dinwoodie, 1996). These areas of crystallites are much shorter than a cellulose molecule, at 60nm in length (Desch and Dinwoodie, 1996). Molecules can pass through these areas of crystallinity as well as areas of low or no crystallinity, where bonding is

loose. These molecules often become part of the next crystalline structure, forming high amounts of longitudinal structures to form a unit of indefinite length, called microfibrils (fig 11) (Desch and Dinwoodie, 1996). Of all cellulose within cell wall, 60-70% is in crystallite form (Haygreen and Bowyer, 1982).

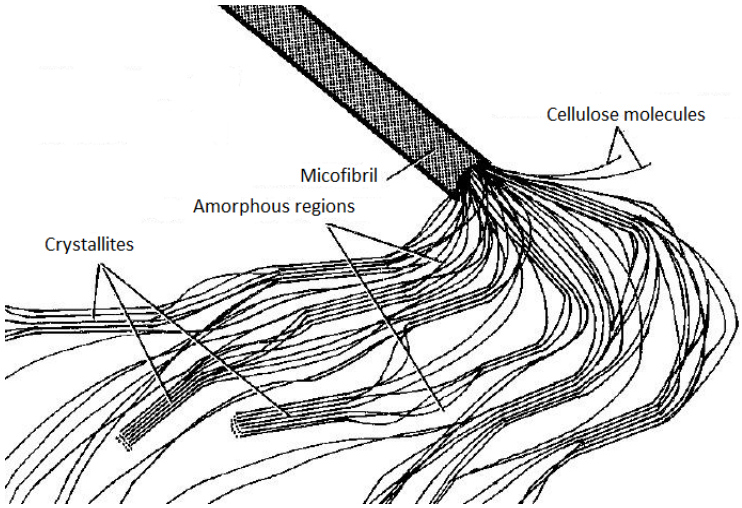


Figure 11: Structure of a micofibril (Haygreen and Bowyer, 1982)

1.9.2.2 Hemicellulose

Hemicellulose is the second carbohydrate and accounts for 20-40% dry wood mass (Desch and Dinwoodie, 1996). Hemicellulose is a polysaccharide, built up from a mix of sugar units, (monosaccharides) to form a branched chain structure (Desch and Dinwoodie, 1996). Sugars that makeup hemicellulose include mannose, xylose, galactose and arabinose (Desch, 1996; Rowell, 1984). Each hemicellulose molecule contains far fewer sugar units (150-200) compared to cellulose and has a lower degree of crystallinity. As different proportions of monosaccharides make up a hemicellulose, each with different components, there are different types of hemicellulose (Rowell, 1984). Hemicelluloses found within softwood species are noticeably different from those found in hardwoods. The most abundantly observed hemicelluloses include; Galactoglucomannan, Arabinoglucuronoxylan, Arabinogalactan, Glucomannan, and Glucuronoxylan (Rowell, 1984). The latter two types are found in hardwoods. In general, hardwood species have a greater proportion of hemicelluloses than softwoods (Desch and Dinwoodie, 1996).

1.9.2.3 Inorganics

Inorganics exist in wood in two ways. They can be an integral part of substances, made by living cells.; Magnesium is required to produce chlorophyll and sodium and potassium are needed to form the nucleus of new cells (Desch and Dinwoodie, 1996). Or they can exist as inorganics and are brought up in through roots in suspension and deposited such as silica (Desch and Dinwoodie, 1996). In total, inorganics account for 0.1-1.0% dry wood weight in temperate species, but the percentage has been recorded as high as 5% in tropical species.

1.9.2.4 Extractives

The name "extractives" is used to encompass a large number of organic compounds that can be extracted from wood, in polar and non-polar solvents. These extractives do possess some functions including energy reserves and are responsible for wood odour, colour and decay resistance (Rowell, 1984). These extractives can be easily removed from wood, without altering structure (Desch and Dinwoodie, 1996). The types and quantities of extractives vary with genus and family and can vary within the wood cell types that are present in heartwood. Extractives are absent from sapwood, as it is rich in food (Haygreen and Bowyer, 1982). For this reason, heartwood durability varies across species and is generally agreed that the darker the heartwood, the more extractives are present (Desch and Dinwoodie, 1996).

Examples of extractives include terpenes, phenolic compounds, waxes, fats, alkaloids, proteins, simple sugars, pectins, gums, starches and oils (Desch and Dinwoodie, 1996; Rowell, 1984).

1.9.2.5 Acidity

Wood is naturally acidic, with a few exceptions. The heartwood is relatively more acidic than sapwood (Desch and Dinwoodie, 1996). Wood acidity varies with species and can be as low as pH 3 , but is commonly between 4.5-5.5pH (Desch and Dinwoodie, 1996). In the presence of moisture, hydrolysis occurs, freeing acetic acid and wood can erode metal in direct contact or through corrosive vapours (Desch and Dinwoodie, 1996).

1.9.3 Cell wall structure

The cell wall is made up of millions of micofibrils and can be subdivided into, which are identified by how the micofibrials are arranged (Desch and Dinwoodie, 1996). Figure 12 depicts the microstructure of the cell wall (Desch and Dinwoodie, 1996).

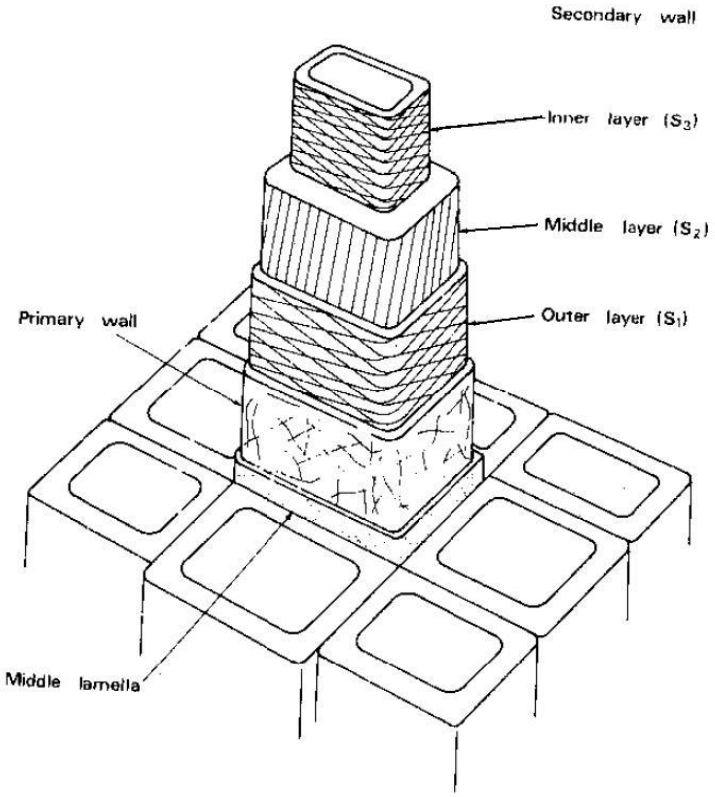


Figure 12: The structure of the cell wall (Desch and Dinwoodie, 1996)

The middle lamella surrounds the primary wall and is without cellulose. The outer most cell wall is the original cell wall, laid down during cambial division called the primary wall. Primary wall thickness through organic (cellulose) material deposition, which is not haphazard but highly accurate to form microfibrils (Haygreen and Bowyer, 1982). Cellulose units are laid in neat parallel fashion, very precisely into crystal like structures, hence these regions are called crystallites (Haygreen and Bowyer, 1982). The S_1 layer is very thin, making up less than 10% of the cell wall. In the S_1 layer, the micofibrils lay parallel to each other on an axis of 50^o - 70^o depending on the tree species (Haygreen and Bowyer, 1982). The S_3 layer is the innermost layer of the cell wall and similar to the S_1 layer (Haygreen and Bowyer,

1982). Together the S_1 and S_3 layer play a crucial role in strengthening the cell wall against lateral deformation and providing horizontal stiffness to the wood (Ansell, 2015). The S_2 layer makes up the greatest proportion of the cell wall, approximately 85% (Desch and Dinwoodie, 1996). The arrangement of the micofibrils lay parallel but in a spiral form on an axis of 10^o- 30^o (Desch and Dinwoodie, 1996). It is the arrangement of these micofibrils in the S_2 layer that are responsible for the performance of the wood and implicates dimensional stability, stiffness and strength (Desch and Dinwoodie, 1996).

1.9.4 Decay fungi

Many indoor decay fungi are spread across a number of orders and families within in the phyla, Basidiomycota (Schmidt, 2007). Fungi usually colonise timber through the rays and penetrate the cells through pits and bore holes. The fungi hyphae secrete extracellular enzymes and other agents and depolymerise cell wall materials, which are then absorbed into the fungal hyphae where they are assimilated and further metabolised (Carll and Highley, 1999). Broadly speaking, wood decaying fungi can be divided into brown rot, white rot, dry rot and soft rot categories. Wood decaying species exhibit characteristic substrate preferences such as sapwood, softwoods or hardwoods or heartwoods (Martin, 2013). Some species may be able to colonise and decay all substrates (generalist fungi), whereas others are restricted to one or a few wood species (Martin, 2013).

1.9.5 Brown rot fungi

Brown rot fungi are characterised by their ability to decay structural carbohydrates and their lack of ability to decay lignin (Pandey and Pitman, 2003). These brown rot fungi mainly colonise softwoods but can be found on a few hardwoods (Rowell, 2012). The decay process leaves the wood a darker brown colour due to remains of the lignin, hence the name (Carll and Highley, 1999; Rowell, 2012). In the natural environment, this lignin residue resists further decay and adds to the carbon pool in humic soils (Martin, 2013).

These fungi extensively and rapidly decay wood by depolymerisation of the carbohydrate (cellulose and hemicellulose) components of the wood, leaving the

lignin behind as a polymeric residue (Martin, 2013; Rowell, 2012). This breakdown of the carbohydrates causes wood and wood-based structures to quickly lose their strength, even in the early stages of decay (incipient decay) (Carll and Highley, 1999; Curling et al., 2001; Rowell, 2012). This is markedly different to the gradual cellulose degradation by hydrolytic enzymes of other fungi (Martin, 2013; Rowell, 2012).

Gloeophyllum species are other common indoor decay-fungi that can destroy coniferous timbers and products (Schmidt, 2007). It is especially common in damp roofing and window timber frames. Other brown rot species include *Lentinus lepideus* (common in damp cellars), *Tapinella panuoides* (common in cellars) and *Daedalea quercina* (attacks oak timbers) (Schmidt, 2007).

1.9.6 White rot fungi

White rot fungi are characterised by their ability to degrade all three of the major wood components (cellulose, hemicellulose and lignin) (Martin, 2013; Rowell, 2012). These fungal species are most commonly found growing on hardwood species but it is known to colonise and degrade softwoods too (Rowell, 2012).

As white rot decays the wood, the wood becomes bleached where the lignin is removed, creating 'white' zones (Rowell, 2012). White rot decayed wood does not crack like brown rot or soft rot wood until it is severely degraded (Carll and Highley, 1999; Rowell, 2012). The unique ability to decay lignin is sometimes considered as a strategy to access carbohydrate polymers in plant cell walls (Martin, 2013).

White rot fungi employ two major techniques of decay. The first technique employed by some species is simultaneous decay of cellulose, hemicellulose and lignin. During this simultaneous decay, the hyphae leave erosion troughs in the wood and the cell walls become gradually thinner and holes developed between cells as the decay advances (Martin, 2013). The second is the selection of lignin and hemicelluloses, which are removed at a faster rate than cellulose. This is known as preferential white rot decay (Martin, 2013; Pandey and Pitman, 2003). In contrast to simultaneous decay, the cell walls retain their structure during selective decay (Martin, 2013). A characteristic of preferential white rot decay is that the wood, it retains its structure for some time and becomes 'spongy' as the strength properties

are gradually reduced (Rowell, 2012). Example white rot species include *Phanerochaete chrysosporium*, a selective fungi and *Coriolus versicolor* a simultaneous white rot fungi (Pandey and Pitman, 2003)

1.9.7 Dry rots

Dry rot fungi or water conducting fungi pose a slightly greater threat to building structures. Whereas other species require the presence of sufficient water for initial colonisation and decay, dry rot fungi are able to transport water to dry wood and cause decay (Carll and Highley, 1999). The hyphae of dry rot fungi become intertwined into root-like strands, forming water conducted structures, which carries water to wherever it is needed (Carll and Highley, 1999). However, this feature is not limited to dry rot fungi, other species such as *Coniophora* do form root-like strands of hyphae. *Serpula lacrymans* is a dry rot fungus, that degrades amorphous regions of cellulose in a non-enzymatic cellulose degradation process (Schmidt, 2007). This fungus is considered to be the most destructive wood decaying fungi and the least controllable, due to its ability to transport nutrients over long distances (Schmidt, 2007)

1.9.8 Soft rots

Soft rot fungi are related to moulds and occur in environments where the wood substrate is constantly wet (Carll and Highley, 1999; Rowell, 2012). The name soft rot refers to the fact that these fungi only attack wood when its surface is wet or soft under anaerobic or near anaerobic conditions (Carll and Highley, 1999). Characteristically, when this decayed wood is dried the surface is cracked and fissured but under the surface the wood is relatively untouched. The wood becomes darker (dull brown to blue-gray in colour) when decayed by soft rot fungi (Rowell, 2012).

1.9.9 Moulds

Mould fungi are quite different to decay fungi. Moulds survive on wood substrates, feeding off the starches and free sugars stored in the parenchyma cells of the wood or on surface detritus deposits (Carll and Highley, 1999; Singh, 1999). Where decay

fungi can cause significant damage to wood structures, mould damage only the surface of the wood and have little effect on strength properties (Rowell, 2012; Singh, 1999). Therefore they are traditionally considered as affecting only the aesthetics of wood. The depth of penetration and subsequent damage a mould fungi causes to a surface is dependent upon the mould species (Rowell, 2012). To a point, it also depends on the structure of the wood itself; Softwoods of a small pore structure only experience surface damage that can often be planed off, whereas hardwoods may experience deeper penetration due to their larger pore sizes (Rowell, 2012). Moulds are distinctive by their fluffy or powdery growth on a substrate and their different colours (Rowell, 2012; Singh, 1999).

Common moulds found within all buildings include *Cladosporium, Chaetomium, Trichoderma, Penicillium, Alternaria, Stachybotrys* and *Aspergillus* (Griffith et al., 2007; Polizzi et al., 2011; Segers et al., 2015, 2016; Singh et al., 2010). *Aspergillus versicolor* and *Penicillium chrysogenum* are particularly abundant in areas that have experienced water damage or direct moisture (Segers et al., 2016).

Moulds have also shown great potential for different means of utilisation in industry. Moulds in the phylum Ascomycota have been widely used in the cheese industry such as *Penicillium* in blue cheese, namely *Penicillium roquefortii* in Roquefort and *P. camembertii* used to turn cottage cheese into Camembert (Tudge, 2002). Most significant of all is the discovery of penicillin from *Penicillium chrysogenum* (Griffith et al., 2007; Nielsen, 2003).

1.10 Indoor contamination

Several global trends have been identified that contribute to increased levels of microbial pollution. The first is the increase in energy conservation measures to improve efficiency of buildings (WHO, 2009). This has led to tighter buildings and more cases of buildings of inadequate ventilation and improper insulation leading to a build-up of moisture within buildings. The second is increased urbanisation, increasing areas of human migration, urban degradation and greater density of buildings (WHO, 2009). This also enhances the effects of the urban microclimate. The third is climate change, increasing frequency of extreme weather conditions

and shifting climate zones (WHO, 2009). The final trend is the quality and globalisation of building materials and components, construction techniques and concepts (WHO, 2009) that are not always appropriate for certain countries' climates. The contamination of fungi in the indoor environment are influenced by other factors such as climate and season, species of fungi, construction, building age, the building's primary use and ventilation rate (Segers et al., 2016; WHO, 2009).

As previously discussed, the root problem with poor indoor air quality is the lack of adequate ventilation and air flow, especially in new buildings. Considering the biological pollution, this increased air tightness results in a build-up of moisture in the indoor environment, particularly in cavity walls, loft spaces and crawl spaces (Singh et al., 2010). This build-up of moisture ultimately leads to the growth and proliferation of fungi and moulds (Singh et al., 2010). It has been estimated that 25% of housing in the European Union experience fungal growth (Moularat et al., 2008; Segers et al., 2016). Although in the UK, data suggests that as high as 45% of buildings suffer from mould growth (Nielsen, 2003). However this growth can be an area covering a few cm^2 to widespread severe fungal growth (Nielsen, 2003). Indoor environments contain a complex mixture of live (viable) and dead microorganism fragments and therefore toxins, allergens and microbial VOCs and mycotoxins. Mattresses are a particularly good reservoir of mould with measured concentrations of 10^3-10^7 spores g^{-1} of dust (WHO, 2009).

Indoor levels of microbial pollution are usually lower than outdoor but levels naturally increase inside damp buildings (WHO, 2009). Indoor contamination can take many forms including, fungal growth, spore and mycotoxin contamination and fungal fragments. The dispersal of fungal fragments and matter, and subsequent inhalation, results from two major mechanisms. The first is the active discharge from the mould or fungus into the atmosphere or by air movements and human or pet activity. The second is the resuspension of settled fungal matter from physical disturbance such as human activity (WHO, 2009). The environmental factors that affect the rate of spores and fragment release include air velocity, time, colony structure, desiccation stress, moisture conditions and vibration (WHO, 2009).

Airborne concentrations of viable fungi in indoor environments are in the order of a few several thousand colony forming units (CFU) per m^3 (WHO, 2009). Spores ubiquitous in outdoor air range from levels of 100 to more than 10^5 spores/m^3 (Griffith et al., 2007; WHO, 2009). Airborne spores are typically 2-10µm in length and can stay airborne for very long periods of time and may be deposited in the respiratory system and smaller spores can reach the alveoli (WHO, 2009). Crawl spaces and cellars often have fungal growth due to the damper environments. Studies have shown that spores can be easily transported into a building from these areas, even cavity wall structures (WHO, 2009). Fungal fragments are derived from broken or fractured spores and hyphae. Some of these fragments can be less than 1 µm in length. Such small fragments can also be deposited into the respiratory tract (Nielsen, 2003; WHO, 2009).

1.10.1 Mycotoxins

Fungi produce many secondary metabolites that cause a toxic response in vertebrates, called mycotoxins (Griffith et al., 2007; Nielsen, 2003). These mycotoxins are volatile metabolites and are thought to play a crucial role in their natural habitats (Nielsen, 2003). Some of these compounds play a functional role in biocontrol mechanisms as toxins against plants, bacteria, parasites and other fungi (Griffith et al., 2007; Nielsen, 2003; Stoppacher et al., 2010). Some metabolites and MVOCs are also used between organisms as a form of communication (Stoppacher et al., 2010). Mycotoxins can be classified by their distinct chemical structures and reactive functional groups including primary and secondary amines, hydroxyl groups, carboxyl acids, amides and phenolic groups (WHO, 2009). Mycotoxins can also be classified in accordance with a researcher's subject. For example, a chemist may categorise based on substrate, a biologist on the taxonomy of the fungi and a toxicologist may categorise them based on cellular responses and diseases caused (Jarvis and Miller, 2004).

The quantity and type of mycotoxins produced from a single fungal species is species specific and can change depending on the substrate on which it is growing (WHO, 2009). The mycotoxins are released from any size of mould colony, individual spores and colony fragments (Nielsen, 2003). In a building environment

mycotoxins can be harmful to humans, especially if they are airborne and mycotoxins of all varieties have been identified on most building materials and in dust (Nielsen, 2003; WHO, 2009). Mycotoxins have also been found in higher concentrations in damp buildings, where fungal growth is proliferating and airborne spore concentrations are high (Nielsen, 2003; WHO, 2009). Even in dry conditions, moulds can still produce metabolites and mycotoxins at low RH and temperatures (Nielsen et al., 2004).

Scientific research of mycotoxins produced from fungi in the built environment is a multi-disciplinary subject. It demands knowledge in a number of areas including, mycology, toxicology, chemo-toxicology, fungal metabolism and biosynthetic pathways, fungal physiology growth and analytical chemistry (Nielsen, 2003).

1.10.2 Microbial VOCs

Fungi produce microbial volatile organic compounds (MVOCs) (Griffith et al., 2007; Polizzi et al., 2012b; Van Lancker et al., 2008; Wady and Larsson, 2005; WHO, 2009). These comprise of a mixture of organic compounds that can be common to a family or genus of fungi or are species specific (Polizzi et al., 2012b; WHO, 2009). The difference between organic compounds and other microbial compounds is their emissions source i.e. mould or substrate material (Griffith et al., 2007; WHO, 2009). The emission of the MVOCs is a consequence of competition between moisture and some chemicals for adsorption sites (WHO, 2009). These microbial VOCs are produced during all stages of growth as intermediate and end products of various metabolic pathways (Griffith et al., 2007; Moularat et al., 2008; Nielsen, 2003; Polizzi et al., 2012b; Stoppacher et al., 2010). Fungus like odours can be detected at 35 ng/m^3 MVOC and very strong odour of fungus at >160 ng/m^3 (Wang et al., 2008)

It is these MVOCs that give the characteristic musty smell we all recognise in damp buildings (Nielsen, 2003; Singh et al., 2010). More than 500 of these MVOCs have been identified and include alcohols, aldehydes, ketones, terpenes, esters, aromatic compounds, hydrocarbons and amine (Griffith et al., 2007; Polizzi et al., 2012b; WHO, 2009). Another example is

Formaldehyde, which is found naturally in the environment and can be a result of oxidation of hydrocarbons during biological degradation of biomass (Roffael, 2006).

Fungal growth and MVOC production is a complex interaction between fungi, substrate, temperature and water availability (Ezeonu et al., 1994; Polizzi et al., 2011; Radványi et al., 2014; Van Lancker et al., 2008). The MVOC chemical profile emitted from any one fungal species can vary according to the substrate on which it is growing, although some species do produce species specific MVOCs that are always produced (Griffith et al., 2007; Nielsen, 2003; Nilsson et al., 1996; Polizzi et al., 2011; Radványi et al., 2014; Van Lancker et al., 2008). The type of MVOC emitted from a colony can vary with time and age of the colony. Some MVOCs that are present during initial colonisation may not be present in later stages of colonisation (Polizzi et al., 2012b). The relative humidity of a room or building influences MVOC production, whereas temperature has been found to only influence a few specific types (Polizzi et al., 2011). The changes in MVOC production observed is largely due to stress reactions and changes in metabolism of fungi under different environmental conditions such as nutritional imbalances (Polizzi et al., 2011, 2012a). The changes observed in MVOC production are also species dependant, where some may hardly change their emissions profile, increasing or decreasing production quantity or remain the same. Whereas other species may change the type of MVOCs emitted drastically and produce MVOCs that were not previously produced (Polizzi et al., 2012a). For this reason, the study of MVOCs is also a multidisciplinary subject that requires knowledge in many different areas and a good understanding of all the variables that influence MVOC emissions.

However, these MVOCs can be very helpful for building occupants and investigators. This 'chemical signature' of some mould species can be used to help to identify mould contamination and poor indoor air quality within buildings, where mould growth is not visible (Griffith et al., 2007; Polizzi et al., 2012b; Radványi et al., 2014; Wady and Larsson, 2005) for example in crawl spaces and cavity walls (Singh et al., 2010). Solid phase micro-extraction (SPME) and gas chromatography (GC) coupled with mass spectrometry (MS) (SPME/GC-MS) analysis can be used to identify MVOCs emitted from indoor moulds and where they have colonised in a building (Griffith et al., 2007; Nilsson et al., 1996; Stoppacher et al., 2010; Van Lancker et al., 2008; Wady and Larsson, 2005). A study conducted by Griffith et al., (2007) showed that a chemical profile, almost like a fingerprint of common moulds

can be developed. The study highlighted the differences in MVOCs emissions between species. *Stachybotrys chartarum* emitted significantly more dodecanoic acid and oxirane, whereas *Penicillium chrysogenum* emitted higher amounts of hexanoic acid and very little dodecanoic acid (Griffith et al., 2007). *Aspergillus versicolor* was the only mould tested found to emitted arsenous acid. Knowledge of individual mould species MVOCs is important to aid in determining the extent of contamination, as moulds and fungi appear in a colonising succession, dependant on substrate water activity. However, it is not without its own complications as a number of VOCs emitted from moulds have a number of other emission sources. Wady and Larsson, (2005) also evaluated the use of SPME/GC-MS to identify MVOCs released from *Chaetomium globosum, Aspergillus versicolor* and *Stachybotrys chartarum.* This SPME technique was found to be an effective means of evaluating MVOCs and found that *C. globosum* had the greatest MVOC intensity of peaks of the moulds tested but this was largely due to its higher amount of growth on its agar substrate. This technique also has the potential for use for identifying lignocellulosic degradation markers (Lattuati-Derieux et al., 2006). Historical documents and artefacts slowly decay over time and SPME can help to identify the extent of deterioration and decay of important papers or books. As stated previously, the MVOCs emitted can vary with substrate, therefore experiment on agar media may result in misleading expectations of an MVOC in indoor environments.

1.11 Human Health

For many centuries it has been known that some fungal species have hallucinogenic properties which have shaped philosophies and social hierarchies of entire cultures; also some species are highly toxic if consumed such as *Armillaria* species (Tudge, 2002). There are very strong and historical link between damp buildings, materials and mould growth associated with poor indoor air quality. There exists a biblical reference (Leviticus, ch. 14 V. 33-35) to indoor mould growth, which shows that it has been a long recognised problem (Nielsen, 2003). Often fungi are parasitic and can cause some serious diseases in humans. Some are merely irritating like ringworm but some can invade the lungs and some can spread further into the

body (Tudge, 2002). However there are more dangerous diseases caused by fungi such as bronchopulmonary aspergillosis (Singh et al., 2010).

In the built environment fungi are associated with physical and aesthetic damage. Fungi are also associated with human health problems such as allergic, irritation and toxic reactions (Airaksinen et al., 2004; Cooley et al., 1998; Jarvis and Miller, 2004; Mensah-Attipoe et al., 2015; Nielsen, 2003; WHO, 2009). However, the type of agent released from fungi and moulds can result in a diverse range of symptoms (Nielsen, 2003).

1.11.1 Sick Building Syndrome

Biological agents that affect indoor air quality and are associated with human health range from: pollen, spores, bacteria, fungi, algae and some protozoa (WHO, 2009). There is sufficient evidence that indoor dampness-related agents (fungi and moulds) cause adverse health effects including asthma exacerbation, upper respiratory symptoms, coughing, wheezing, asthma development and dyspnoea (laboured breathing) (Griffith et al., 2007; WHO, 2009). Fungal species can also have adverse effects on the respiratory system, nerve system and blood vessels (Polizzi et al., 2011).

As previously discussed, SBS is a serious issue that affects many people in their day to day lives. There is evidence from epidemiological studies that MVOCs released from fungi are also partially responsible for some of the non-specific symptoms such as eye redness and skin irritation, even at low concentrations (Abbott, 2002; Cooley et al., 1998; Polizzi et al., 2011; Sahlberg et al., 2013; Sari et al., 2004; Van Lancker et al., 2008; Wady and Larsson, 2005). Microbial volatile organic compounds (MVOCs) are often similar to industrial chemicals (WHO, 2009) emitted from other materials within a building. As such, identification of the source and types of MVOCs is complicated to achieve in indoor environments. However, it is known that like other VOCs, MVOCS are also irritants causing asthma and eye irritation (Arts et al., 2008; Griffith et al., 2007; Jarvis and Miller, 2004; WHO, 2009). Microbial VOCs naturally vary in their toxicity but some can be quite dangerous such as a the cytotoxic MVOC 1-octen-3-ol (Griffith et al., 2007; Polizzi et al., 2012b). Additionally, MVOCS have also been noted to be pre-cursors for

mycotoxin production such as trichodiene a precursor for trichothecene mycotoxin (Van Lancker et al., 2008). Mycotoxins can have their own adverse health effects on humans, see section 1.12.3. It has however been noted that indoor MVOCs do not occur in high enough concentrations to stimulate SBS symptoms in building environments (Polizzi et al., 2011; Van Lancker et al., 2008) unless there is significant water damage and fungal growth.

Structural elements of fungi, such as β-1,3-Glucans can also adversely affect human health by triggering inflammatory reactions similar to the reactions of endotoxins (Nielsen, 2003). Spores and fungal fragments are considered to cause irritation in humans (WHO, 2009). Epidemiological studies have shown that respiratory and irritative symptoms are linked to indoor moulds and mould odour (WHO, 2009). Perceived mould odours can also result in stress responses and nonspecific symptoms such as headaches and nausea (WHO, 2009).

1.11.2 Allergens

Biological agents such as moulds can also release allergens that induce an immune response in humans (defined as the production of specific antibodies) (Polizzi et al., 2011; Radványi et al., 2014; WHO, 2009). An allergen can refer to a single molecule or a mixture of molecules or even a single particle (viable or not) from which an allergen molecule can be released (WHO, 2009). Allergic responses to high concentrations of airborne fungal spores are caused by many fungal species such as *Cladosporium, Penicillium* and *Serpula* (Singh et al., 2010).

Due to the variety of sources of allergens, fungal allergens themselves comprise of a large number of macromolecular structures from low molecular mass sensitizers such as chemicals, to higher molecular weight sensitizers, such as proteins and carbohydrates (WHO, 2009). Some fungal allergens are gylcopeptides with enzymatic properties and are found in spores, hyphae and fungal fragments (WHO, 2009). Even non-viable (dead) fungal fragments and spores can release allergens but at lower concentrations (WHO, 2009). Some allergens are produced continuously by fungi and some are specific to the activity of the fungi. For example, glycopeptide allergens are released in the greatest amounts during germination and mycelial growth (WHO, 2009).

Humans of an atopic nature (vulnerable to allergies) are sensitive to moulds and experience more allergic responses, (asthma and allergic rhinitis) to mould exposure (Jarvis and Miller, 2004). Such responses are a result of inhalation when exposed to fungi. However, exposure can take different forms including ingestion and epidermal exposure (Jarvis and Miller, 2004). Fungal species produce type I allergens and immunoglobulin (Ig)E immune response to common mould species such as *Penicillium*, *Aspergillus* species (Nielsen, 2003; WHO, 2009). *Cladosporium* species are strongly associated with allergenic respiratory disease such as asthma and produce other allergens (WHO, 2009). Mould *Penicillium* and *Aspergillus* species are also sources of type III allergens and are very common in many houses (WHO, 2009). Some fungi are known to cause hypersensitive pneumonitis (extrinsic allergic alveolitis), an inflammation of the alveoli within the lungs caused by hypersensitivity to organic particles (WHO, 2009). Exposure to high spore concentrations emitted from *Cladosporium* and *Penicillium* species are common causes of hypersensitive pneumonitis (Singh et al., 2010). *Trichoderma* is known to produce allergens and can provoke immediate hypersensitivity in human (Polizzi et al., 2011). It has also been suggested that dry and wet rot fungi can cause hypersensitive pneumonitis (Singh et al., 2010; WHO, 2009). Other allergic responses include rhinitis (inflammation of the inside of the nose), eczema (skin irritation) and asthma (Nielsen, 2003; Singh et al., 2010; van Laarhoven et al., 2015).

1.11.3 Mycotoxins

The biological effects of many fungal secondary metabolites are poorly documented and very few have been conducted in animal studies (Nielsen, 2003). However, laboratory studies have shown that metabolite production is influenced by medium composition, temperature and water activity. This indicates that in real life scenarios, the types and quantity of metabolites are likely to vary considerably. Moulds can still colonise materials and grow in sub optimal conditions and even at low humidities, and where substantive growth may be retarded or prevented spores and mycotoxins can still be released (Abbott, 2002; Nielsen et al., 2004). Non-viable (dead) fungal fragments and spores are known to contain potentially harmful compounds such as mycotoxins and glucans (WHO, 2009).

The World Health Organisation International Agency for Research determined that many mycotoxins have carcinogenic, toxic or cancer promoting characteristics (Griffith et al., 2007; Segers et al., 2016; WHO, 2009). Other studies have shown that mycotoxins can cause neurotoxicity and inflammation in the nose and brain (Griffith et al., 2007). Mycotoxins such as aflatoxins released by *Aspergillus flavus* growing on ground nuts and cereals can kill thousands a year (Tudge, 2002). Mycotoxins are also known to interfere with RNA synthesis and may cause DNA damage (WHO, 2009). Some mould species of *Aspergillus* produce aflatoxin, a potent carcinogen (WHO, 2009). The water activity (a_w) of a substrate also influences the type and quantity of mycotoxins released. The higher the a_w (at least 0.9) on the surface of construction materials, the greater the mycotoxin production (Griffith et al., 2007; Nielsen, 2003). Therefore, a building will experience a worst case scenario of mycotoxin pollution if it experiences water damage with fungi and moulds intrusion and severe growth. Followed by a period of drying that encourages spore and fragment dispersal and disposition (Nielsen, 2003). There are also concerns that exposure to a mixture of mycotoxins and other secondary metabolites can produce synergistic effects in humans (Nielsen, 2003). Indeed not all mycotoxins are harmful. *Penicillium* produces a mycotoxin, Penicillin, which is a most useful antibiotic (WHO, 2009). Roquefortine C is consistently produced by *Penicillium chrysogenum* and is a very common mould use for blue cheese fermentation (Nielsen, 2003).

A number of representative examples of typical fungi genera found in homes and mycotoxin release detailed below.

Stachybotrys

Stachybotrys chartarum is a black fungus that is found on moisture saturated building materials such as gypsum board and those with high cellulose content (Gravesen et al., 1999; Singh et al., 2010). This fungus has received a lot of attention as it is known to cause reoccurring cold-like symptoms, skin rashes and causes idiopathic pulmonary hemosiderosis (a bleeding lung disease) (Jarvis and Miller, 2004; Nielsen, 2003; Singh et al., 2010). Although active toxins and mechanisms remain unclear (Nielsen, 2003). It has been found that *Stachybotrys* contain higher

quantities of secondary metabolites, which suggests that they play an important role in the biology of the mould (Nielsen, 2003). The mycotoxins emitted from this species are spread over a wide range, resulting in enzyme inhibition, cytotoxicity, neurotoxicity and thrombosis (Nielsen, 2003). *S. chartarum* has also been found to produce highly cytotoxic macrocyclic trichothecenes that inhabit protein synthesis (Nielsen, 2003). However studies have shown that less than 50% of strains actually produce macrocyclic trichothecenes (Andersen et al., 2002), hence not all genera can be described in the same way.

Aspergillus

Aspergillus species are very frequently found within damp buildings and are known to contribute to SBS (Ezeonu et al., 1994; Gravesen et al., 1999). *Aspergillus versicolor* is the most prevalent species within buildings as it is able to grow on very nutrient poor materials such as concrete (Gravesen et al., 1999; Nielsen, 2003). *Aspergillus versicolor* is almost unique in that it produces a consistent chemical profile, generating high quantities of carcinogenic mycotoxins called sterigmatocystin and other related compounds (Ezeonu et al., 1994; Jarvis and Miller, 2004; Nielsen, 2003). *Aspergillus flavus* is less common in buildings but it does produce the most potent naturally occurring carcinogen, aflatoxin B_1 and aspergillic acid (Nielsen, 2003). *Aspergillus niger* also produces a wide range of mycotoxins such as ochratoxin A, 1-octen-3-ol, tetracyclic compounds, kotanin and nigragillin (Griffith et al., 2007; Nielsen, 2003; Schuster et al., 2002). However, with the exception of *Aspergillus versicolor* mycotoxin production from *Aspergillus* species is limited in the indoor environment (Nielsen, 2003). This highlights the importance of understanding how a fungal species responds to its environmental conditions and the substrate upon which it grows as these combined factors influence mycotoxin production.

Chaetomium

Chaetomium globosum is the most common of all *Chaetomium* species found within building environments and is known to produce highly cytotoxic chaetomins and chaetoglobosins that inhibit cell division and glucose transport (Nielsen, 2003;

Ueno and Hsieh, 1985). Importantly with this mould species is that it produces the same mycotoxin profile when it is isolated from different materials; plasterboard, wood and textiles (Nielsen, 2003).

Penicillium

Penicillium expansum, another common mould found within buildings growing on wood based substrates, has been shown to produce high toxic mycotoxins, patulin, citrinin, chaetoglobosins and the less toxic roquefortine C (Nielsen, 2003). *Penicillium chrysogenum* another common toxic *Penicillium* found within buildings, has received some intense scrutiny, since penicillin was derived from this species (Griffith et al., 2007; Nielsen, 2003). It has been found that the toxin secalonic D has been emitted from this mould, however only in laboratory conditions and not isolates from the indoor environments (Nielsen, 2003).

Trichoderma

Trichoderma species isolated from buildings are also known to emit many mycotoxins. This can be attributed to its production of antifungal products (Šegvić Klarić et al., 2007) that enable it to outcompete other fungal species (Ghisalberti and Sivasithamparam, 1991; Wiest et al., 2002). *Trichoderma* species can also produce mycotoxins and other metabolites that can inhibit a plant's resistance to fungal pathogens, rendering it defenceless (Stoppacher et al., 2010). *T. virens* produces viridin, a fungistatic substance and gliotoxin (Nielsen, 2003). Other metabolites produced include cytotoxic proteins that inactivate ribosomes, membrane active peptides and compounds, that damage the plasma membrane of sperm cells (Lin et al., 1991; Nielsen, 2003; Polizzi et al., 2011).

1.12 Mitigation

Once a fungal or mould infestation has begun it will continue and proliferate for as long as environmental conditions are favourable or until the material can longer sustain fungal colonies (Singh et al., 2010). Thus initial mitigations are very important in preventing fungal establishment within buildings. Preventative measures against all wood decaying fungi are generally the avoidance of general

building defects such as leaky roofs, water seeping through masonry and insufficient ventilation (Schmidt, 2007). Proliferation of moulds is a result of bad buildings practices such as lack of ventilation, misconnection of drains and inadequate maintenance leading to build up of moisture (Singh et al., 2010). Nutrient sources to support fungal growth are ubiquitous in all buildings, as fungi will grow on any organic and inorganic material (Singh et al., 2010). Therefore as the nutrient sources cannot be removed, mitigation processes are based around reducing and controlling moisture conditions.

The easiest method to determine the fungal and mould contamination of a building is to evaluate the moisture dynamics of the building. Careful inspection for signs such as blistering of finishes, discolouration, severe salt efflorescence and condensation can indicate the likelihood and level of contamination (Singh et al., 2010).

1.12.1 Legislation and guidelines

Individual microbes and other biological agents responsible for adverse health effects are very difficult to identify because humans are exposed to multiple microbiological agents simultaneously and will present a large of number of different symptoms (WHO, 2009). As quantitative guidelines cannot be provided for the many different biological agents, recommendations and simple guidelines have been developed in the interest of human health and risk factors have been identified. The World Health Organisation published the '*Guidelines for indoor air quality; Dampness and mould*' which identifies the main health risks associated with damp buildings, the associated microbial growth and contamination of buildings and describes relevant guidelines to protect human health (WHO, 2009).

1.12.2 Building design and ventilation

The building design is vital to ensuring a good air quality within a building. There are 3 major known problems associated with well-insulated buildings that can result in increased fungal contamination (Gullbrekken et al., 2015). The first is that the outer part of construction becomes colder and therefore RH is higher in such areas. Second, drying time for built in moisture increases with increased material

thickness. Thirdly, increased insulation thickness provides increased potential for internal convection in insulation layer, causing moisture redistribution within the building.

The internal building environment varies significantly between rooms depending on occupant activity, crowding, utilisation and the season. Microclimates within the building vary with the building envelope of the internal building fabric (Singh et al., 2010). This is another reason why ventilation is so important. Ventilation is key to improving indoor air quality. Ventilation if properly designed and utilised, will remove and dilute pollutants and maintain the temperature and lower the relative humidity inside the building (Schmidt, 2007; WHO, 2009). However, as exact values for adequate ventilation cannot be provided for every single pollutant, it is therefore not possible to determine the necessary ventilation rates (WHO, 2009). Moisture can migrate throughout a building as liquid, vapour or carried as humid air infiltration (Singh et al., 2010). Buildings can be specially designed with moisture barriers, water-proof membranes or other damp-proofing techniques (Singh et al., 2010). Building design is important in the prevention of fungi growth. Incorrect vapour barriers, insulation, foundations of building and roof structure can all lead to seepage and build-up of condensation inside a building (Schmidt, 2007).

Ventilation can also have adverse effects on human health (WHO, 2009). If not properly designed, installed and maintained, it can allow entry of harmful substances. Most importantly, if the ventilation system is not adequately controlled the relative humidity and moisture can build-up within the indoor environment and encourage fungi and mould growth (Schmidt, 2007). Domestic humidifiers and air-conditioning systems are important sources of micro-flora (Singh et al., 2010). Maintenance of ventilation systems is vital as mould and fungi can grow in cooling-coils, cooling towers and drip pans, which are able to emit biological pollutants into the indoor environment, thus decreasing air quality and leading to human health problems such as ‘humidifier fever’ and legionnaires disease (WHO, 2009).

2 Benchmarking of commercial MDF

2.1 Introduction

Building materials must have adequate properties required to deal with loadings and hazards encountered during their service life. Therefore, to ensure that the material is appropriate for its appointed task, there are a number of mechanical, physical, hygric and microbiological tests that are used to evaluate their performance and properties. As modifications to boards could affect these properties, baseline values of appropriate properties were determined for commercial panels. The values could then be used as comparative minimum requirements for boards manufactured during this study.

2.2 MDF Panels

Three MDF panels were obtained from Kronospan (Chirk, UK). The panels were produced using urea-formaldehyde (UF) resin, to 12mm thickness with no laminate to and were approximately 1.2 m x 1.8 m (4 x 6 ft.).

2.3 Sample Preparation

The panels were cut and prepared at the BioComposites Centres Bio-Refining Technology Transfer Centre (Mona, Anglesey, UK).

Samples for each of the following tests were taken from three different panels and from different positions on each different panel, to account for variability between and within the panels, as per standard EN 326-1. The remaining panel pieces were placed into storage for any subsequent testing.

As these panels were obtained from a commercial supplier, the panels had already endured an 'off-gassing' of formaldehyde period. Individual test samples were conditioned at 65% ±5 RH and 20 ±2 ^{o}C until a constant mass was reached.

2.4 Mechanical

The mechanical properties of a construction material refer to its strength properties and how well a material can withstand an external force imposed on it. All solid materials have a limit to the amount of force they can endure before the force

exceeds a maximum limit and deformations in the material are permanently formed. When a solid is extended or compressed by an external force (N) the dimensions of the solid change. Stress is a measure of the force that acts on a solid and strain is a measure of the solid's response to stress. Stress (N/m^{-2}) on a solid is described as force (f) over the area (A). There are 4 modes in which a force is applied to a material: Tension, bending, shear and compression (McArthur and Spalding, 2011). This study evaluates the tension, bending and internal bond strength of commercial MDF.

2.4.1 Modulus of Rupture (MOR) and Modulus of Elasticity (MOE)

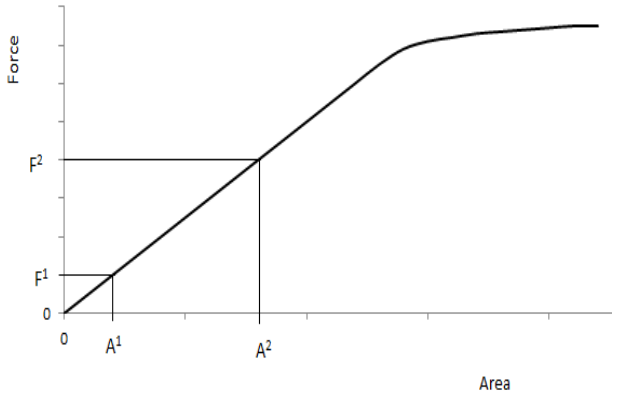
The principle of this test is to determine the modulus of elasticity in bending (Kollman and Côté, 1968). A material is said to be elastic when the material recovers its original state and any deformations disappear after the applied, normally low, loads are removed. Above a certain load, termed the elastic limit, permanent deformations or failure will occur.

2.4.1.1 Sample Dimensions

The samples were rectangular in shape, 50 ±1 mm in width (*W*) with the length (*L*) set at a value 20 times the panel thickness (*T*), with at least 100mm additional length to ensure samples remains on the support (fig 13). In total 6 replicates were cut from across the MDF panel

2.4.1.2 Procedure

The samples were tested in accordance with EN 789 (2004) using an INSTRON 3345 testing machine. The sample was placed on two supports, equally spaced from the centre of the sample, (20x the sample thickness) and a load was applied at constant rate, on the sample (fig 13).



A) Equipment setup B) Deflection curve

Figure 13: Modulus of rupture and elasticity determination

The deflection at the load point was measured and the maximum load recorded. The results are expressed:

$$MOE \text{ (N mm}^{-2}) = \frac{L_1^2 (F_2 - F_1)}{4\,WT^3 (A_2 - A_1)} \qquad \text{[Equation 1]}$$

$$MOR \text{ (N mm}^{-2}): = \frac{3\,F_{max}\,L_1}{2\,WT^2} \qquad \text{[Equation 2]}$$

Where

L_1	is the span between supports (mm)
W	is the sample width (mm)
T	is the sample thickness (mm)
F_1	is 10% of the maximum load (N) (fig 13B)
F_2	is 40% of the maximum load (N) (fig 13B)
A_1	is extension at F_1 (mm) (fig 13B)
A_2	is extension at F_2 (mm) (fig 13B)
F_{max}	is the maximum load (N)

2.4.2 Internal Bond strength (IB)

The principle of this test is to determine the resistance to tension (loads resulting in elongation) of a material, perpendicular to the material's surface. Internal bond strength measures the maximum stress a material can withstand before being pulled apart. More brittle materials will break sharply without deformation. Other materials, such as plastics, will deform or 'neck' before failure. Such materials are more ductile.

2.4.2.1 Sample dimensions

The samples were square in shape at 50 ±1 mm in width (*W*) and length (*L*) at nominal thickness (*T*). Sanding of the surface of these materials was not necessary as they were pre-sanded, prior to delivery. 8 replicates were prepared.

2.4.2.2 Procedure

The samples were tested in accordance with EN 319:1993. Each sample was bonded to a loading block with standard glue and hot glue gun, on both surfaces of the sample and allowed to cure. The sample was then placed into the grips of the INSTRON 3345 and a load applied, at a constant rate, applying the tension force to the sample, until failure (fig 14). Any partial failures or glue line failures of a tested sample were rejected.

Figure 14: Internal bond strength setup

The maximum load and extension of the sample were recorded and the result expressed as:

$$\text{IB (N mm}^{-2}) = \frac{F_{max}}{L\,W} \qquad \text{[Equation 3]}$$

Where

L is sample length (mm)

W is the sample width (mm)

F_{max} is the maximum load (N)

2.4.3 Results

The standard that specifies the requirements for dry process MDF panels is defined by EN 622-5:2009. For general purpose MDF boards in dry conditions at 12mm thickness, the required MOE, MOR and IB is 2200 N mm^{-2}, 20 N mm^{-2} and 0.55 N mm^{-2}, respectively. Table 9 summarises the mechanical strength properties of the commercial MDF. The MDF panels tested did meet the standard requirements for general purpose MDF and exceeded the minimal requirements set by EN 622-5 for general purpose MDF in humid conditions (MDF.H).

Table 9: Mechanical properties of commercial MDF

	No: replicates	**N mm^{-2}**	**S.dev**	**Max Load (N)**	**S.dev**	**EN 622-5 Requirements for general purpose MDF**	**EN 622-5 Requirements for MDF.H**
MOE	6	3966.21	185.73	1185.62	120.34	2200	2400
MOR	6	39.16	3.51			20	24
IB	8	0.76	0.06	1936.00	172.91	0.55	0.75

2.5 Physical

The physical properties of the panel refer to the properties and composition of the material.

2.5.1 Bulk density (BD)

The purpose of this test is to determine the average density of the whole panel. The samples were square in shape at 50 ±1 mm in width (*W*) and length (*L*) at nominal thickness (*T*). Three replicates were prepared.

2.5.1.1 Procedure

The samples were tested in accordance with EN 323:1993. The samples were measured and weighed once a constant mass was reached after conditioning at 65% ±5 RH and 20 ±2 ^{o}C. A micrometer was used to determine the thickness, width and length of each sample. A four-figure balance was used to measure the mass. The results are expressed as:

$$BD\ (\text{kg m}^{-3}) = \frac{M}{W_1\, x\, W_2\, x\, T}\ x\ 10^6 \qquad \text{[Equation 4]}$$

Where

M is sample mass (g)

W_1 is sample width (mm)

W_2 is sample length (mm)

T is sample thickness (mm)

2.5.2 True density

The true density of the panels was obtained using a helium pycnometer. There is not a European standard for this experiment, but a standard BC procedure was used (Kwon et al., 2007). The dimensions of the sample cut from the MDF panels were 10 x 20 mm at panel thickness of 12 mm. Three replicates were prepared.

2.5.2.1 Procedure

The samples were oven dried at 105 ^{o}C overnight. The samples were then placed in the small chamber of the helium pycnometer and flooded with helium. The density is calculated using the sample displacement of helium compared to an empty chamber. The results are given in g mm^{-3}.

2.5.3 Ash content (inorganic content)

The principle of this test was to determine the ash (inorganic) content of the tested material, following BSEN 14775:2009. The ash content was determined by the mass of the residue remaining after the sample was heated to 550 °C under controlled conditions. Three replicates, representative of the MDF panel were cut from across the panel. The sample dimensions were not important but the sample mass was a minimum of 1g and able to fit inside an inert porcelain crucible. The sample and crucible were then oven dried at 105 °C. Three replicates were prepared.

2.5.3.1 Procedure

The porcelain dish was oven dried prior to the testing. This was cooled in a desiccator and weighed to record the oven-dried mass using a four figure balance. The sample was then placed into the dish and the mass recorded again to the nearest 0.1 mg. The dish containing the sample was placed into a cold furnace and the temperature steadily increased to 550 °C. The temperature was maintained for at least 120 minutes. Once the furnace cooled the dish was removed carefully and placed in a desiccator to cool to ambient temperatures. The dish was then weighed and the mass recorded on a four-figure balance. The ash content was then determined on a dry basis and expressed as a percentage of the dry mass of the sample.

$$\textit{Inorganic content}\ (\%) = \frac{(\boldsymbol{C}-\boldsymbol{A})}{\boldsymbol{S_o}}\ \boldsymbol{x}\ \mathbf{100} \qquad \text{[Equation 5]}$$

Where

C is the dry crucible and ash mass (g)

A is the dry crucible mass (g)

S_o is the original sample mass (g)

2.5.4 Moisture content

The principle of this test is to determine the moisture content of a material on a basis of wet and dry mass. The shape and size of the sample were not important but was a minimum mass of 20g and free of sawdust or any lose pieces. Three replicates were conducted to determine the average moisture content of the MDF panel. Six replicates were prepared.

2.5.4.1 Procedure

The initial sample mass was weighed to an accuracy of 0.01g. The samples were then placed in a ventilated oven at a temperature of 103 ±2 ^{o}C for 24hours. The samples were then removed and placed into a desiccator and allowed to cool to ambient temperature conditions. Once cool the samples were re-weighed to an accuracy of 0.01g as quickly as possible to ensure that no moisture was taken up by the sample. The results are expressed as a percentage of mass (H) to nearest 0.1% using the following formula:

$$\text{MC} = \left(\frac{(m_h - m_o)}{m_o}\right) x\ 100 \qquad \text{[Equation 6]}$$

Where

m_h is the initial sample mass (g)

m_o is the mass of the sample after drying (g)

The moisture content of the board is calculated as the mean of the replicates values and expressed as a percentage to one decimal place.

2.5.5 Results

Table 10 summarise the physical properties of the commercial MDF.

Table 10: Physical properties of commercial MDF

Property	Number of replicates	Result	Standard deviation
Bulk density	3	0.76 g cm^{-3}	14.75
True density	3	1.3964 g cm^{-3}	0.004
Ash content	3	0.223 %	0.018
Moisture Content	6	7.9 %	0.280

2.6 Hygric properties

Sources of moisture can be separated into three categories: construction sources (evaporation of moisture trapped within materials can be important during the first few years of a building's life), interior moisture (cooking, showers and respiration) and external moisture sources (infiltration, vapour diffusions and capillarity) (McArthur and Spalding, 2011). The presence of moisture in the atmosphere is given as relative humidity (RH) expressed as a percent (%). Moisture in buildings can result in a cold, damp and uncomfortable internal environment and can result in mould and fungal growth resulting in the deterioration of materials. Therefore it is desirable for constructions materials to possess buffering or hydrophobic properties.

There are some materials that are dimensionally unaffected by moisture such as gypsum plaster and plasterboards. Changes in response to changing moisture conditions can be reversible or irreversible. It is therefore important to understand the material's hygrothermal performance (water and moisture transport and storage). Water/moisture is directly or indirectly responsible for a number of physical (bulking, weathering, freeze/thaw and dimensional changes), chemical (sulphate attack, corrosion and hydration of oxides) and degradation processes.

2.6.1 Water absorption coefficient

The principle of this test was to quantify the absorption of liquid water, by capillary action and the transport of liquid into the surface of the material, in accordance with EN 15148:2002. This test is used as a standard method to indicate the liquid transport performance of a material. The water absorption coefficient (W_{ac}) measures the mass of water absorbed by a material per area per square root of time (kg m^{-2} $s^{-0.5}$).

2.6.1.1 Sample Dimensions and Preparation

The samples were square in shape with a constant cross section to ensure one-dimensional water flow (EN15148). The samples were cut to 60 ±1 mm in width (*W*) and 60 ±1 mm in length (*L*) and at nominal thickness (mm) (*T*). The sides of the samples were sealed with a water and vapour tight flexible silicone sealant (UNIBOND flexible bathroom sealant, purchased through Amazon.com).

2.6.1.2 Procedure

Once the sealant had cured, the samples were weighed to an accuracy of 0.1 %, after conditioning. The sample was then placed into a tank on two supports, which kept the sample's bottom face off the bottom of the tank. Sufficient tap water was poured into the tank so that 5 mm of the sample was immersed in water and a timer started. After 5 minutes the samples were carefully removed. The bottom surface blotted dry of free water and re-weighed on a four-figure balance. This was repeated after 20 minutes, 1 hour, 2 hours, 4 hours and 8 hours after first immersion in water. The final weight was taken after 24 hours of immersion. If water was observed on the top surface of a sample, before the end of the 24 hours period, the test was terminated for that sample.

The first step of the analysis is to determine the mass change at each weighing compared to the initial sample weight:

$$M_T\,(\mathrm{g}) = \frac{(\boldsymbol{M_t} - \boldsymbol{M_i})}{\boldsymbol{A}} \qquad \text{[Equation 7]}$$

Where

M_t is sample mass at each time measured (g)

M_I is the initial mass of the sample (g)

A is the area of the bottom surface of the sample (m^2)

Results were plotted graphically in accordance with the standard EN ISO 15148, which can generally result in either of two graphs. In the case of the MDF panels tested, the resulting graph was type A (fig 15). The graphical plot was assessed using the following calculations:

$$W_{ac}\,(kg\ m^{-2}\ hr^{-1}) = \frac{(\Delta \boldsymbol{M_{tf}}\ \boldsymbol{x}\ \Delta \boldsymbol{M_0})}{\sqrt{\boldsymbol{T_f}}} \qquad \text{[Equation 8]}$$

Where

tf is the duration of the experiment (24hours)

M_{tf} is the value of M on the straight line at the time of tf ($kg\ m^{-2}$)

M_o is the Y intercept

The accuracy of these results depends upon the handling and drying of the sample, therefore care was taken to ensure that the same steps were taken for each sample.

2.6.2 Water Vapour Transmission

This test was conducted in accordance with EN 12572:2001 to determine the water vapour permeance and permeability of the test material, under isothermal conditions. The samples are exposed to different environments with varying partial vapour pressures so that a vapour flow occurs. To determine the rate of water vapour transmission the samples are periodically weighed.

2.6.2.1 Sample Dimensions and Preparation

In accordance with the standard, the exposed surface was at least 0.005 m^2. Six replicates were cut from each board at 60 ±1 mm in width (W) and 60 ±1 mm in

length (*L*) and at nominal thickness (mm) (*T*). Using a water and vapour tight, flexible, silicone sealant the sides of the samples were sealed and glued to an inert plastic waterproof cup that is free of holes and cracks. Three of these cups contained a desiccant, calcium chloride ($CaCl_2$) creating an RH of 0% (dry cup) at 23^{o}C. The other 3 cups contained an aqueous solution of potassium chloride (KCl) creating an RH of 85% (wet cup) at 23^{o}C.

2.6.2.2 Procedure

Each sample and cup assembly was weighed using a four-figure balance. The dry cups were placed into a climate chamber, set to 23^{o}C and 85% RH. The wet cup samples were placed into a different climate chamber set to 23^{o}C and 0 % RH.
Each sample was weighed every 24 hours until the change in mass was a constant ± 5 % of the mean value for the sample.

From this experiment a number of calculations were made:

1. The mass change was plotted against time to facilitate determining mass change rate (ΔM_{12}).

$$\Delta M_{12}\,(\text{kg s}^{-1}) = \frac{(\boldsymbol{m_2 - m_1})}{(\boldsymbol{t_2 - t_1})} \qquad \text{[Equation 9]}$$

Where

m_1	is the mass of the test assembly at time t_1 (kg)
m_2	is the mass of the test assembly at time t_2 (kg)
t_1 and t_2	are the successive times of weighing (s)

2. A regression line was determined by plotting mass versus time and the gradient determined (*G* in kg s^{-1}).

3. The gradient of the slope was then used to calculate the density of water vapour flow rate ($\dot{g}$), which is a measure of the mass of the water vapour transferred through the sample.

$$\dot{g}\ (kg/(m^{-2}\,s^{-1})) = \frac{G}{A} \qquad \text{[Equation 10]}$$

Where

A is the exposed area of the test specimen (m^2)

4. The water vapour permeance (W) is calculated by:

$$W\ (kg/\ (m^{-2}\,s^{-1})) = \frac{G}{(A \times \Delta p_v)} \qquad \text{[Equation 11]}$$

Where

Δp_v is the water vapour pressure difference across the sample (Pa).

5. Water vapour resistance (Z) is calculated by:

$$Z\ (kg/\ (m^{-2}\,s^{-1})) = \frac{1}{W} \qquad \text{[Equation 12]}$$

6. Water vapour permeability factor (δ) is given by:

$$\delta\ ((kg / m \cdot s)) = W \cdot t \qquad \text{[Equation 13]}$$

Where

t is the nominal thickness of the sample (m)

2.6.3 Dynamic Vapour Sorption

Dynamic vapour sorption (DVS) is designed to accurately measure mass changes of a sample (less than 10 mg) as it absorbs and desorbs moisture at differing relative humidities and temperatures.

2.6.3.1 Procedure

Only a small amount of material is required for DVS analysis, approximately 10mg. This was carefully sliced off from a conditioned MDF sample. The sample was suspended in a microbalance within a sealed thermostatically controlled chamber, where a constant flow of dry nitrogen gas was passed over the sample at a flow rate of 200 cm^3 s^{-1} and a temperature of 21 ± 0.2 °C (Popescu et al., 2013). The inert gas carried a controlled quantity of water, maintaining a set RH. The schedule for the DVS was set to start at 0% RH and then increase in 5% steps up to 95% for the adsorption phase and the reverse for the desorption phase (Popescu et al., 2013). The DVS was maintained at a given RH until the mass change of the sample was less than 0.002 % min^{-1}. Any change in mass readings was recorded every 20s and at each set point, an algorithm was set to ensure that equilibrium had been reached when the ratio of change in mass in relation to change in time was less than 0.002 % min^{-1} for at least 10 minutes.

2.6.3.2 Analysis

From the data derived from the DVS, sorption and desorption isotherms can be produced for the tested material by plotting mass change against relative humidity (RH) and the hysteresis analysed.

2.6.4 Thickness swell (TS)

The principle of this test is to determine the material's swelling in thickness when immersed in water for 24 hours. The samples were square in shape at 50 ±1 mm in width (*W*) and length (*L*) at nominal thickness (*T*). The mass (M_t) of the sample was also recorded using a four figure balance.

2.6.4.1 Procedure

The procedure followed EN 317:1993. A thermostatically controlled water bath was prepared to a pH of 7 ±1 and temperature of 20 ±1 ^{o}C. Each sample was weighed using a four decimal place balance and the thickness measured using a micrometer to two decimal places. The samples were placed in a cage, separated from each

other and then immersed into the water vertically. After 24 hours of immersion, the samples were reweighed and the thickness re-measured as above. The swelling in thickness was calculated as a percentage of the initial thickness and mass:

$$TS\ (\%) = \frac{T_2 - T_1}{T_1}\ x\ 100 \qquad \text{[Equation 14]}$$

Where

T_1 is sample thickness prior to immersion

T_2 is sample thickness post immersion

2.6.5 Results

2.6.5.1 Water absorption coefficient

The Water absorption coefficient for general purpose MDF was determined to be 3.25 $kg^{-1}m^{-2}hr^{-1}$ with a standard deviation of 0.02. Figure 15 shows the change in mass over time during immersion which reveals that the capillary uptake of water is linear. The fact that the graph is linear with no change in slope, shows that the liquid water had not reached the top surface of the MDF panel by the end of the test.

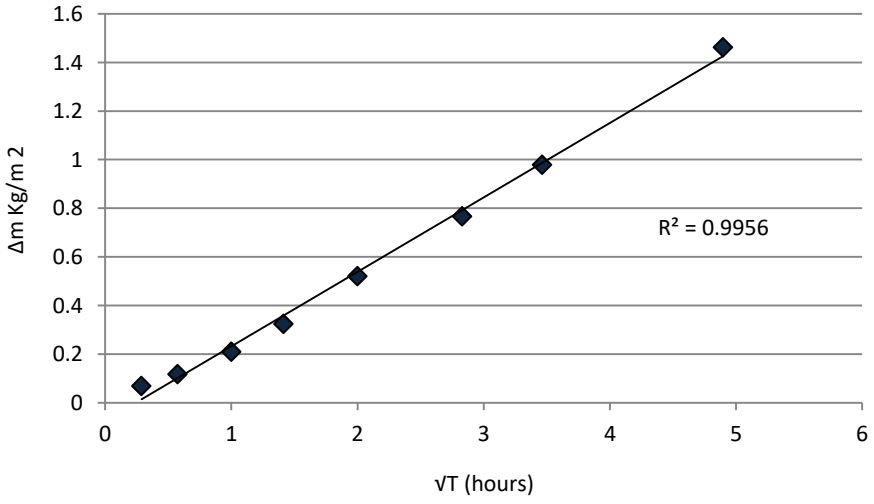


Figure 15: Mass change of MDF over time, submerged in water

2.6.5.2 Water Vapour Transmission

The vapour transmission properties determined from EN 12572:2001 are water vapour flow rate, permeance, permeability and water vapour resistance are shown in Table 11. The water vapour resistance is a measure of how resistant the material is to water vapour movement through the sample; the lower the value, the easier it is for water vapour to move through the sample. Figure 16 (dry cup) samples and Figure 17 (wet cup) show the mass change over time plots which were used to determine the water vapour flow rate through the specimen (gradient).

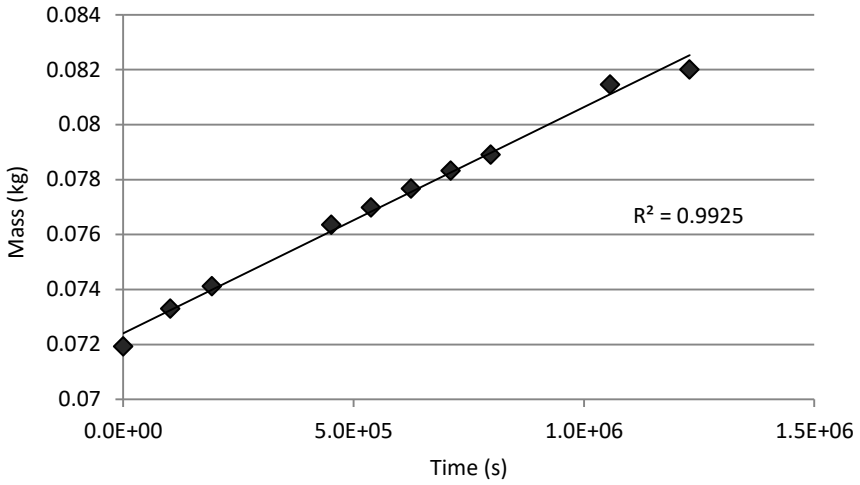


Figure 16: Dry cup mass change over time

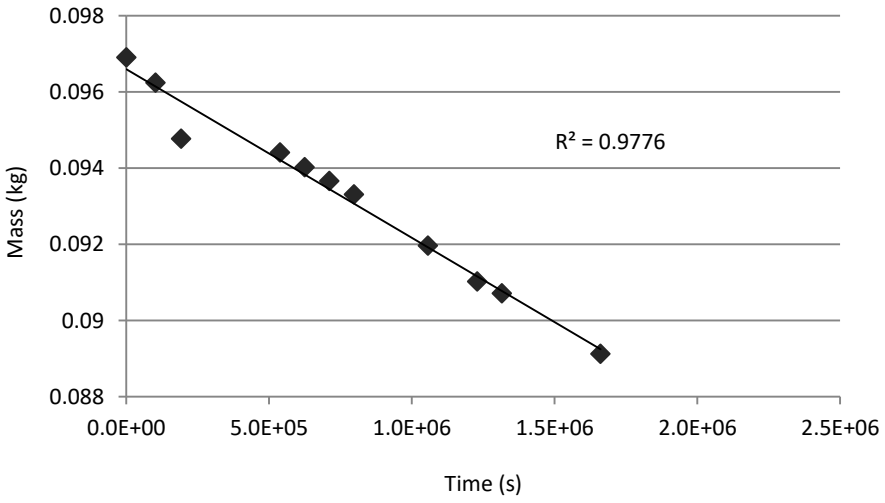


Figure 17: Wet cup mass change over time

Table 11: Water vapour transmission properties of commercial MDF

	Water vapour flow rate (g) ($kg\ s^{-1}\ m^2$)	**Water vapour permeance (*W*) ($kg\ (m^2\ s)$)**	**Water vapour resistance (Z) ($kg\ (m^2\ s)$)**	**Water vapour permeability factor (δ) ($kg\ (m^2\ s)$)**
Wet cup	1.2963E-06	1.2E-09	8.3E+08	6.74964E-08
Dry cup	2.22222E-06	7.5E-12	1.33E+11	4.17E-10

2.6.5.3 Dynamic Vapour Sorption

From the data recorded using the DVS, a sorption/desorption isotherm was produced (fig 18), which shows a typical type 2 form with evidence of hysteresis. This hysteresis is caused by the difference between the sorption (wetting) and desorption (drying) stages. From figure 19, it is evident that the greatest difference between wetting and drying is between 70 and 80% RH. This data will be important for determining any differences between the modified MDF and commercial MDF panel's behaviour when exposed to changes in RH. In many natural materials, the moisture content is higher on the drying (desorption) cycle for a particular RH due to pore filling and emptying dynamics. The equilibrium moisture content was also determined at 95% RH, to be 17.46%.

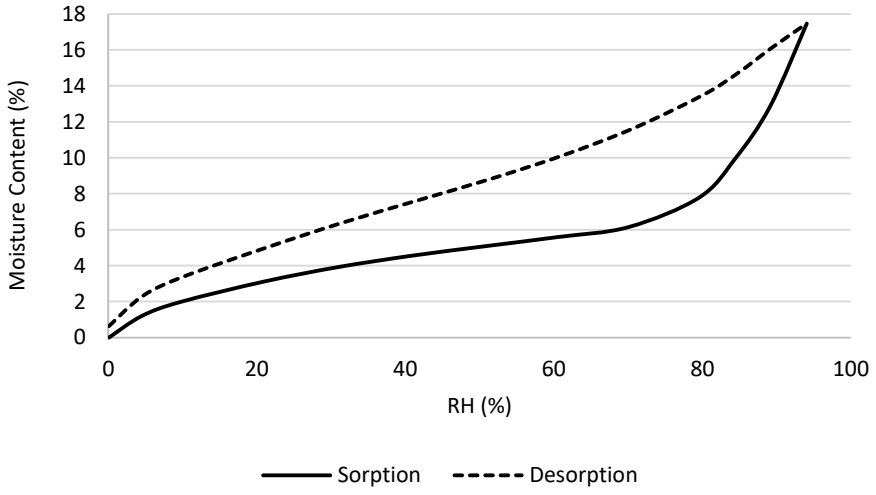


Figure 18: DVS isotherm of MDF panel

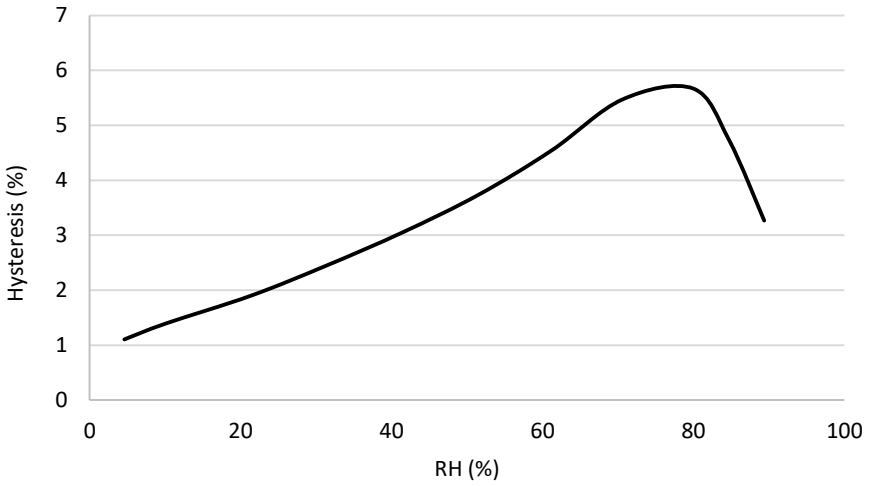


Figure 19: Hysteresis of MDF panel

2.6.5.4 Thickness swell

The standard that specifies the requirements for dry process MDF panels is defined by EN 622-5:2009. For general purpose MDF boards in dry conditions at 12 mm thickness, the required thickness swell is less than 12%. The swelling thickness for MDF boards was found to be 3.15% with a standard deviation of 0.13. According to the standard, these boards meet the requirements for general purpose MDF, general purpose MDF in humid conditions and loading bearing general purpose MDF.

2.7 Microbiology

Biodeterioration is a result of biotic processes from microorganisms (Falkiewicz-Dulik *et al* 2015). Saprophytic organisms such as mould and decay fungi are the main agents responsible for the decomposition and recycling of dead organic matter. In a building environment fungi and moulds are associated with physical and aesthetic damage to materials and human health problems such as allergic and toxic reactions (Nielsen 2003 and Jarvis and Miller, 2005). Therefore when considering the materials used in buildings it is important to consider its microbiological resistance.

This section benchmarks the MDF panel's resistance to decay, mould attack, loading of microbiota and ease of colonisation.

2.7.1 Basidiomycete Decay resistance

The decay fungi are called Basidiomycetes and there are at least 30,000 known species of these fungi (Falkiewicz-Dulik *et al* 2015). BSEN standard 12038: 2002 was used to determine the material's decay resistance. After a period of pre-conditioning (ageing) the samples were exposed to 4 pure culture of basidiomycetes: *Pleurotus ostreatus* (40c), and *Trametes* (*Coriolus*) *versicolor* (CTB 863A) (both white rot fungi), *Gloeophyllum trabeum* (108N) and *Coniophora puteana* (PWB E11) (both brown rots). After a prescribed period of incubation, the loss in dry mass resulting from the fungal attack was determined and compared with a mass loss of control samples. This procedure is used to determine resistance to fungal decay.

2.7.1.1 Sample Dimensions

For this experiment, 4 different sample sets of samples were tested; the MDF test samples, moisture check specimens, size control samples, fungal strain and virulence samples. Solid wood of Scots pine (*Pinus sylvestris*) and Beech (*Fagus sylivatica*) were tested for the fungal virulence samples. These solid wood blocks were carefully checked for good quality with no cracks, checks, decay or other defects. In accordance with the standard, the pine samples comprised entirely of sapwood with 2.5-8 growth rings per 10mm and the beech wood had an even grain of 2-6 growth rings per 10mm. The test and moisture check samples were square in shape at 50 ±0.5 mm at nominal thickness (12mm) (*T*). The size control samples, both pine and beech samples were square in dimension at 50 ±0.5 mm at the thickness of the wood-based panels being tests. The virulence samples had dimensions of 50 ±0.5 mm in length, 25 ±0.5 mm in width and 15 ±0.5 mm in height. The longitudinal faces of the virulence samples had parallel to the direction of the grain, in accordance with the standard. 6 replicates were cut and prepared for all samples, for each of the four basidiomycetes used.

2.7.1.2 Procedure

All the samples were pre-conditioned together at 60% ±5 RH and 21 ±2 °C, under a vacuum to draw off any free formaldehyde. When a constant mass had been

reached, each sample was weighed for its initial mass (m_0) to the nearest ±0.05g. All samples excluding the moisture check samples were placed individually into labelled bags and parcelled into sets for each fungal exposure, and sent to STERIS, Applied Sterilisation Technologies, Reading for gamma radiation at a dose of 30.2kGy.

2.7.1.3 Moisture check samples

These samples are used to give the moisture content factor (F_i) of the samples exposed to the basidiomycete fungi. The moisture check samples were placed into an oven at 103 ±2 °C for 24 hours. The samples were then cooled in a desiccator and weighed to the nearest 0.01g. The moisture content factor (F_i) was determined using the following equation:

$$\boldsymbol{F_i = 1 - \left(\frac{(m_o - m_1)}{m_o}\right)} \qquad \text{[Equation 15]}$$

Where

m_0 Is the initial conditioned mass (g)

m_1 Is the oven dry mass (g)

A mean is then calculated for each type of panel tested (F_{im}) and used to determine the calculated dry mass of the equivalent set of test samples (m_2).

$$\boldsymbol{m_2 = F_{im} \text{ x } m_0} \qquad \text{[Equation 16]}$$

Where

m_0 Is the initial conditioned mass (g)

F_{im} Is the calculated mean moisture factor (g)

The calculated moisture content (m_3) of the sample exposed to fungi degradation is then determined.

$$m_3 = \left(\frac{(m_o - m_2)}{m_2}\right) \mathbf{x\ 100} \qquad \text{[Equation 17]}$$

Where

m_0 Is the initial conditioned mass (g)

m_2 Is the calculated dry mass of the sample prior to fungi exposure

2.7.1.4 Culture preparation and inoculation

The culture vessels used were 90mm in diameter and 80mm deep. A 4% malt agar culture medium was made using 40g malt extract (Thermo Scientific Oxoid) and 20g agar powder (Fisher BioReagents) mixed in 1 litre of deionised water. 60ml of this culture medium was poured into each vessel and sealed with a ventilated aluminium lid. Each jar was then sterilised in an autoclave at 121^{o}C for 30 minutes. Once these vessels were cool two 6mm diameter inocula from the appropriate test fungi were transferred under aseptic conditions to the media and placed at opposite ends (fig 20). These inoculated vessels were stored in a dark room at 70% ± 5 RH and 22 ± 1 ^{o}C for two weeks or until the fungi had covered the surface of the media (fig 21). If any vessels became contaminated, they were removed from the experiment.

After the two weeks, a sterile inert plastic support was introduced using aseptic techniques to each cultured vessel and positioned centrally. The corresponding test sample was then planted on top of the support, making sure it did not come into contact with the original inocula. Figure 22 depicts the setup used. For the virulence samples, two were planted and kept separated in one vessel. The vessels were then resealed and stored in a dark chamber at 70% ±5 RH and 22 ±1 ^{o}C for 16 weeks.

Figure 20: Agar inoculation

Figure 21: Fungal growth over the agar

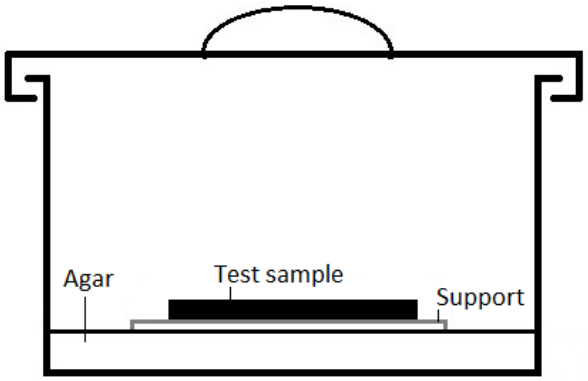


Figure 22: Vessel set up for basidiomycete decay test

2.7.1.5 Assessment

All samples were removed from the incubation chamber and from the vessels. The adhering mycelium was carefully removed and each sample weighed to the nearest 0.01g to determine the wet mass (m_2). Any waterlogging or contamination was recorded. All samples were then placed in an oven at 103 ±2 ^{o}C until a constant mass was reached. The samples are then cooled in a desiccator and then weighed to determine the dry mass (m_4) to the nearest 0.01g. From this, the percent mass loss (m_5) can be determined.

$$m_5 = \left(\frac{(m_2 - m_4)}{m_2}\right) \mathbf{x\ 100} \qquad \text{[Equation 18]}$$

Where

m_2 Is the calculated dry mass of the sample prior to fungal exposure (g)

m_4 Is the dry mass of the sample after fungal degradation (g)

If the mean mass loss is found to be greater than 3 %, then the materials are declared to be susceptible to basidiomycete decay and therefore the decay susceptibility index (DSI) must be calculated.

$$\text{DSI} = \left(\frac{T}{S}\right) \mathbf{x\ 100} \qquad \text{[Equation 19]}$$

T Is the percentage loss in mass of an individual test specimen

S Is the mean percentage loss in mass of the appropriate set of size control specimens

2.7.2 Dilution plating

This method was conducted on thin samples of wood based material. The principle of this test is to expose a sample material to fungi or bacteria for a set period of time under specific conditions. After which the samples are evaluated for fungal growth.

2.7.2.1 Sample Dimensions

The material samples were square in shape at 50 ±1 mm in width (*W*) and length (*L*) at nominal thickness (*T*). Additional virulence samples of pine and beech wood were prepared to dimensions of 50 ±0.5 mm x 25 ±0.5 mm x 15 ±0.5 mm. These were cut and planed in accordance with BSEN 12038. Size control beech and pine square samples were also prepared to 50 ±0.5 mm and at MDF test material thickness (12mm) in accordance to BSEN 12038.

2.7.2.2 Procedure

The samples were conditioned at 65% ±5 RH and 20 ±2 ^{o}C until a constant mass was reached and left in an open environment within the laboratory for 6 months. Inside a CAT 2 fume hood, the samples were then placed into 20g sterilised water and shaken for 2 minutes to remove any spores or microbial fragments on the sample. Of this solution, 100µl was removed and diluted into 10ml of sterile water (1 in 10) and shaken for 1 minute. Of this second solution, 100µl was removed and placed into 10µl (1 in 100) and shaken for one minute. This step was repeated a third time (1 in 1000). From each solution, 200µl was removed using a sterilised pipette onto sterile nutrient agar. Using a sterilised glass rod, the solution was evenly spread over the agar. Each agar plate was sealed with parafilm, suitably labelled and then stored in a dark chamber at 70% ±5 RH and 22±1 ^{o}C for 4 weeks. Three replicates were produced for each sample at each dilution.

2.7.2.3 Analysis

The agar plates were regularly checked over the 4 weeks for colony forming units. At the end of the 4 weeks, the number of individual species was counted and recorded. A record was also made of the number of uncountable species and bacterial smears that were present. The number of colony forming units (CFU) was then calculated on a basis of the sample mass:

$$\text{CFU} = \frac{(\boldsymbol{c}\ \mathbf{x}\ \mathbf{100})}{\boldsymbol{m}} \qquad \text{[Equation 20]}$$

Where

c Is the species count on the agar plate

m Is the mass of the sample (g)

2.8 Results

2.8.1 Basidiomycete decay

EN 12038:2002 declares that a material is resistant to wood-rotting basidiomycetes if the mean mass loss of the test samples is less than 3% and if all replicates of the material experienced a mass loss of less than 5%. Figure 23 shows the results of MDF

panel, pine and beech size control decay by the 4 decay fungi. The results show that the MDF panel was heavily decayed by *Coniophora puteana* (brown rot fungi) seeing over 40% mean mass loss. White rot decay by *Pleurotus ostreatus* and *Trametes* (*Coriolus*) *versicolor* was significantly less but still exceeding 3% mean mass loss. The DSI was calculated for these 3 fungi in accordance with the standard (Table 12). A DSI value of 100 indicates the same decay resistance as that of the timber used for the size control and a lower DSI indicates that the MDF panel is more resistant to decay. However, when compared to the virulence samples run, the mean mass loss was less than the required 20%. Thus the brown rot fungus *Gloeophyllum trabeum* was not virulent and did not adequately cause decay, the results are invalid and not included in DSI results.

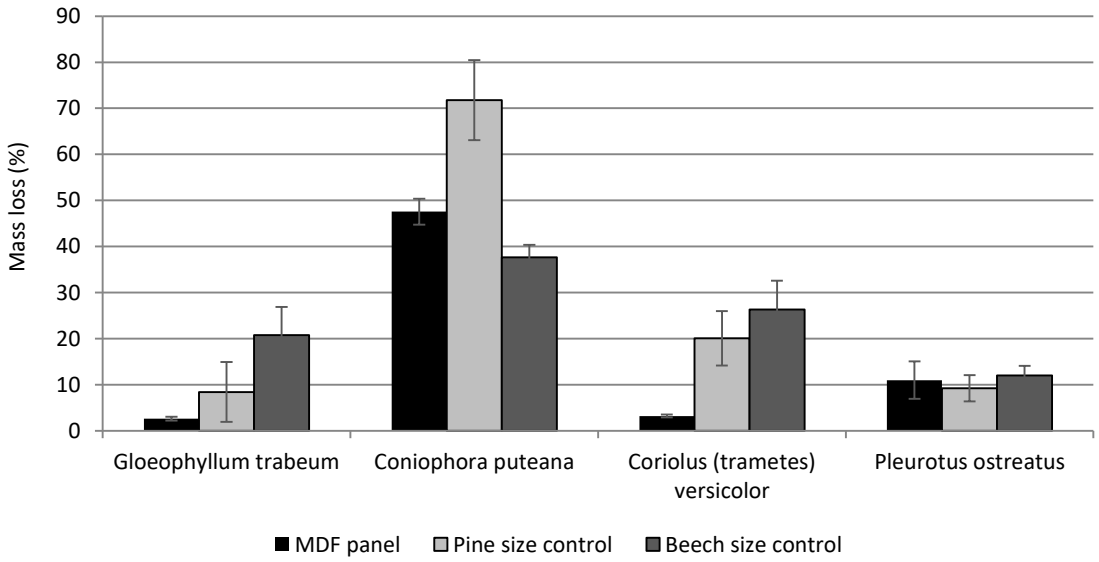


Figure 23: Basidiomycete decay of MDF panel and pine and beech size controls

Table 12: The decay susceptibility index for MDF panel

Decay fungi	DSI
Coniophora puteana	66.27
Coriolus (Trametes) versicolor	12.14
Pleurotus ostreatus	91.63

2.8.2 Microbial loading

The results of the microbial loading test are shown in Table 13. No fungal colonies were counted in the 1 in 100 and 1 in 1000 dilutions. For the 1 in 10 dilutions, the CFU was found to be 101.75 CFU g^{-1}.

Table 13: Colony forming unit (CFU) of MDF panel

Sample	Dilution			Other observations
	1 in 10	1 in 1000	1 in 1000	
MDF	101.75	0	0	Bacteria smears

2.9 Chapter summary

Table 14 shows a summary of all the data collected for benchmarking purposes of commercial MDF panel. The primary factors that govern the performance, physical and mechanical, of MDF panels are the fibre properties, fibre orientation, panel density and fibre to fibre adhesion (Groom et al., 2004). The hygric properties of a wood-based panel product are highly influential on the microbiological susceptibility of the product. The purpose of this chapter was to benchmark these influencing properties of current, commercially available MDF produced for general purpose use. The results for each of these tests will be used to compare the properties of MDF panels, modified to absorb and sequester indoor air pollutants. Each of the above tests described will be performed on MDF panels produced for this study.

Table 14: Summary of MDF panel characteristic properties

Property		Result		Property		Results	
Mechanical	Modulus of rupture (N mm^{-2})	39.16		**Physical**	Bulk density (g cm^{-3})	0.76	
	Modulus of elasticity (N mm^{-2})	3966.21			True density (g cm^{-3})	1.40	
	Internal bond strength (N mm^{-2})	0.76			Ash content (%)	0.223	
					Moisture content (%)	7.9	
Hygric	Water absorption coefficient (kg m^{-2} hr^{-1})	3.25		**Microbiology**	Basidiomycete decay (DSI)	*Coniophora puteana*	66.27
	Water vapour transmission	Wet cup	Dry cup			*Coriolus (trametes) versicolor*	12.14
	Water vapour flow rate (kg/(sec*m^2))	1.30E-06	2.22E-06				
	Water vapour permeance (kg/(sec*m^2*Pa))	1.20E-09	7.5E-12			*Pleurotus ostreatus*	91.63
	Water vapour resistance ((sec*m^2*Pa)/kg)	8.30E+08	1.33E+11				
	Water vapour permeability (kg/(sec*m*Pa))	6.75E-08	4.17E-10		Dilution plating (Colony forming unit, 1 in 10)	101.75	
	Equilibrium moisture content (EMC) (%) at 95% RH	17.46					
	Thickness Swell (%)	3.15					

3 Physical and Mechanical Modifications

3.1 Introduction

Historically, there has been considerable research into the reduction of emissions from their original source, such as replacing formaldehyde based resins with bio-based resins or synthetic resins such as Methylene Diphenyl di-isocyanate (MDI) or polymeric MDI (pMDI) (Jiang et al., 2002; Pratelli et al., 2013). However, using isocyanate-based resins does not prevent all panel emissions and can result in molecularly heavier VOC emissions (Jiang et al., 2002). Therefore, other methods are sought to reduce or absorb formaldehyde released from other materials from the atmosphere. This chapter examines a mechanical and a physical modification that can be made to MDF panels to sequester VOCs and formaldehyde from the atmosphere. The mechanical modification made was to vary the refining pressure during MDF wood fibre production and the physical modification was the addition of a scavenger to the MDF panel with both methods designed to actively scavenge formaldehyde and VOCs.

3.2 Mechanical Modification – Refiner pressure

3.2.1 Rationale

There is some research (Groom et al., 2004; Kelley et al., 2005; Labosky et al., 1993; Xing et al., 2006a) that indicates that changes to the refining process can alter the fibre's properties. During the refining process, the wood chips are put through a "digester", where the chips are squeezed, compressed and heated with steam at 6-10 bar (87-145 psi) pressure. Here the wood chips are fed into the centre of two rotating metal disks. One disk remains stationary while the second rotates at approximately 1500 rpm. This generates an internal temperature of 175-190^{o}C (Widsten *et al* 2004). The high temperature aids the refining process by softening the fibre (Aisyah *et al* 2013). The combined pressure, rotational forces and temperature result in the lignin becoming plasticised and cause the separation of the fibres at the lignin rich middle lamella region resulting in reduced fibre dimensions. A fine material is therefore produced by the partial or full collapse of the fibre and by the surface material becoming detached (Monica *et al* 2009).

Some research has indicated that this refining stage in MDF production can alter the fibres and have adverse effects on the final MDF panel mechanical properties (Zawawi *et al* 2013). Krug and Kehr (2001) suggested that, due to the shorter fibre lengths, the MDF panel will have lower strength and elastic properties, although swelling properties may be improved (Cheng *et al* 2006). This was also observed by Zawawi *et al* (2013) who highlighted that a reduced fibre length resulted in MDF panels with a lower modulus of rupture, modulus of elasticity and internal bond strength, mainly due to poor fibre contact.

The mechanical process of producing fibre for MDF can also alter the properties of the fibre in other ways. The percentage of extractives and glucose, for example, increases with refining pressure whilst xylan, galactan and mannan quantities decrease (Kelley *et al* 2005). Different refining conditions can also alter the morphology of fibres and thus surface roughness (Gustafsson et al., 2003; Snell et al., 2005). High refining pressures coupled with high temperatures produce very fine fibres, while mild conditions produce a mixture of fibrillated and unbroken fibres, increasing roughness (Aisyah *et al* 2013). This research shows that changes to the refining of the wood fibre alter its structure, therefore it is possible that different functional groups may be more accessible.

Research has also been conducted into the effects of refining of different wood species and other lignocellulosic materials. The woodchip obtained from Kronospan was a mixture of spruce, pine and fir. Cheng *et al* 2006 reported the effects of refining black spruce and the implications it has on mechanical properties. The woodchip was refined at 6, 9 and 12 bar and at different retention times of 3, 5 and 7 minutes, for each pressure and composite boards produced. The results obtained revealed that steam pressure had a significant effect on the modulus of rupture (flexural strength), modulus of elasticity, thickness swell and water sorption, whereas the retention time significantly affected internal bond strength. It was concluded that the steam pressure should be considered the most important factor in refining spruce. Krug and Kher (2001) found that increased fibre pressure reduced the strength and modulus of elasticity of pine fibre based panels (Aisyah *et al* 2013).

Bhardwaj *et al* (2007) studied the effects of refining of fibre for paper making. The main aim of refining is to improve fibre to fibre bonding and make the fibres'

chemical components more accessible. Fardim and Durán (2003) also analysed the effects of refining on kraft pulp fibres and also stated that fibre length shortens and fibrillation of the cell wall occurs. Fardim and Durán (2003) studied the surface chemical composition and found that the refining process increased the carbohydrate coverage and decreased lignin coverage. This is a result of the refining changing the distribution of surface components, leading to increased exposure to carbohydrates. It was also found that during this process, extractives and xylan were released and adhered to the fibre surface and the sodium oleate (a surface-active compound), thus changing its surface chemistry.

As refining pressure does influence surface chemistry and final panel strength properties, an investigation to determine how different refining pressures influence the absorption and desorption of formaldehyde was conducted in this study.

3.2.2 Wood fibre production

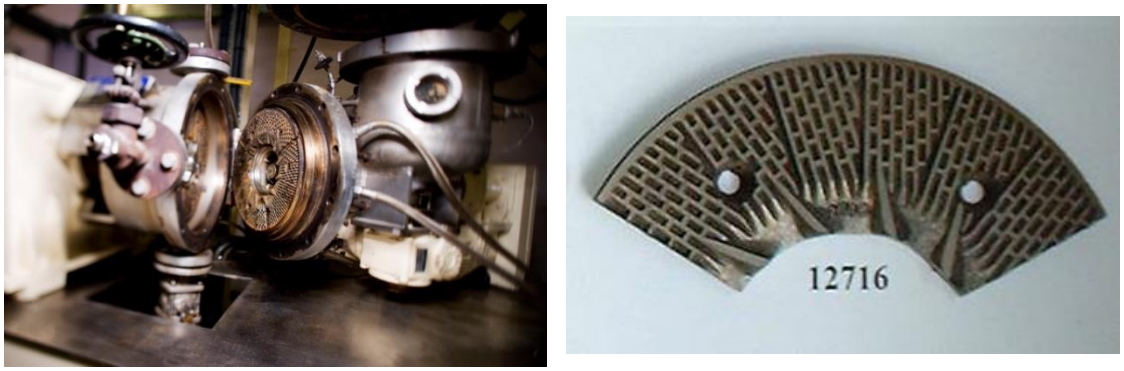
The wood chip was obtained from Kronospan (Chirk, North Wales) and was a mix of fir, spruce and pine. The chips were then taken to the BioComposites Centre's Bio-Refining Technology Transfer Centre (Mona, Anglesey, UK), where they were refined using an ANDRITZ SPROUT-BAUER 12" pressurised refiner at different refining pressures; 6 bar (87 psi or 6 x10^5 Pa), 8 bar (116 psi or 8 x10^5 Pa) and 10 bar (145 psi or 10 x10^5Pa).

Figure 24: Hopper and MSD infeed

The wood chips were first screened for contaminants and other potential equipment damaging pieces such as stone and metal. The wood chips were then poured into a hopper and fed into a modular screw device (MSD) (fig 24) and passed through a 2.6 metre long cooker to a 60 litre digester (fig 25).

Figure 25: 60 litre digester

From the 60 litre digester, the wood material was fed by a screw conveyor to the centre of two stationary refiner disks (fig 26). The maximum throughput of the refiner is 45kg of wood chips per hour. The required pressure was applied to the refining system by a steam boiler and the material was held in a pressurised environment for a minimum of 4 minutes. The refiner plates are designed for either rolling, cutting or grinding actions and the gap between them can be adjusted in accordance with the material being refined.



A B

Figure 26: Refiner setup, (A) Refiner plate setup and (B) Refiner plate

The now refined fibre was then vented through a 9mm stainless steel pipe called the blow-line. The blow-line can be used to inject the resin and wax required for board manufacture but for the purpose of this test, the blow-line connected the refiner to a 120m long flash drier. The diameter of the dryer was 59mm with an air velocity of 29 m s^{-1} and the fibre remained in the flash dryer for only a few seconds. The temperature of the flash dryer was kept in the range of 115-125°C using a hot oil heat exchanger, which took air from the outside environment. A cyclone system separated the dry fibre from the wet fibre and directed it into bags or, if an MDF panel was immediately being produced, to a mattress former. To maintain comparability between the refined fibres, refiner feed screw settings, energy consumption and plate gap width were maintained at the same levels throughout fibre production. The fibre produced at each refiner pressure was collected and sealed in plastic bags to ensure the moisture content (approximately 7%) was maintained (fig 27).

Figure 27: Sealed MDF wood fibre for storage

Results and discussion

It was noticed that the wood fibre refined at 6 bar pressure was much longer in length and lighter in colour than those refined at 8 and at 10 bar pressure (fig 28), which were a much darker brown. This agrees with Groom et al., (2004) observations who also noted that the number of fines (fibres were powder-like) increased with increasing refiner pressure, up to a maximum pressure of 18 bar.

Figure 28: The colour variation between 6 bar (left), 8 bar (middle) and 10 bar (right) refined fibre

This colour difference immediately reveals that the different refiner pressures affected the fibre structure and suggests some damage to the fibre surface structure. Woodchip refined at lower pressures produces fibre that has a smoother surface, with surface tears (Groom et al., 2004), whereas woodchip refined at higher pressures produce fibre that is highly fragmented with a higher proportion of fines fraction (Groom et al., 2004; Kelley et al., 2005).

3.2.3 Moisture behaviour

The fibres refined at different pressures were also subjected to dynamic vapour sorption (DVS) to determine if refining woodchip at different pressures affected the hydroscopic behaviour when exposed to water vapour. Determination of fibre mass change with changing relative humidity was carried out using the same method as described in chapter 2, section 2.6.3.

3.2.3.1 Results and discussion

The equilibrium moisture content (EMC) at 95% RH of the wood fibres refined at 6, 8 and 10 bar pressures are 20.57%, 20.14% and 20.54% respectively. Figure 29 shows the isotherm results of woodchips refined at 6, 8 and 10 bar pressure and reveals that hysteresis is evident. Hysteresis is common in materials and natural fibres with a microporous structure. Hysteresis is the difference in EMC values at the same RH value observed on wetting and drying of the material and is readily evident in vapour sorption isotherms of natural fibre materials (Hill et al., 2009). Figure 30 depicts the hysteresis of the refined fibre, revealing that there is little difference between the absorption and desorption curves of the fibres. However, fibres refined at 10 bar seem to have the greatest hysteresis at lower RH than the 6 and 8 bar refined fibre. The higher hysteresis observed in 10 bar refined fibre is due to the fibres' higher lignin content than the 6 and 8 bar refined fibre. This is because the lignin network within material fibres is able to deform to accommodate water within in the cell wall, expanding the microcapillaries (Hill et al., 2009). This swelling exposes new OH sites for hydrogen bonds with water molecules, therefore desorption occurs at a different rate to absorption (Hill et al., 2009).

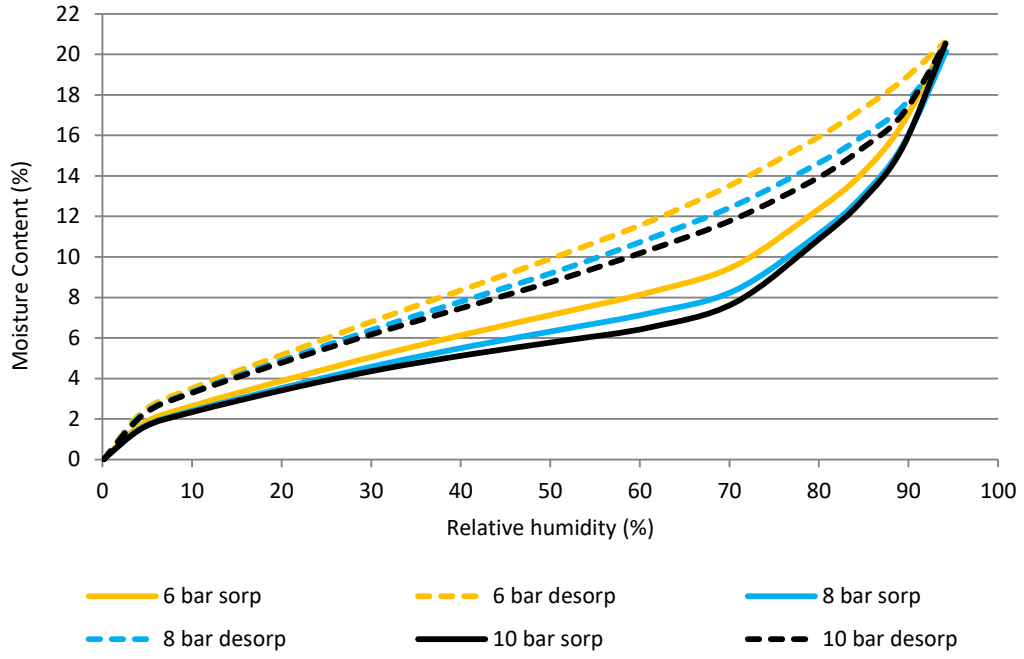


Figure 29: DVS isotherm of 6, 8 and 10 bar refined fibre

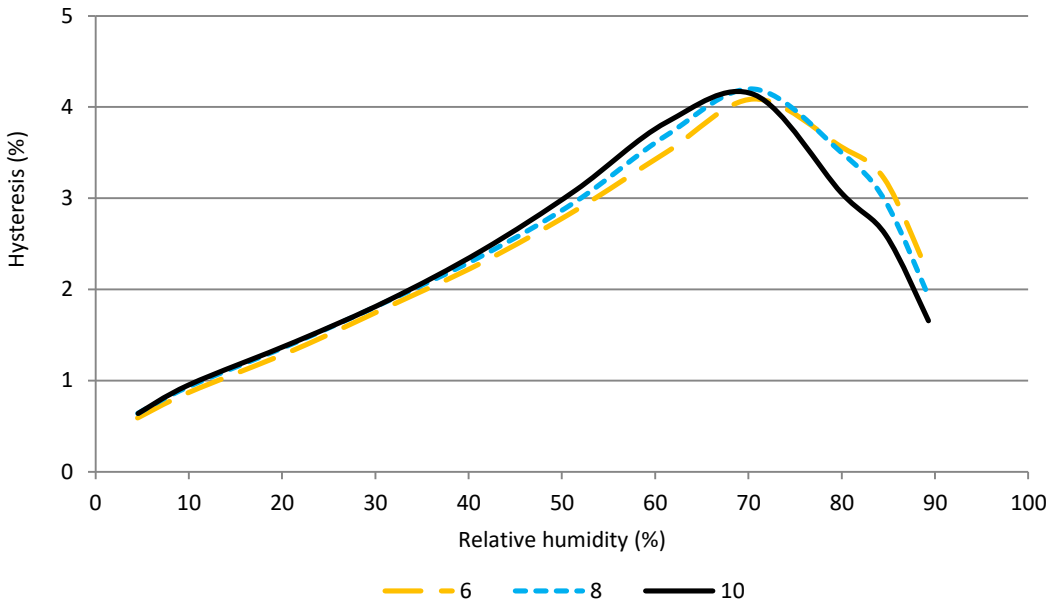


Figure 30: Hysteresis of 6, 8 and 10 bar refined fibre

3.2.4 Formaldehyde Absorption

The fibres produced under the three refiner pressures of 6, 8 and 10 bar were each evaluated for the absorption capabilities using the Dynamic Vapour Sorption (DVS) equipment.

3.2.4.1 Method

The DVS is designed to accurately measure mass changes of a sample (less than 10mg), as the sample absorbs controlled concentrations of formaldehyde. The water reservoir in the DVS system was filled with a 9.25% solution of formaldehyde in water (diluted with deionised water from a 37% formaldehyde solution supplied by Sigma-Aldrich UK). The formaldehyde was carried over the sample using nitrogen inert gas, while the relative humidity was precisely controlled. The mass changes indicated sorption and desorption characteristics of the sample. The nitrogen gas was passed over the sample at a rate of 200 cm^3 s^{-1} and at a temperature of 21 ±0.2 °C. The schedule for the DVS was set up to run 6 cycles whereby the RH would begin from 0% until a constant mass was reached and then the RH increased to 90% until constant mass was reached and then the RH was reduced to 0% again. The mass change data was acquired every 20s (Curling *et al* 2012). To ensure the reliability of the results obtained, an absorption/desorption cycle was repeated 6 times over the same sample. This helped to ensure that a true maximum value of formaldehyde absorption was obtained.

Results and discussion

Figure 31 depicts an example of the six DVS cycles. Point A shows the initial dry mass of the sample and point B is the sample mass after the first exposure it to formaldehyde. The difference in mass of the sample after each cycle indicates that the sample had absorbed formaldehyde. The difference between the initial mass and final mass at the end of the 6^{th} cycle gives the total amount of formaldehyde adsorbed by the wood fibre. Figure 32 shows the maximum formaldehyde absorption results of 6, 8 and 10 bar refined fibre. The results show that 6 bar refined fibre absorbed the most formaldehyde, 134.67 mg g^{-1} and 8 bar refined fibre the least, 41.20 mg g^{-1}. It is clear that there is a distinct difference between the formaldehyde absorption capabilities of the fibre refined under different pressures. This could be a result of the change in lignin structure during the refining process and the degradation of hemicellulose due to the high temperatures generated (175-190^{o}C) within the refiner.

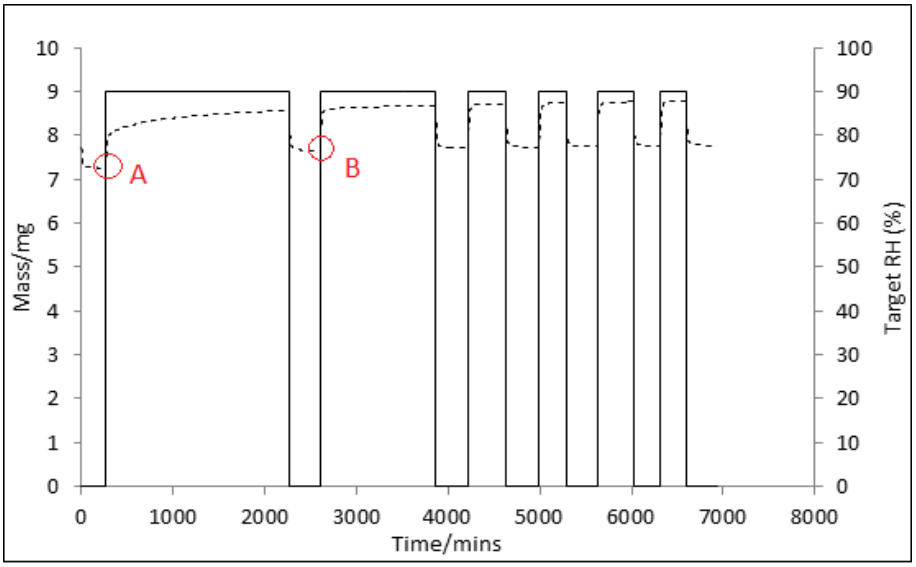


Figure 31: Example of mass change (dotted line) over the six cycles (solid line)

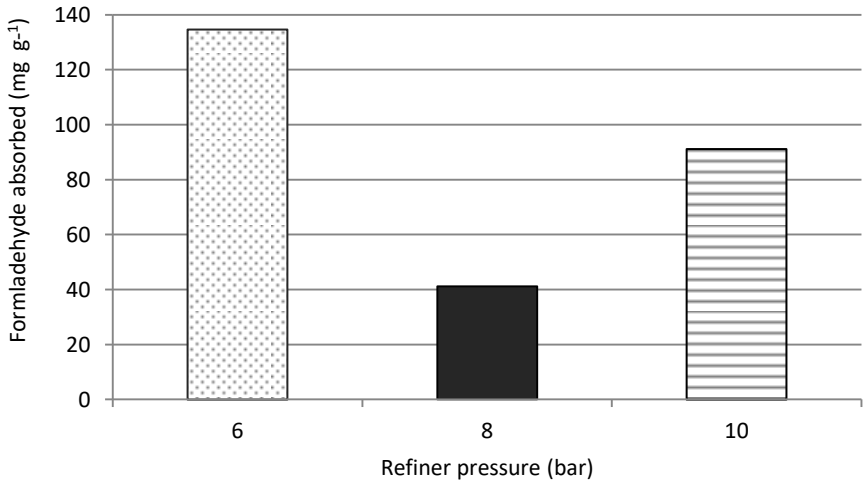


Figure 32: Formaldehyde absorption of MDF wood fibre refined at different pressures

Figure 33 shows the formaldehyde absorption increase with each cycle. It reveals that the absorption of fibre refined at 6 and 10 bar has not reached equilibrium suggesting the fibre has potential to absorb more formaldehyde than stated above. Whereas fibre refined at 8 bar pressure shows very little increase after the third cycle, therefore, it is unlikely it will absorb much more formaldehyde than 41.20 mg g^{-1}.

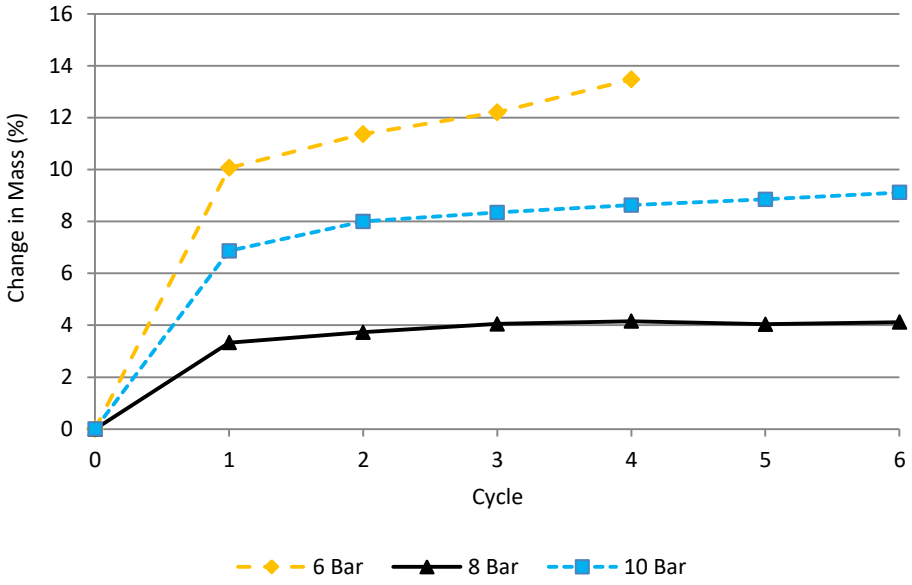


Figure 33: Mass change of refined fibre over six cycles

It is difficult to determine the effect of refining pressure on the properties of wood fibres due to the number of parameters linked with the refining process (Groom et al., 2004). However, there have been previous studies on the refining of woodchips at varying pressures and temperatures, evaluating the changes in the wood fibre structure and chemical composition (Groom et al., 2000, 2004; Kelley et al., 2005). The refining process is known to alter the fibre structure and the proportions of the three fundamental components of the wood, cellulose, hemicellulose and lignin, as well as extractive content (Kelley et al., 2005). Groom et al., (2000) reported that with increasing refiner pressure, the fibre surface becomes increasingly more torn and rough, thus affecting other properties such as surface area. Moreover, increasing refiner pressure decreases the proportion of hemicellulose sugars such as xylose and galactose due to hydrolysis (Groom et al., 2000; Kelley et al., 2005). As a result of hydrolysis, a large proportion of the carbohydrate fraction is lost in the refining processes, which accounts for the darkening in colour of the fibre, as the proportion of the lignin content becomes greater. This also affects the cellulose in the wood fibre generally increasing the average crystallinity following the increasing refiner pressure, as the concentration of amorphous cellulose and hemicellulose components decrease (Kelley et al., 2005). All of the above-mentioned changes are most pronounced at 8 bar refined fibre (Kelley et al., 2005).

The proportion of lignin has been reported to remain the same (Groom et al., 2000). However, at higher refiner pressures, the glass transition temperature of lignin polymer is reduced. As a result, the lignin is more unstable at lower temperatures and therefore the lignin molecules can move more freely within the fibre structure. This movement of the hydrophobic lignin could explain the changes in hydroscopic behaviour of the fibre. Groom et al., (2000) also reported that at low refining pressures, a substance appeared to be deposited on the surface of the fibre and at higher pressures the deposit 'flowed' together to form a large homogenous coating. This could be evidence of the lignin moving to the surface of the fibre changing the surface characteristics.

3.2.5 Small MDF panel production

The next stage of the mechanical modification assessment was to produce and evaluate MDF panels produced from the 6, 8 and 10 bar refined fibre. Small scale MDF boards were produced using the fibre refined as described in section 3.2.2 at BioComposites Centre (Bangor, UK) (fig 34). The dimensions of the MDF boards were 300 x 300 x 12mm thickness at a final density of 760 k gm^{-3}. The urea-formaldehyde (UF) resin was obtained from Kronospan (Chirck, UK) and stored in a fridge at -2 ±1 °C until it was required for panel production.

Figure 34: Small scale press

3.2.5.1 Method / Production

The principle of making the MDF boards on a small scale is the same as the pilot scale. The fibre was weighed out to the nearest 0.1kg into a pre-weighed bin. The fibre was then emptied into a clean drum blender and spun to produce a fine 'curtain' of falling fibre. This fibre was left spinning for 3 minutes to ensure the fibre was fluffed and broken up (fig 35A). 156.20g of UF resin was weighed out to the nearest 0.1g and sprayed onto the fibre inside the drum blender at a steady constant rate. The fibre was then removed from the drum blender and placed evenly into a forming box of 0.3m^2 and 1m deep. The fibre was then pre-pressed to reduce the mat thickness to less than 30cm so that it fitted between the two hot plates of the press (fig 35B). The fibre was then placed into pre-heated hot press plates at 180 ±2 °C and pressed to a thickness of 12mm for 3 minutes to ensure resin curing.

A B C

Figure 35: Three main stages of MDF panel production; wood fibre (A), pre-pressed fibre mat (B) and final MDF panel (C)

The MDF panels (fig 35C) were removed from the press and cooled under a ventilated hood to off-gas any free formaldehyde. Three replicates were produced from each of the three different refined fibres. After a week of off-gassing, the panels were cut in accordance with EN 326-1, where samples for property testing were taken from the 3 replicate panels and from different positions in the panel to account for variability between and within the panels. The cut samples were labelled accordingly to their cut position, replicate and panel, then conditioned to a constant mass at 65% ±5 RH and at 20 ±2 ^{o}C.

3.2.6 Mechanical properties

The panels underwent a number of tests to determine the effect of the mechanical modification on MDF panel properties and formaldehyde absorption properties.

3.2.6.1 MOE and MOR

The modulus of elasticity (MOE) and modulus of rupture (MOR) were determined following the same method as described in chapter 2, section 2.4.1 with six replicates.

The modulus of rupture (flexural strength) is a measurement of the strength of the material when it ruptures or fractures. The modulus of elasticity (flex modulus) measures the stiffness of the material, the higher the value the lower the amount of deformation the material experiences under an applied load.

Results and discussion

Table 15 shows the maximum load at break, MOR and MOE results of the panels produced using fibre refined under different refiner pressures. There is no statistical difference between the results for either of the panels produced from the 6, 8 or 10 bar refined fibre. Figures 36 and 37 depict maximum load applied to the MDF panels before failure, the MOR and MOE respectively. Panels produced using fibre refined at 10 bar pressure had the lowest maximum load, MOR and MOE of 222.53N, 11.37 N mm^{-2} and 1713.06 N mm^{-2}, respectively. Panels produced using 6 bar refined fibre had the highest maximum load and MOR at 271.75N and 13.6 N mm^{-2}, respectively. The greatest MOE 2053.39 N mm^{-2} observed was for panels produced using 8 bar refined fibre.

Table 15: The average maximum load, MOR and MOE of MDF panels refined at different pressures (6 replicates)

Board	Maximum Load		Modulus of Rupture		Modulus of Elasticity	
	(N)	StD	(N mm^{-2})	StD	(N mm^{-2})	StD
MDF 6 bar	271.75	32.91	13.60	1.58	1868.99	101.40
MDF 8 bar	269.45	48.84	13.34	1.74	2053.39	360.89
MDF 10 bar	222.53	30.47	11.37	1.76	1713.06	281.54

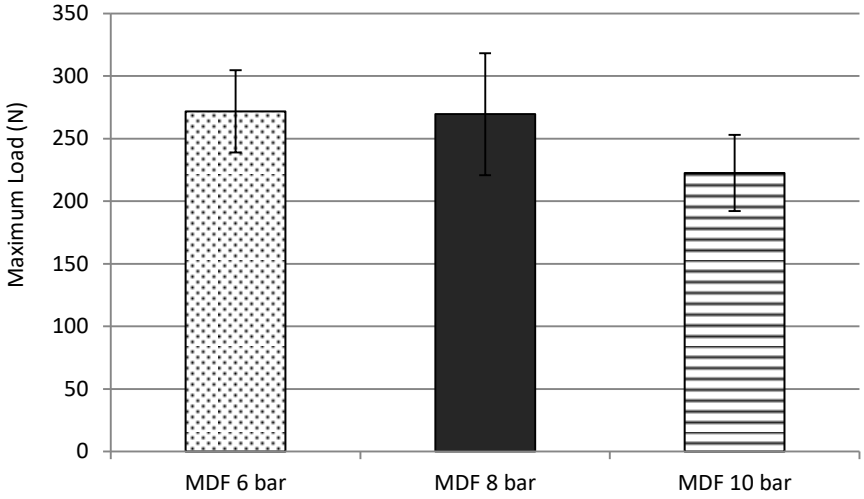
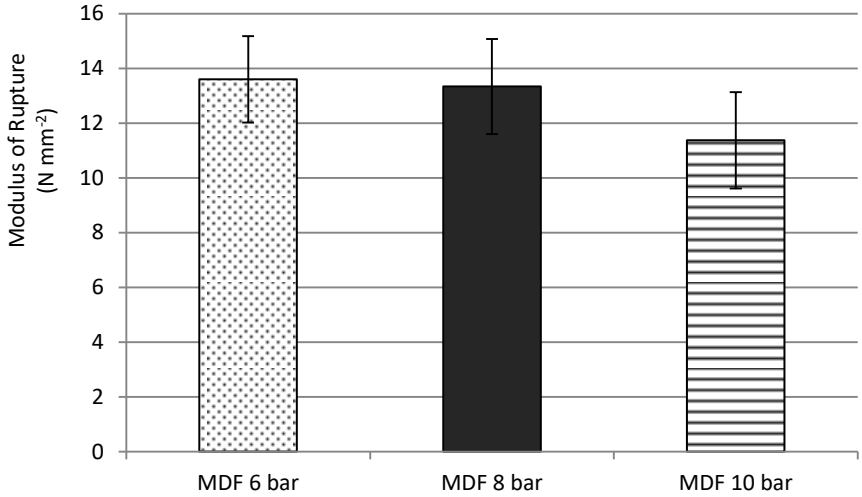
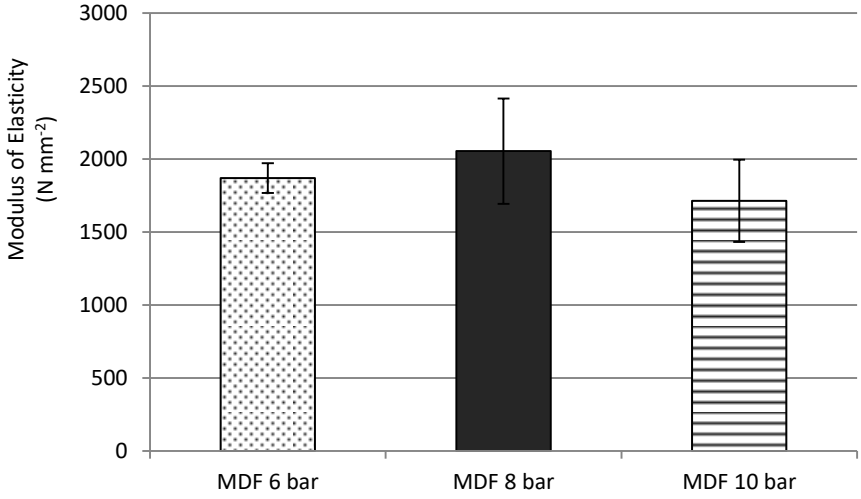


Figure 36: Maximum load of MDF panels refined at different pressures



A



B

Figure 37: MOR (A) and MOE (B) of MDF panels refined at different pressures

During the production process, the resin migrates through the cell wall and coats the fibre lumen surface by capillary action and through pairs of pits (Groom et al., 2004). With refined fibre, the resin will also migrate through cell wall cracks, which generally follow the microfibril angle of the S2 layer (Groom et al., 2004). Therefore it is expected that this will improve bonding between individual fibres and increase the mechanical properties of the final MDF panel. However, drum-blending is done on relatively dry fibres, which move slowly enough for fibre to fibre interactions, compared to fibre resonated directly in the blow-line (Groom et al., 2004). This slowly moving fibre results in thicker and poorer distribution of resin on the fibre surface (Groom et al., 2004). This is evident in Figure 35C by the presence of the resin spots. The same better distribution of resin on the fibre in the blow-line and stronger bonding was observed by Kelley et al., (2005) who reported that fibreboards produced from 8 bar refined fibre, had the highest MOE and was related to fibre surface properties such as fibre aspect ratio (width: length). The reduction in strength of boards produced using 10 bar refined fibre is due to the reduction in fibre length. This changes the aspect ratio of the fibre and affects the matrix of the MDF panel, thus reducing its strength.

3.2.6.2 Ash test

The ash content of the modified panels was also determined to quantify the inorganic content. The method was the same as described in chapter 2 section 2.5.3.

Results and discussion

Figure 38 depicts the ash content (%) of the MDF panels. Panels produced from 6 and 8 bar refined fibre had the lowest proportion of inorganics, 0.19 % and 0.16% respectively. The highest amount of inorganics was found to be in panels produced from 10 bar refined fibre at 0.25%.

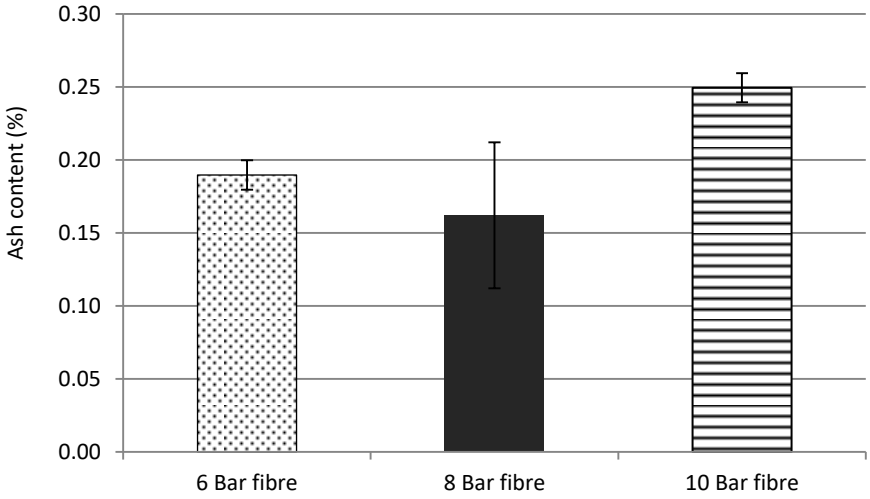


Figure 38: Ash content of MDF panels refined at different pressures

The higher amount of inorganics observed in panels produced with 10 bar refined fibre is a result of the refining process. During the refining process, there is evidence of a significant increase in extractive content with increasing refining pressure (Kelley et al., 2005). Extractives are categorised as either inorganic or organic including phenolics, waxes, fats, salts and oils (Desch and Dinwoodie, 1996; Rowell, 1984). The increased percentage of inorganics in 10 bar refined fibre MDF results from the loss of organic extractives during refining at high pressures.

3.2.7 Formaldehyde Absorption

The main purpose of the physical modification to the MDF panel was to determine any difference in the refined fibres' ability to absorb formaldehyde from the atmosphere. Whilst the mechanical properties are important to maintain for obvious reasons, the fibres must still be able to absorb formaldehyde from indoor air and not just any free formaldehyde that may exist after board production from the UF resins. This absorption is necessary for the physical modifications to be successful. Therefore, the MDF panel produced from the different refined fibres were reevaluated using DVS for formaldehyde absorption using the same method described in section 3.2.4

Results and discussion

Figure 39 and Table 16 show the maximum formaldehyde absorption of MDF panels made from fibre refined at different pressures. The highest value of formaldehyde absorption was observed for MDF panels made from 8 bar refined fibre, 127.66 mg g^{-1}. Whereas the least amount absorbed was by MDF panels produced from 6 bar refined fibre, 63.23 mg g^{-1}.

Table 16 also shows the average percentage net gain in mass from formaldehyde absorption as a proportion of the sample weight. It shows that the mass of MDF panels produced with 8 bar refined fibre increased by 13%. Whereas panels produced from 6 bar and 10 bar refined fibre, had a net increase of 7%.

Table 16: Maximum formaldehyde absorption by modified MDF panels

Board	Formaldehyde absorbed (mg g^{-1})	Standard deviation	Net gain (%)	Standard deviation
6 Bar	63.23	13.58	6.56	1.04
8 Bar	127.66	0.0071	12.77	1.64
10 Bar	65.69	0.007	6.57	0.0005

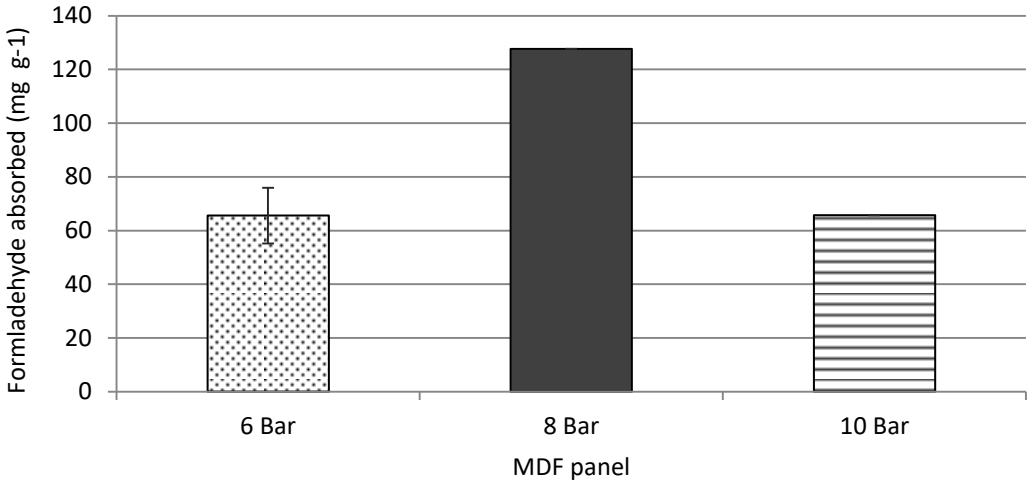


Figure 39: The maximum formaldehyde absorption of MDF panels refined at different pressures

The results for modified MDF panel and formaldehyde absorption show a reverse relationship compared to formaldehyde absorption by loose fibre refined at

different refiner pressure (section 3.2.4.2). Where loose (not in board form) 8 bar refined fibre previously absorbed the least formaldehyde, it absorbed the most when used to produce an MDF panel. The percent mass gain of the modified panels highlights that MDF panels made using 8 bar refined fibre absorb twice the amount of the formaldehyde than MDF panels made from 6 and 10 bar refined fibre. This shows that the MDF panel production process had an effect on the fibre's capabilities of absorbing formaldehyde.

It is possible that the additional exposure to heat and high pressure has further altered the structural state of the fibre. If this is the case, then the fibre's surface structural state is important in influencing its formaldehyde absorption capabilities. Figure 40 depicts a theoretical chart showing changes in the fibre state after refining, hot pressing and formaldehyde absorption. It is possible that fibre refined at 6 bar (state 1) sees a structural shift during hot pressing to a different, state 2. Fibre refined at 8 bar refined fibre at structural state 2 shifts to a 3rd state. Fibre refined at 10 bar, state 3 shifts to a 4^{th} state, that fibre would if some fibre was refined at 12 bar pressure. This would suggest that fibre at different structural states absorbs different amounts of gaseous formaldehyde. The additional exposure to the heat and high pressure may have caused further movement of the lignin proportion in the fibre towards the fibre surface, reducing its surface area and access to functional groups. Therefore reducing the number of accessible formaldehyde binding sites.

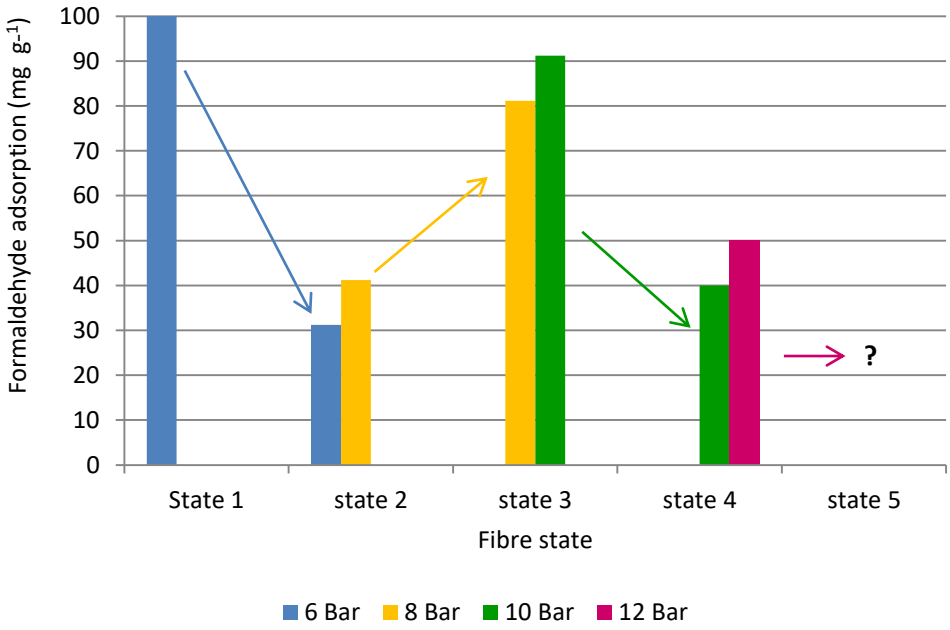


Figure 40: Theoretical shift of structural state

To further understand any structural differences between the modified MDF panels the panel surface area and porosity characteristics were determined to interpret why MDF panels produced with 8 bar refined fibre absorbed the most formaldehyde.

3.2.7.1 Surface area

The surface area of the modified MDF panels was determined using a Micromeritecs Gemini surface area analyser and using a nitrogen absorption method and the Brunauer, Emmett and Teller (B.E.T) theory (Ryu et al., 2003).

Method

The samples, after de-gassing, were oven dried overnight at 50°C. The samples were then placed into a glass tube connected to the Gemini analyser. The glass tubes were mechanically lowered into liquid nitrogen which was used as a sample coolant to ensure temperature stability. The surface area was then determined by Micromeritecs Stardriver software using the B.E.T. theory, based on the volume of nitrogen absorbed at different partial pressures (zeroed for background pressure).

Results and discussion

The surface area of MDF panels made from 6, 8 and 10 bar refined fibre were 1.0578 $m^2 g^{-1}$, 0.8961 $m^2 g^{-1}$ and 0.8442 $m^2 g^{-1}$ respectively. Figure 41 shows the surface area results for modified MDF panels.

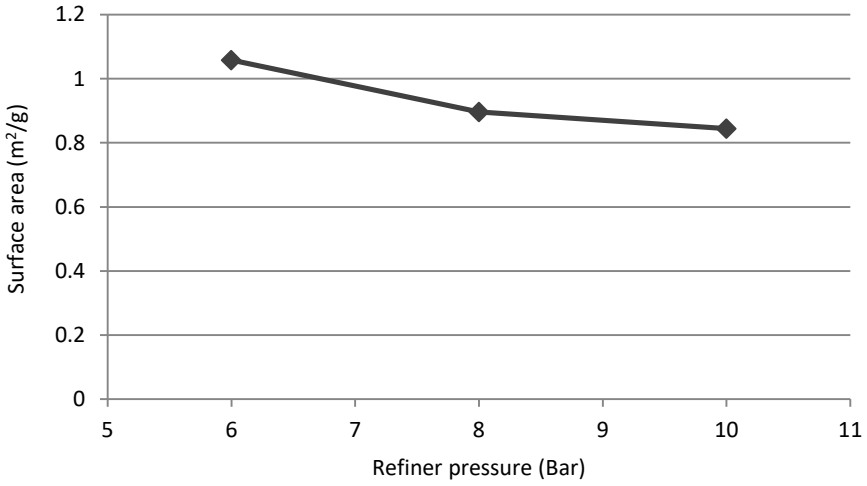


Figure 41: Surface area of MDF panels refined at different pressures

The results show that with increasing refiner pressure, the fibre surface area decreases. It would be expected that with increasing refiner pressure, the surface area would increase as the fibre lengths become shorter and rougher. However, it is more likely that the movement of lignin has formed a smooth coating over the fibre surface, thus reducing surface area. This helps to explain and understand why formaldehyde absorption by wood fibre decreases with increasing refiner pressure. This movement of lignin may be obscuring access to functional groups (formaldehyde binding sites) or boards produced using 8 bar refined fibre have optimal amounts of available sites at a surface area of 0.8961 $m^2 g^{-1}$ and beyond this point, the surface area decreases as the lignin forms a smooth coating on the fibre surface.

3.2.7.2 Porosity

Using the same piece of equipment and method to determine surface area, the porosity of the modified MDF panel can be determined using the BJH theory. Three pore sizes can be determined and are classified into microporous (<2nm),

mesoporous (2nm-50nm) and macroporous (>50nm). The data is presented in 3 graphs, porosity isotherms, cumulative pore volume and pore diameter distribution.

Results and discussion

Porosity isotherm

The isotherm graph shows the sorption and desorption of nitrogen into the MDF panel structure. Figure 42 shows the isotherm for MDF panels made from 6 bar refined fibre and that there is very little hysteresis between the absorption and desorption curves, which is indicative of a macroporous structure. MDF panels produced from 8 bar (fig 43) and 10 bar (fig 44) refined fibre have a more defined hysteresis which indicates a shift towards a mesoporous structure.

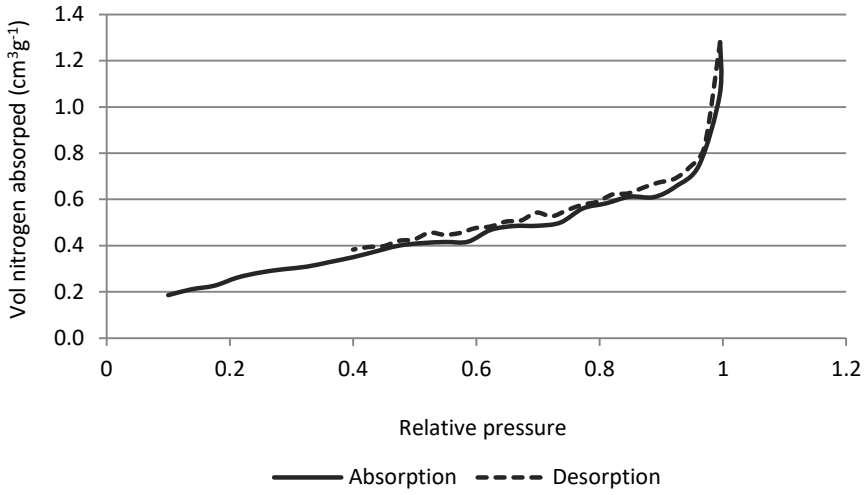


Figure 42: Porosity Isotherm of 6 Bar refined fibre

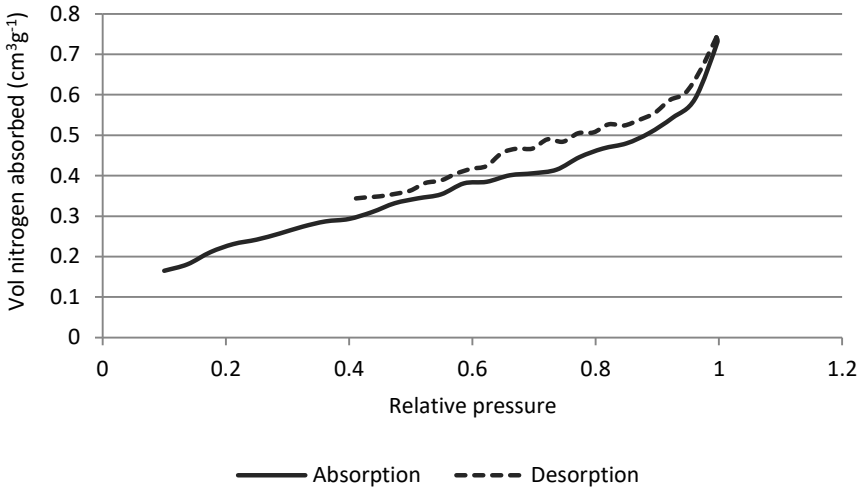


Figure 43: Porosity Isotherm of 8 Bar refined fibre

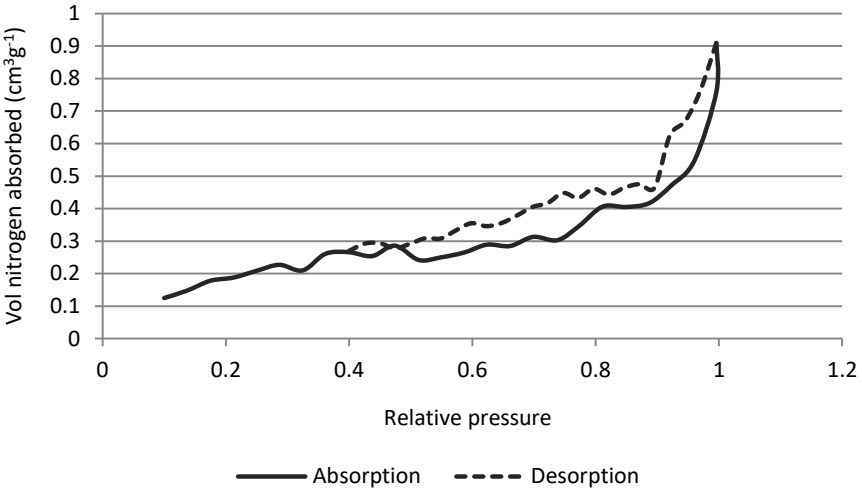


Figure 44: Porosity Isotherm of 10 Bar refined fibre

Cumulative pore volume

The cumulative pore volume shows absorption behaviour differences. Figure 45 depicts the cumulative pore volume of the different diameters of pores. The graph shows that MDF panels produced from 6 bars refined fibre have a greater pore volume of larger pores, confirming a macroporous structure of the fibre and MDF panel. Figure 45 also shows that MDF panels produced from 8 bar refined fibre also have more, larger pores than 10 bar refined fibre panels. MDF panels produced from 10 bar refined fibre have a greater mesopore cumulative volume than 8 bar refined fibre panels and a higher mesopore cumulative volume than 6 bar refined fibre

panels. This confirms that panels produced from 10 bar refined fibre have a mesoporous structure.

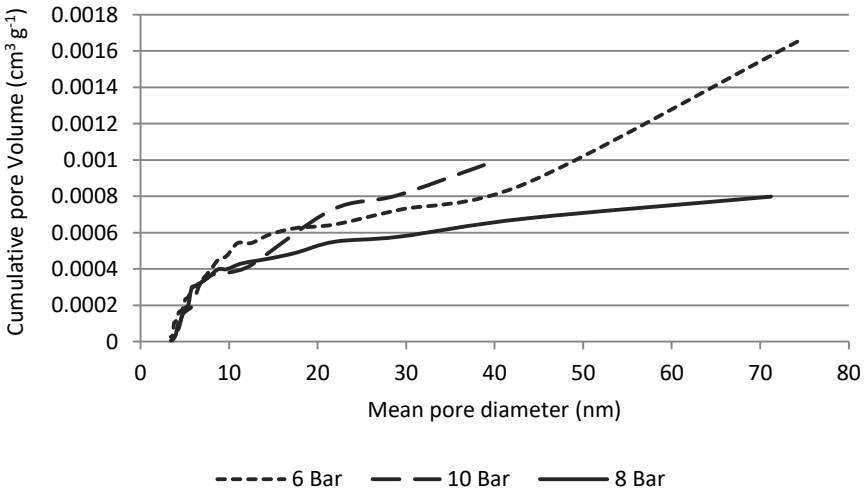


Figure 45: Cumulative pore volume of modified MDF boards

Figure 46 shows the total pore volume of the modified MDF panels. This figure better shows that the MDF panels produced from 6 bar refined fibre had a higher total cumulative pore volume of 1.65 x 10^{-3} cm^3 g^{-1}. MDF panels produced from 8 bar refined fibre, had the smallest pore volume of 7.98 x 10^{-4} cm^3 g^{-1}.

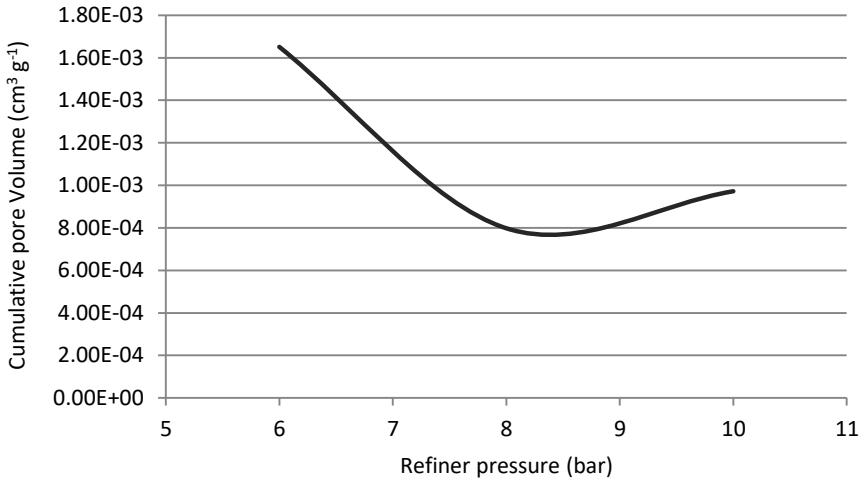


Figure 46: Total pore volume of modified MDF boards

Pore size distribution

The pore size distribution determination shows the proportion of pores at different pore diameters. The data reveals that if any micropores (<2nm) are present they are not detected in either of the three modified MDF panels, as the method is mainly optimised for mesopores. Figure 47A shows that MDF panels produced from 6 bar refined fibre consist predominantly of pores <10nm and macro-pores >50nm, with a high proportion of pores greater than 70nm in diameter. Figure 47B confirms that MDF panels produced from 8 bar refined fibre have a predominantly mesoporous structure, with the majority of pores with a diameter of <10nm. Figure 47C shows that MDF panels produced with 10 bar refined fibre also possesses mesopores of a diameter >10nm. However, in contrast to the other modified MDF panels, there is a greater proportion of pores between 15-25nm. This is evidence that during the refining and panel production process, the fibre structure is changing more significantly at higher refiner pressures. This is a result of the movement of the lignin towards the outer surface of the fibre, essentially filling in the macro-pores and reducing surface area and porosity. The reduction in the number of macropores in 8 bar refined fibre suggests that at this refiner pressure the lignin has begun to move and is filling in the macropores within the fibre structure. At greater refiner pressure, 10 bar, pores of a diameter greater than 40nm are no longer present.

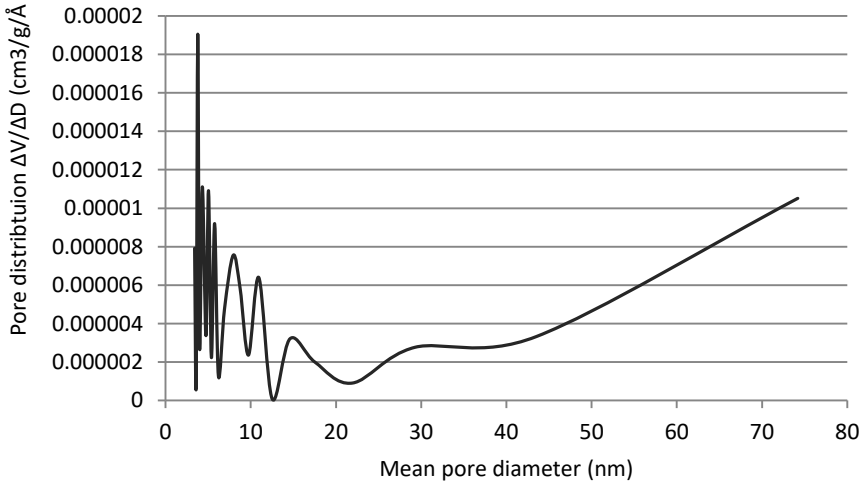


Figure 47A: 6 bar

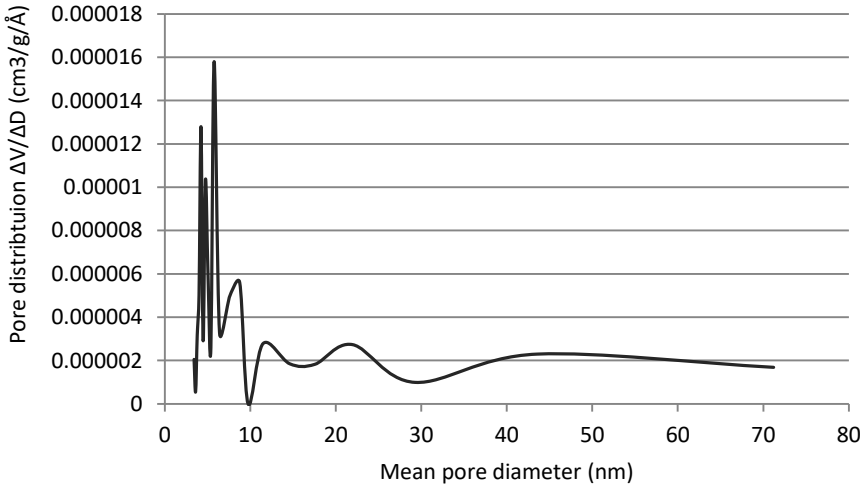


Figure 47B: 8 bar

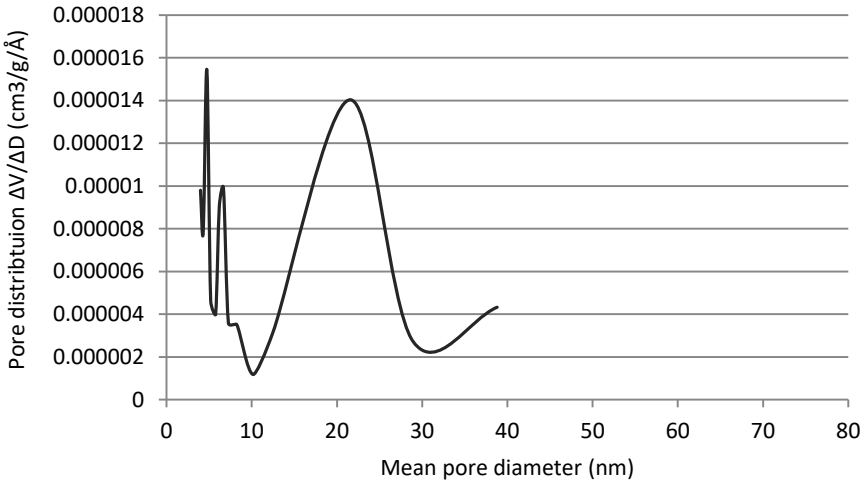


Figure 47C: 10 bar

Figure 47: Pore size distribution of MDF fibre refined at different pressures

3.3 Conclusion

The purpose of this study was to determine if a mechanical modification to the wood fibre affects the panels' formaldehyde absorption properties and mechanical properties. Woodchip was refined at 6 bar, 8 bar and 10 bar refiner pressures. Initial results revealed that the fibre was a lighter colour when refined at lower pressures and darker fibre is produced at higher refiner pressures. This is due to the removal of hemicelluloses during refining and increases the proportion of lignin content. The moisture behaviour of the fibre was also evaluated on the DVS and the results revealed little difference in sorption and hysteresis between the fibres refined at different pressures. Exposing the fibre to formaldehyde using DVS revealed that wood fibre does absorb formaldehyde. It was found that fibre refined at 6 bar pressure absorbed the most formaldehyde 134.67 g kg^{-1} and 8 bar the least, 41.20 g kg^{-1}. However, panels made from 8 bar refined fibre absorbed the most formaldehyde 127.66 g kg^{-1} and MDF panels produced from 6 bar refined fibre absorbed the least, 63.23 g kg^{-1}. Currently, it is unknown what causes this change in formaldehyde absorption between loose fibre and MDF panels, therefore further study is required.

The surface area and porosity of the modified MDF panels were evaluated to understand the difference in formaldehyde absorption. It was found that the surface area of the MDF panels reduced with increasing refiner pressure, which does not correlate with formaldehyde absorption.

The porosity data obtained helps to highlight the difference between fibre characteristics refined at different pressures. Fibre refined 6 bar pressure have the greatest cumulative pore volume and the majority of the pores are small mesopores. This helps to explain the greater surface area observed in MDF panels. MDF panels produced from 8 bar refined fibre have a mesoporous structure hence it has a greater surface area than 10 bar MDF panels, despite having a smaller total cumulative pore volume. However, this does not explain the differences observed in formaldehyde absorption.

The difference in formaldehyde absorption is likely to be a result of the movement of lignin towards the surface of the fibres and the removal of hemicellulose.

Unfortunately, the data gathered does not provide evidence for this and further work must be conducted.

3.4 Physical Modification - VOC and Formaldehyde Scavenger

3.4.1 Rationale

As previously described in the literature review, chapter one section 1.6.1.3, organic wastes have shown potential as bio-absorbers of formaldehyde and VOCs. This is worthy of further exploration. Lignocellulosic wastes are quite versatile in their use but what is most interesting for this study is the research conducted in which the wastes are used as bio-absorbents for contaminants and pollutants (Johns et al., 1998; Kazemipour et al., 2008; Kim et al., 2001; Mohamad Nor et al., 2013; Pirayesh et al., 2013; Tan et al., 2008; Tavakoli Foroushani et al., 2016). Section 1.6.1.3 of the literature also describes how and why inorganic materials and proteinaceous wastes have also shown potential as scavengers of formaldehyde and VOCs. The enormous variety of materials available for alternative uses varies significantly in their composition, chemical and physical structure. As such a selection of waste and readily available materials were evaluated for their capability of absorbing formaldehyde and VOCs. Agricultural organic waste, inorganic materials and protein based wastes were evaluated for use as scavengers of indoor air pollutants. These materials could then be incorporated into MDF panels.

3.4.2 Scavenger materials

The agricultural wastes chosen as potential organic scavengers were walnut shells, almond shells, peanut shells, sunflower seed shells, coconut husks and pistachio nut shells (fig 48A-F). Waste paper sludge was also evaluated as an alternative lignocellulosic waste material (fig 48G). The inorganic material evaluated was a nano-clay calcium carbonate and wool fibre was evaluated as the protein-based scavenger (fig 48I and 48H). Appendix B lists the sources of the materials tested. Untreated MDF was also analysed to set a benchmark (minimum requirement) for formaldehyde absorption. As it is likely that a solid additive to MDF panel will adversely affect mechanical properties, the scavenger must be a better absorber than wood fibre alone.

These materials were tested in their original state and were not modified. The lignocellulosic materials were dry milled into <5mm particles and any contaminating materials such as seed or stem were removed. The wool fibre was cut by hand with a pair of scissors into more manageable fibre lengths of approximately 50mm.

A. Walnut shell

B. Sunflower seed shell

C. Almond shell

D. Pistachio shell

E. Peanut shell

F. Coconut husk fibre

G. Paper pulp waste

H. Wool

I. Nano-clay

Figure 48: Potential formaldehyde and VOC scavengers

3.4.3 Formaldehyde Absorption

MDF wood fibre was used as a control for the minimum requirement of formaldehyde absorption. The scavengers added to the panels must absorb more formaldehyde than the fibre or else any physical modification is not worth the alteration. The method used to determine formaldehyde absorption was the same as described in section 3.2.4

Results and discussion

Table 17 shows the formaldehyde absorption of the different scavengers tested by dynamic vapour sorption. Figure 49 graphically shows the difference between the quantities of formaldehyde absorption. The loose wood fibre absorbed 49.69 g kg^{-1} formaldehyde, which is the minimum requirement of formaldehyde absorption for each scavenger. The results show that coconut husk fibre, pistachio, nano-clay and paper sludge absorbed a lower amount of formaldehyde than wood fibre. Wool fibre absorbed only a small amount more than the wood fibre but the other organic lignocellulosic-based scavengers absorbed more formaldehyde. Sunflower seed shell absorbed the most formaldehyde of all the scavengers tested 101.97 g kg^{-1}. Nanoclay absorbed the least formaldehyde 0.01 g kg^{-1}.

Table 17: Formaldehyde absorption of scavengers

Scavenger	**Formaldehyde Absorption (g kg^{-1})**	**Standard deviation**
Walnut shell	90.19	0.91
Almond shell	64.86	0.67
Coconut husk fibre	49.29	0.52
Pistachio shell	31.70	0.49
Peanut shell	81.48	0.43
Sunflower seed shell	101.97	0.22
Wool fibre	49.80	0.35
Wood fibre	49.69	0.57
Nanoclay	0.01	0.004
Paper sludge	10.43	0.64

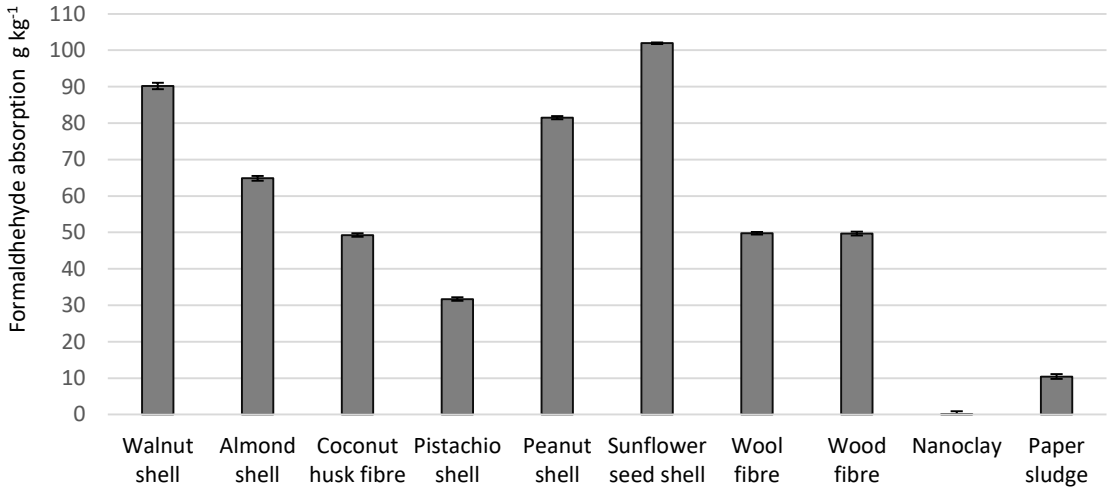


Figure 49: Formaldehyde absorption by scavengers

Table 18 shows the summary results for T-Test analysis of the formaldehyde absorption by the different scavengers evaluated. All scavengers had a significant statistical difference between their ability to absorb formaldehyde, except for wool fibre and coconut husk, wood fibre and coconut husk and wool fibre and wood fibre

Table 18: Summary of T-Test results for scavenger formaldehyde absorption (✓ statistical difference and X no statistical difference)

	Almond shell	Pistachio shell	Sunflower seed shell	Walnut shell	Peanut shell	Coconut husk	Wool fibre	Wood fibre	Nanoclay	Paper sludge
Almond shell	-	✓	✓	✓	✓	✓	✓	✓	✓	✓
Pistachio shell	✓	-	✓	✓	✓	✓	✓	✓	✓	✓
Sunflower seed shell	✓	✓	-	✓	✓	✓	✓	✓	✓	✓
Walnut shell	✓	✓	✓	-	✓	✓	✓	✓	✓	✓
Peanut shell	✓	✓	✓	✓	-	✓	✓	✓	✓	✓
Coconut husk	✓	✓	✓	✓	✓	-	X	X	✓	✓
Wool fibre	✓	✓	✓	✓	✓	X	-	X	✓	✓
Wood fibre	✓	✓	✓	✓	✓	X	X	-	✓	✓
Nanoclay	✓	✓	✓	✓	✓	✓	✓	✓	-	✓
Paper sludge	✓	✓	✓	✓	✓	✓	✓	✓	✓	-

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Figure 50 and 51 depict the mass change of the different scavengers over the 6 cycles of formaldehyde exposure. As can be seen from figure 50 for the coconut husk fibre, wood fibre and paper sludge, the mass does not increase showing that the scavenger formaldehyde absorption had reached a maximum and will not absorb more formaldehyde greater than 49.29 g kg^{-1}, 49.69 g kg^{-1} and 10.43 g kg^{-1}, respectively. The graphs also reveal that the scavengers wool fibre, wood fibre, walnut shell, peanut shell, almond shell, pistachio shell, sunflower seed shell and coconut husk fibre had a rapid mass change in the first cycle and then a gradual increase follows. This indicates that these scavengers may be able to absorb even more formaldehyde than the quantities recorded. To confirm this, the scavengers would have to be exposed to further testing and more sorption and desorption cycles. However, for this study time was a limiting factor.

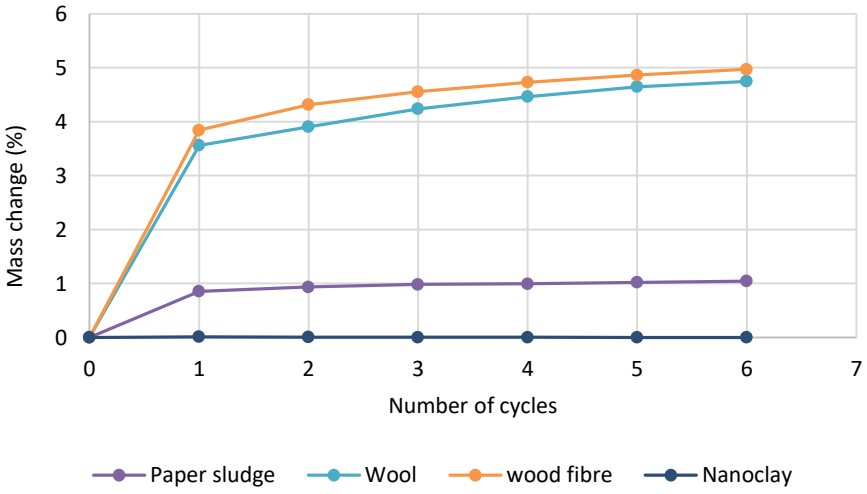


Figure 50: Mass change of paper sludge, wool, wood fibre and nano clay over 6 cycles of formaldehyde exposure

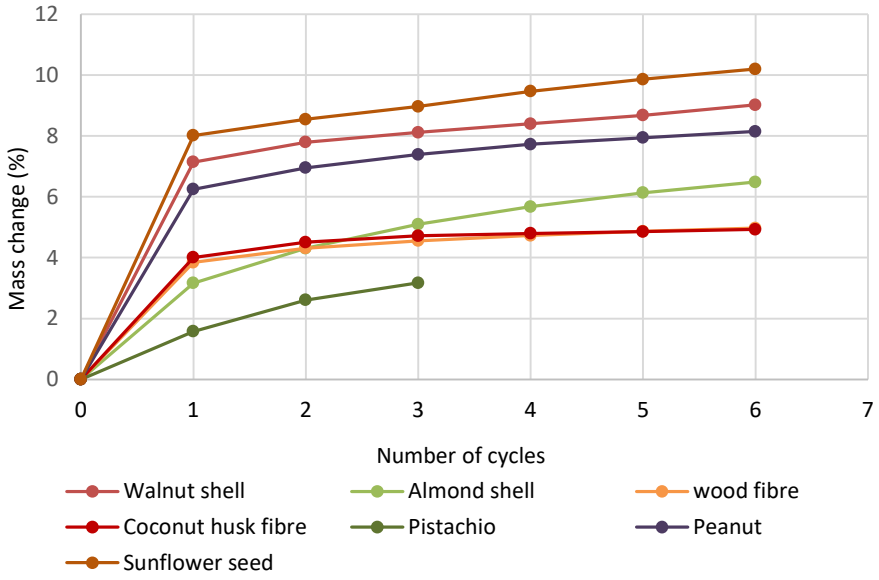


Figure 51: Mass change of wood fibre and organic scavengers over 6 cycles of formaldehyde exposure

To understand the differences observed in the scavengers' capabilities to absorb formaldehyde further tests were conducted. It is known that formaldehyde is highly reactive to proteins (Mansour et al., 2016) and reacts with the side chains of amino acids and amido groups of glucose (Curling et al., 2012). The nitrogen content (as a basis for protein content) was therefore determined using the Kjeldahl method, to assess correlations with formaldehyde sorption.

3.4.4 Kjeldahl / Nitrogen test

To determine the nitrogen content of the waste nut shells and wool fibre, the Kjeldahl method was used. This procedure generally has high reliability and is easy to use with biological materials.

Method

The shell materials were prepared by dry milling the shells into <5mm pieces and removing any contaminating material. The material was then oven dried overnight in a 50^{o}C oven. Between 0.2g and 0.3g of the oven dried waste shell were weighed to four decimal places and placed into digestion tubes to which two Kjeldahl peroxide tablets and 12ml of sulphuric acid were added. The digestion tubes were then placed in a preheated (420^{o}C) digester and left to digest for 1 hour from the

time of first vapour sighting. Once the digestion process was complete and cooled the sample was transferred to the distilling unit. The distillation procedure was run automatically and once completed (pre-prepared boric acid is blue) the distilled sample (now in the Erlenmeyer flask) was removed for titration. The sample was alkaline at this point and hydrochloric acid (HCl) was titrated into the sample until it became neutral (clear) and the volume of HCl used was recorded. The nitrogen content is calculated from the following formula:

$$\% N = 14.01 \text{ x } \left(\frac{(t_s - t_b)}{m}\right) \text{ x } M_{sd} \qquad \text{[Equation 21]}$$

Where:

t_s	volume of titration of sample (ml)
t_b	volume of titration blank (ml)
m	oven dry mas of sample (g)
M_{sd}	molarity of standard HCl (0.01)

Results and discussion

The nitrogen content was analysed to determine a relationship between protein content and formaldehyde absorption. Table 19 and Figure 52, shows the Kjeldahl nitrogen content results of the waste shells and wool fibre. As would be expected, the wool fibre had the highest nitrogen content 17.16% as it is a proteinaceous fibre. Of the shell wastes, sunflower seed shell had the highest value of 4.17% and pistachio shell had the least at 0.10%. The wood refined fibre had a nitrogen content of 0.15%.

Table 19: Nitrogen content of organic waste shells

Scavenger	Nitrogen content (%)	Standard deviation
Wool	17.16	0.02
Walnut shell	1.12	0.22
Almond shell	0.26	0.11
Coconut husk fibre	0.31	0.00
Pistachio shell	0.10	0.01
Peanut shell	0.73	0.03
Sunflower seed shell	4.17	0.18
Wood fibre	0.15	0.01

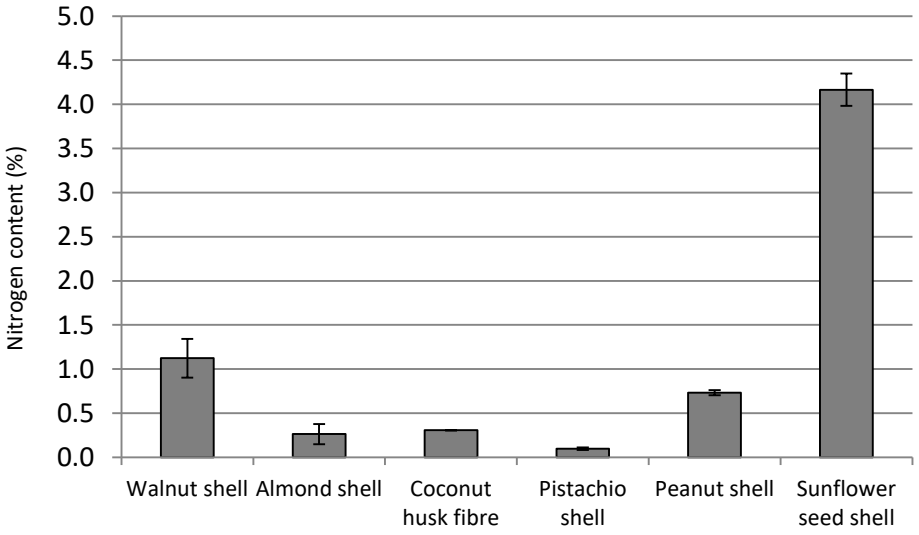


Figure 52: Nitrogen content of the waste nut shells

Figure 52 graphically shows the nitrogen content of the lignocellulosic scavengers and their formaldehyde absorption. The higher nitrogen content of sunflower seed shell, walnut shell and peanut shell (4.17%, 1.12% and 0.73% respectively) correlating with their higher capacity to absorb formaldehyde (101.97 g kg^1, 90.19 g kg^1 and 81.48 g kg^1 respectively). However, it would appear the wool fibre values do not fit into this relationship between nitrogen content and formaldehyde absorbed. Wool has significantly higher nitrogen content 17.16%, as it has a protein structure,

but it absorbed significantly less formaldehyde, 49.80 g kg^{1}, than the top three shell waste scavengers. The Kjeldahl method measures total nitrogen and therefore may detect non-protein nitrogen compounds within the wool. There may also be differences due to access via diffusion into the materials and due to different quantities of active nitrogen sites. In this case, the wool fibres tested, although with a higher nitrogen content, may not have as many free active nitrogen sites as walnut shell and sunflower seed shell. Further investigation is required into the surface energies of the waste shells.

When considering the lignocellulosic organic scavengers and formaldehyde absorption, there is an obvious relationship between absorption and nitrogen content, (fig 53). With increasing nitrogen content of the nutshell wastes, formaldehyde absorption increases. Song et al., (2007) also reported for activated carbons (AC) that the higher the nitrogen content of the AC the more formaldehyde was absorbed.

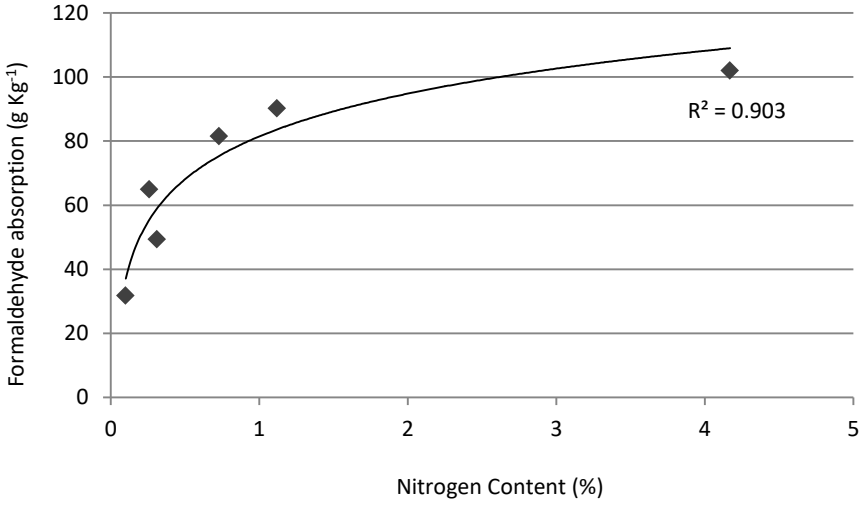


Figure 53: Nitrogen content and formaldehyde absorption

The reactions between formaldehyde and other compounds and molecules are very complex, as formaldehyde has low specificity and will readily react with a number of compounds in different ways (Reddie and Nicholls, 1971). The reactions between wool and formaldehyde are very complex. Polyamides form the backbone of the wool proteins and are comprised of many functional groups, each with varying

reactivity (Reddie and Nicholls, 1971). The wool keratin reacts with formaldehyde and formaldehyde irreversibly binds to asparagine amide groups of the wool (Alexander et al., 1951; Middlebrook, 1949).

It is well reported that formaldehyde will react and bind with amino groups and result in the formation of a methylol derivative (Alexander et al., 1951; Levy and Silberman, 1937; Puchtler and Meloan, 1984; Reddie and Nicholls, 1971). Other crosslinks are formed between amine and amide, amine and phenol and amine and indole groups (Alexander et al., 1951). Lignocellulosic wastes composition contain a wide variety of functional groups (Altun and Pehlivan, 2012; Miretzky and Cirelli, 2010; Okuda et al., 2003; Reddie and Nicholls, 1971; Zitouni et al., 2000). The predominant amino acids found in the lignocellulose material varies with species; walnut contains lysine, almonds cysteine and methionine and peanut contains threonine and methionine (Venkatachalam and Sathe, 2006). These differences in the type, composition and quantity of the functional groups may be key factors in determining the ability of a material to absorb and bind formaldehyde. Determination of the different types of functional groups on these waste nut shells may help to explain the differences observed in the quantity of formaldehyde absorbed by the shells and wool. Physical factors may also play an important role as there may be differences due to access via diffusion into the materials and due to different quantities of active nitrogen sites.

3.4.5 Fourier transform infrared spectroscopy

3.4.5.1 Principle and method

Fourier transform infrared spectroscopy (FTIR) analysis was performed on the nutshell scavengers to determine chemical components of the organic materials. The FTIR technique uses infrared light to scan a sample and thus obtain an infrared spectrum of absorption and reflectance of the material. This technique enables the determination of qualitative data on the functional groups within samples.

The analysis was conducted using a Thermo Nicolet 800 FTIR with a Pike Industries GladiATR Vision unit. The FTIR spectrometry was performed directly onto the scavenger surface, with tight close contact with the sample and probe. Each sample was scanned 32 times, over wavenumbers from 4000 to 600cm^{-1} and the spectra

acquired on the attached computer. Three replicates were conducted for each sample and an average spectrum produced. A blank spectrum was also obtained before any testing of the scavenger samples and after every three sample runs to ensure that background noise of water vapour and CO_2 peaks relating to background environment was accounted for.

3.4.5.2 Results and discussion

Figure 54 depicts the six FTIR spectra obtained for each of the lignocellulosic scavenger samples. The spectra reveal that there is little difference between the components of the lignocellulosic scavengers. Table 20 summarises the component characteristic absorption.

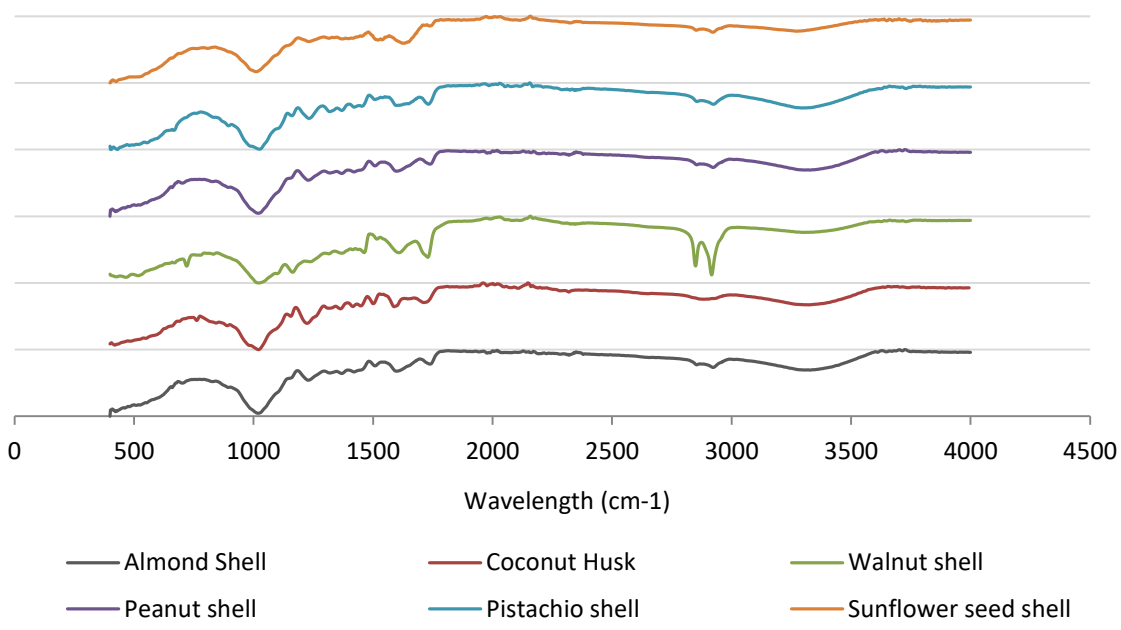


Figure 54: FTIR spectra of lignocellulosic scavengers

Table 20: Wavenumbers for typical absorptions for lignocellulosic scavengers

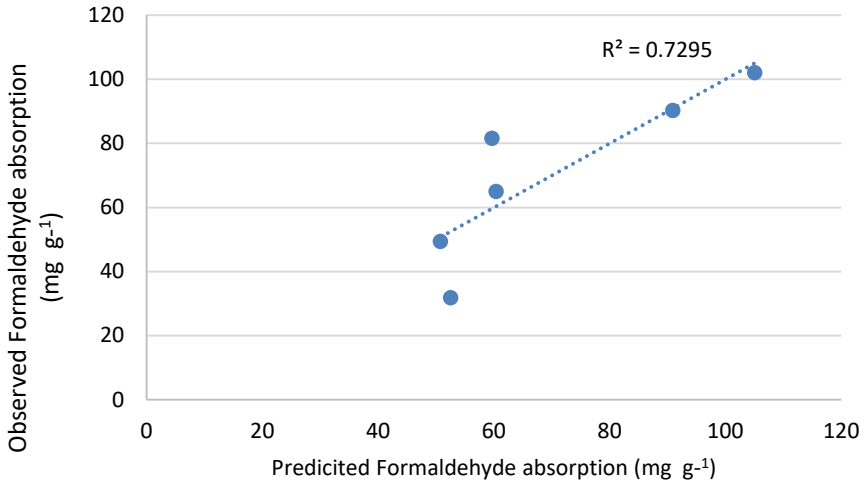
Wavenumber (cm^{-1})	**Functional group**	**Description**
3338 - 3284	C-OH	Cellulose
3000 - 2700	NH	NH stretch
2970-2950	CH_3	Asymmetric vibrations
2935-2915	CH_2	Asymmetric vibrations
2880-2860	CH_3	Symmetric vibration
2865-2845	CH_2	Symmetric vibration
1732	Ester	Esters
1595	Aromatic ring	Lignin aromatic ring vibration and C=O stretch
1510	Aromatic ring	Lignin aromatic ring vibration
1422	CH - OH	C-O stretch and CH or OH bending in cellulose and hemicellulose
1420	Aromatic ring	Lignin aromatic ring vibration
1375	CH	CH bend in cellulose
1100	C-O-C	CO stretch in cellulose and hemicellulose
1096	C-OH	C-OH bending in hemicellulose
1064	C-O	Cellulose C-O stretch at C3
1022		Cellulose C-C and C-O stretch

(El Mansouri and Salvadó, 2007; Jääskeläinen et al., 2003; Liu et al., 2006; Sills and Gossett, 2012; Sun et al., 2005)

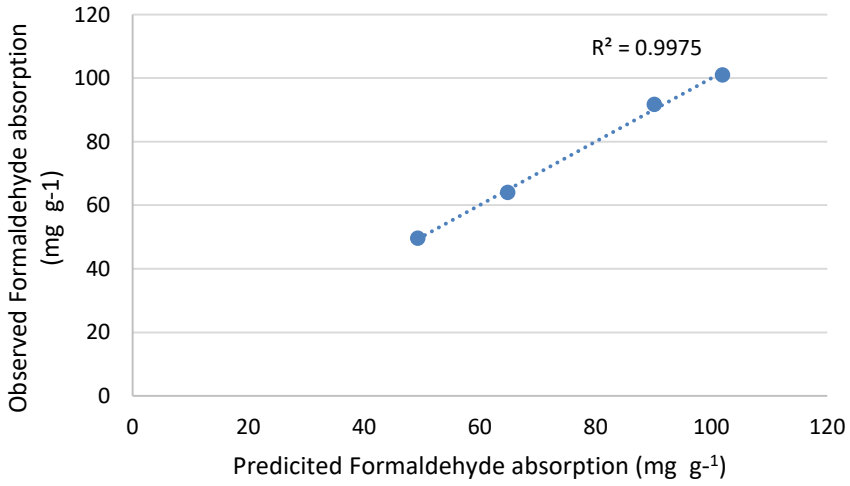
Formaldehyde absorption and FTIR

From the previous experiment, there appears to be a correlation between formaldehyde absorption and nitrogen content. This indicates that there is something specific about their chemical structure and functional groups that influence the material's capabilities to absorb and trap formaldehyde. The obtained FTIR spectra were analysed in conjunction with the formaldehyde absorption data using Partial Least Square regression (PSL). The PLS variance of importance (VIP) data was used to identify the areas of the FTIR spectra which explain the modelled

correlation of the organic scavengers and its capabilities to absorb gaseous formaldehyde. The PLS was conducted using Origin 9.2 statistical analysis software. Figure 55 shows the PLS regression model of the scavengers and formaldehyde absorption.



A.



B.

Figure 55: PLS regression model of FTIR-ATR spectra correlating to formaldehyde absorption. (A) all lignocellulosic scavengers. (B) Lignocellulosic scavengers, sunflower seed shell, almond shell, coconut husk shell and walnut shell

The principle of the regression model is to show any correlation between observed and predicted values, based on the data provided. The R^2 value of the PLS regression in Figure 55 was 0.7295 and there are two distinct out-layers of this model for formaldehyde absorption. The two out-layers were the peanut shell and pistachio

shell. After removing these two components from the PLS model the R^2 value was increased from 0.7295 to 0.9975. This reveals that, based on the current data used for this PLS model, there is a correlation between the lignocellulosic scavengers' chemical structure and their capabilities to absorb gaseous formaldehyde.

The VIP was used to determine the areas within the FTIR spectra that explain the differences in the formaldehyde absorption capabilities between the four lignocellulosic scavengers (walnut shell, sunflower seed shell, almond shell and coconut husk) according to the PLS model (fig 56).

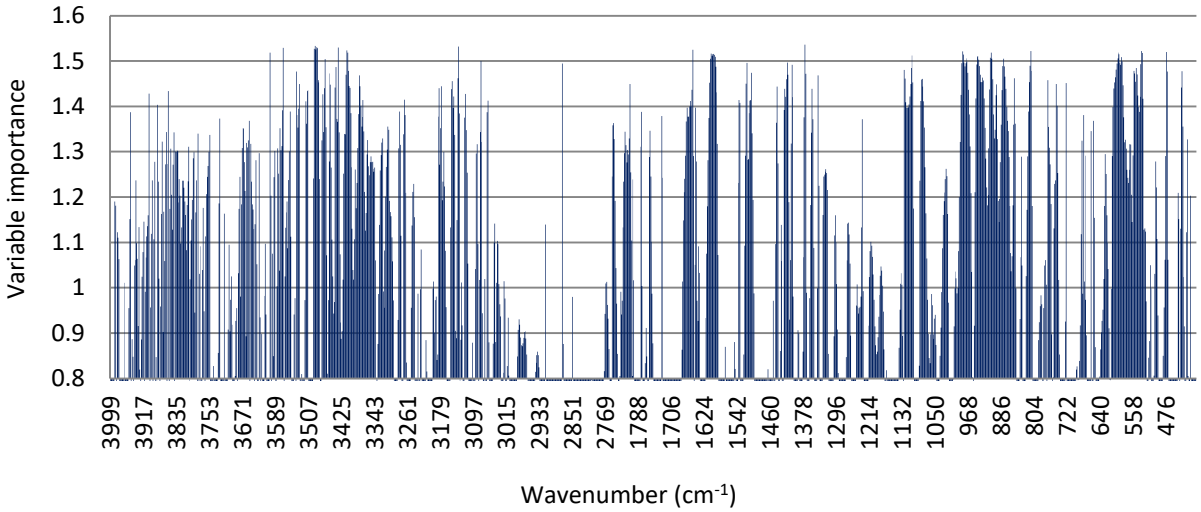


Figure 56: Variable importance of PLS regression of formaldehyde absorption

In accordance with Pérez-Enciso and Tenenhaus (2003), peaks with a VIP value of <0.8 show no major contribution to the prediction model and could be excluded without significantly affecting the model. According to Figure 56, there are seven major areas of the FTIR spectra with VIP>0.8 that fit the PLS model. These areas are between wavenumbers of 3750-4000 (cm^{-1}), 3680-3600 (cm^{-1}), 3500-3270 (cm^{-1}), 3200-3000 (cm^{-1}), 1670- 1470 (cm^{-1}), 1020-800 (cm^{-1}) and 630- 500 (cm^{-1}). These spectra areas influence the model most and explain the correlation between the FTIR spectra and formaldehyde absorption of this data set. The peaks between 3500-3270, 1670-1470 (which have 3 distinct peaks) and 1020-800 could be related to the presence of primary and possible secondary amines in the scavengers. It is possible that the amines are significantly affecting the formaldehyde absorption.

However, as the formaldehyde-exposed samples were different from the control FTIR samples further testing is required using the same sample before and after the exposure to formaldehyde in order to better understand the influence (if any) of the amines to the absorption properties. The use of sample for both experiments could be used to improve the model and may be able to be used on other types of lignocellulosic scavengers as well.

However, peanut shell and pistachio nut shell do not fit this PLS model the same as the rest of the samples. Although peanut shell has the third highest nitrogen content (0.73%), the PLS data indicates that it is not the chemical differences between the scavengers that is responsible for peanut shells being the third best at formaldehyde absorption (81.48 g kg^{1}). It could be hypothesised that there is an aspect of its physical structure that probably explains the peanut shell's ability to absorb gaseous formaldehyde. Song et al., (2007) reported for some ACs tested the surface area was quite low compared to other but had a higher formaldehyde absorption. Following this, the lignocellulosic scavengers were evaluated for their surface area.

3.4.6 Surface area

The surface area of the lignocellulosic scavengers was determined using a Micromeritecs Gemini surface area analyser following the same method as described in section 3.2.7.1.

Results and discussion

Table 21 and Figure 57 depict the surface area of each of the six lignocellulosic scavengers. Peanut shell had the highest surface area, 0.76 $m^2 g^{-1}$ and pistachio nut shell had the lowest, 0.14 $m^2 g^{-1}$. The second highest surface area was observed in walnut shells, 0.58 $m^2 g^{-1}$ and the third in sunflower seed shell 0.49 $m^2 g^{-1}$. This high surface area observed in peanut shell could explain the higher formaldehyde adsorption. This reveals that the scavengers' physical structure and surface influence its ability to absorb formaldehyde as well as its chemical composition.

Table 21: Surface area of lignocellulosic scavengers

Scavenger	Surface area (m^2 g^{-1})	Standard deviation
Almond shell	0.16	0.03
Pistachio shell	0.14	0.09
Sunflower seed shell	0.49	0.02
Walnut shell	0.58	0.07
Peanut shell	0.76	0.09
Coconut husk fibre	0.46	0.06

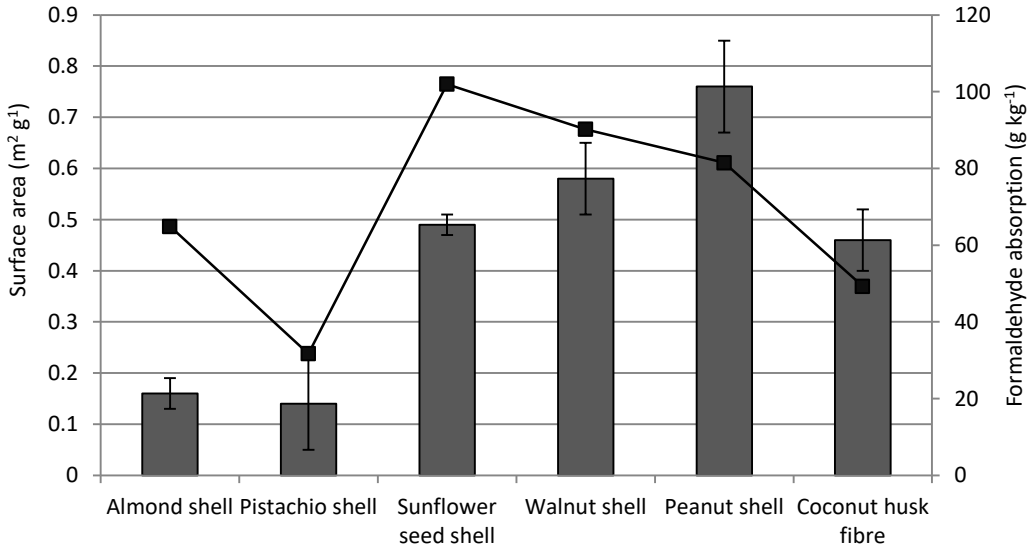


Figure 57: Surface area (line) and formaldehyde absorption (bar) of lignocellulosic scavengers

Statistical analysis

Table 22 shows the results for the T-Test analysis of the surface area of the lignocellulosic scavengers. The results show there is no statistical difference between pistachio shell and almond shell (p- value 0.356) nor between coconut husk and sunflower seed shell (p-value 0.49). There was a statistical difference between all other lignocellulosic scavengers.

Table 22: Summary of T-Test results for lignocellulosic scavenger surface area (✓ statistical difference and X no statistical difference)

	Almond shell	Pistachio shell	Sunflower shell	Walnut shell	Peanut shell	Coconut husk
Almond shell	-	X	✓	✓	✓	✓
Pistachio shell	X	-	✓	✓	✓	✓
Sunflower seed shell	✓	✓	-	✓	✓	X
Walnut shell	✓	✓	✓	-	✓	✓
Peanut shell	✓	✓	✓	✓	-	✓
Coconut husk	✓	✓	X	✓	✓	-

3.5 Conclusion

The study reveals that all the six shell types can absorb formaldehyde, with pistachio nut shell absorbing the least and sunflower seed shell absorbing the greatest amount. The wood fibre was used as a control, absorbing 49.69 g Kg^{1}. Walnut shell, sunflower seed shell, almond shell and peanut shell absorbed more formaldehyde than wood, with the potential to absorb more. Coconut husk absorbed similar amounts of formaldehyde as the wood fibre, but not sufficiently enough to warrant its use as a scavenger. The nano clay material absorbed negligible amounts of formaldehyde, likely due to its inert nature. The paper sludge absorbed the second least quantity of formaldehyde, 10.43 g Kg^{1}, likely due to the ink contained in the paper sludge. The only scavengers effectively able to absorb formaldehyde were the shell lignocellulosic agricultural wastes. The Kjeldahl results revealed that the quantity of formaldehyde absorbed increased as the nitrogen content within the waste shells increased. However, as the values for the wool fibre did not fit the relationship it can be seen that factors other than simple nitrogen (protein) content also influence the absorption properties of the materials.

3.6 Chapter summary

The aim of this work was to investigate two modifications to an MDF panel that actively removed formaldehyde and VOCs from the atmosphere and surrounding materials. Mechanical and physical modifications were employed to achieve this.

It was found that refining woodchip at different refiner pressures, 6, 8 and 10 bar did influence the wood fibre properties and the final MDF panel produced. Increasing the refiner pressure was found to darken the fibres, reduce surface area, change the porosity structure from mesoporous to macroporous and increased ash content. Wood fibre refined at 6 bar pressure absorbed the most formaldehyde whereas MDF panels produced with 8 bar fibre absorbed more formaldehyde than MDF panels produced with 6 bar refined fibre. Therefore, wood fibre, refined at 8 bar were further investigated and used to produce pilot scale MDF panel.

The chosen physical modification was to incorporate a solid, unmodified scavenger into the panel. Different formaldehyde scavengers were evaluated for their ability to absorb formaldehyde. It was found that the best scavengers were lignocellulosic nutshell wastes. The top three formaldehyde absorbing scavengers were walnut shells, peanut shells and sunflower seed shells due to their high nitrogen content and available binding sites for formaldehyde. Therefore these three scavengers were used to produce a pilot scale MDF panel.

4 Modified MDF Panel

4.1 Modified MDF panel

The next stage of this study was to develop a pilot scale, modified MDF panel that would actively adsorb formaldehyde and VOCs from the atmosphere. All MDF panels produced had an area of $1m^2$ at 12mm thickness and at a density of 750 k gm^{-3}. All panels were produced using 8 bar refined fibre, one as a control with no scavenger addition and nine others with the addition of the three different lignocellulosic scavengers; walnut shell, peanut shell and sunflower seed shell. These scavengers were added to the MDF panel at three different loadings, based on wet weight, 5%, 10% and 15%. The purpose of this was to determine if there was a limit of addition after which the properties of the MDF panels were impaired.

4.1.1 Production

The pilot scale MDF panels were produced at the Biocomposites Centres' Bio-Refining Technology Transfer Centre (Mona, Anglesey, UK) using the fibre produced as previously described in chapter 3 section, 3.2.2, at 8 bar refiner pressure. Appendix C details the mass of scavenger, fibre and resin used to produce an MDF panel.

The required fibre was weighed out to the nearest 0.1kg into a pre-weighed bin. The fibre was then emptied into a drum blender (fig 58A) and rotated for approximately 3 minutes to break up and re-fluff the fibre after it had been in storage. The pre-weighed scavenger was then placed into the drum blender with the fibre and spun again. After approximately 3 minutes of mixing, the pre-weighed resin was sprayed onto the falling curtain of MDF fibre. The UF resin was obtained from Kronospan (Chirk, UK) the day before the panels were produced.

A B C

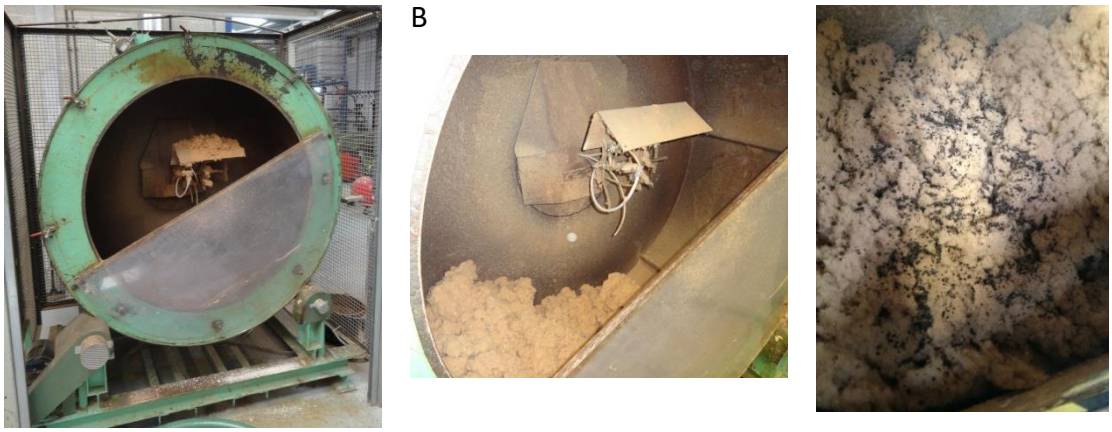


Figure 58: The drum blender (A), loose wood fibre (B) and addition of walnut scavenger

This fibre was then removed from the blender into the flash dryer using vacuum suction. The purpose of this was to break up any clumps of fibre in the cyclone, that may have formed in the drum blender (fibre balling) and prevent resin spots in the final MDF panel. The fibre was then directed into a $1m^2$ forming unit, where the fibre was manually spread out, (fig 59A). The fibre in the former was then transported to a pre-press, where it was compressed into a solid mat at a reduced thickness, ready for the press, (fig 59B).

The pre-pressed fibre board was then transported to the press and slid between the two hot plates (fig 60A). Once the panel was immediately in position, the heated platens (at 180°C) were closed and the press schedule started. The platens were closed until the thickness of the panel reached 12mm and held for 3 minutes to ensure curing of the resin. The panels were then removed (fig 60B), labelled with a corresponding panel number and placed under a vented, cooling rack to remove any formaldehyde fumes.

B

A.

C.

Figure 59: Forming unit (A), pre-pressed fibre (B) and pre-pressed fibre with sunflower seed shell scavenger (C)

A B

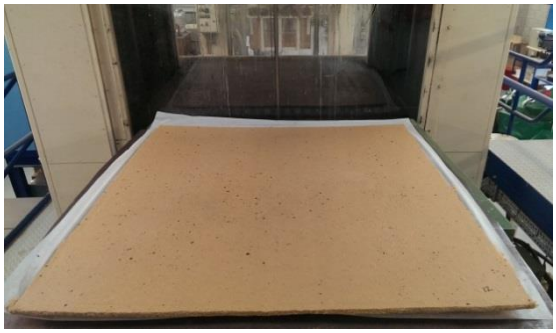
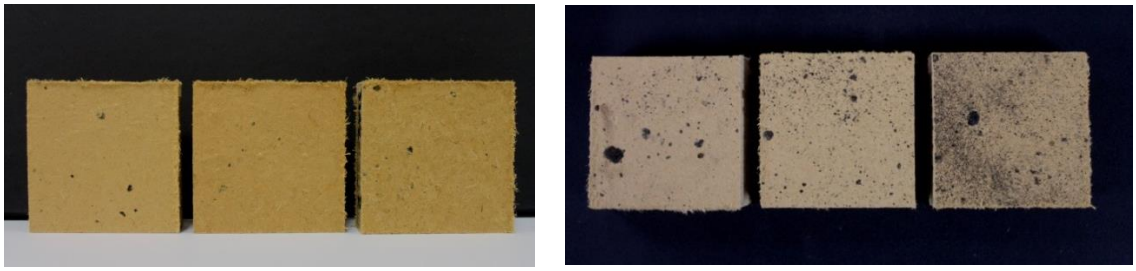


Figure 60: Pre-pressed panel in press (A) and final MDF panel (B)

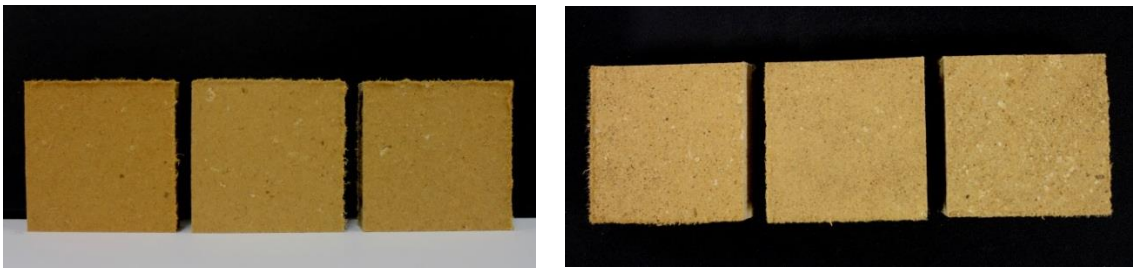
When the panels had sufficiently cooled they were cut and labelled in accordance with their intended experiment. Appendix D depicts the cutting plan for all the panels and lists the dimensions of each sample required for each experiment. Samples for each of the following tests were taken from three different panels and from different positions on each panel to account for variability between and within the panels, as per standard EN 326-1. Each sample was then placed in a conditioning room at 65% ±5 RH and 20 ±2 ^{o}C until constant mass was reached.

Discussion

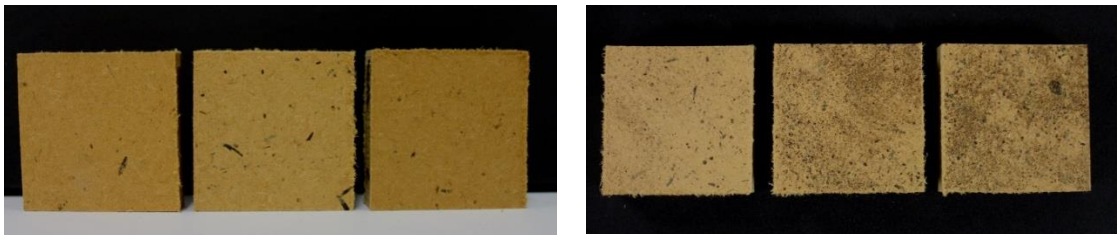
Figure 61 shows the surface of the modified MDF panels with 5% scavenger loading (left), 10% scavenger loading (middle) and 15% scavenger loading (right).There is little immediate aesthetic difference between the scavenger loadings and between the types of scavengers. However, when observing the bottom of the MDF panels (fig 61) it is evident that the finer particles of the scavengers have fallen to the bottom of the panel. The finer particles of the scavengers that have fallen to the bottom are distinctly obvious in the panels containing walnut shell and sunflower seed shell due to their darker colour (fig 61A and fig 61C). During the MDF panel production process, the fibres and scavengers are mixed together in the drum blender, which does lead to balling of the resinated fibre. To reduce the impact of this on the final product the fibre and scavengers were extracted through the flash dryer into a cyclone. This is also likely to break up the scavengers especially the sunflower seed shell which is quite brittle and increase the proportion of particulate matter. Hence the much darker bottom surface of the panel.



A) Walnut shell MDF



B) Peanut shell MDF



C) Sunflower seed shell MDF

D) Control MDF panel

Figure 61: Control and Modified MDF panel top (left) and bottom (right) surface

The bottom surface of the MDF panels containing the peanut shell shows little discolouration between panels of different scavenger loading (fig 61B). The bottom surface of the control MDF panel reveals a little contamination of heavier particles of dust and possibly, scavenger shells (figure 61D). This is a result of the control MDF panels being produced after the modified MDF panels. Any small shell particles left

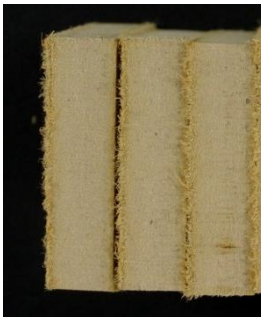
in the flash dryer system during the production of the modified panels may have made their way out and into the cyclone and mat former. Figure 62D shows the cross section of the control MDF panel and no other contamination can be observed in the panel.

Figure 62 shows images taken of the cross-section of the MDF panels with scavengers. The top surfaces of the panels are on the right-hand side and the bottom surface on the left. It can be seen that the scavenger particles are equally spread throughout the panel and has not massed towards the bottom of the panel. It would appear that only the smaller, finer particles of the scavengers have fallen to the bottom of the panel.

A) 5, 10 and 15% Walnut shell MDF

B) 5, 10 and 15% Peanut shell MDF

C) 5, 10 and 15% Sunflower seed shell MDF



D) Control MDF panel

Figure 62: Cross-sectional image of control and modified MDF panels

It has also been observed during the MDF panel cutting preparations, that although scavenger distribution is consistent in the thickness of the panel, it is not across the MDF panel length. Figure 63 shows the MOE/MOR samples cut from 15% walnut MDF panels reveals that the walnut shell distribution shows the greatest

concentration in the centre (right) of the panel and least towards the edge of the panel (left).

Figure 63: 15% walnut shell MDF panel for MOE/MOR testing

This is a result the production method used to produce the MDF panel. Where the fibre and scavenger are deposited into the MDF mat former, it was in the centre of the $1m^2$ former (fig 59). The fibre was then manually distributed evenly throughout the former. This movement of the fibre and scavenger agitates the fibre, causing the heavier, more circular shape of the scavenger to fall towards the bottom of the panel and concentrating in the centre of the former. This is likely to have an adverse effect on some of the properties of the MDF panel. To overcome this variation, samples cut from the whole panel were taken from different places across the board and where appropriate, with different orientations (such as MOE/MOR), see Appendix D. The same was not observed in MDF panels containing peanut shell or sunflower seed shell scavengers. This is likely due to their aspect ratio and lower density enabling the shells to be trapped within the fibre and therefore could be better distributed throughout the whole MDF panel.

4.2 Modified MDF Panel Analysis

The modified MDF boards were exposed to a series of tests to evaluate the physical modifications of the MDF panels. These were: formaldehyde absorption, emissions profile, absorption of VOCs; limonene, dodecane and toluene, the physical properties, mechanical strength properties and hygric properties.

4.2.1 Formaldehyde Absorption

The modified MDF panels with different scavenger loadings were exposed to formaldehyde using the DVS, following the same method as described in chapter 3, section 3.2.4. The total formaldehyde absorption was determined and mass change recorded over six cycles, Table 23. Due to time constraints and machine malfunction, only one replicate of 5% sunflower seed shell modified MDF was tested for formaldehyde absorption.

Results and discussion

Table 23 shows the formaldehyde absorption of control MDF panel and modified MDF panels. Control MDF panel absorbed 116.06 mg g^{-1} of formaldehyde. Peanut shell and walnut shell modified MDF panel absorbed a lower amount of formaldehyde than the control MDF panel on average. Indeed for 15% peanut shell and 5%, 10% and 15% walnut shell MDF panels, some replicates absorbed much greater amounts of gaseous formaldehyde than control MDF panel. MDF panels containing walnut shell was found to have a high absorption efficiency of formaldehyde by da Silva et al., (2017). Analysis of variance (ANOVA) was conducted on the control MDF panels and peanut shell and walnut shell modified MDF panels to determine any significant difference. The results showed that there was no statistical difference between the control MDF panels and peanut shell MDF panels (p-value 0.3470) and walnut shell MDF panels (p-value 0.8810). The large standard deviation is due to the variation in scavenger loading from the centre of the board, outwards as previously described (fig 63). For example, in samples taken from 5% walnut boards, one sample absorbed 118.10 mg g^{-1} and another, taken from the edge of the of the panel, absorbed 66.89 mg g^{-1} of formaldehyde. Another possibility for the large standard error bars could be due to the fact that small samples are used to determine the formaldehyde absorption using the DVS. Therefore the exact percentage loading of scavenger within the sample could be higher or lower than expected. To overcome this, many more replicates would have to be evaluated for formaldehyde absorption or another method used to determine formaldehyde absorption.

The 5% sunflower seed shell MDF absorbed a greater amount of formaldehyde than the control MDF panel at 116.71, however without replications it cannot be confirmed that the 5% sunflower seed absorbed significantly greater amounts than the control MDF panel. However, it does suggest promise that a sample taken from the edge of the MDF panel, absorbed very similar amounts of the gaseous formaldehyde as the control MDF panel. A greater loading of sunflower seed shell could absorb significantly more formaldehyde than control MDF panel. Further study is required to determine how effective sunflower seed shell is at absorbing formaldehyde in an MDF panel.

Table 23: Formaldehyde absorption of control MDF panel and modified MDF panels over 6 cycles

Board	**formaldehyde absorption ($mg\ g^{-1}$)**	**Standard deviation**
Control MDF	116.05	8.91
5% Peanut shell	72.04	8.91
10% Peanut shell	87.25	12.20
15% Peanut shell	98.18	35.66
5% Walnut shell	97.09	26.81
10% Walnut shell	99.70	20.23
15% Walnut shell	107.60	22.55
5% sunflower seed shell	116.71	-

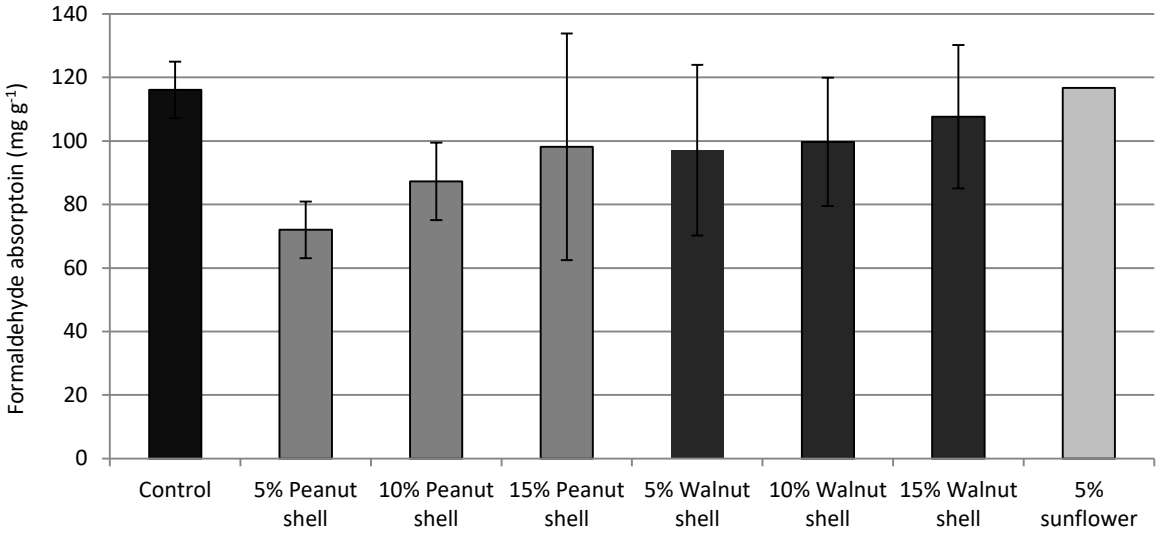


Figure 64: Formaldehyde absorption of control MDF panel and modified MDF panels

Most important of all, the results show that the peanut shell, walnut shell and sunflower seed shell are still active scavengers of gaseous formaldehyde within the MDF panel. Despite the scavengers being exposed to the additional breakages during production, resination and high temperatures and pressures, the scavengers combined with wood fibre, absorbed more formaldehyde than the scavengers alone. Except for 5% peanut shell, where less gaseous formaldehyde was absorbed by the modified panel than peanut shell alone. However with increasing peanut shell loading the formaldehyde absorption increases. The ANOVA test was conducted to determine if there was a statistical difference in formaldehyde absorption between control MDF panel and modified MDF panel. The results show that there was no statistical difference between the control MDF panel and panels modified with peanut shell (p-value 0.35) and walnut shell (p-value 0.88).

Figure 65 shows the average percentage mass change of MDF boards modified with peanut shell increase over the six cycles. The results show that the 5%, 10% and 15% peanut shell MDF panel did not reach equilibrium, suggesting the modified panels have the potential to absorb more gaseous formaldehyde. Modified MDF panels with 5% peanut shells absorbed the least and 10% peanut shell absorbed the highest. 5% and 15% peanut shell MDF panels absorbed similar amounts of formaldehyde in cycle one and two, whereas 10% peanut absorbed high amounts in

the very first cycle. This increase absorption by 10% boards could be a result of the lower absorption readings observed in 15% peanut MDF panels, pulling down the average percentage mass change over the 6 cycles. However, the figure does show the rate of mass change is similar in all three modified MDF panels.

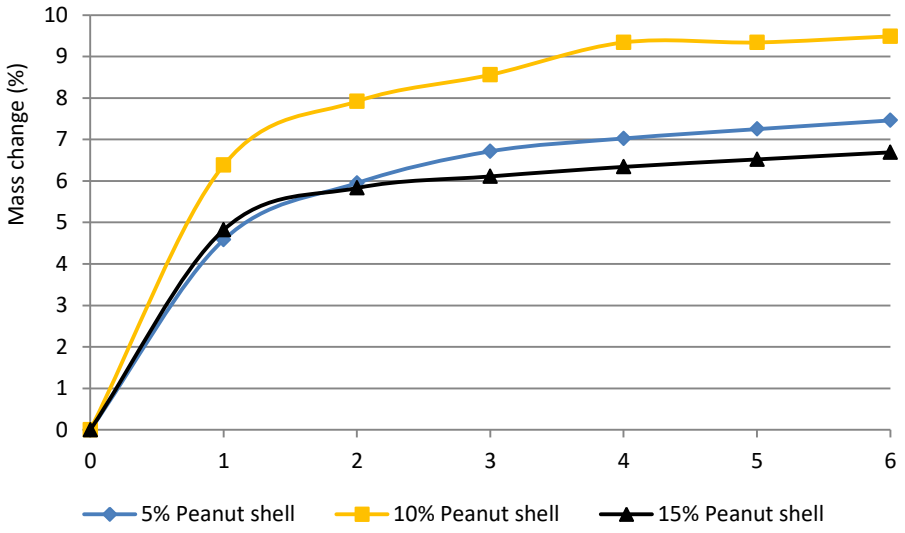


Figure 65: Mass change of peanut shell modified MDF panel over 6 cycles of formaldehyde absorption

Figure 66 shows the average percentage mass change of MDF boards modified with walnut shell increase over the 6 cycles. The results show that panels modified with 5% walnut shell did not reach equilibrium and has the potential to absorb more gaseous formaldehyde. Whereas MDF panels modified with 10% and 15% peanut appear to have reached equilibrium in the fourth and 5th cycle respectively. This suggests that these panels may not absorb much if any, more gaseous formaldehyde. However, the variation observed in the scavenger loading and subsequent variation in formaldehyde absorption should also be considered and that a greater percentage loading of walnut shells, may increase formaldehyde absorption. The samples tested with lower mass change (lower percentage loading) will have brought down the average mass change.

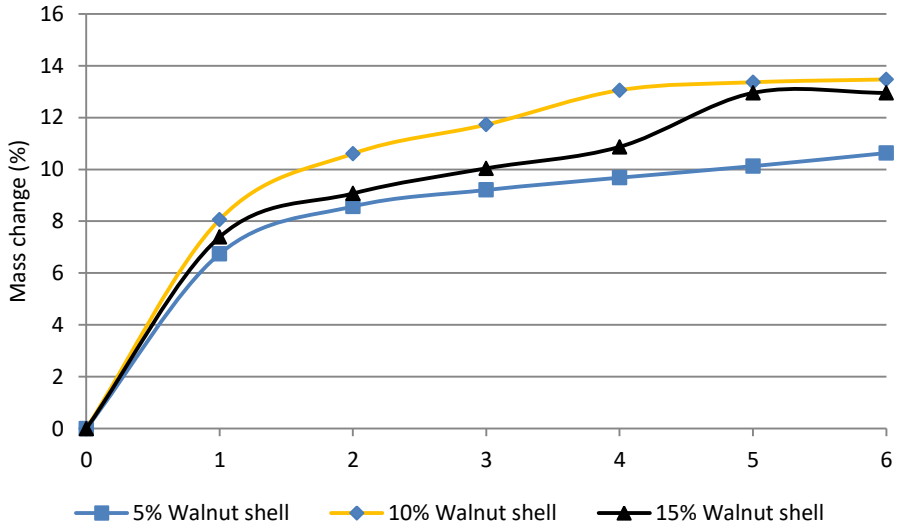


Figure 66: Mass change of walnut shell modified MDF panel over 6 cycles of formaldehyde absorption

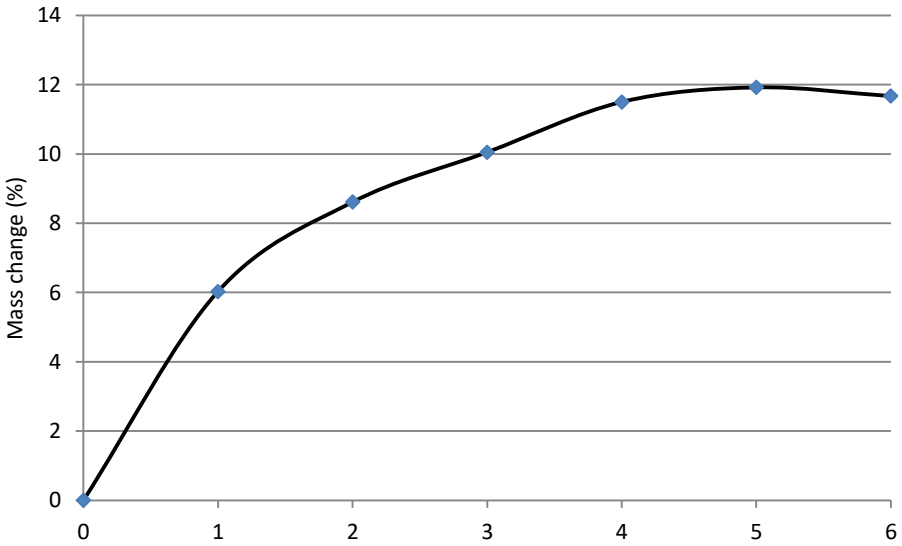


Figure 67: Mass change of sunflower seed shell modified MDF panel over 6 cycles of formaldehyde absorption

Figure 67 shows the percentage mass change of MDF boards modified with sunflower seed shell increase over the six cycles. The figure shows an increase in mass change over the first five cycles and a drop in the mass change in the sixth cycle. This suggests that the formaldehyde absorbed may not be chemically bound in the modified MDF panel but only physically trapped within the panel pores and that

the formaldehyde can be emitted back into the atmosphere over time. However, further replicated must be conducted before conclusions can be determined.

4.2.2 Volatile Organic Compound (VOC) absorption

To represent the enormous range of different types of VOCs found in indoor air, three major types of VOCs were chosen: toluene (T) representing aromatic compounds, dodecane (D) representing straight chain and non-polar compounds and limonene (L), representing cyclic and non-polar compounds.

4.2.2.1 Method

To determine the absorption capabilities of the modified MDF panel the method described by Mansour et al., (2016) was used, whereby the sample is exposed to gaseous VOCs for a set length of time, using a microchamber (fig 68). Samples were cut from the modified panels to 20 x 20 mm at nominal thickness (a volume of 480 cm^3) and conditioned until a constant mass was reached, as described previously. Three replicates were conducted. Due to time constraints of the project, only the scavengers peanut shell, walnut shell and sunflower seed shell, control MDF panel and modified panels with 15% scavenger loading were evaluated.

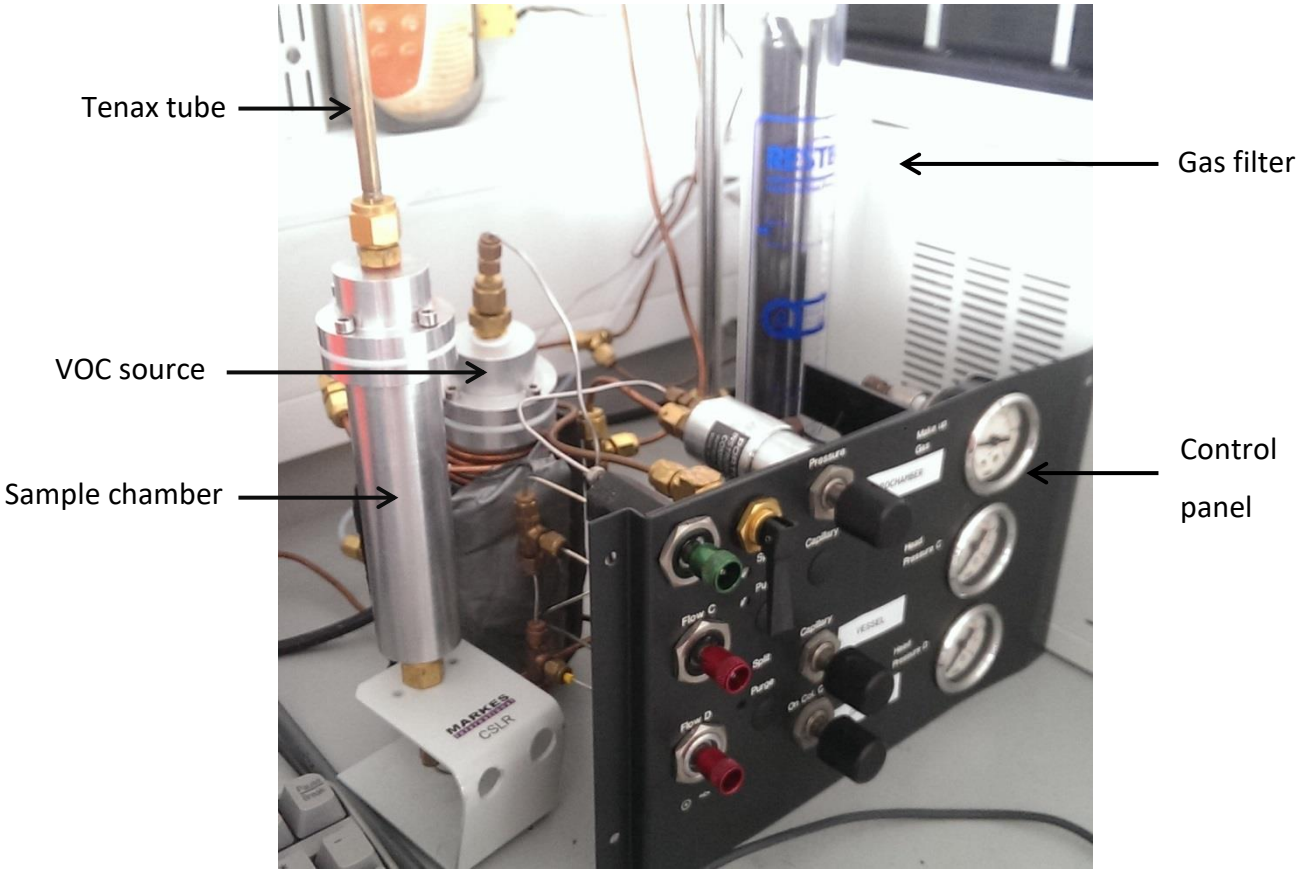


Figure 68: Microchamber set up for VOC absorption analysis

The sample was placed into a sealed vertical vessel connected to a microchamber. This microchamber houses the liquid VOC sources, together in another sealed vessel. A flow of pure nitrogen gas was passed into the vessel containing the VOC sources. The outlet gas flow was controlled at a flow rate of 2.5 ± 0.5 ml/min with an additional flow of clean nitrogen gas at 2.5 ±5 ml/min. This controlled flow was then fed into the vessel containing the MDF sample and flowed over the sample for 5 hours. The gas passed through the inner chamber and out of the top into an inert stainless steel tube (89 x 6.4mm) containing 200mg of Tenax TA that trapped any VOCs not absorbed by the sample. After the 5 hours of steady exposure, the TA tube was removed from the microchamber set up and analysed using gas chromatography coupled with a flame ionisation detector (GC-FID). Three replicates were run for each sample evaluated and blank samples were run at the beginning of the test and after every three samples, in order to calculate the quantity of VOC absorbed by the samples.

Results

Table 24 and Figure 69 show the results for the toluene, limonene and dodecane absorption of the lignocellulosic scavengers. Initial results show that the three scavengers were able to absorb toluene, limonene and dodecane.

Table 24: VOC absorption by lignocellulosic scavenger (µg cm^{-3})

Lignocellulosic scavenger	Toluene	Standard deviation	Limonene	Standard deviation	Dodecane	Standard deviation
Peanut shell	3.76	0.14	3.53	0.32	6.96	0.37
Walnut shell	4.25	0.26	5.34	0.31	7.25	0.25
Sunflower seed shell	1.85	0.40	3.20	0.28	7.27	0.18

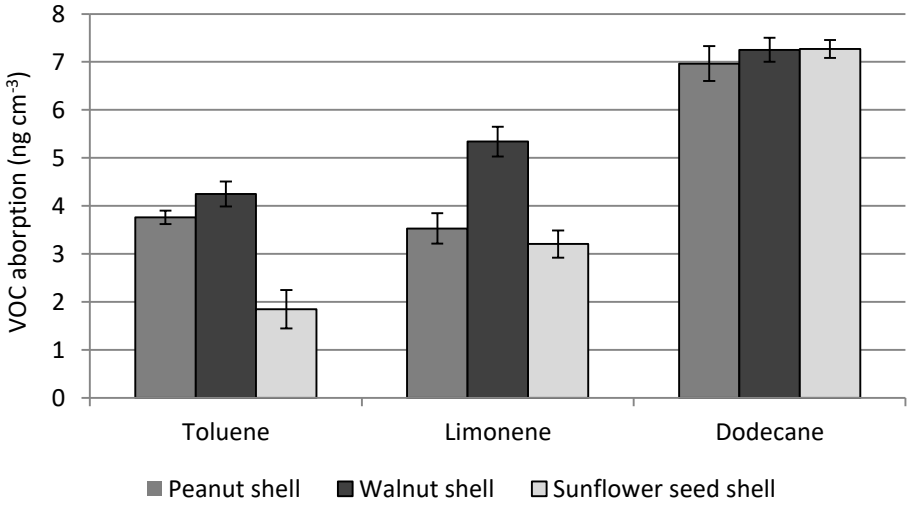


Figure 69: VOC absorption by lignocellulosic scavenger (µg cm^{-3})

It would seem that peanut shell, walnut and sunflower seed shell can all absorb similar amounts of dodecane, 6.96 µg cm^{-3}, 7.25 µg cm^{-3} and 7.27 µg cm^{-3}, respectively. Sunflower seed shell absorbed the highest amount of dodecane but absorbed the least toluene and limonene, 1.85 µg m^{-3} and 3.20 µg cm^{-3}, respectively. This suggests that sunflower seed shell has better properties such as functional groups or surface polarity to absorb straight chain, non-polar compounds and polar VOCs (formaldehyde) than VOCs that are cyclic or aromatic compounds. The same can be said for peanut shell that absorbed more dodecane than any other VOC. The

shell's natural chemical composition significantly influences its capabilities to act as a scavenger and absorb pollutants from the atmosphere, compounds such as phenolic compounds play a role in determining VOC sorption properties (Pirayesh et al., 2013). A study conducted by Weisz et al., (2009) into the phenolic compounds of sunflower seed shells found that the phenolic content of the shells varies with maturity of the shell as well its silviculture. Sunflower seed shell sourced from Italy had a much lower phenolic content 2938 mg $100g^{-1}$ whereas those from France had a phenolic content of 4176 mg $100g^{-1}$ (Weisz et al., 2009). This difference in chemical composition may influence the VOC sorption properties of the sunflower seed shell and should be further investigated.

Walnut shell absorbed a higher amount of limonene, 5.34 μg cm^{-3} than peanut shell, 3.53 μg cm^{-3} and sunflower seed shell, 3.20 μg cm^{-3}. Walnut shell also absorbed a higher amount of toluene, 4.25 μg cm^{-3}, than peanut shell, 3.76 μg cm^{-3}, and sunflower seed shell, 1.85 μg cm^{-3}. This suggests that walnut shell is a better scavenger for cyclic and non-polar VOCs. Walnut shell is known to have functional groups such as alcoholic, carbonylic, carboxylic and phenolic groups, which are potentially involved in bonding with sorbed pollutants (Altun and Pehlivan, 2012). Pirayesh et al., (2013) described how the polyphenolic content of the walnut shell is responsible for its ability to bind to formaldehyde and subsequently reduce emissions from particle board. The tannins and extractives in the walnut shell are likely to be responsible for the VOC absorption also. Peanut shell is also reported to have phenolic compounds approximately 33.4 to 71.3 mg/g of hulls, depending on the age of the peanut shell (Gow-Chin et al., 1993). This may influence peanut shell's ability to absorb VOCs but further investigation is required.

Table 25 shows the summary results of the ANOVA results for the VOC absorption of the scavengers, peanut shell, walnut shell and sunflower seed shell. The results confirm no statistical difference in the scavenger's ability to absorb dodecane. The results show that there is significant difference in the scavenger's ability to absorb toluene and limonene.

Table 25: Summary of ANOVA results for VOC absorption (✓ statistical difference and X no statistical difference)

VOC	Scavenger	Peanut shell	Walnut shell	Sunflower seed shell
Toluene	Peanut shell	-	✓	✓
	Walnut shell	✓	-	✓
	Sunflower seed shell	✓	✓	-
Limonene	Peanut shell	-	✓	X
	Walnut shell	✓	-	✓
	Sunflower seed shell	X	✓	-
Dodecane	Peanut shell	-	X	X
	Walnut shell	X	-	X
	Sunflower seed shell	X	X	-

Table 26 and Figure 70, show the results of the modified MDF boards with the three lignocellulosic scavengers and control MDF panel. As is evident the results show a difference in the viability of the scavengers to absorb VOCs when they have been used to modify an MDF panel.

Table 26: VOC absorption by control MDF panel and lignocellulosic scavenger modified MDF panel (µg cm^{-3})

Board	Toluene	Standard deviation	Limonene	Standard deviation	Dodecane	Standard deviation
Control MDF	1.52	0.40	1.67	0.65	0.40	0.15
peanut shell	2.39	0.46	0.51	0.12	6.14	0.45
Walnut shell	0.90	0.68	0.78	0.28	0.24	0.06
Sunflower seed shell	4.17	0.20	5.42	0.84	6.88	0.54

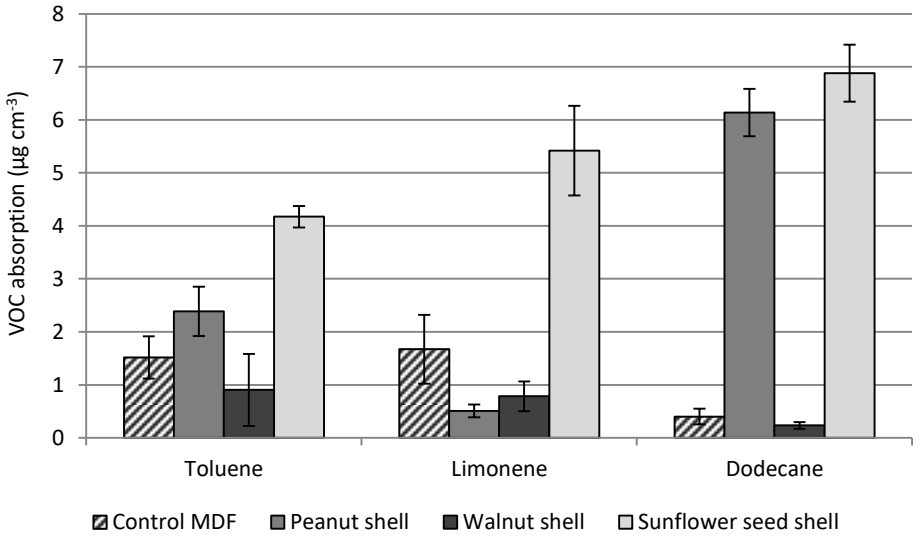


Figure 70: VOC absorption by control MDF panel and modified MDF panel (µg cm^{-3})

The results show that control MDF panel can also absorb a small amount of toluene, limonene and dodecane, 1.52 µg cm^{-3}, 1.67 10 µg cm^{-3} and 0.40 µg cm^{-3}, respectively. Boards modified with peanut shell absorbed the least limonene, 0.51 µg cm^{-3} and board modified with walnut shell absorbed the least toluene and dodecane, 0.90 µg cm^{-3} and 0.24 µg cm^{-3} respectively. Boards modified with sunflower seed shells absorbed the most toluene, limonene and dodecane, 4.17 µg cm^{-3}, 5.4 µg $cm^{-3}$and 6.88 µg cm^{-3} respectively.

Table 27 shows the summary ANOVA results for the toluene, limonene and dodecane absorption by the MDF panels modified with 15% scavenger, compared to control MDF panel. The results show that MDF panels modified with walnut shell do not statistically absorb more or less of either VOC than the control MDF panel. Unsurprisingly, MDF panel modified with sunflower seed shell absorbed significantly more toluene, limonene and dodecane than the control MDF panel. MDF panels modified with peanut shell statistically absorbed more toluene and dodecane than the control MDF panel, but not significantly more limonene.

Table 27: Summary of ANOVA results for VOC absorption by modified MDF panel (✓ statistical difference and X no statistical difference)

Board	VOC		
	Toluene	Limonene	Dodecane
Peanut shell	✓	X	✓
Walnut shell	X	X	X
Sunflower seed shell	✓	✓	✓

The results show that when in a board form, the scavengers absorbed lower amounts of VOCs than scavengers alone. This suggests that the process of board production, exposing the scavengers to high temperatures and pressures, changes the surface polarity of the scavengers. This change in surface polarity may have altered the level of interaction between VOCs and surface of the modified MDF panel. This suggests that it may be possible to tailor the production and treatment of the scavengers to absorb specific VOCs. However, boards modified with sunflower seed shell still absorbed high amounts of dodecane after board production. This suggests that the production method had little influence on sunflower seed shell ability to absorb straight chain and non-polar compounds.

It should also be noted that the high density of the modified MDF panels may have influenced the absorption capabilities of the scavengers. This may be due to the lack of accessibility and therefore VOCs may have been absorbed by those scavengers close to the board's surface.

From these figures, the quantity of toluene, limonene and dodecane absorbed on a larger scale can be modelled by determining the uptake of 1 cubic cm and calculating the equivalent uptake of a $1m^2$ board. Table 28 shows the theoretical absorption of an MDF panel and modified panels with 15% percentage loading of lignocellulosic scavengers.

Table 28: Model VOC absorption by control MDF panel and lignocellulosic scavenger modified MDF panel (μg m^{-3})

Board	Toluene	Limonene	Dodecane
8 Bar control	18.20	20.05	4.80
15% Peanut shell	28.63	6.08	73.68
15% Walnut shell	10.85	9.40	2.83
15% Sunflower seed shell	50.08	65.03	82.58

As is shown in Table 26, the quantity of the toluene, limonene and dodecane absorbed by a $1m^2$ MDF panel over five hours is significant and could effectively remove indoor air pollutants. However, this can only be treated as estimation as other variables would likely affect the total absorption of the MDF panel, namely bulking effects, density, vapour flow rates and surface area. It would be interesting to investigate the sorption properties of the modified MDF panel on larger scales. Another investigation for future study would be to investigate the absorption capacity of the modified MDF panels, exposed to different RH. da Silva et al., (2017) reported that formaldehyde and polar VOC absorption at higher RH might be reduced as these polar compounds compete with water vapour molecules for binding sites in the scavengers.

4.2.3 MDF panel emissions

As well as the absorption of VOCs, the VOC emissions from the modified MDF panels must also be considered. A novel multifunctional product designed to absorb VOCs within an enclosed space should not increase the initial emissions and should absorb more VOCs than it emits. To determine the emissions released from MDF fibre, control MDF board and modified MDF with sunflower, peanut and walnut shell were evaluated using SPME (Solid Phase Micro Extraction) and GC-MS (Gas Chromatography–Mass Spectrometry).

Principle

The principle of this test was that the Volatile organic compounds emitted from the sample panels were trapped onto the SPME fibre. The VOCs were then injected into

a GCMS, thermally desorbed and were individually separated using capillary columns in a gas chromatograph and were identified with a mass spectrometric detector.

Method

The materials tested for emissions were the three boards modified with the maximum loading of the scavenger at 15% of walnut shell, peanut shell and sunflower shell and the control board produced using 8 bar refined fibre. Three samples were cut from random positions in the MDF boards at 20 x 20 mm at panel thickness of 12mm. Alongside these samples, 2g of loose MDF fibre, refined at 8 bar (produced in chapter 2 section X) was also evaluated for emissions. The samples were conditioned at 65% ±5 RH and 20 ±2 ^{o}C for 6 months to ensure the release of free formaldehyde and any emissions detected would better represent emissions later during the service life of an MDF panel.

The samples were then placed into an inert glass vessel, with an airtight lid to prevent the release of any emissions or external contamination. The samples were left to stand for 30 minutes prior to testing. An empty vessel (Blank) was also tested as a control in order that background peaks could be identified and discarded. For this experiment, grey SPME fibres were used which were coated with divinylbenzene/Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS), suitable for volatile absorption. Once equilibrated, a 3mm grey fibre was carefully inserted through a small hole in the top of the lid and left to absorb for 30 minutes.

The fibre was then carefully removed and retracted into the holder to prevent any further absorption. The fibres were then desorbed into the GC-MS injector at 250°C, one at a time for 1 minute, under a constant flow of hydrogen. The analysis ran for 42 minutes and mass spectra recorded. The GC-MS system was controlled by Turbomass software, equipped with a mass spectral library to enable peak identification

Results and discussion

Figure 71 shows a chromatogram obtained from the GC-MS of the control MDF panel as an example, the other chromatograms can be found in Appendix E. Each peak was identified using the inbuilt compound library of the GC-MS but only those

peaks with a probability >50% were recorded. Table 29 lists the all the compounds recorded and from which samples they were detected. A total of 45 different compounds were identified and 11 of these peaks were identified in the background of the blank vessel, but only 3 were found to be present from all other samples; carbon dioxide, decanal and Hexanedioic acid bis(2-ethylhexyl) ester. Control MDF panel emitted the most VOCs (22 compounds identified) and loose MDF fibre, the least (6 compounds identified).

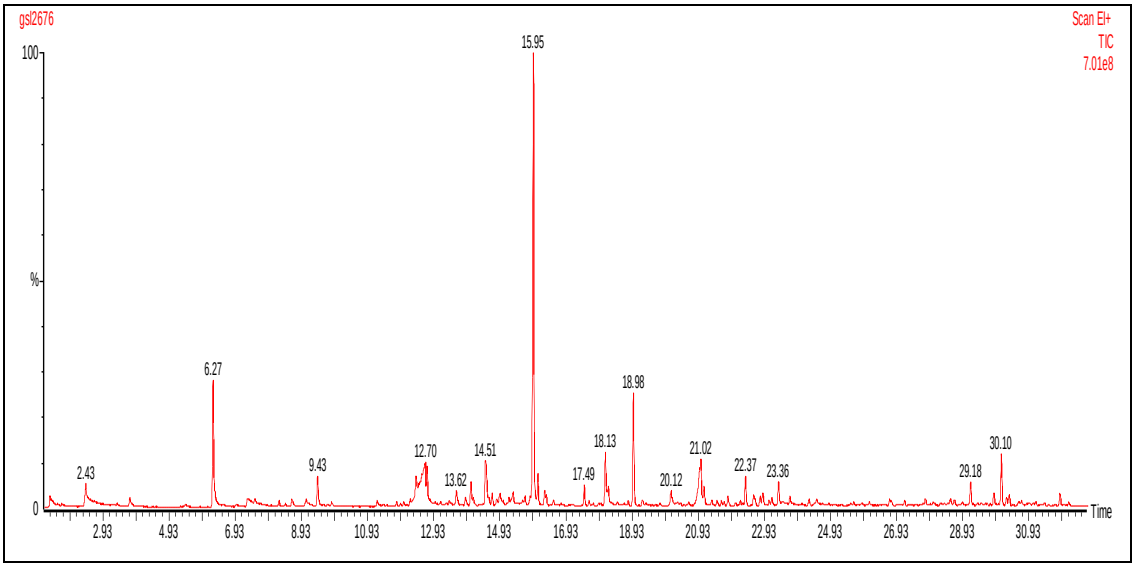


Figure 71: Example chromatogram of control MDF panel emissions

Table 29: VOC emissions from modified MDF panel and 8 bar refined fibre

Compound		Formula	No sample	MDF fibre	Control MDF panel	MDF + Peanut	MDF + Walnut	MDF + Sunflower
1	Carbon Dioxide	CO_2	/	/	/	/	/	/
2	Silanediol	H_4O_2Si	/	-	-	-	-	-
3	Dimethyl-1-heptene	C_9H_{18}	/	-	-	-	-	-
4	Limonene	$C_{10}H_{16}$	/	-	-	-	-	-
5	Nonanal	$C_9H_{18}O$	/	-	-	/	-	/
6	Cyclopentasiloxane	$Cl_8O_4Si_4$	/	/	-	-	-	-
7	Cyclotetrasiloxane, demamethyl	$C_{10}H_{30}O_5Si_5$	-	/	-	/	-	/
8	Decanal	$C_{10}H_{20}O$	/	/	/	/	/	/
9	Ethanol	C_2H_6O	/	-	-	-	-	-
10	Methanobenzocyclodecene	$C_{15}H_{26}$	/	-	/	/	/	/
11	Heptasiloxane	$C_{16}H_{48}O_6Si_7$	/	-	-	-	-	-
12	Hexanedioic acid bis(2-ethylhexyl) ester	$C_{22}H_{42}O_4$	/	/	/	/	/	/
13	Isopropyl myristate	$C_{17}H_{34}O_2$	-	/	-	-	-	-
14	Acetic acid	CH_3COOH	-	-	/	-	/	/
15	Pentanal	$C_5H_{10}O$	-	-	/	-	-	-
16	Hexanal	$C_6H_{12}O$	-	-	/	/	-	/
17	Furaldehyde	$C_5H_4O_2$	-	-	/	-	-	-
18	Hexanal, 4-methyl-	$C_7H_{14}O$	-	-	/	-	-	-
19	Heptanal	$C_7H_{14}O$	-	-	/	/	/	/
20	Hexanoic acid	$C_6H_{12}O$	-	-	/	/	-	/
21	Octanol	$C_8H_{18}O$	-	-	/	/	-	/
22	Hexane	C_6H_{14}	-	-	/	-	-	-

23	Heptanoic acid	$C_7H_{14}O_2$	-	-	/	-	-	-
24	Nananol	$C_9H_{18}O$	-	-	/	-	/	-
25	Hexanoic acid, 2-ethyl-	$C_8H_{16}O_2$	-	-	/	-	-	-
26	Cylcopentasiloxane, decamethyl	$C_{10}H_{30}O_5Si_5$	-	-	/	-	-	-
27	Octanoic acid	$C_8H_{16}O_2$	-	-	/	-	-	-
28	Nonanoic acid	$C_9H_{18}O_2$	-	-	/	/	/	/
29	Propanoic acid	$C_3H_6O_2$	-	-	/	/	/	-
30	Cylcononasiloxane, octadecamethyl-	C18H54O9	-	-	/	-	-	-
31	2,3-Butanediol	$C_4H_{10}O_2$	-	-	-	-	/	-
32	Octane	C_8H_{18}	-	-	-	-	/	-
33	Octanal	$C_8H_{18}O$	-	-	-	-	/	-
34	Tridecane	$C_{13}H_{28}$	-	-	-	-	/	-
35	Cyclopentasiloxane, decamethyl	$C_{10}H_{30}O_5Si_5$	-	-	-	-	/	-
36	Pentanoic acid	$C_5H_{10}O_2$	-	-	-	-	/	-
37	Silanediol dimethyl	$C_2H_8O_2Si$	-	-	-	/	-	-
38	Furfural	$C_5H_4O_2$	-	-	-	/	-	/
39	Furan, 2-pentyl	$C_9H_{14}O$	-	-	-	/	-	/
40	Propanoic acid	$C_3H_6O_2$	-	-	-		-	
41	Propanoic acid, 2 methyl-, 3-hydroxyl-2,4, 4-trimethylpentyl ester	$C_{12}H_{24}O_3$	-	-	-	/	-	/
42	1- Octen-3-ol	$C_8H_{16}O$	-	-	-	-	-	/
43	3-Octen-2-one	C8 H14 O	-	-	-	-	-	/
44	Ethanol, acetate	$C_4H_8O_2$	-	-	/	/	-	/
	Total number of peaks		11	6	22	17	16	18

The results also show that some of the compounds (peaks, 2,3,4,9 and 11) were not present in vessels containing fibre or the modified MDF panels, suggesting that the samples' emissions masked their presence or they were absorbed by the sample.

Comparing the 8 bar refined fibre and the control MDF panel, there is an increase in the number of compounds detected, from 6 to 22 respectively. This is a result of the use of the urea-formaldehyde resin during production, increasing emissions after production even after 6 months of conditioning.

Of the MDF panels containing scavengers, the least number of compounds detected was observed in panels containing peanut shell (16 compounds), then walnut shell (17 compounds) and the most were observed in panels containing sunflower seed shell (18 compounds). Peanut shell MDF and sunflower seed shell MDF had 11 compounds also found to be emitted from the control MDF panel. Whereas walnut shell MDF panel was found to only emit 9 compounds that were also identified from control MDF panels. This reveals that the addition of the scavengers can reduce some VOC emissions emitted from the MDF panel or mask them but also changes the emissions profile observed. MDF panels containing walnut shell emitted 6 compounds (compounds 31 – 36) that were not observed in any other sample. These VOCs are a mixture of hydrocarbons (tridecane, which is a respiratory irritant in high quantities), organic alcohols (2,3-Butanediol) and aldehydes (octanal). This is important to understand the different emissions from a modified panel, as it may add to the problem of poor indoor air quality, rather than help to mitigate the pollution. MDF panels containing peanut shell and sunflower seed shell had very similar emissions profile to each other but not to panels modified with walnut shell. Peanut shell and sunflower seed shell emitted the same VOCs with 3 exceptions. Dimethyl silanediol was found to be emitted only from panels modified with peanut shell and 1-Octen-3-ol and 3-Octen -2-one emitted only from sunflower seed shell MDF. According to Markowicz and Larsson, (2014) the detection of 1-octen-3-ol indicates the presence of moulds. This suggests that mould were growing on the sunflower seed shell prior to use in production or the presence of moulds growing on the modified MDF panel after production. This requires further investigation to determine how susceptible modified panels are too mould growth and emissions from the raw lignocellulosic scavengers.

Some of these VOCs may be more hazardous than others, or could chemically react with other VOCs to produce other secondary VOCs'. A further study would be to look closer at the individual VOCs emitted from the panels and study the VOCs chemical profile and determine if they contribute to poor indoor air quality and SBS.

4.3 Panel properties

4.3.1 Physical

The physical properties, bulk density, ash content, surface area and porosity were re-evaluated to characterise the modified MDF panel.

4.3.1.1 Bulk Density

The bulk density was determined as an average of the whole panel. The bulk density was determined following the same procedure as described in chapter 2, section 2.5.1

Results and discussion

Table 30 and Figure 72 show the results for the density of the modified MDF panels. The highest average density was observed in 5% peanut MDF panel and the least in 10% sunflower MDF panel.

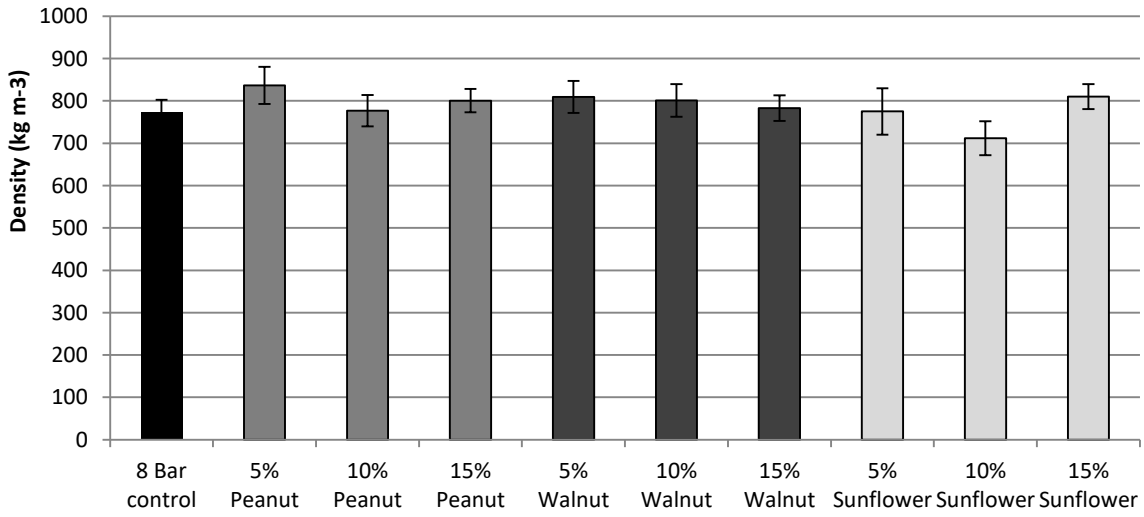


Figure 72: Bulk density of modified panels

Table 30: Bulk density of modified panels

Board	Average Density (kg m^{-3})	Standard deviation
Control MDF	774.25	28.14
5% Peanut shell	836.75	43.98
10% Peanut shell	776.83	36.99
15% Peanut shell	800.67	27.54
5% Walnut shell	809.67	37.89
10% Walnut shell	801.00	38.60
15% Walnut shell	783.00	30.15
5% Sunflower seed shell	775.17	54.57
10% Sunflower seed shell	712.17	39.96
15% Sunflower seed shell	810.00	29.40

Analysis of variance (ANOVA) was conducted to analyse the differences between the control MDF panel and scavenger modified MDF panels. Bulk density is an important aspect of the MDF panel and any variation between control MDF panel and modified panels could help later when analysing the difference in other panel properties.

Table 31: Summary of ANOVA results for physical properties (✓ statistical difference and X no statistical difference)

Physical Test	Scavenger Modification		
	Peanut	Walnut	Sunflower
Bulk Density	X	X	✓

The ANOVA results for bulk density (Table 31) show that there is no statistical difference in density between control MDF panel and panels modified with peanut shell (p-value 0.06) and walnut shell (p-value 0.36) scavengers. This shows that the maximum loading of 15% peanut shell or walnut shell scavenger can be added to the MDF panel without affecting the bulk density of the product. However, there is a

statistical difference between the control MDF panel and sunflower seed shell (p-value 0.005), therefore, a T-Test assuming equal variances was also conducted.

Table 32: T-Test assuming equal variance for bulk density (✓ statistical difference and X no statistical difference)

Board		Control MDF	Sunflower seed shell		
			5	10	15
Control MDF		-	X	✓	✓
Sunflower seed shell	5	X	-	✓	X
	10	✓	✓	-	✓
	15	✓	X	✓	-

Table 32 reveals that there is no statistical difference between control MDF panel and 5% scavenger loading but there is a difference between 10% and 15% scavenger loading. This shows that increasing scavenger percentage loading does significantly increase bulk density. Therefore it shows that 5% sunflower seed shell can be added to the MDF panel without affecting bulk density.

4.3.1.2 Ash content

The ash content was determined following the same method as described in chapter 2, section 2.5.3. Samples (10 x 10 mm) were oven dried, weighed and placed in a muffle oven at 925^{o}C for five hours. The samples were then reweighed to give the ash (inorganic) content.

Results and discussion

The ash content for each of the panels is described in Table 33. The control MDF panel had an ash content of 0.19% and was the panel with least percentage of inorganics. The greatest ash content was observed in 15% walnut MDF, 2.48%. With increasing scavenger loading (%) the ash content increased. The least increase was observed with the addition of peanut shell and the greatest increase with walnut shell.

Table 33: Inorganic content of modified panels

Board	Ash content (%)	Standard deviation
8 Bar fibre	0.19	0.05
5% Peanut shell	0.45	0.06
10% Peanut shell	0.46	0.2
15% Peanut shell	0.58	0.2
5% Walnut shell	0.94	0.08
10% Walnut shell	1.64	0.2
15% Walnut shell	2.48	0.02
5% Sunflower seed shell	0.48	0.09
10% Sunflower seed shell	0.68	0.3
15% Sunflower seed shell	0.84	0.08

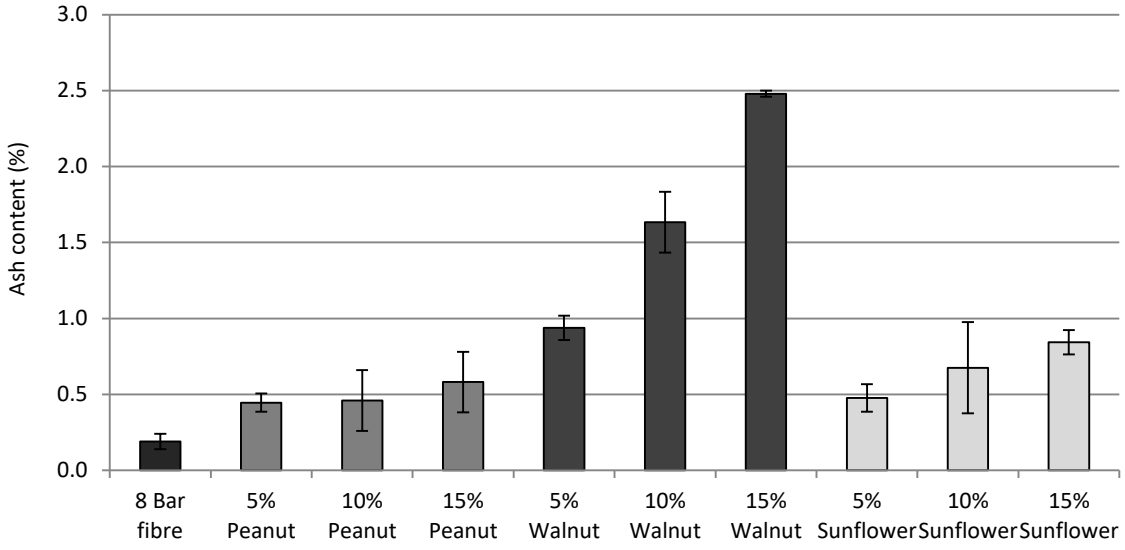


Figure 73: Inorganic content of modified panels

As was expected, increasing the addition of the lignocellulosic scavenger increased the ash content of the modified MDF panels. The data shows that walnut had the highest percentage of inorganics, which is due to the walnut shell's high extractive content. Interestingly, scavenger loading of peanut shell from 5% to 15% did not significantly increase the ash content, revealing that peanut shell had little inorganic content. Table 34 summarises the ANOVA results for the inorganic content of the

control MDF panel and modified MDF panels. ANOVA results for ash content show that there is a statistical difference between MDF panels modified peanut shell (p-value 0.026), walnut shell (p-value 2.7 $x10^{-7}$) and sunflower seed shell (p-value 0.004).

Table 34: Summary of ANOVA results for physical properties (✓ statistical difference and X no statistical difference)

Physical Test	**Scavenger Modification**		
	Peanut	Walnut	Sunflower
Ash content	✓	✓	✓

To determine where the variation is between scavenger loading and control MDF panel, the T-Test assuming equal variances was determined for each of the scavenger loading (5%, 10% and 15%) compared to the control MDF panel. Table 35 shows that there is a statistical difference in ash content of the control MDF panel and modified panels containing the lignocellulosic scavenger at either loading percentage. There is no statistical difference between peanut shell loading, whereas with the walnut shell there is a statistical difference between walnut shell loadings. This confirms that increasing walnut shell percentage, the ash content of the MDF panel increases (fig 73). In regards to sunflower seed shell, there is no statistical difference between shell loading of 5% and 10% or between 10% and 15% but there is between 5% and 15% loading.

Table 35: Summary of T-Test assuming equal variance for inorganic content (✓ statistical difference and X no statistical difference)

Board		Control MDF	Peanut shell			Walnut shell			Sunflower seed shell		
			5	10	15	5	10	15	5	10	15
Control MDF		-	✓	✓	✓	✓	✓	✓	✓	✓	✓
Peanut shell	5	✓	-	X	X	-	-	-	-	-	-
	10	✓	X	-	X	-	-	-	-	-	-
	15	✓	X	X	-	-	-	-	-	-	-
Walnut shell	5	✓	-	-	-	-	✓	✓	-	-	-
	10	✓	-	-	-	✓	-	✓	-	-	-
	15	✓	-	-	-	✓	✓	-	-	-	-
Sunflower seed shell	5	✓	-	-	-	-	-	-	-	X	✓
	10	✓	-	-	-	-	-	-	X	-	X
	15	✓	-	-	-	-	-	-	✓	X	-

4.3.1.3 Surface area

The surface area of the modified MDF panel and control panel were determined following the same method as described in chapter 3, section 3.2.7.1 using the Micrometerics Gemini.

Results and discussion

The surface area of the control panel was 1.02 m^2 g^1. Figure 74 depicts the changes in surface area with increasing scavenger loading. With the addition of peanut shell scavenger loading, the surface area of the panel sees little variation, whereas the surface area increases with increasing walnut shell scavenger. MDF panels modified with sunflower seed shell showed a much lower surface area than the control or MDF panels modified with walnut shell and peanut shell. The lowest surface area was observed in 5% sunflower seed shell MDF panel, 0.36 m^2 g^1. Even with increasing percentage of the sunflower seed shell within MDF panels, the surface area of the panel does not significantly increase the surface area.

Table 36: Surface area of modified boards

Board	Surface area (m^2 g^1)	Standard deviation
8 Bar control	1.02	0.02
5% Peanut shell	0.98	0.03
10% Peanut shell	1.03	0.03
15% Peanut shell	0.99	0.03
5% Walnut shell	0.44	0.02
10% Walnut shell	0.65	0.03
15% Walnut shell	0.89	0.06
5% Sunflower seed shell	0.36	0.09
10% Sunflower seed shell	0.38	0.07
15% Sunflower seed shell	0.46	0.12

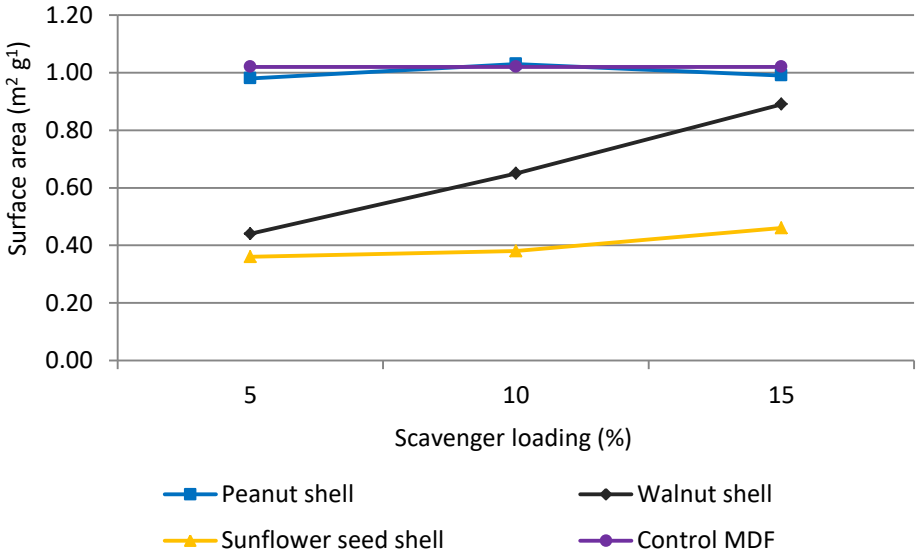


Figure 74: Surface area of modified panels

ANOVA was also conducted to determine to analyse the differences between control MDF panels and modified MDF panels (Table 37). Determining if the modifications cause a significant difference in surface area is important as the results could help to explain the panel's performance in other properties such as formaldehyde adsorption.

Table 37: ANOVA results for surface area (✓ statistical difference and X no statistical difference)

Physical Test	Scavenger Modification		
	Peanut	Walnut	Sunflower
Surface area	X	✓	✓

The ANOVA results for the surface area results show that there is no statistical difference between control MDF panel and peanut shell scavenger (p-value .087), therefore the maximum loading of 15% peanut shell can be applied without changing the surface area values. The ANOVA tests reveal that there is a statistical difference between MDF control panel and walnut shell scavenger (p-value $1.6x10^{-1}$) therefore a T-Test was conducted.

Table 38: T-Test assuming equal variance for surface area (✓ statistical difference and X no statistical difference)

Board		Control MDF	Walnut shell			Sunflower seed shell		
			5	10	15	5	10	15
Control MDF		-	✓	✓	✓	✓	✓	✓
Walnut shell	5	✓	-	✓	✓	-	-	-
	10	✓	✓	-	✓	-	-	-
	15	✓	✓	✓	-	-	-	-
Sunflower seed shell	5	✓	-	-	-	-	X	X
	10	✓	-	-	-	X	-	X
	15	✓	-	-	-	X	X	-

The T-Test reveals that there is a statistical difference between the control MDF panel and loading of walnut shell scavenger at 5, 10 and 15%. This shows that the addition of walnut shell to the MDF panel significantly reduces the surface area. Figure 37 shows that the surface area increases with the addition of walnut shell scavenger. Therefore if more than 15% of walnut shell could be added, a greater

surface area could be achieved that is not statistically different to the control MDF panel.

The ANOVA results show that there is also a statistical difference in surface area of the control MDF panel and sunflower seed shell panels (p-value 4.62 x 10^{-6}). Revealing that adding sunflower seed shell significantly reduces the surface area of the MDF panel. The T-Test result (Table 38) shows there is a statistical difference in surface area between the control MDF panel and 5%, 10% and 15% sunflower seed shell MDF panels. However, there is not a statistical difference in surface area between the sunflower seed shell percentage loading. The addition of the sunflower seed reduced the surface area, therefore, a higher percentage loading of sunflower seed shell would need to be applied to increase the surface area.

4.3.1.1 Porosity

The porosity of the modified MDF panels was determined following the same method as described in chapter 3, section 3.2.7.2.

Results and discussion

The porosity isotherm graphs, pore size distribution graphs and cumulative pore volume graphs can be found in Appendix F.

The porosity isotherm graphs show there is little hysteresis between the absorption and desorption curves, except in MDF panels modified with walnut shell scavenger. This is indicative of macroporous structure within the peanut shell and sunflower seed shell. The modified MDF panels with walnut shells that have a more defined hysteresis indicate a mesoporous structure instead.

Table 39 shows the total cumulative pore volume of the modified MDF panels. The greatest total cumulative pore volume was observed in 10% peanut shell MDF panel (0.0016 $cm^3\ g^{-1}$) and the lowest observed in control MDF panel, 10% walnut shell, 15% sunflower seed shell MDF panel (0.0008 $cm^3\ g^{-1}$). The graphs in Appendix F also reveal that micropores (<2nm) were not present or were not detected in any of the modified MDF panels or control MDF panel. The modified panels and control MDF panel reveal that the pore structure was predominantly <5nm and macro-pores >30nm. This helps to confirm that the structure of the panels consists of mainly

mesopores. MDF panels containing 10% peanut shell, 15% peanut shell and 15% walnut shell had a greater number of macropores (>50nm). The observed differences are a result of the sample variation in the distribution of the scavenger in the sample. As figure 63 shows that along the length of the panel, the distribution of the scavenger is not uniform, with samples from the centre of the panels containing a greater proportion of the lignocellulosic shell. Overall it does not appear that the addition of lignocellulosic scavenger to the MDF panel, at either percentage loading, adversely affects the porosity characteristics of the MDF panel. This is likely to be a result of the MDF panel production method, whereby all the panels are made to the same density profile and pressed to the same thickness of 12mm.

Table 39: Total cumulative pore volume of control and modified MDF panels

Board	Total cumulative pore volume ($cm^3 g^{-1}$) (10^{-3})	Standard deviation
8 Bar control	0.79	0.05
5% Peanut shell	1.21	0.07
10% Peanut shell	1.57	0.04
15% Peanut shell	1.26	0.05
5% Walnut shell	1.03	0.09
10% Walnut shell	0.78	0.06
15% Walnut shell	0.96	0.01
5% Sunflower seed shell	0.95	0.06
10% Sunflower seed shell	0.95	0.04
15% Sunflower seed shell	0.85	0.06

4.3.2 Mechanical

The mechanical properties of the modified panels were also evaluated to determine the adverse effect (if any) of adding the lignocellulosic scavenger to the strength properties.

4.3.2.1 Internal Bond Strength

The internal bond strength of the modified MDF panels was determined following the same method and procedure as described in chapter 2, section 2.4.2.

Results and discussion

Table 40 shows the results for the IB strength of the modified and control MDF panels. The IB strength for the control MDF panel was 0.49 N mm^{-2} and panels containing 15% peanut shell, 10% and 15% walnut shell and all loadings of sunflower seed shell exceeded this value, showing that the IB strength increased with scavenger loading. The highest IB strength was observed in panels modified with 10% sunflower seed shell. 5% and 10% peanut shell and 5% walnut shell reduced the IB strength of the MDF panel. The lowest IB strength was observed in panels modified with 5% peanut shell.

Table 40: Internal bond strength of modified MDF panels and control MDF panel

Board	Internal bond strength (N mm^{-2})	Standard deviation
Control	0.49	0.10
5% Peanut shell	0.46	0.12
10% Peanut shell	0.47	0.11
15% Peanut shell	0.50	0.07
5% Walnut shell	0.47	0.05
10% Walnut shell	0.52	0.11
15% Walnut shell	0.50	0.12
5% Sunflower seed shell	0.62	0.11
10% Sunflower seed shell	0.68	0.06
15% Sunflower seed shell	0.55	0.09

The BSEN standard 622-5:2006 states that the minimum requirement for general purpose MDF panel is 0.55 N mm^{-2}. The fact that the control MDF panel did not meet this standard may be due to the limitations of the production method at Biocomposites centres' Bio-Refining Technology Transfer Centre. The variation

within the results shows that the all modified MDF panels, except those modified with 5% walnut has exceeded the minimum requirement for general purpose MDF panels. However, the average of these results states that only MDF panels modified with sunflower seed shell exceeded the minimum requirement for general purpose MDF panels.

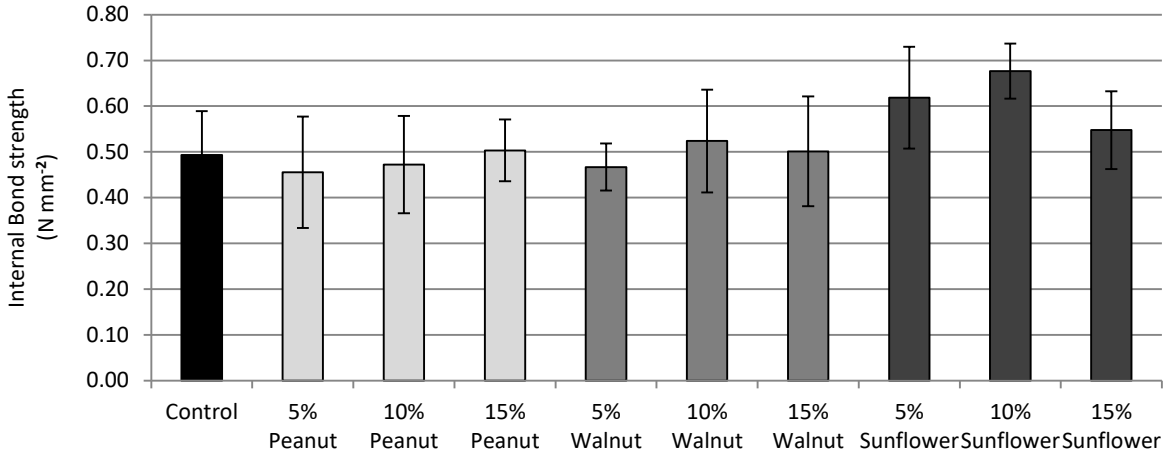
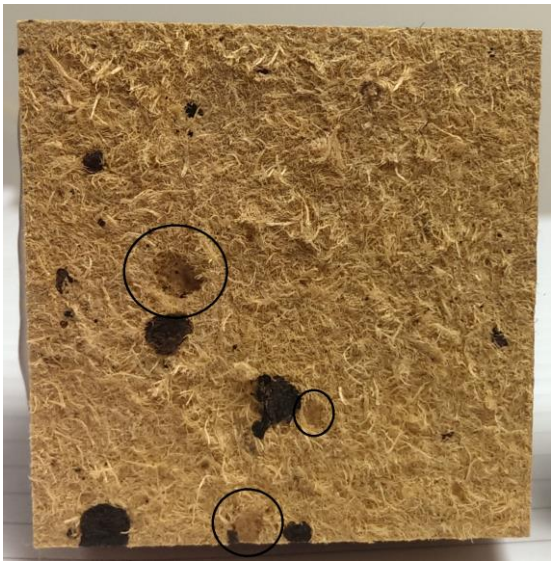


Figure 75: Internal Bond Strength of modified MDF panel and control MDF panel

Sunflower seed shell has a long and thin shape and this aspect ratio may increase the matrix of cross shell and fibre within the MDF panel, improving bonding strength (Groom et al., 1999). Whereas peanut shell has a squarer shape that may inhibit the internal matrix of the fibres. Peanut shell has a white waxy internal layer and this may prevent adhesion between the shell particle and wood fibre. This inner layer is also not strongly bound (weaker IB strength) to the outer shell of the peanut shell, which may cause many small areas of weaker areas within the MDF panel and more easily break when under tensile stress. Increasing IB strength with walnut shells is surprising, as the scavenger has a rounder shape that is not flat. It was assumed that these particles would create many cavities (fig 76) within the fibre matrix, reducing its tensile strength. However, there appears to be no significant reduction in IB strength with the addition of walnut shell.

A. Peanut shell inner wax layer



B. Walnut shell cavities

C. Sunflower seed shell

Figure 76: Example IB strength fracture surfaces of modified MDF panels

Figure 75 depicts the results of IB strength and the standard deviation. As is visible the standard deviation error bars are quite large. This could be a result of the problem of the distribution of the scavenger across the panel as described in section 4.1.1 and figure 63, whereby the MDF panels have a higher concentration of scavenger towards the centre of the panel and lower towards the edges. This could account for the large variation (as indicated by the graphical error bars) between IB strength of central IB samples and samples taken closer to the edge of the MDF panel. The primary purpose of the MDF panel is to be used as a construction panel

and any modifications made to the MDF panel, should not impact its mechanical strength properties. ANOVA test was conducted to determine if the variation observed was significant or not.

Table 41: ANOVA results for IB strength versus control MDF (✓ statistical difference and X no statistical difference)

Mechanical Test	**Scavenger Modification**		
	Peanut	Walnut	Sunflower
Internal Bond Strength	**X**	**X**	**X**

According to the ANOVA results (Table 41), there was no statistical difference between the IB strength of control MDF panels, walnut shell (p-value 0.99), peanut shell (p-value 0.77) and sunflower seed shell (p-value 0.13) MDF panels. Therefore, statistically speaking, the addition of either lignocellulosic scavenger does not impact the internal bond strength of the MDF panel at either loading percentage.

4.3.2.2 Modulus of Rupture and Elasticity

The modulus of rupture (MOR) and modulus of elasticity (MOE) were determined following the same procedure and methods as described in chapter 2, section 2.4.1.

Results and discussion

Table 42 shows the MOR and MOE of modified MDF panel and control MDF panel. The MOR and MOE results of the control panel, were 19.35 N mm^{-2} and 2139 N mm^{-2}, respectively. According to the BSEN standard 622-5:2006 the minimum requirement for general purpose MDF is 2200 N mm^{-2} and 20 N mm^{-2} for MOE and MOR respectively.

Table 42: MOR and MOE of modified MDF panel and control MDF panel

Boards	MOR ($N\ mm^{-2}$)	Standard deviation	MOE ($N\ mm^{-2}$)	Standard deviation
Control	19.35	1.99	2139.30	259.89
5% Peanut shell	20.50	2.14	2346.35	227.40
10% Peanut shell	13.92	2.44	1608.13	257.46
15% Peanut shell	18.41	2.07	2112.05	231.99
5% Walnut shell	16.90	2.56	1745.23	258.87
10% Walnut shell	19.13	2.68	1818.82	249.84
15% Walnut shell	16.83	2.47	1581.42	246.05
5% Sunflower seed shell	23.43	3.29	2254.75	292.25
10% Sunflower seed shell	19.81	3.51	1940.68	343.38
15% Sunflower seed shell	17.20	3.43	1875.68	340.11

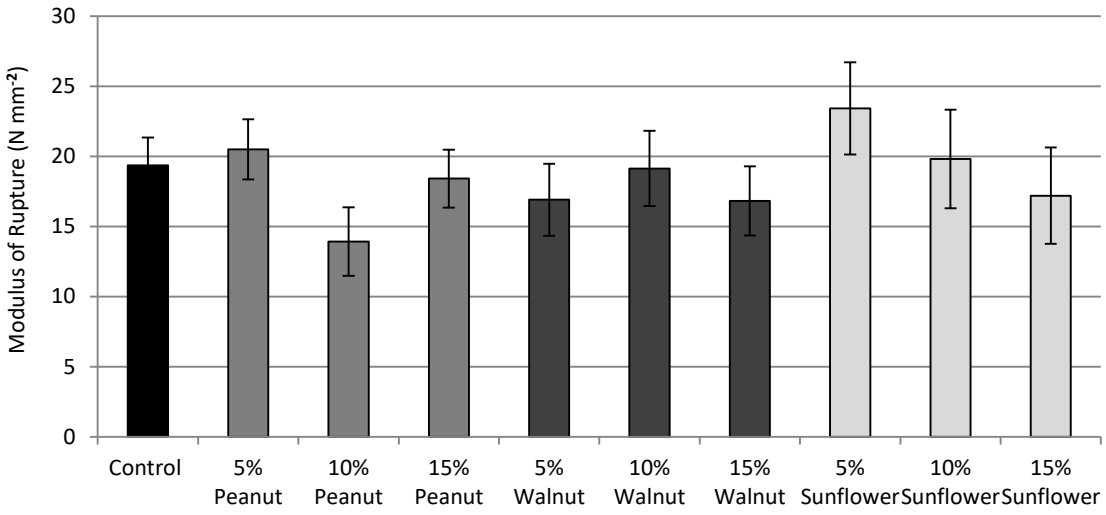


Figure 77: Modulus of rupture of modified MDF panel and control MDF panel

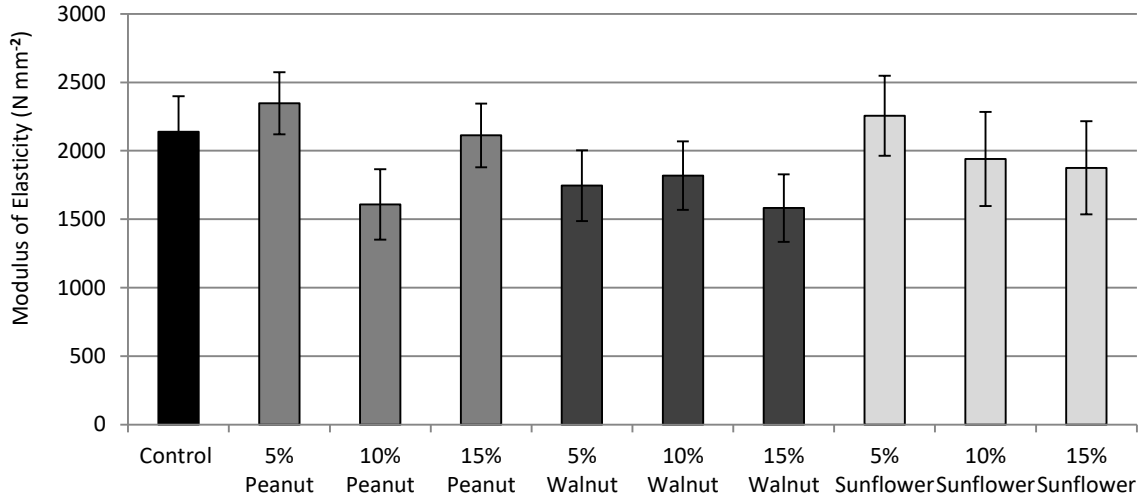


Figure 78: Modulus of elasticity of modified MDF panel and control MDF panel

Table 43: ANOVA results for MOE and MOR versus control MDF (✓ statistical difference and X no statistical difference)

Mechanical Test	**Scavenger Modification**		
	Peanut	Walnut	Sunflower
Modulus of Rupture	✓	**X**	✓
Modulus of Elasticity	✓	✓	**X**

There were statistical differences found between MOR of control MDF panel and peanut shell (p-value 2 x 10^{-4}) and sunflower seed shell (p-value 0.02) MDF panels. Whereas MOR of control MDF panel and walnut shell (p-value 0.16) MDF panel showed no statistical difference. Therefore MDF panels could be modified with walnut shell at either percentage loading without adversely affecting MOR properties. There was a statistical difference found between MOE of control MDF panel and peanut shell (p-value 3.5 x 10^{-4}) and walnut shell (p-value 8.7 x 10^{-3}) MDF panels. There was no statistical difference found with sunflower seed shell (p-value 0.16) MDF panels. Therefore MDF panels could be modified with sunflower seed shell at either percentage loading without adversely affecting MOE properties

To determine where the variation lies in the mechanical properties, T-Test assuming equal variances was determined for each of the scavenger loading (5%, 10% and 15%) compared to the control MDF panel (Table 44).

Table 44: Summary of T-Test assuming equal variance for modulus of rupture (✓ statistical difference and X no statistical difference)

Mechanical Test		Control MDF	Peanut shell			Sunflower seed shell		
			5	10	15	5	10	15
Control MDF		-	X	✓	X	✓	X	X
Peanut shell	5	X	-	✓	X	-	-	-
	10	✓	✓	-	✓	-	-	-
	15	X	X	✓	-	-	-	-
Sunflower seed shell	5	✓	-	-	-	-	✓	✓
	10	X	-	-	-	✓	-	X
	15	X	-	-	-	✓	X	-

Table 45: Summary of T-Test assuming equal variance for modulus of elasticity (✓ statistical difference and X no statistical difference)

Mechanical Test		Control MDF	Peanut shell			Walnut shell		
			5	10	15	5	10	15
Control MDF		-	X	✓	X	✓	✓	✓
Peanut shell	5	X	-	✓	X	-	-	-
	10	✓	✓	-	✓	-	-	-
	15	X	X	✓	-	-	-	-
Walnut shell	5	✓	-	-	-	-	X	✓
	10	✓	-	-	-	X	-	✓
	15	✓	-	-	-	✓	✓	-

Table 44 shows that MOR of MDF panels with peanut shell loading of 5% and 15% are not statistically different from control MDF but the panel with 10% peanut shell are. This could be a result of the lower density observed in 10% peanut shell MDF panel (776.83 kg m^{-1}) compared to 5% and 15% peanut shell MDF panels, 836.75 kg m^{-1} and 800.67 kg m^{-1}, respectively.

Table 44 also shows that there is a statistical difference in MOR between control MDF panel and 5% sunflower MDF panel but not between 10% and 15% sunflower MDF panel. This shows statistically that MOR of MDF panels is greater with 5%

sunflower seed shell. This could be due to the sunflower seed shell being tougher than individual fibres and acts as a reinforcement of the MDF panel. However, at a loading greater than 5%, the modified MDF MOR reduces, showing that the addition of the sunflower seed shell disrupts the matrix of the panel, reducing its MOR.

From the ANOVA there was no statistical difference between the control MDF panel and walnut shell MDF panels but there was with the sunflower seed shell MDF panels, whereas the opposite was observed in MOE results. The T-Test on the MOE of the control MDF panel and walnut shell MDF panel shows that there was a statistical difference between all three loadings (Table 45). All three percentage loadings of walnut shell resulted in statistically lower MOE of the final MDF panel. The MOE results of peanut shell modified MDF panels show the same relationship as observed in MOR results. This again is probably due to the lower density of the 10% peanut shell MDF panel.

4.3.3 Hygric

The hygric characteristics of the modified panels were re-evaluated to determine the adverse effect (if any) of adding the lignocellulosic scavenger on the moisture and vapour properties.

4.3.3.1 Thickness swell

The thickness swell of the modified panels, was determined following the same procedure and methods as described in chapter 2, section 2.6.4.

Results and discussion

The thickness swell of the control MDF panel was 46.49%, almost doubling in thickness (Fig 46). The BSEN standard states that the thickness swell should not exceed 12% and Table 46 shows that no MDF panel met this requirement.

Table 46: Thickness swell of modified MDF panel and control MDF panel

Boards	Thickness Swell (%)	Standard deviation
Control	46.49	1.56
5% Peanut shell	48.53	1.60
10% Peanut shell	36.86	1.21
15% Peanut shell	39.67	0.93
5% Walnut shell	43.83	2.04
10% Walnut shell	36.48	2.74
15% Walnut shell	33.64	1.48
5% Sunflower seed shell	35.04	5.65
10% Sunflower seed shell	37.59	1.36
15% Sunflower seed shell	37.61	0.98

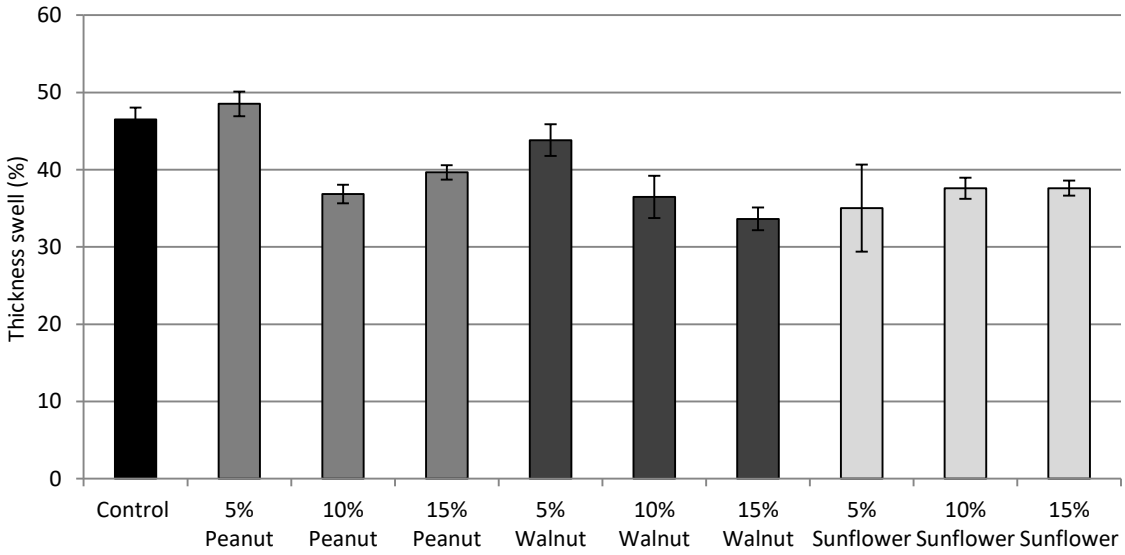
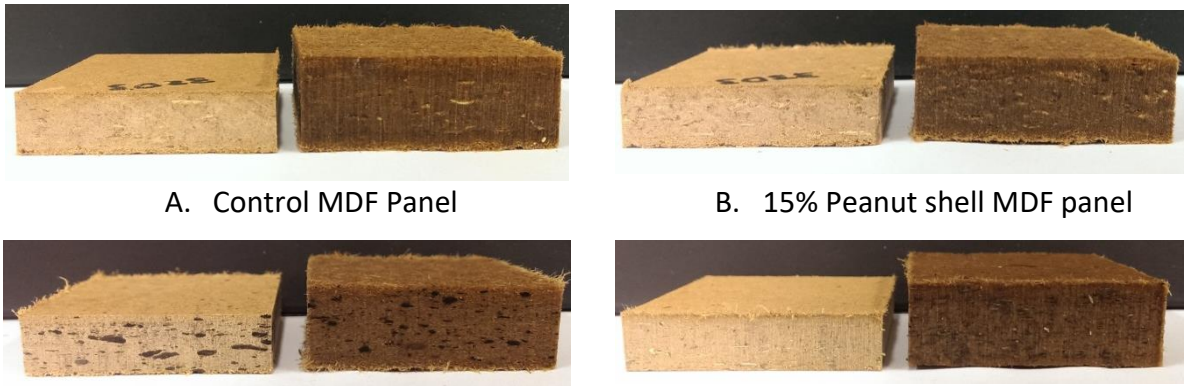


Figure 79: Thickness swell of modified MDF panel and control MDF panel

The fact that no panel met the required BSEN 622-5:2006 standard is due to the fact that no wax was added to the MDF panel during production as this may have masked effects of the scavengers on thickness swell. Indeed, Figure 79 shows that with increasing walnut shell and peanut shell the thickness swell decreases. However, 15% peanut shell had a higher thickness swell than 10% peanut MDF panel. The addition of sunflower seed shell with increasing percentage loading does

not seem to have an influence on the thickness swell but all three MDF panels had a lower thickness swell than the control MDF panel. The larger standard deviation observed in 5% sunflower seed MDF panel could be a result of the spread of the sunflower seed shell across the MDF panel. Concerning the MDF panels modified with walnut shell, the thickness swell decreases with increasing walnut shell loading percentage. This suggests that the walnut shell absorbs less water than wood fibre and increasing the percentage of walnut shell reduces the proportion of fibre in the MDF panel. Hence the thickness swell of the MDF panel is reduced.



A. Control MDF Panel B. 15% Peanut shell MDF panel

C. 15% Walnut shell MDF panel D. 15% sunflower seed shell MDF panel

Figure 80: Example thickness swell of control and scavenger modified MDF panel (untested, left and tested, right)

Moisture within buildings can be categorised into 3 categories; construction sources (moisture trapped within the building during construction), interior moisture (such as cooking and showers) and external sources (such as infiltration and capillarity). The presence of moisture within a building can cause adverse conditions such as dampness, cold and resulting in mould and fungal growth, generating an uncomfortable internal environment. In extreme conditions, the build-up of moisture coupled with biodegradation can lead to structural deterioration and collapse. Hence, construction materials should possess moisture buffering properties and any modifications should not adversely affect such properties. ANOVA was conducted to analyse the differences in thickness swell between the control MDF panel and scavenger modified MDF panels (Table 47).

Table 47: ANOVA results for thickness swell (✓ statistical difference and X no statistical difference)

Hygric Test	Scavenger Modification		
	Peanut	Walnut	Sunflower
Thickness Swell	✓	✓	✓

According to the ANOVA test, at p=0.05 there is a statistical difference between the thickness swell of control MDF panel and peanut shell (p-value 3.22 x 10^{-12}), walnut shell (p-value 9.23 x 10^{-10}), and sunflower seed shell (p-value 1.35 x 10^{-5}) MDF panels. This shows that the addition of either lignocellulosic scavenger does impact the internal bond strength of the MDF panel at either loading percentage. Therefore, T-Test assuming equal variance was determined for each of the scavenger loading (5%, 10% and 15%) compared to the control MDF panel (Table 48).

Table 48: Summary of T-Test assuming equal variance for Thickness swell (✓ statistical difference and X no statistical difference)

Board		Control MDF	Peanut shell			Walnut shell			Sunflower seed shell		
			5	10	15	5	10	15	5	10	15
Control MDF		-	✓	✓	✓	✓	✓	✓	✓	✓	✓
Peanut shell	5	✓	-	✓	✓	-	-	-	-	-	-
	10	✓	✓	-	✓	-	-	-	-	-	-
	15	✓	✓	✓	-	-	-	-	-	-	-
Walnut shell	5	✓	-	-	-	-	✓	✓	-	-	-
	10	✓	-	-	-	✓	-	✓	-	-	-
	15	✓	-	-	-	✓	✓	-	-	-	-
Sunflower seed shell	5	✓	-	-	-	-	-	-	-	X	X
	10	✓	-	-	-	-	-	-	X	-	X
	15	✓	-	-	-	-	-	-	X	X	-

Table 48 also shows that there is a statistical difference in thickness swell between the control MDF panel and either scavenger loading of peanut shells and walnut

shell. Figure 79 shows that with increasing scavenger loading of peanut shells and walnut shell, the thickness swell decreases. This indicates that the addition of peanut and walnut shell increases the hydrophobicity of the MDF panel. It also indicates that increasing the loading over 15% could reduce the thickness swell even further. The T-Test also shows that regardless of the scavenger loading percentage, the addition of sunflower seed shell does not affect the thickness swell, either adversely or positively.

In future work, modified MDF panels can be produced with the addition of a liquid wax during the blending stage. This would most likely reduce the thickness swell to the standard requirement of 12%. Another future piece of work would be to look at the moisture dynamics of the lignocellulosic scavenger in their pure state, using the dynamic vapour sorption (DVS) as described in chapter 2, section 2.6.5.3. It would also be interesting to see if this addition of wax, to reduce thickness swell had any influence on the VOC and formaldehyde absorption properties. It might be that the wax blocks binding sites on the fibre and scavengers as it effectively creates an impermeable layer over the fibres and scavengers.

4.3.3.2 Water absorption coefficient

The water absorption coefficient (W_{ac}) was determined following the same procedure as described in chapter 2, section 2.6.1.

Results and discussion

The purpose of this test is to quantify the absorption of liquid water by capillary action and the transport of water to the surface of the material. The W_{ac} of the control MDF panel was 4.11 kg m^{-2} hr^{-1}. Panels with lower W_{ac} than the control MDF panel were 10% and 15% peanut shell, 15% walnut shell and 5% and 15% sunflower seed shell MDF panel. The lowest W_{ac} 3.89 kg m^{-2} hr^{-1} was observed in 10% and 15% peanut shell MDF panels. This indicates that these panels have a lower liquid transport performance than the control. This shows that the transport of water, by capillary action is at a slower rate than observed in the control. This could have implications on the panels' susceptibility to basidiomycete decay as water is the driving factor in biodegradation.

Table 49: Water absorption coefficient of modified MDF panel and control MDF panel

Board	Water absorption coefficient ($kg\ m^{-2}\ hr^{-1}$)	Standard deviation
Control	4.11	0.09
5% Peanut shell	4.16	0.07
10% Peanut shell	3.89	0.10
15% Peanut shell	3.89	0.09
5% Walnut shell	4.28	0.15
10% Walnut shell	4.18	0.15
15% Walnut shell	4.05	0.17
5% Sunflower seed shell	3.90	0.11
10% Sunflower seed shell	4.18	0.15
15% Sunflower seed shell	4.00	0.11

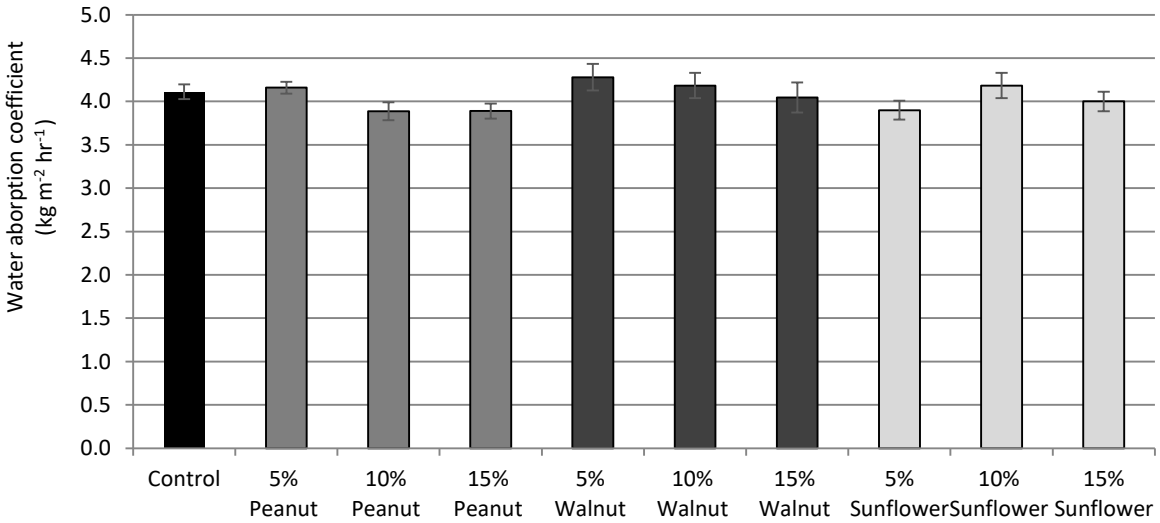


Figure 81: Water absorption coefficient of modified MDF panel and control MDF panel

All other panels had a higher W_{ac} than the control MDF panel, with the exception of MDF panels produced with 5% and 15% sunflower seed shell. The greatest W_{ac} was observed in 5% walnut shell MDF panel, 4.28 kg m^{-2} hr^{-1}. However, Figure 81 shows that with increasing walnut shell percentage loading the W_{ac} reduces. This suggests

that if the walnut shells were applied to the MDF at a higher percentage the W_{ac} could be further reduced. However, ANOVA tests (Table 50) reveals there is no significant difference between control MDF panel and MDF panels with walnut shells (p-value 5.79 x 10^{-2}).

Table 50: ANOVA results for water absorption coefficient (✓ statistical difference and X no statistical difference)

Hygric Test	Scavenger Modification		
	Peanut	Walnut	Sunflower
Water absorption coefficient	✓	X	✓

The ANOVA test for the hygric results showed there was a significant difference in water absorption coefficient between control MDF and peanut shell (p-value 1.30 x 10^{-5}) and sunflower seed shell (p-value 2.06 x 10^{-2}). No significant difference was seen with MDF panels modified with walnut shells (p-value 5.79 x 10^{-2}) To determine the where the variation lies in the mechanical properties, T-Test assuming equal variances was performed for each of the scavenger loading (5%, 10% and 15%) compared to the control MDF panel (Table 51).

Table 51: Summary of T-Test assuming equal variance for water absorption coefficient (✓ statistical difference and X no statistical difference)

Board		Control MDF	Peanut shell			Sunflower seed shell		
			5	10	15	5	10	15
Control MDF		-	X	✓	✓	✓	X	✓
Peanut shell	5	X	-	✓	✓	-	-	-
	10	✓	✓	-	X	-	-	-
	15	✓	✓	X	-	-	-	-
Sunflower seed shell	5	✓	-	-	-	-	✓	X
	10	X	-	-	-	✓	-	✓
	15	✓	-	-	-	X	✓	-

Table 51 shows that there is a statistical difference in water absorption coefficient between the control MDF panel and peanut shell modified MDF panels with 10% and 15% loading. This confirms that with increasing peanut shell loading the water uptake by capillary action of the MDF panel decreases. This also indicates that the addition of the peanut shell increases the hydrophobic properties and the absorption of water and transport of water through the panel reduces. However, at least 10% of peanut shell should be added to the MDF panel to have an impact on the hygric properties of the panel. Table 51 shows that there is a statistical difference in the water absorption coefficient of 5% and 15% loading of sunflower seed shell and control MDF, but not at 10%. This could be a result of the distribution of sunflower seed shell throughout the MDF panel. The samples evaluated for water absorption coefficient may have had a lower percentage of the scavenger than 10% and therefore resulting in having a similar result to the control MDF panel. Whereas the addition of 15% sunflower seed shell has statistically reduced the water absorption coefficient of the MDF panel.

4.3.3.3 Water Vapour Transmission

The water vapour transmission properties of the modified panels were determined following the same procedure described in chapter 2, section 2.6.2.

Results and discussion

Table 52 summarises the four water vapour transmission results derived using the dry cup method for the modified boards; water vapour flow rate, water vapour permeance, water vapour resistance and water vapour permeability factor. The water vapour permeability factor is a measure of the water vapour resistance and water vapour permeability of air with respect to partial pressures. The results were found to be the same for all samples in dry cup and wet cup experiments. This is not surprising as the samples were tested together under the same conditions. The dry cup results show the results for the movement of water vapour through the top surface of the MDF panel into the cup and the wet cup shows the results for the movement of water vapour through the bottom surface of the MDF panel.

Figure 82 shows the result for the water vapour flow rate of the control MDF panel and modified MDF panel, for the dry and wet cup. The chart shows there is a difference in the water vapour flow rate between wet cup (drying) and dry cup (wetting). Wet cup samples have a higher water vapour flow rate than the dry cup samples. The wet cup samples had an internal RH of 85% and were placed into an oven at 23°C and 0% RH. Under these different partial pressures, water vapour is moving out of the cup, through the sample and into the oven. The dry cup had an internal RH of 0% in the cup and was placed in a climate chamber of 85% RH and at 23°C. Water vapour moved from the outside, through the sample and into the cup. This difference shows that the modified MDF panels and control MDF panel exhibit hysteresis between wetting and drying. The larger uncertainty bars observed on the wet cup samples could be a result of the placement of the sample within the oven. The temperature and air flow within the oven may not have been uniform, thus affecting the rate of water vapour moving through the sample. Some areas of the oven, such as towards the back and top may have had greater airflow compared to the bottom of the oven.

Table 52: Water vapour transmission data for dry cup and wet data

Board	Density of Water Vapour flow rate (kg s^{-1} m^2) (10^{-7})				Water vapour permeance (kg (m^2 s)) (10^{-10})				Water vapour resistance (kg (m^2 s)) (10^9)				Water vapour permeability factor (kg (m^2 s)) (10^{-2})			
	Dry Cup	SD	Wet cup	SD	Dry Cup	SD	Wet cup	SD	Dry Cup	SD	Wet cup	SD	Dry Cup	SD	Wet cup	SD
Control	5.00	0.60	9.65	3.39	4.68	0.56	9.04	3.17	2.16	0.28	1.22	0.49	1.2	0	1.2	0
5% Peanut shell	4.85	0.49	8.19	4.05	4.55	0.46	7.68	3.79	2.21	0.21	1.50	0.62	1.2	0	1.2	0
10% Peanut shell	6.28	0.33	11.47	0.84	5.88	0.31	10.66	0.78	1.70	0.09	0.94	0.07	1.2	0	1.2	0
15% Peanut shell	6.00	0.44	7.63	0.98	5.62	0.41	7.15	0.92	1.78	0.13	1.41	0.18	1.2	0	1.2	0
5% Walnut shell	7.38	0.83	10.26	3.59	6.92	0.78	9.62	3.37	1.46	0.16	1.12	0.34	1.2	0	1.2	0
10% Walnut shell	7.13	0.80	8.74	4.48	6.68	0.75	8.19	4.17	1.51	0.16	1.43	0.63	1.2	0	1.2	0
15% Walnut shell	7.13	0.80	9.37	2.53	6.68	0.75	8.78	2.37	1.51	0.16	1.19	0.28	1.2	0	1.2	0
5% Sunflower seed shell	6.48	0.42	8.31	3.45	6.07	0.40	7.79	3.24	1.65	0.11	1.43	0.55	1.2	0	1.2	0
10% Sunflower seed shell	6.67	0.28	9.46	1.00	6.25	0.26	8.87	0.94	1.6	0.07	1.14	0.12	1.2	0	1.2	0
15% Sunflower seed shell	8.15	0.85	8.73	2.42	7.64	0.79	8.18	2.27	1.32	0.14	1.29	0.37	1.2	0	1.2	0

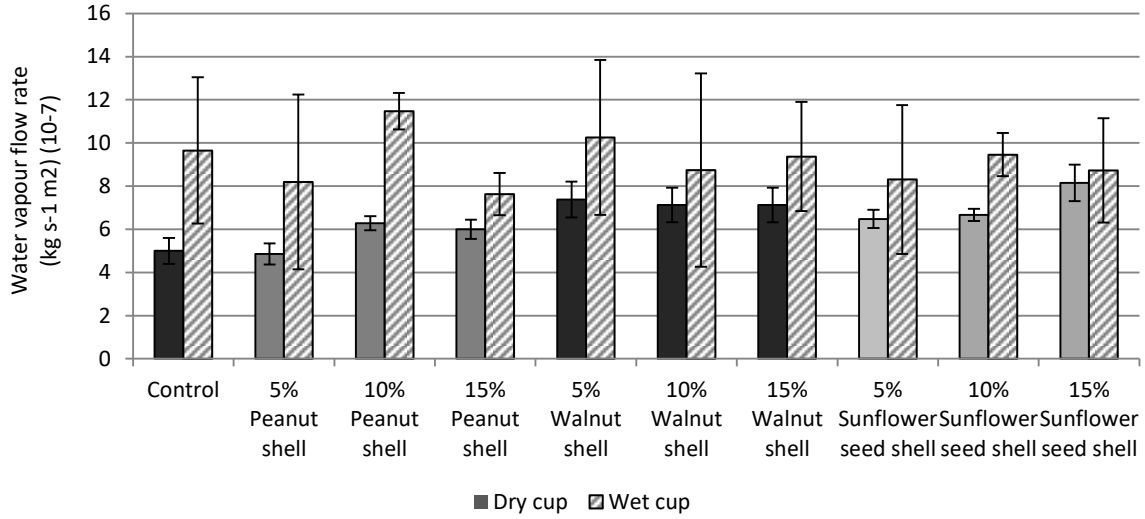


Figure 82: Water vapour flow rate of modified MDF panel and control MDF panel

Figure 83 shows the result for the water vapour permeance of the control MDF panel and modified MDF panels, for the dry and wet cup. Water vapour permeance is a measure of the permeability of the material to water vapour. Again what is evident is that the wet cup samples have a higher water vapour flow rate than the dry cup samples. This is evidence of a hysteresis effect occurring between wetting and drying of the materials. The control MDF panel had a water permeance of 4.68 kg (m^2 s) dry cup and 9.04 kg (m^2 s) wet cup. Only the modified boards with 5% peanut shell had a lower water vapour permeance in both dry and wet cup, 4.55 kg (m^2 s) and 7.68 kg (m^2 s), respectively. However, wet cup results of 15% peanut (7.15 kg (m^2 s)), 10% and 15% walnut (8.19 kg (m^2 s) and 8.78 kg (m^2 s)) and 5%, 10% and 15% sunflower seed shell (7.79 kg (m^2 s), 8.87 kg (m^2 s) and 8.18 kg (m^2 s)) MDF panels had a lower water vapour permeance than the control MDF panel.

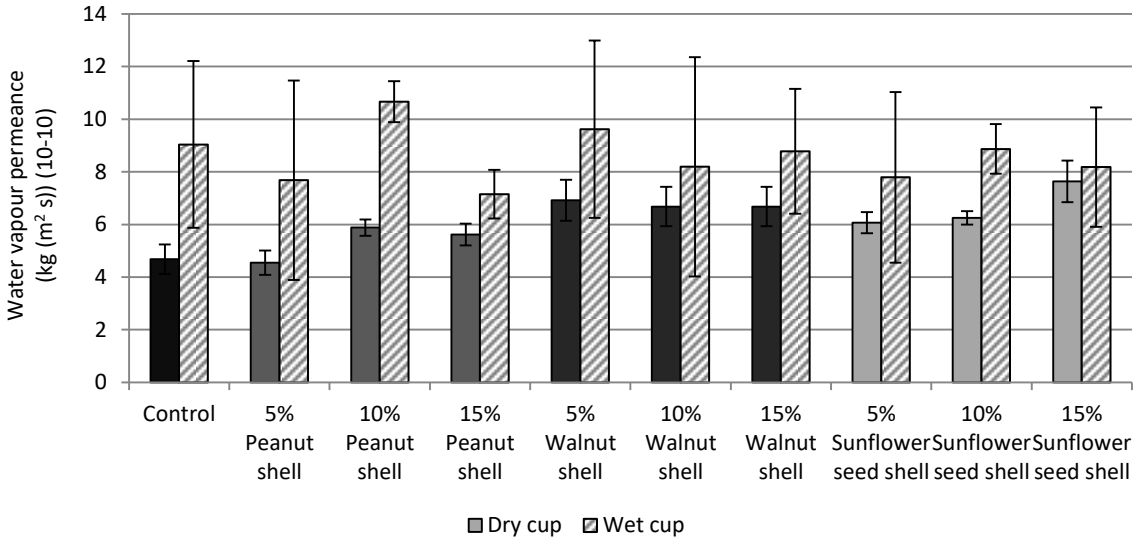


Figure 83: Water vapour permeance of modified MDF panel and control MDF panel

Figure 84 shows the result for the water vapour resistance of the control MDF panel and modified MDF panels, for the dry and wet cup. Water vapour resistance is a measure of a material's reluctance to allow water vapour to pass through the material. The higher the value shows that the water vapour will pass through the thickness of the material more slowly. In comparison to other tests, the dry cup samples had a higher water vapour resistance than the wet cup samples. The water vapour resistance of the control MDF panel was 2.16 kg (m^2 s) for the dry cup samples and 1.22 kg (m^2 s) for the wet cup samples. All modified MDF panels had a lower water vapour resistance value than the control MDF panel, except for 5% peanut shell MDF panel for dry cup samples. For the wet cup samples, only 5% peanut (0.94 kg (m^2 s)), 5% walnut kg (m^2 s)), 15% walnut (1.19 kg (m^2 s)) and 10% sunflower seed shell (1.14 kg (m^2 s)) MDF panel had a lower water vapour resistance value than the control MDF panel.

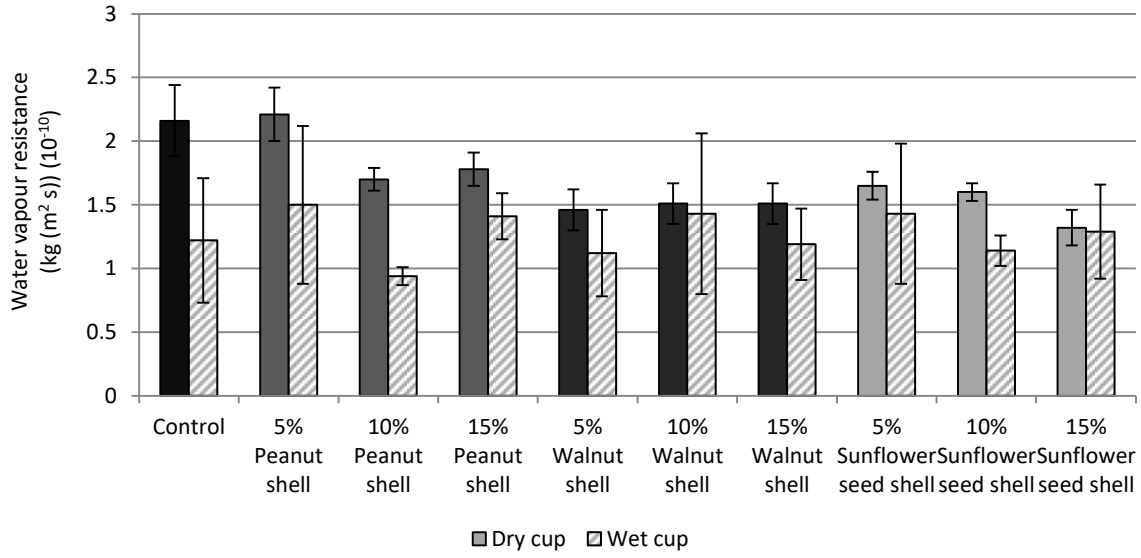


Figure 84: Water vapour resistance of modified MDF panel and control MDF panel

Table 53 summarises the ANOVA results. The ANOVA test reveals that there is no statistical difference in the vapour transmission properties of the wet cup samples between the control MDF panel and the modified MDF panels: peanut shell ($\dot{g}$ p-value 0.51, *W* p-value 0.51 and *Z* p-value 0.63), walnut shell ($\dot{g}$ p-value 1.51, *W* p-value 0.98 and *Z* p-value 0.98) and sunflower seed shell ($\dot{g}$ p-value 2.51, *W* p-value 0.85 and *Z* p-value 0.91). Whereas for the dry cup samples the data showed a statistical difference between control MDF panel and MDF panels modified with scavengers; peanut shell ($\dot{g}$ p-value 0.028, *W* p-value 2.75×10^{-2} and *Z* p-value 0.04), walnut shell ($\dot{g}$ p-value 3.07×10^{-2}, *W* p-value 3.07×10^{-2} and *Z* p-value 0.02) and sunflower seed shell ($\dot{g}$ p-value 2.6×10^{-3}, *W* p-value 0.003 and *Z* p-value 0.005). This indicates that there is a difference in the hygric performance of the modified MDF panels when exposed to different partial pressures.

Table 53: ANOVA results for vapour transmission properties compared to control MDF (✓ statistical difference and X no statistical difference)

Board	Scavenger Modification					
	Peanut		Walnut		Sunflower	
	Dry cup	Wet cup	Dry cup	Wet cup	Dry cup	Wet cup
Density of Water Vapour Flow Rate ($\dot{g}$)	✓	X	✓	X	✓	X
Water Vapour Permeance (W)	✓	X	✓	X	✓	X
Water Vapour Resistance (Z)	✓	X	✓	X	✓	X

Table 54: Summary of T-Test assuming equal variance for Density of Water Vapour Flow Rate of dry cup samples (✓ statistical difference and X no statistical difference)

Board		Control MDF	Peanut shell			Walnut shell			Sunflower seed shell		
			5	10	15	5	10	15	5	10	15
Control MDF		-	X	✓	X	✓	✓	✓	✓	✓	✓
Peanut shell	5	X	-	✓	✓	-	-	-	-	-	-
	10	✓		-	X	-	-	-	-	-	-
	15	X	✓	X	-	-	-	-	-	-	-
Walnut shell	5	✓	-	-	-	-	X	X	-	-	-
	10	✓	-	-	-	X	-	X	-	-	-
	15	✓	-	-	-	X	X	-	-	-	-
Sunflower seed shell	5	✓	-	-	-	-	-	-	-	X	✓
	10	✓	-	-	-	-	-	-	X	-	✓
	15	✓	-	-	-	-	-	-	✓	✓	-

Table 55: Summary of T-Test assuming equal variance for Water Vapour Permeance of dry cup samples (✓ statistical difference and X no statistical difference)

Board		Control MDF	Peanut shell			Walnut shell			Sunflower seed shell		
			5	10	15	5	10	15	5	10	15
Control MDF		-	X	✓	X	✓	✓	✓	✓	✓	✓
Peanut shell	5	X	-	✓	✓	-	-	-	-	-	-
	10	✓	✓	-	X	-	-	-	-	-	-
	15	X	✓	X	-	-	-	-	-	-	-
Walnut shell	5	✓	-	-	-	-	X	X	-	-	-
	10	✓	-	-	-	X	-	X	-	-	-
	15	✓	-	-	-	X	X	-	-	-	-
Sunflower seed shell	5	✓	-	-	-	-	-	-	-	X	✓
	10	✓	-	-	-	-	-	-	X	-	✓
	15	✓	-	-	-	-	-	-	✓	✓	-

Table 56: Summary of T-Test assuming equal variance for Water Vapour Resistance (✓ statistical difference and X no statistical difference)

Board		Control MDF	Peanut shell			Walnut shell			Sunflower seed shell		
			5	10	15	5	10	15	5	10	15
Control MDF		-	X	✓	X	✓	✓	✓	✓	✓	✓
Peanut shell	5	X	-	✓	✓	-	-	-	-	-	-
	10	✓	✓	-	X	-	-	-	-	-	-
	15	X	✓	X	-	-	-	-	-	-	-
Walnut shell	5	✓	-	-	-	-	X	X	-	-	-
	10	✓	-	-	-	X	-	X	-	-	-
	15	✓	-	-	-	X	X	-	-	-	-
Sunflower seed shell	5	✓	-	-	-	-	-	-	-	X	✓
	10	✓	-	-	-	-	-	-	X	-	✓
	15	✓	-	-	-	-	-	-	✓	✓	-

Table 54, 55 and 56 show the T-Test results for the water vapour transmissions for the dry cup samples only, as the results for wet cup results showed no statistical

difference from the control MDF panel. The results show that for the three expressions of results, the relationships (statistical analysis) are the same between control MDF panel and MDF panels modified with lignocellulosic scavengers and between the different percentage loadings of lignocellulosic scavenger. Hence, from this point, the results will be collectively analysed as water vapour transmission.

The T-Test shows there is no statistical difference in water vapour transmission between the control MDF and modified MDF panel modified with 5% and 15% peanut shell. The statistical difference observed between control MDF panel and modified MDF panels with 10% peanut shell is due to the lower density observed in this modified MDF panel. It also shows there is a statistical difference between 5%, 10% and 15% peanut shell MDF Panels. This suggests that with increasing percentage loading of peanut shell the water vapour resistance increases.

The T-Test also reveals that there is a statistical difference between control MDF and walnut shell MDF panels however, there was no statistical difference between the 5%, 10% and 15% loadings. This suggests that any further addition of walnut shell to the MDF panel would not significantly change the water vapour resistance.

The T-Test also reveals that there is no statistical difference between the control MDF panel and 5% sunflower seed shell MDF panel. However there is a difference between the control MDF panel and 10% and 15% sunflower seed shell. This shows statistically that increasing the percentage loading of sunflower seed shell increases the water vapour resistance of the panel and suggests that increasing the loading of sunflower seed shell to 20% could increase the water vapour resistance even further.

4.4 Chapter Summary

The aim of this chapter was to develop a modified MDF panel using 8 bar refined fibre and lignocellulosic scavengers, peanut shell, walnut shell and sunflower seed shell.

MDF panels produced with the lignocellulosic scavengers showed little aesthetic differences in the top surface of the panel, however, the bottom surface of the walnut shell and sunflower seed shell revealed an accumulation of small particles of the scavenger. Transverse cut through the MDF panels revealed that large particles

of the scavengers were evenly distributed through the thickness of the panels. Longitudinal cuts through the panel, from the panel centre outwards, did reveal the accumulation of walnut scavenger in the centre. This was a result of the production method and the effects of this accumulation of scavenger is reflected in the standard deviation of some of the mechanical, hygric and physical properties of the modified MDF panel.

4.4.1 Formaldehyde, VOC absorption and emission properties

Formaldehyde Absorption

The formaldehyde absorption tests revealed that the scavengers are still active within the MDF panels, after production and can absorb recordable amounts of gaseous formaldehyde. Statistically, only the MDF panels modified with walnut shell did not absorb less formaldehyde than the control MDF panel. Statistically, the peanut shell absorbed less than the control, however, Figure 65 and 66 show the breakdown of the six cycles conducted for formaldehyde absorption for walnut shell and peanut shell modified MDF panels. It shows that MDF panels containing walnut shell and peanut shell had not reached equilibrium, suggesting that if run for a longer period of time, the boards could have absorbed more formaldehyde. The one sample of panel modified with sunflower seed shell did absorb slightly more than the control MDF, however figure 67 shows that equilibrium was reached, so it is unlikely to absorb more formaldehyde. More testing is required to understand the formaldehyde absorption capabilities of the sunflower seed shell panels. Further tests could also be conducted to evaluate the mechanisms taking place in which formaldehyde is absorbed by the modified panels. Sorption and desorption cycles of formaldehyde absorption and then water absorption sequentially run could reveal how the formaldehyde is absorbed. Formaldehyde is polar therefore exposing a sample, which physically and chemically absorbed formaldehyde to a water cycle will cause any physisorbed formaldehyde to dissipate, therefore leaving only the chemisorbed formaldehyde. This data could be used to determine the buffering effects of the modified MDF panel.

VOC absorption

The volatile organic compounds absorption tests revealed that these lignocellulosic scavengers have the capabilities to absorb toluene, dodecane and limonene. The test also proved that the scavengers also remained active after MDF panel production, to absorb the different VOCs. The results also showed that the scavengers absorbed different amount of the three VOCs. MDF panels containing sunflower seed shell absorbed the most of the three VOCs. MDF panels absorbed the least of all three VOCs and boards modified with peanut shell absorbed dodecane but were very poor at absorbing toluene and limonene. There was a marked difference in the VOC absorption of the scavenger before and after use in MDF panel. This suggests that MDF panels can be modified and produced with specific tailoring (temperature and heat exposure) altering the surface polarity of the scavengers to absorb targeted VOCs.

MDF panel emissions

Across all the wood fibre and MDF panels, 34 different compounds were emitted (not including background noise from GC-MS) and only 3 of these were found to be emitted from the MDF panels. These three compounds are likely to be emissions from the UF resin used. 6 VOCs were emitted from the wood fibre and when combined with resin and pressed into a panel, 16 additional compounds were emitted. MDF panels with peanut shell were found to emit 17 VOCs, with walnut shell 16, and with sunflower seed shell 18. The results showed that some of the VOCs emitted from the wood fibre, empty jar (background) emissions and control MDF panel, were not present in the emissions profile of the modified MDF panels. This suggests that the MDF panels are absorbing these VOCs or masking their presence. However, MDF panels modified with walnut shell were found to emit 7 other compounds that were not present in any other MDF panel or fibre emission profile. These results show that the lignocellulosic scavengers can prevent the release of VOCs and emit other VOCs otherwise not observed in unmodified MDF panels, thus showing that such modifications can change the emissions profile of the MDF panel. If properly understood then lignocellulosic scavengers can be selected

for their use as specific VOC scavengers and MDF panels can be specially tailored to absorb targeted indoor air pollutants.

4.4.2 Physical properties

Bulk density

Statistically, there was only a difference in density of the control MDF panel and sunflower seed at 10% and 15% loading. Therefore 5% of scavenger could be added to the MDF panel before density is affected. To overcome this, more fibre or sunflower seed scavenger could be added to the panel during production to increase the density. This, however, will mean that the percentage of sunflower scavenger would be either higher or lower than 10%. There was no effect of peanut shells and walnut shell on the density of the MDF panel.

Inorganic content

The use of a lignocellulosic scavenger in MDF panels had higher inorganic content than unmodified MDF panels. The increase in walnut scavenger loading increases the inorganic content of the MDF panel. A maximum of 10% sunflower seed shell could be used before the inorganic content of the MDF panel is significantly affected. Peanut shell scavenger had low inorganic content and increasing the percentage loading did not statistically affect the inorganic content.

Surface area

Statistically, there was found to be no difference between surface area of control MDF panel and peanut shell MDF panels at either percentage loading. However, there was between control MDF panels and boards modified with walnut shell and sunflower seed shell. The addition of these scavengers significantly reduced the surface area. Surface area can influence other properties of the MDF panel such as emissions and absorption of VOCs and formaldehyde, therefore if the percentage loading of walnut shells was increased the surface area increases. However, the addition of walnut shell could adversely affect other properties such as internal bond strength, MOE, MOR and swelling thickness.

4.4.3 Mechanical properties

Internal bond strength

According to the statistical analysis, there is no difference in internal bond strength between control MDF panels and MDF panel modified with either lignocellulosic scavenger at any percentage loading.

Modulus of rupture and elasticity

It was found that the different loading of scavengers has a different effect on modulus of elasticity and modulus of rupture. There was found to be no statistical significant difference between the control MDF panel and walnut shell loading in MOR but there was in MOE. Increasing the percentage loading of walnut shell in MDF panel decreased the MOE. There was found to be no significant difference between control MDF and sunflower seed shell loading in MOE but there was with MOR. Increasing the percentage loading of sunflower seed shell decreased MOE. The addition of peanut shell to the MDF panel did not significantly change the MOE or MOR of the panel except when loaded at 10%, which is likely due to the lower density of the overall panel.

In terms of mechanical properties alone, 5% sunflower seed shell MDF panel is the most suitable modification as it has the least adverse impact on the mechanical properties (primary function) of the MDF panel. Indeed, this modification seems to improve the mechanical properties.

4.4.4 Hygric properties

Thickness swell

ANOVA results showed that the addition of lignocellulosic scavenger affected the thickness swell of the MDF panel. The T-Test analysis revealed that there was significant in thickness swell and the increased loading of walnut shell and peanut shell scavenger. The increased addition of either these scavengers, reduced the thickness swell of the MDF panel. However, the addition of sunflower seed shell at either percentage loading did not statically affect thickness swell.

Water absorption coefficient (W_{ac})

Statistically the addition of peanut shells was found to reduce the W_{ac} of the MDF panel, up to a loading of 10%. The addition of sunflower seed shells to the MDF panel was also found to, statistically, reduce W_{ac}. The addition of walnut shell, at either percentage loading was found not to influence W_{ac}, positively or negatively.

Water vapour Transmission properties

The water vapour transmissions properties are evaluated on a wet cup and dry cup basis. ANOVA results shows no statistical difference in water vapour transmission results between control MDF panels and MDF panels modified with lignocellulosic scavengers, for the wet cup samples. However, there was in the dry cup samples. Water vapour transmission increased with increasing peanut shell percentage loading. The addition of walnut shell did not statistically increase water vapour transmission past a percentage loading of 5%. Panels modified with sunflower seed shell did not show any statistical difference in water vapour resistance at 5% loading but there was at higher percentage loadings. This suggests that the water vapour transmission could be reduced further with increasing addition of sun flower seed shell.

5 Modification Discussion

It has been recognised that the build-up of total chemical compound emissions and increased air-tightness of non-industrial buildings is a potential hazard to human health (Yu and Kim, 2010). This indoor air pollution of chemical emissions (VOCs) contributes to poor indoor air quality (IAQ) and subsequently can cause a number of adverse on humans, namely sick building syndrome (SBS). The reduction of VOCs and the improvement of IAQ can be tackled on four different levels: occupants, architects and developers, manufacturers and government. Occupants can improve IAQ by increasing ventilation, opening windows and reducing their use of cleaning agents, scented candles and odorants (Wolkoff et al., 2000). Occupants should also be encouraged to purchase and use products with low emissions. Architects and developers should consider IAQ during building design and construction, taking special consideration of the appropriate ventilation system for the building and substituting materials for low emissions products. Governments should take responsibility for ensuring that building regulations are followed, develop mandatory IAQ guidelines as well sponsor, fund and support research and development into alternative, novel materials and into toxicology of VOCs. Manufacturers should ultimately test their products for types and quantities of emissions and where possible, should collaborate with researchers and developers to investigate alternative compositions and production methods to reduce a product/materials' emissions. There is scientific evidence that simple measures such as storing and drying wood for longer, increasing production press times and temperatures can reduce wood-based products emissions (Hun et al., 2010; Roffael, 2006; Salem and Böhm, 2013) and using different wood species can reduce emissions (Costa et al., 2013a; Gabriel et al., 2015). Production processes can also influence emissions from a product and oven drying has been shown to reduce emissions (Boruszewski et al., 2011). Physical modifications can also be applied to the material to reduce emissions such as different surface treatments including photocatalytic coatings (Hoffmann et al., 1995; Mo et al., 2009b; Salthammer and Fuhrmann, 2007) and material surface treatments (Hematabadi et al., 2012; H. Zhang et al., 2013). Resin modifications have also proved to be an effect means of

reducing emissions and changing emissions profile with the use of tannins and extractives (Bisanda et al., 2003; Ping et al., 2012; Roffael et al., 2000; Valenzuela et al., 2012), altering molar ratio (Astarloa Aierbe et al., 2000; Park et al., 2006; Tohmura et al., 2000; Zorba et al., 2008) and substitution of fossil fuel based resins with agricultural and protein wastes. The addition of absorbing scavengers into the products has also shown to have great potential in reducing emissions and absorbing VOCs from the atmosphere. The scavengers can be inorganic such as chemicals (Costa et al., 2013b; Johnsson et al., 2014) or silica, clay and pozzolanic materials (Ashori and Nourbakhsh, 2009; Gedikoglu et al., 2012; Kim, 2009b; Kosuge et al., 2007; Lei et al., 2008). Organic scavengers such as lignocellulosic wastes (Ayrilmis et al., 2013; Buyuksari et al., 2010; Cosereanu et al., 2014; Kamireddy et al., 2014; Mothé and Miranda, 2009; Nemli and Çolakoğlu, 2005; Pirayesh and Khazaeian, 2012; Tavakoli Foroushani et al., 2016; van Dam et al., 2004) and protein based scavengers (Du et al., 2009; Huang et al., 2007; Mcafee et al., 2001; Middlebrook, 1949; Middlebrook and Phillips, 1947; Monier, 2012) have been well investigated for their potential to reduce emissions from a product.

The aim of this study was to develop a modification that can be applied to wood-based construction material, MDF, to produce a multifunctional material that will actively absorb formaldehyde and VOCs to improve IAQ.

5.1 Identifying modifications

Formaldehyde is always present within indoor and outdoor environments as it is emitted from a vast variety of sources, including wood, human, volcanoes, furniture, construction materials and electronic equipment (Meyer and Boehme, 1997; Trézl et al., 1997; WHO, 2010). Consequently, a “zero emissions” wood-based panel is not achievable (Meyer and Boehme, 1997; Roffael, 2006; Weigl et al., 2009). Therefore, the first objective of this study was to identify ways in which MDF can be modified to absorb external sources of formaldehyde, rather than attempt to reduce emissions from the MDF panel. The chosen modification were to alter the refining pressure during MDF fibre production (mechanical) and adding a formaldehyde and VOC scavenger to the MDF panel (physical).

5.2 Mechanical modification

Refining at different pressures

Evidence gathered in the literature review revealed that changes to the refining process can alter the fibres properties. The percentage of extractives and glucose, for example, increase with refining pressure whilst xylan, galactan and mannan quantities decrease (Kelley *et al* 2005). Different refining conditions also can alter the morphology of fibres and thus surface roughness. High refining pressures coupled with high temperatures produce very fine fibres, while mild conditions produce a mixture of fibrillated and unbroken fibres, increasing roughness (Aisyah *et al* 2013). This research shows that changes to the refining of the wood fibre alter its structure. Therefore, it is possible that different functional groups may be more accessible.

There were immediate differences observed in the fibre refined at different pressures. Fibre refined at 6 bar pressure was much longer in length and lighter in colour than those fibres refined at 8 and at 10 bar pressure, which were a much darker brown.

5.2.1 Formaldehyde absorption performance

MDF fibre

The result revealed that the fibre refined at 6 bar absorbed the most formaldehyde, 134.67 g kg^{-1} and 8 bar refined fibre the least, 41.20 g kg^{-1}. Fibre refined at 10 bar absorbed 91.17 g kg^{-1} of formaldehyde but it was found to reach equilibrium in formaldehyde absorption and would not absorb more. Whereas fibre refined at 6 bar and 8 bar showed potential to absorb more than the amount of formaldehyde recorded. The refining process is known to alter the fibre structure and the proportions of the three fundamental components of the wood, cellulose, hemicellulose and lignin, as well as extractive content (Kelley et al., 2005). Increasing refiner pressure decreases the proportion of hemicellulose sugars such as xylose and galactose due to hydrolysis (Groom et al., 2000; Kelley et al., 2005). The cellulose in the wood fibre generally increases the average crystallinity following the increasing refiner pressure, as the concentrations of amorphous cellulose and hemicellulose

components decrease (Kelley et al., 2005). The proportion of lignin has been reported to remain the same (Groom et al., 2000). However, at higher refiner pressures, the glass transition temperature of lignin polymer is reduced. As a result the lignin is more unstable at lower temperature and therefore the lignin molecules can move more freely within the fibre structure. This movement of the hydrophobic lignin could explain the changes in hydroscopic behaviour of the fibre. Looking at the moisture dynamics of the refined fibre in the DVS, the EMC at 95% of the 6, 8 and bar refined fibre is not significantly different. However, looking at the moisture content of the fibres at relative humidities less than 80%, fibre refined at 10 bar has a lower MC. This is evidence of the movement of the lignin, which is hydrophobic, to the surface of the fibre, reducing moisture uptake by the fibre.

Groom et al., (2000) and Groom et al., (2004) reported that with increasing refiner pressure, the fibre surface becomes increasingly more torn and rough. Fibre refined at intermediate pressures (8 bar) are reported to have a granulated surface suggesting the redisposition of constituent parts during the refining process (Groom et al., 2004). It is clear that the refining process does have an effect on the wood fibre chemistry and its structure. These changes in wood chemistry ultimately led to measureable changes in hygroscopicity, decay, strength and stiffness (Winandy and Krzysik, 2005). A further investigation to better understand the physical effects of refining on wood fibre would be to look at the surface area of the fibres, pore structure and porosity when loose before being pressed into a MDF panel.

Small scale MDF panel

The next stage of the mechanical modification assessment was to produce and evaluate MDF panels produced from the 6, 8 and 10 bar refined fibre.

Formaldehyde absorption

The greatest formaldehyde absorption was observed in boards produced using 8 bar refined fibre, 127.66 g kg^{-1}. Whereas the least amount absorbed was by MDF panels produced from 6 bar refined fibre, 63.23 g kg^{-1}. This is unexpected and an important area that requires further investigation. Winandy and Krzysik,(2005) suggested that during the hot pressing stage of MDF panel production, temperatures exceeding

150°C alter the chemical composition of wood fibre further. This in turn would ultimately influence the formaldehyde absorption capabilities of the MDF panel. It can be hypothesised that there is a further structural and chemical shift in the wood fibre during the high temperature and high pressure pressing of MDF production. Evidence for structural shift can be seen in Chapter 3, section 3.2.7.1 which shows the results for the surface area of the MDF panel produced using the modified fibre. The results show that the surface area decreases with increasing refiner pressure. The change in pore structure chapter 3, section 3.2.7.2, is also evidence for a change in the fibre structure with different refiner pressures. Figure 47A, B and C depicts the distribution of the different pore sizes within the mechanically modified MDF panel. It can be seen that with increasing refiner pressure there is a reduction in the number of large pore diameters within the panel. This could be a result of the movement of lignin towards the surface of the individual fibres, filling in the pores and surface cracks and tears. It is known that the glass transition temperature of lignin is reached when fibres are refined at 10 bar, but not reached when fibres are refined at 6 and 8 bar (Groom et al., 1999). So it is likely that the lignin has moved in the fibre structure, affecting its properties, such as the surface area, which was found to reduce with increasing refiner pressure. A marked reduction in the cumulative pore volume in MDF panels produced with 6 bar refined fibre and 8 bar and 10 bar refined fibre was also observed.

The moisture of the fibre used to produce the MDF panel will also have an effect on the chemical structure of the MDF fibre. If the fibre had a high MC going into the press, the steam expelled from the board during the hot pressing can cause degradation of the hemicelluloses, lignin and cellulose within the fibre (Winandy and Krzysik, 2005). Winandy and Krzysik, (2005) also described how hemicelluloses arabinose and galactan (side chains of hemicellulose) are reduced and hemicellulose is hydrolysed during exposure to high temperatures. These changes reduce the hygroscopity of fibre boards (Winandy and Krzysik, 2005). It is important to understand the dynamic changes occurring and where the VOCs and formaldehyde are binding to, as the loss of hemicellulose may also be the reason for the reduced formaldehyde absorption. Hemicellulose is hydrophillic, so if the formaldehyde is

binding to the water within the fibre, then increased hydrophobicity of the fibre would possibly reduce the amount of formaldehyde absorbed. However, this would only be true if the cellulose is responsible for the absorption of formaldehyde. Evidence of this can be seen in chapter 3, section 3.2.3 with the moisture dynamics of the refined fibre and moisture isotherms (fig 29), the hysteresis of the 10 bar refined fibre is less than the fibre refined at 6 and 8 bar pressure. This could be a result of the removal of hydrophilic components of the fibre and the movement of hydrophobic lignin towards to fibre surface. This, in turn, would also have knock on effects on the thickness swell and mechanical properties of the final MDF product (Winandy and Krzysik, 2005).

It is also important to understand the effect of formaldehyde release from the MDF panels produced from fibre refined at different pressures. As formaldehyde emission from a board is governed by the moisture content (Boruszewski et al., 2011) reducing the initial MC of the wood fibre prior to hot pressing is important in reducing emissions of the MDF panel.

Further work would be to study the effects of long press times and different press temperatures on refined fibre and their formaldehyde sorption and fibre composition and the influence the change in schedule has on a panel's capabilities for formaldehyde absorption. This would be an important area of research as this study shows that the absorption capabilities of an MDF panel are not only governed by the pressure at which the wood chip is refined but also temperature and lignin and sugar composition. Another piece of future work would be to determine which component of the wood fibre, lignin, cellulose or hemicellulose that the formaldehyde and other VOCs bind too. It would be helpful and important to determine how the cumulative thermal exposure (refining and hot pressing) the fibres are subject to and the effect on formaldehyde and VOC absorption capabilities. This would also help to prove the theory described in chapter 3 section 3.2.7 that the fibres undergo a structural state shift before and after hot pressing that will affect the formaldehyde absorption of the fibre.

Mechanical properties

The mechanical properties modulus of rupture (MOR) and modulus of elasticity (MOE) of the mechanically modified MDF panels were evaluated. Statistically, there was found to be no difference between the MDF panels produced from fibres refined at difference pressures. Although, there is a visible decrease in the MOR of MDF panels produced from 10 bar refined fibre, compared to those produced using 6 and 8 bar refined fibre. This is due to the reduction in the aspect ratio of the fibres and fibre lengths, when refined at 10 bar, which affects the matrix of the MDF panel, reducing its strength, due to the poor physical interlocking, by fibre to fibre contact (Groom et al., 2004). The slight increase in MOE observed in MDF panels produced from 8 bar refined fibre could be a result of the increase in cracks and tears in the fibre structure, when refined at intermediate pressures. This enables higher resin migration and penetration ultimately resulting in better fibre to fibre bonding and higher mechanical strength properties. However, too high a refining pressure increases the number of fines in the MDF fibre and reduces the aspect ratio which reduces cross-linking between fibres, thus reducing mechanical strength properties. This shows that a balance must be struck between these two factors.

5.3 Physical modification

As the number of sources of VOCs and formaldehyde is vast, it is impractical to try to prevent all emissions from their prospective sources and production streams completely. Emissions should, of course, be eliminated where possible, such as replacing formaldehyde based resin with bio-based resins. The indoor atmosphere will always contain VOCs and it is unlikely that formaldehyde concentrations could be lower than 20μgm^{-3} (Salthammer et al., 2010). Therefore, formaldehyde and VOC scavengers can be employed to actively absorb pollutants from the atmosphere and improve IAQ. Lignocellulosic wastes are quite versatile in their use and have shown great potential as bio-scavengers of formaldehyde and VOCs. A great advantage of wood-based panels such as MDF is that they can be easily modified to incorporate scavengers to enhance the panel's sorption capacities (Tittarelli et al., 2015).

5.3.1 Formaldehyde absorption

The materials that were tested as potential scavengers were walnut shells, almond shells, peanut shells, sunflower seed shells, coconut husks and pistachio nut shells, waste paper sludge, nano-clay calcium carbonate, wool fibre and wood fibre.

The formaldehyde absorption capability of the scavengers was determined using DVS, described in chapter 3 section 3.4.3. Results showed that wood fibre absorbed 49.69 g kg^{-1} and only four scavengers were found to absorb more than the wood fibre; sunflower seed shell, walnut shell, peanut shell and almond shell in that order. Nano-clay was found to be the poorest of scavengers. Evidence in the literature suggested that nano-clay could be used as a filler to modify thermosetting resin for wood-based materials and reduce formaldehyde emissions, as it would would react and bind to aldehyde groups (Ashori and Nourbakhsh, 2009; Lei et al., 2008; Lin et al., 2006). However, the nano-clay used in this study was found to absorb only 0.01 g kg^{-1}. The nano-clay reported in the literature review was most commonly silica based, whereas the nano-clay used was calcium carbonate. This shows that all nano-clays should not be discarded or willingly used as a scavenger, as the composition of the nano-clay greatly influences its sorption capabilities.

A material's absorption capacity is not easily determined as this property is governed by the physical and chemical properties of the material and the target VOC (Deng et al., 2012). In an attempt to determine the properties that govern the scavenger's ability to absorb formaldehyde the protein content of the scavengers was determined. It has been noted in literature that protein based materials have potential to be used as natural fillers in adhesive to improve bonding in wood-based panels. Bisanda et al., (2003), Guezguez et al., (2013), Lorenz et al., (1999), Pizzi and Mittal, (2003) and Wang et al., (2011) all showed that protein based wastes such as soybean, cashew nut sell liquid (CNSL), soy protein, whey from cheese making and casein could be used as filler to improve resin crosslinking. Such additives to resins are rich in functional groups such as hydroxyl and amino groups that readily react with aldehyde and isocyano groups. These additional reactions occurring during the curing process reduce the emissions of free formaldehyde and can generate stronger panels. It has also been reported that the amino groups in the protein structure of wool fibre are responsible for the high amounts of formaldehyde

absorption observed (Curling et al., 2012; Huang et al., 2007; Middlebrook, 1949; Salthammer et al., 2010). As the proteins within the scavengers are most likely to be responsible for the absorption of formaldehyde, the nitrogen content of the lignocellulosic scavengers was determined.

5.3.1.1 Nitrogen content

The nitrogen content of the waste nut shells and wool fibre, was determined using the Kjeldahl method, as described in chapter 3, section 3.4.4. Figure 53 revealed that with increasing nitrogen content of the nut shell wastes, the formaldehyde absorption increases. However, wool fibre does not fit this relationship, revealing that it is the structure of the nut shell wastes that is responsible for its formaldehyde absorption capabilities. Other physical and chemical properties must be influencing the formaldehyde absorption properties.

5.3.1.2 FTIR / PLS

The nut shell wastes underwent Fourier transform infrared spectroscopy (FTIR). This technique enables the determination of qualitative data on the functional groups within samples. The spectra (fig 54) revealed that there was little difference between the components of the lignocellulosic scavengers. There appears to be a correlation between formaldehyde absorption and the nitrogen content of the lignocellulosic scavengers. This indicates that there is something specific about their chemical structure and present functional groups that influence the material's capabilities to absorb and trap formaldehyde.

The obtained FTIR spectra were analysed in conjunction with the formaldehyde absorption data using Partial Least Square regression (PSL). The PLS variance of importance (VIP) data was used to identify the areas of the FTIR spectra's which explains the modelled correlation of the organic scavengers and its capabilities to absorb gaseous formaldehyde. There were 7 major areas of the FTIR spectra that explain the fit of the PLS model. It is these areas on the spectra that show were the chemical differences are that are responsible for the differences in the scavengers' ability to absorb formaldehyde. These areas are likely to be the protein structures that relate to hydroxyl groups and amino groups (functional groups), which readily

bind to aldehyde groups (Wang et al., 2011). It is the presence or absence of these functional groups that is most likely to be responsible for formaldehyde absorption. Buyuksari et al., (2010) concluded that the phenolics within lignocellulosic materials are also responsible for formaldehyde absorption. It would be interesting to determine the phenolic content of the scavengers and identify individual compounds that could be isolated for formaldehyde scavenging, although this was outside the scope and timeframe of the current study. (Johns et al., 1998; Tavakoli Foroushani et al., 2016; Witek-Krowiak et al., 2011) reported the use of peanut shell and pistachio nut shell use as bio-absorbents of pollutant in aqueous solutions, however they required chemical activation. It may be the case that to significantly improve these scavengers, they would need to be activated. However this would ensue rising production costs.

Figure 56 showed the regression model of the scavengers and formaldehyde absorption. The PLS model showed that for 4 of the 6 lignocellulosic wastes, it is their chemical structure that is responsible for the difference between their ability to absorb formaldehyde. Although this model works, it was improved by removing two outliers, peanut shell and pistachio nut shell. However, peanut shell absorbed the 3rd most formaldehyde of the lignocellulosic scavengers but the PLS data indicates that it is not the chemical differences between the scavengers that is responsible, i.e. the chemical structure of peanut shell and pistachio nut shell is not responsible for the differences observed in formaldehyde absorption between the scavengers. Therefore another property of the peanut shell and pistachio nut shell must be responsible for the observed differences in formaldehyde absorption.

5.3.1.3 Surface area

The surface area of the waste nut shells was evaluated to determine if there was a significant difference between them. It was found that the surface area of the peanut shell was the highest between the scavengers and the lowest was pistachio nut shell. Walnut shell and sunflower seed shell had the second and third highest surface area. This helps to show that the chemical structure of these waste shells plays a larger role in their ability to absorb gaseous formaldehyde.

5.4 Scavenger modified MDF panels

The top three scavengers that absorbed the most formaldehyde, peanut shell, walnut and sunflower seed shell were then used to produce modified MDF panels, containing 5%, 10% and 15% loading. The benefits of the absorption capabilities of the modified MDF panels with lignocellulosic scavengers are described below

5.4.1 MDF with Peanut shell Scavenger

Formaldehyde and VOC sorption

It was found that MDF panels modified with peanut shell absorbed a lower quantity of formaldehyde on average than the control MDF panel. However, increasing the percentage loading of peanut shell increased the amount of formaldehyde absorbed by the modified MDF panel. The MDF panels modified with 5% peanut shell absorbed the least formaldehyde which was less than the quantity of formaldehyde absorption observed in peanut shell alone. Some of the replicate samples absorbed far more than the control MDF panel, hence the large uncertainty bars. This could be result of the variation in peanut shell loading across the MDF panel and the fact that samples used with DVS were very small. Looking at the cycles of absorption, it can be seen that equilibrium was not reached, so there is scope for further absorption if the DVS was run for a greater number of sorption and desorption cycles.

Despite the lower average of formaldehyde absorption of the peanut shell modified panels, this study has shown that the peanut shell is active within the panel after being exposed to high temperatures and pressures during MDF panel production. If the shells had been deactivated during production due to the high temperatures and pressure, then the formaldehyde absorption would decrease as the formaldehyde absorbing MDF fibre is replaced by increasing peanut shell loading.
The results for the VOC absorption properties of the peanut shell, however, show that the MDF panel production process does have an effect on the VOC absorption by the peanut shell. In its raw form, peanut shell was best at absorbing dodecane, then toluene with limonene absorbed the least. This suggests that the peanut shells are better at absorbing straight chain and non-polar compounds. However, once combined into an MDF panel, the quantity of the limonene and toluene absorbed is reduced. Dodecane remains the most absorbed VOC and limonene the least

absorbed and less than the quantity of limonene absorbed by the control MDF panel. This suggests a change in the surface chemistry of the peanut shell during hot pressing. There could have been a change in polarity of the surface chemistry altering the interaction between VOCs and surface of the modified MDF panel.

VOC emissions

The VOC emissions from the control MDF panel and modified MDF panels were also determined. It is important to understand if the emissions from an MDF panel will be influenced by any modifications, as the modifications should not increase the emissions and they themselves reduce IAQ. MDF panels modified with peanut shell were found to emit 11 major types of emissions (minus the background emissions). The emissions profile of these panels was found to be similar to the emission profile of MDF boards containing sunflower seed shell. There were no unique peaks identified on SPME-GCMS results (Table 29) and all peaks were all found to be emitted by other modified panels and the control MDF panel.

Hygric

The hygric properties of a wood-based panel can have an influence on a number of other properties of the panel such as dimensional changes, chemical and biodegradation processes. Therefore, it is very important to understand the hygric performance of a material.

It was found that increasing the percentage loading of peanut shell into the MDF panel, decreases the thickness swell and was found to be better than control MDF panel. It was also found that increasing the percentage loading decreases the water absorption coefficient up to 10% loading as there no significant differenced observed between panels containing 10% and 15% peanut shell.

The vapour transmission data revealed a small hysteresis present between wet cup and dry samples, showing that water vapour can be trapped within the small pore structure. The small sorption hysteresis and the pore size distribution graphs (appendix F, fig 122B) show that the peanut shell structure is predominantly macropores (hence the small hysteresis and the gases and liquids can easily desorb from the peanut structure. The water vapour transmissions data revealed that the

water vapour flow rate was greater than the control MDF panel, showing that the addition of peanut shells increases the flow rate of water vapour through the sample. Increasing the percentage loading of peanut shells was also found to increase the water vapour permeance showing that the MDF panel is more permeable than the control MDF panel. This may be due to the larger pore structure and the increased cumulative pore volume observed in peanut shell modified MDF panels. The hygric properties can be improved by adding a wax to the resin in MDF panel production which would increase liquid water and vapour water resistance. The water vapour transmission properties of a panel are important to understand as a reduction in vapour resistance may cause the release of greater formaldehyde and VOC emissions as water vapour governs the emission of formaldehyde from a material. No significant difference was observed in the vapour transmission properties of the control MDF panel and MDF panels modified with 5% peanut shell.

This large pore structure also explains why little formaldehyde was absorbed by peanut shell modified MDF panels. It suggests that formaldehyde is only physically bound in the MDF panel, not chemically and can be easily emitted from the panel again. However, this may be a beneficial property of the MDF panel, as the peanut shell MDF panels would act as a buffer to indoor pollutants, rather than a permanent sink. When concentrations of indoor pollutants are high (when there is high activity within a room) the panels would absorb formaldehyde and VOCs and when the activity decreased, the panels emit the VOCs and formaldehyde to be ventilated out of the room.

Mechanical strength

The primary function of the MDF panel is use in construction. The results for the mechanical properties showed no significant difference in the internal bond strength was observed between control MDF panels and modified MDF panels with peanut shell. Despite there being a higher inorganic content of these panels (inorganics can interfere with the resin bonding) and the difference in aspect ratio between fibre and peanut shell there was no significant difference in MOE and MOR between control MDF panels and panels modified with 5% and 15% peanut shell. It is possible

that due to peanut shell's larger pore structure, the resin could easily migrate through the scavenger creating a panel of similar strength to an unmodified panel despite the disruption of the internal matrix of the fibre. There was a significant difference in MOR and MOE observed between control MDF panel and MDF panels modified with 10% peanut shell. However, this is a result of the lower density than other panels due to a fault in the manufacturing process.

5.5 Walnut shell Scavenger

Formaldehyde and VOC absorption

The formaldehyde absorption results showed that there was no statistical difference in formaldehyde absorption between control MDF and modified MDF panel with walnut shell. There was however, a slight increase in formaldehyde absorbed with increasing walnut shell loading. The DVS cycles revealed that panels modified with 5% walnut shell had the potential to absorb more formaldehyde, but panels modified with 10% and 15% walnut shell did not. This suggests that the walnut shell scavenger quickly reached equilibrium in formaldehyde absorption and would not have a buffer effect of indoor pollutants. The results from the FTIR and PSL show that the formaldehyde is likely to chemically combine with the hydroxyl groups and amino groups present in walnut shell (Pirayesh et al., 2013). Therefore these sites become bound (used) and as there are only a finite number of them present within the walnut shell structure, the scavenger becomes saturated. Therefore, use of this scavenger would act as permanent sink, not as a buffer for indoor air. The working life-span of such a scavenger would need to be further investigated, as it maybe that this scavenger becomes saturated quickly and would not help to improve indoor air quality throughout the MDF panel's service life.

In terms of VOC absorption walnut shell absorbed the most toluene and limonene of the three scavengers. This suggests that the walnut shells are better at absorbing aromatic compounds and cyclic and non-polar compounds than peanut shell and sunflower seed shell. Walnut shell absorbed similar quantities of dodecane to sunflower seed shell and peanut shell. However, when incorporated into an MDF panel, the VOC absorption capabilities of the walnut shell changed significantly. The

walnut shell modified MDF panels did not absorb either VOC better than the control MDF panel or the other scavengers. One possible mechanisms is that the walnut shells undergo a change in the walnut shell's surface chemistry during MDF production, whereby the high temperatures and pressures, change the polarity of the surface altering the interaction between VOCs and surface of the modified MDF panel. It may be that the chemical binding sites of the walnut shells are used up by the UF resin, however, there was no significant difference observed in the internal bond strength and MOR between the modified MDF panel and control MDF panel. Therefore, it is not likely to be the case or else a much weaker MDF panel would be observed as the resin would not be binding fibre to scavengers.

VOC emissions

The VOC emissions profile from walnut shell modified panels was found to have 14 major emissions (minus background emissions), 6 of which were not identified in any other emissions profile. These VOCs were found to be mix of hydrocarbons, aldehydes and organic alcohols. This and the absence of the background (blank jar) emissions, suggests that the unique emissions are secondary VOCs that are a product of chemical reactions taking place between the VOC and walnut shell scavenger. However it can also be true that these emissions from the walnut shell are masking the presence of other VOCs.

Hygric

It was found that the walnut shell does affect the hygric properties of the MDF panel. With increasing percentage loading of walnut shell, the thickness swell of the MDF panel decreased although the water absorption coefficient showed no significant difference between the control MDF and the walnut shell modified panels. The water vapour flow rate results showed an increase in the vapour flow rate compared to the control MDF panel but there was no significant difference observed between the different percentage loading of walnut shell. The same can be said of the water vapour permeance, showing that the addition of walnut shell, increased the permeability of the MDF panel. This correlates with a reduction in water vapour resistance but there was no significant difference with percentage

loading of walnut shell. Water vapour resistance was the same whether the MDF panel had been modified with 5% or 15% walnut shell. This increased uptake of moisture and movement of water vapour can be attributed to the walnut shell MDF panel's greater cumulative pore volume than control MDF panel. The porosity data also showed that the panels had large pores as well as small, but still predominantly small pores, which accounts for the hysteresis observed in the sorption and desorption isotherms (appendix F, fig 122A) and increasing percentage loading of walnut shell, increased the surface area.

Mechanical properties

The addition of walnut shell on the mechanical properties of the MDF panel showed no significant difference in the internal bond strength and MOR between the control MDF panel and walnut shell modified MDF panels. However, the results for the MOE were lower than the control and MOE decreased with increasing percentage loading of walnut shell. This reduction in the modulus of elasticity could be caused by the different shape of the walnut shell disrupting the internal matrix of the MDF panel. The stiffness and strength of MDF panels is dependent upon the properties of the individual fibres and how these fibres are combined (Groom et al., 1999). The fibres within the panel form a three dimensional fibre network/matrix and the walnut shell is disrupting this internal structure, creating voids, ultimately reducing the stiffness and strength of the MDF panel. The very high inorganic content of the walnut shells may also have disrupted the resin bonding, especially if full of silicone compounds. Walnut shell is also reported to have a high quantity of hydroxyl groups which may have interrupted the bonding of fibre to scavenger during production. Pirayesh et al., (2013) reported that these polar hydroxyl groups are responsible for hydrogen bonds which can affect adhesion between wood and shell, making the overall panel weaker mechanically.

5.6 Sunflower seed shell scavenger

Formaldehyde and VOC absorption

Only MDF panel with 5% sunflower seed shell could be evaluated for formaldehyde absorption. The results showed no significant difference in absorption between

control MDF panel and the sunflower seed shell modified MDF panel. Although, the formaldehyde absorption was greater in 5% sunflower MDF panels that the other scavenger modified MDF panels. However, looking at the mass gain over the six sorption cycles, the scavenger appears to have reached equilibrium in formaldehyde absorption. Evaluating the FTIR and PLS data shows that the chemistry of the sunflower seed shell is responsible for formaldehyde absorption, hence it is likely that the formaldehyde is chemically bound to the surface functional groups and may have become saturated. Therefore, MDF panels modified with sunflower seed shell would act as a sink to formaldehyde and VOCs, like panels modified with walnut shell and not like a buffer to indoor air pollutants. Again, the life-span of such a scavenger would need to be further investigated, as it may be that this scavenger becomes saturated quickly and would not help to improve indoor air quality throughout the MDF panel's service life.

It can be hypothesised that the formaldehyde absorption would increase with increasing sunflower seed shell loading. The cumulative pore volume of the sunflower seed shell modified panels is greater than the control MDF panel which may aid in the increase of formaldehyde absorption, however the surface area of these MDF panels is significantly lower than the control. Another piece of further work would be to investigate if increasing the percentage loading of sunflower seed shell would increase the formaldehyde absorption capabilities of the MDF panel.

In terms of VOC absorption, MDF panels modified with sunflower seed shells absorbed the most toluene, limonene and dodecane of the three scavengers. Of the three VOCs, dodecane was absorbed the most and toluene the least, suggesting sunflower seed shell is better at absorbing straight chain and non-polar compounds. When incorporated into an MDF panel, the absorption of the VOCs does decrease but not as drastically as observed with the other two scavengers. This shows that the sunflower seed shell does not experience the same change in surface chemistry observed in peanut shell and walnut shell scavengers and still is able to absorb much higher quantities of VOCs than the control MDF panel.

VOC emissions

The emissions profile of sunflower seed shell modified MDF panels was found to be similar to MDF panels modified with peanut shells. However, these MDF panels were found to emit the most compounds emitted from the different modified MDF panels. Three unique emissions were found in the emissions profile of MDF panels modified with sunflower seed shell. This suggests that the VOCs in the atmosphere could be reacting with the surface chemistry of the modified MDF panel, resulting in the emissions of secondary VOCs. These emissions could also be emissions from the sunflower seed shell alone. This requires further study.

Hygric properties

The thickness swell of MDF modified with sunflower seed were found to be significantly less than the control MDF panels, however, there was no significant difference between thickness swell and percentage loading (i.e. increased percentage loading of sunflower seed did not increase or decrease thickness swell).
Only panels modified with 5% sunflower seed shell had a lower water absorption coefficient than control MDF panels. A higher percentage loading of sunflower seed shell increased the rate at which liquid water moved through the MDF panel. This could be result of the change in porosity of the panel. The addition of sunflower seed shell increased the cumulative pore volume of the MDF panel, compared to the control MDF panel. This change in pore structure appears to be enough to increase the rate at which liquid water passes through the MDF panel.

The water vapour flow rate was higher than the control and found to increase with increasing percentage loading of sunflower seed shell. The addition of sunflower seed shells to the MDF panel increased the permeability and decreased its water vapour resistance. This can also be related to the increase in the cumulative pore volume of the MDF panel. The porosity isotherms (appendix F) also show that the sunflower seed shell creates a greater hysteresis between vapour sorption and desorption, showing that vapour entering the MDF panel becomes trapped within its structure and takes longer to desorb from the material. This can impact on the emissions of the MDF panel and its resistance to microbiological attack.

Mechanical strength

The addition of sunflower seed shell to the MDF had no significant impact on the internal strength property of the MDF panel. The addition of up to 5% loading of sunflower seed shell was found to increase the modulus of rupture of the MDF panel. However, increasing the percentage loading of the scavenger greater than 5% reduced the MOR overall but there was no significant difference in MOR between the control MDF panel and MDF panels containing 10% scavenger. Therefore, a maximum of 10% sunflower seed shell can be to the MDF panel before the mechanical properties are impaired. Statistically, the addition of the sunflower seed shell did not have an impact of the modulus of elasticity of the MDF panel. The higher cumulative pore volume of the sunflower seed modified MDF panels, compared to the control MDF panel, may have initially benefitted the mechanical strength properties of the panel, as the resin will have migrated through the pores and improved bonding between fibre and scavenger. However, it was noted that increasing the loading of sunflower seed shell, decreased MOE also. A high percentage loading would likely reduce the MOE and MOR statistically lower than the control MDF panel, as the aspect ratio of the sunflower seed shell will have also disrupted the internal matrix of the panel, making it weaker to mechanical stresses.

5.7 Comparison with commercial MDF panel

Building materials are required to have adequate properties to for fill the role in which they are designed. The boards produced at Mona Tech Transfer facility are produced on a much smaller scale than those produced at Kronspan, Chirk. Therefore, a direct comparison is not suitable, but the results obtained in chapter 2 can be used to calculate a percentage difference (equation 23) between commercially produced MDF panels and results for MDF panels produced at Mona Tech Transfer Centre. This percentage difference could then be used to determine if boards produced at full scale with the lignocellulosic scavengers, would still meet the BSEN standards for general purpose MDF.

Difference (%) = $\left(1 - \frac{mMDF}{cMDF}\right) x\ 100$ [Equation 23]

Where:

mMDF is the result for MDF panel produced at Mona Tech Transfer Centre

cMDF is the result for commercially produced MDF panel

5.7.1 Physical properties

Table 57 shows the percentage difference in the inorganic content of modified MDF panels and commercially produced MDF panel. The MDF panels modified with lignocellulosic scavengers all had an inorganic content at least 100% greater than the commercial MDF panel.

Table 57: Percentage Difference of inorganic content of modified MDF panels and commercial MDF panels

Board	Inorganic content
5% Peanut shell	101.79
10% Peanut shell	106.28
15% Peanut shell	160.09
5% Walnut shell	321.52
10% Walnut shell	635.43
15% Walnut shell	1012.11
5% Sunflower seed shell	115.25
10% Sunflower seed shell	204.93
15% Sunflower seed shell	276.68

MDF panels modified with 5% peanut shell had the least percent difference in inorganic content (101.79%) and MDF panels modified with 15% walnut shell had the greatest (1012.11%).

5.7.2 Mechanical

Table 58 shows the percentage difference in mechanical properties between modified MDF panels and commercially produced MDF panel. Modified panels must have a percent difference no greater than 28% or they will not meet the required standard if produced at full scale. The results show that the MDF panels modified with peanut shell and walnut shell had an internal bond strength at least 30% less than the commercial MDF panel. This shows that if commercial MDF panels were produced with either of these lignocellulosic scavengers the MDF panels would be at least 30% weaker and therefore not meet the requirements of EN 622-5:2009. However, MDF panels modified with sunflower seed shell at either percentage loading had a percent difference less than 28%. The full-scale panel produced with 5%, 10% and 15% sunflower seed would have an IB strength 18.42%, 10.53% and 27.63%, respectively, weaker than an unmodified MDF panel. This shows that these panels would still meet the EN standard for general purpose MDF.

Table 58: Percentage difference (loss) of IB strength, MOR and MOE of modified MDF panels and commercial MDF panels

Board	Internal bond strength	MOR	MOE
5% Peanut shell	39.47	47.65	40.84
10% Peanut shell	38.16	64.45	59.45
15% Peanut shell	34.21	52.99	46.75
5% Walnut shell	38.16	56.84	56.00
10% Walnut shell	31.58	51.15	54.14
15% Walnut shell	34.21	57.02	60.13
5% Sunflower seed shell	18.42	40.17	43.15
10% Sunflower seed shell	10.53	49.41	51.07
15% Sunflower seed shell	27.63	56.08	52.71

Table 58 also shows the result for the MOR and MOE. Modified panels must have a percent difference no greater than 49% for MOR and 45% for MOE or they will not meet the required standard if produced at full scale. The only modified MDF panels

that meet this limit are those modified with 5% peanut shell and 5% sunflower seed shell. MDF panels modified with walnut shell show a percentage difference of, at least 50% for MOE and MOR. This shows that MDF panels made on a commercial scale with the addition of walnut shell would have only half the strength. As previously discussed this could be a result of the aspect ratio and size of the walnut shells or it is their high inorganic content that is disrupting the curing of the resin. Further tests could be conducted on MDF panels produced with a different resin and/or use a much finer size of walnut shells. If commercial grade MDF panels were to be produced with 5% sunflower seed shells would still meet the requirements for general purpose MDF, however, increasing the loading of sunflower seed shell reduces the strength below the required strength of the EN standard.

Therefore, in terms of maintaining adequate strength properties, the one modified MDF panel that would meet the required standard, for IB, MOR and MOE, is 5% sunflower seed shell. MDF panels modified with 5% peanut shell would meet the requirements for MOR and MOE only, but the IB strength would be reduced by almost 40%. Therefore, further investigation is required into how peanut shell and walnut shell could be added to the MDF panel without impairing the strength properties. It must be remembered however that drum blending is done on relatively dry fibre, where fibres move slowly in the drum blender and therefore have little fibre to fibre contact (Groom et al., 2004), whereas in industry, the fibres are resinated in a blow-line and not a drum blender. In the blow-line fibres have a higher moisture content and contact angle of the resin is much lower as the fibres move through the blow line at significantly higher speeds and the resin in very thinly distributed on the fibre surface (Groom et al., 2004). This change in production parameters might change the dynamics occurring in terms of strength properties as well as formaldehyde and VOC absorption, especially if the moisture content of the fibres is higher.

5.7.3 Hygric

5.7.3.1 Thickness swell and Water absorption coefficient

Table 59 shows the percentage difference in the thickness swell of modified MDF panels and commercially produced MDF panel. The results show that all the

modified panels have a thickness swell almost 100% greater than commercial MDF panels and do not meet the standard requirements for general purpose MDF. However, it must be remembered that the commercial MDF panels have other additives such as waxes to improve the permeability of the MDF panel. The thickness swell could be significantly improved however the addition of the waxes may impair the scavenging of VOC capabilities of the modified MDF panels. Therefore further investigation and optimisation is required to ensure that British and European standards are met and that scavengers are able to actively absorb VOCs from the atmosphere, improving indoor air quality.

Table 59: Percentage Difference of Thickness Swell and Water absorption coefficient of modified MDF panels and commercial MDF panels

Boards	Thickness Swell	Water absorption coefficient
5% Peanut shell	93.51	21.88
10% Peanut shell	91.45	16.45
15% Peanut shell	92.06	16.45
5% Walnut shell	92.81	24.07
10% Walnut shell	91.37	22.25
15% Walnut shell	90.64	19.75
5% Sunflower seed shell	91.01	16.67
10% Sunflower seed shell	91.62	22.25
15% Sunflower seed shell	91.62	18.75

Table 59 also shows the results for water absorption coefficient (W_{ac}). The commercial MDF had a water absorption coefficient of 3.25 kg m^{-2} hr^{-1}. There is not a standard requirement for water absorption coefficient for MDF panels but the results show that the addition of lignocellulosic scavengers increases the water absorption coefficient. The addition of 5% walnut shell increased W_{ac} the most by 24% and the addition of 10% and 15% peanut shell increase W_{ac} the least by 16.45%. This increase in the amount of water that is absorbed by the MDF panel by capillary action is an important change in the properties of the MDF panel, especially considering the conditions this type of construction material might have to endure

during its service life time, such as flooding and creeping (rising) damp. Ideally a modification should improve properties but as described previously the addition of greater percentage of peanut shell might improve the W_{ac}.

5.7.3.2 Water Vapour Transmission

Tables 60, show the percentage difference in the vapour transmission properties of modified MDF panels and commercially produced MDF panel. The results for water vapour flow rate, show that the modified MDF panels were at least 66% greater than the commercial MDF. Water vapour permeance and water vapour resistance was almost 100% lower than commercial MDF panel. This difference is most likely a result of the methods of production. During commercial grade MDF panels industry pneumatically controlled sifters (classifiers) and filters remove any clumps of fibres and lay individual fibres without forming layers in the fibre mat. This generates a close knit and relatively uniform fibre layering within the panel and forms a close fibre to fibre bonding. Close fibre to fibre bonding is likely to reduce porosity and therefore increase vapour resistance and reduce water vapour flow rates. However, porosity would have to be investigated to confirm this is the case. Commercial MDF panels are also produced with resins, waxes and hardeners, hence the addition of these additives would increase the water vapour resistance. If the modified panels with lignocellulosic scavenger were produced in the same way as the commercial boards, it is likely that the water vapour transmission properties of the panel would be improved.

Table 60: Percentage difference of Water Flow rate of modified MDF panels and commercial MDF panels

Board	Water Vapour flow rate		Water Vapour Permeance		Water vapour resistance	
	Dry Cup	Wet cup	Dry Cup	Wet cup	Dry cup	Wet cup
5% Peanut shell	78.15	37.00	98.35	36.00	98.34	44.67
10% Peanut shell	71.71	99.12	98.72	99.11	98.72	11.70
15% Peanut shell	72.97	41.31	98.67	40.42	98.66	41.13
5% Walnut shell	66.76	99.21	98.92	19.83	98.90	25.89
10% Walnut shell	67.88	32.77	98.88	31.75	98.86	41.96
15% Walnut shell	67.88	27.92	98.88	26.83	98.86	30.25
5% Sunflower seed shell	70.81	36.08	98.76	35.08	98.76	41.96
10% Sunflower seed shell	69.95	27.23	98.80	26.08	98.80	27.19
15% Sunflower seed shell	63.29	32.85	99.02	31.83	99.01	35.66

6 Modifications and Microbiology – Fungi and Moulds

6.1 Introduction

Indoor fungal growth is ubiquitous around the world; according to the European Union 25% of dwellings of social housing experience fungal growth (Moularat et al., 2008; Segers et al., 2015). Many materials are susceptible to fungal growth but wood and wood-based construction materials are particularly vulnerable to microbiological attack, resulting in biodegradation and biodeterioration. Saprophytic organisms such as moulds and decay fungi are the main organisms responsible for biodeterioration and biodegradation, respectively of materials. These microorganisms can be transported into and around buildings on surfaces of new materials, clothing, pets, and can penetrate into buildings via ventilation systems (WHO, 2009). Moulds will readily colonise lignocellulosic materials but can also attack synthetic floor coverings, aeroplane fuels, oils, glues, paints and textiles (Pasanen et al., 1992; Schmidt, 2006). Subsequently, fungal and mould spores can be found in every building, on every surface, but only if the environmental conditions are adequate will the spores germinate and cause microbial pollution.

The contamination of microbiota in the indoor environment is influenced by a number of factors such as season, climate, fungal species, construction, building use, building age and ventilation rates (Segers et al., 2016; WHO, 2009). As previously discussed in chapter 1, section 1.11, microbial pollution does contribute to poor indoor air quality. A lack of adequate ventilation designed for a building can cause the build-up of moisture in the indoor environment (Singh et al., 2010). It is this moisture that ultimately leads to the proliferation of mould and fungal growth (Singh et al., 2010). This fungal growth can cause aesthetic and structural damage. Moulds and fungi can pose a risk to human health such as allergies, irritation, toxic reactions and in more extreme cases, they can invade the lungs and spread throughout the human body affecting respiratory, blood and nerve system (Airaksinen et al., 2004; Cooley et al., 1998; Jarvis and Miller, 2004; Nielsen, 2003; Polizzi et al., 2011; Tudge, 2002). There is substantial evidence that biological agents such as spores, mycotoxins and microbial VOCs (MVOC) do contribute to sick building syndrome (SBS) and produce symptoms such as coughing, wheezing,

asthma and dyspnoea (Griffith et al., 2007). The productions of such biological agents, their type, quantity and composition do vary with substrate composition, temperatures and water activity. Even where environmental conditions are sub-optimal, spores and mycotoxins can be released into the indoor air (Abbott, 2002; Nielsen et al., 2004). Preventative measures are required to ensure that microbial pollution does not escalate to such levels that human health is at risk. Once a fungal infestation has begun, it will continue until environmental conditions are no longer suitable or the substrate can no longer sustain a fungal colony. Legislation, guidelines and building design and ventilation, as discussed in chapter 1, section 1.13 can be implemented to reduce the risk of microbial pollution and subsequently safeguard indoor air. It is very important that the appropriate construction materials and techniques are utilised to help maintain good indoor air quality.

This section of the thesis assesses the modified MDF panels' resistance to basidiomycete decay and mould colonisation in relation to moisture dynamics. The modified MDF panels were also exposed to VOCs to determine any relationship between the absorption of VOCs and effects on mould colonisation.

6.1.1 Basidiomycete Decay

The basidiomycete decay resistance was determined following the same method and procedure as described in chapter 2, section 2.7.1.

Results and discussion

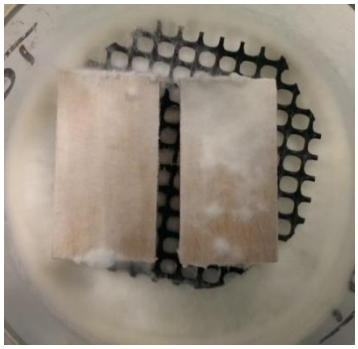
The following results report on the control MDF panels, modified MDF panels and virulence samples exposed to the four basidiomycete fungi: *Pleurotus ostreatus, Coniophora puteana, Coriolus versicolor* and *Gloeophyllum trabeum*. The virulence samples were tested, following the standard BSEN 12038:2002, to determine whether the fungal strain used was virulent and able to adequately decay the solid wood samples. According to the standard, a fungal strain is considered valid if the virulence samples have lost more than 20% of its mass.

Pleurotus ostreatus

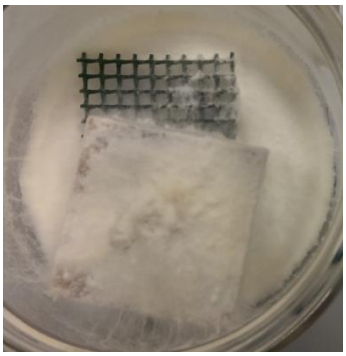
Table 61 shows the final moisture content and average mass loss of the virulence samples, the control MDF panels and the modified MDF panels after 16 weeks exposure to the white rot fungus, *P. ostreatus.* Table 61 shows that the mass loss of the beech virulence samples was below the required 20%. Figure 85 shows example photographs taken of the decay samples after the 16-week exposure to *P. ostreatus* Figure 85B shows the poor fungal growth on the beech virulence samples, respectively. As can be seen the final moisture content of the beech virulence samples was 39.25%, which is high enough to support fungal growth. Therefore, it can be assumed that the fungal strain used, 40C, was not sufficiently virulent for a standardised test. However, in terms of this investigation as the tests were conducted concurrently the results can be validly compared.

Table 61: Final moisture content (MC) (%) and mass loss (%) of samples exposed to *Pleurotus ostreatus*

Board/sample	Final MC (%)	Standard deviation	Mass loss (%)	Standard deviation
Virulence Beech	39.25	1.77	10.47	3.10
Control MDF	94.41	16.20	18.59	4.18
5% Walnut shell	93.39	15.44	21.59	1.55
10% Walnut shell	88.50	8.88	19.51	5.12
15% Walnut shell	104.67	24.91	28.80	2.88
5% Peanut shell	92.42	10.11	22.38	1.17
10% Peanut shell	65.32	6.61	18.85	0.74
15% Peanut shell	69.45	16.73	19.11	1.76
5% Sunflower seed shell	75.05	2.08	20.61	0.61
10% Sunflower seed shell	78.70	5.67	21.46	1.40
15% Sunflower seed shell	97.21	15.85	25.58	2.13

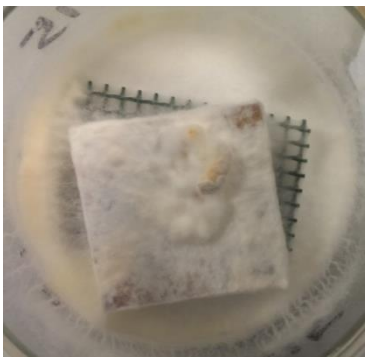


A Beech virulence



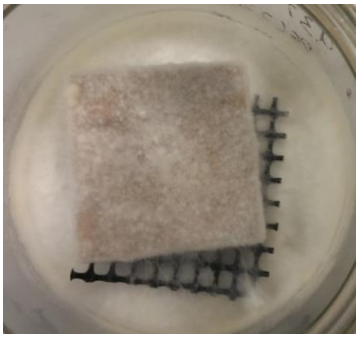
B 5% Walnut Shell

C 10% Walnut shell

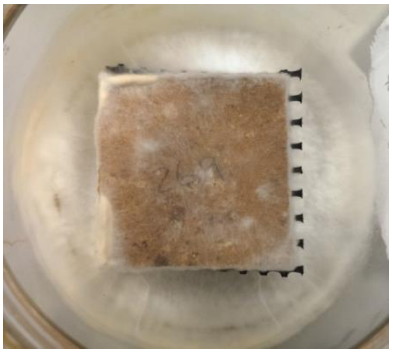


D 15% Walnut shell

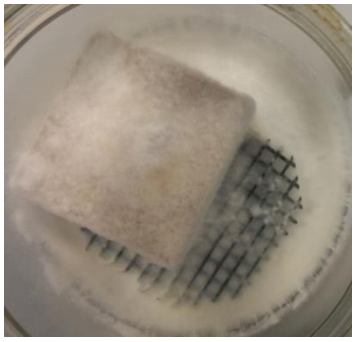
E 5% Peanut shell



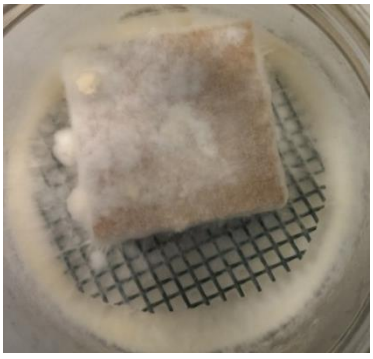
F 10% Peanut shell



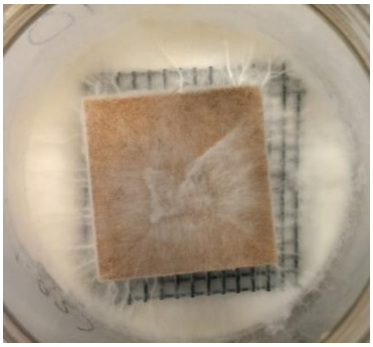
G 15% Peanut shell



H 5% Sunflower seed shell



I 10% Sunflower seed shell



J 15% Sunflower seed shell

Figure 85: Fungal decay by *Pleurotus ostreatus* after 16 weeks

Figure 86 shows the average mass loss of the control MDF panel and the modified MDF panels. The greatest mass loss was observed in 15% walnut MDF panel, 28.80% and the least mass loss of 18.85% in the 10% peanut MDF panel. With increasing

walnut shell loading, the mass loss increases, suggesting that the addition of walnut shells to the MDF panel decreases the resistance to white rot decay. The same can be observed in MDF panels modified with sunflower seed shell.

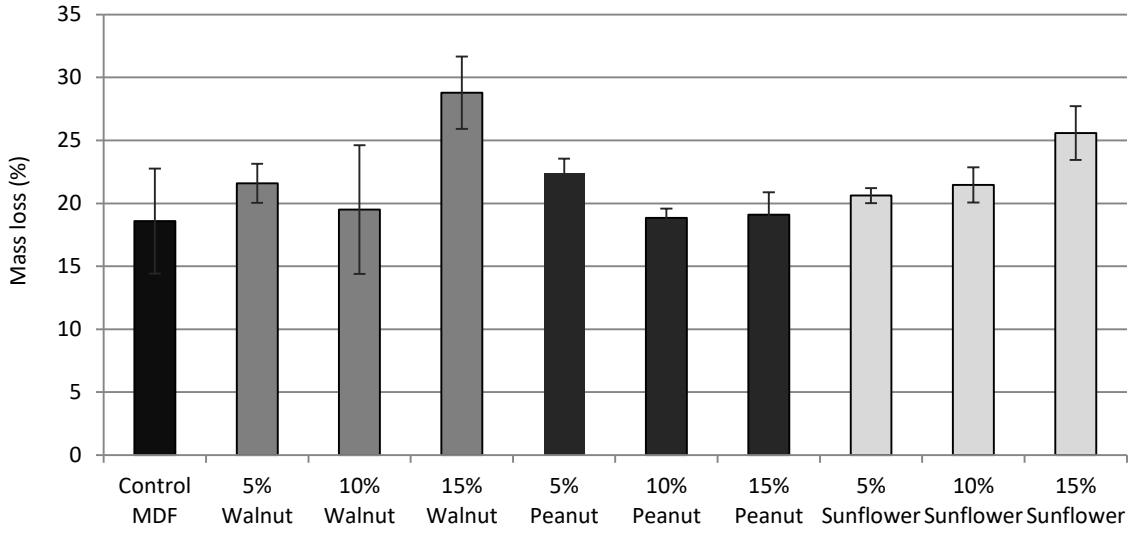


Figure 86: *Pleurotus ostreatus* decay after 16 weeks

This increase in per cent mass loss of the walnut shell and sunflower seed shell modified MDF panels could be a result of the composition of the scavengers, which may naturally be more susceptible to basidiomycete decay. However, it may be possible that the higher final moisture content of the samples, which exceeded 100% MC for walnut shell samples and 95% MC for sunflower samples at 15% loading is responsible for the higher decay. Looking back at the hygric properties of the panel determined in Chapter 4, section 4.3.3, there were no statistical differences in the water vapour resistance or transmission between the control MDF panel and any percentage loading of walnut shell. Nor was there a statistical difference in the water absorption coefficient properties. As a result it may also be likely that the components of the walnut shell, such as carbohydrates, could cause the increase in fungal susceptibility of the MDF panel. It is also known that for every condensation reaction that occurs during fungal decay produces one molecule of water (Moore et al., 2011). Moore et al., (2011) reports that for every one gram of glucose that is broken down, 0.6g of water is produced by basidiomycete fungi. If the walnut shell composition has a high proportion of sugars, then subsequently the

decay of the MDF panels modified with walnut shell would produce high amounts of water from condensation reactions. The decomposition of lignin also results in water production as a by-product (Bugg et al., 2011). As white rot fungi can decompose lignin as well as sugars, then it can be expected that the final moisture content of the modified panels is quite high. Table 61 shows that the final moisture content of the MDF panels modified with walnut shell was greater than other modified MDF panels, except for those modified with 15% sunflower seed shell. This higher final MC could be the result of the higher amounts of decay, rather than greater moisture uptake by the modified MDF panels resulting in higher quantity of decay by the white rot fungi.

Whereas for the sunflower seed shell MDF panels it was observed that an increase in percentage loading increases the water absorption coefficient. This increases the movement of water throughout the sample, increasing the availability of water that is required for the movement of enzymes and degradative agents to the substrate cell wall and for biological reactions thus leading to the breakdown of the material.

Figure 86 shows that MDF panels containing more than 5% peanut shell had the greatest mass loss during basidiomycete decay. This suggests that with increasing peanut shell loading, the susceptibility of the MDF panel decreases. This could be due to the wax content of the peanut shell reducing the moisture content of the modified MDF panel. Table 61 shows that the final moisture content of the MDF panels modified with 10% and 15% peanut shell was less than 70%, whereas the control MDF panel and MDF panel modified with 5% peanut shell was greater than 90%. Indeed when looking back at the hygric data, the water absorption coefficient did decrease with increasing percentage of peanut shells. This is likely due to the peanut shells' waxy composition, preventing the movement of water through the samples and therefore creating less favourable conditions for fungal growth and degradation.

It should be remembered that due to the poor virulence of this fungal strain these results should be taken as indicative only. However, it is clear that the addition of the different lignocellulosic scavengers does influence the susceptibility of the MDF panel to attack by *P. ostreatus*.

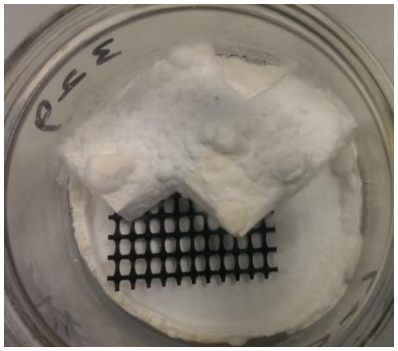
Coriolus versicolor

Table 62 shows the final moisture content and average mass loss of the virulence samples, the control MDF panels and the modified MDF panels after 16 weeks exposure to the white rot fungus, *C. versicolor.* The mass loss of the beech virulence samples was found to be 24.19%, showing that the fungal strain CTB 863A was virile.

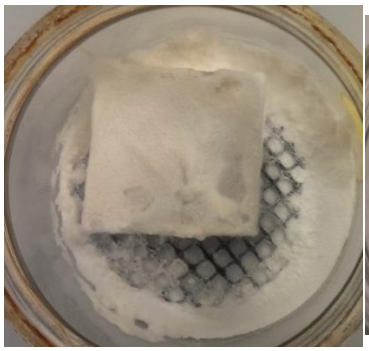
Table 62: Final moisture content (%) and mass loss (%) of samples exposed to *Coriolus versicolor* after 16 weeks

Board/sample	Final MC (%)	Standard deviation	Mass loss (%)	Standard deviation
Virulence Beech	50.22	19.39	24.19	2.94
Control MDF	110.39	9.45	19.28	3.48
5% Walnut shell	125.18	25.86	17.98	3.58
10% Walnut shell	104.12	19.76	16.58	3.75
15% Walnut shell	100.62	7.84	12.23	1.16
5% Peanut shell	72.24	9.19	7.38	0.56
10% Peanut shell	71.09	11.63	9.20	0.94
15% Peanut shell	60.24	15.39	7.70	0.95
5% Sunflower seed shell	75.06	11.67	16.88	1.98
10% Sunflower seed shell	77.61	10.12	11.63	1.52
15% Sunflower seed shell	91.41	7.31	14.11	2.44

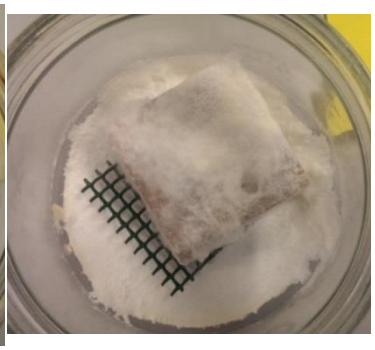
Figure 87 shows a few example photographs taken of the decay samples after the 16-week exposure to *C. versicolor.* As can be seen in Figure 87A the fungal growth on the beech virulence samples is greater than *P. ostreatus* on beech virulence (fig 85A)



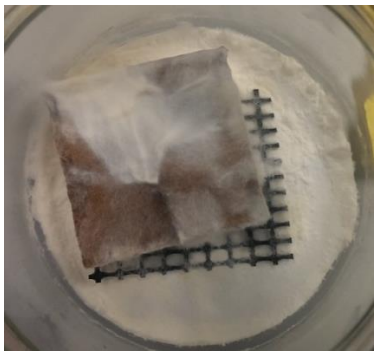
A Beech virulence



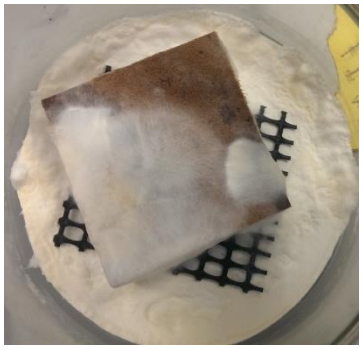
B 5% Walnut Shell



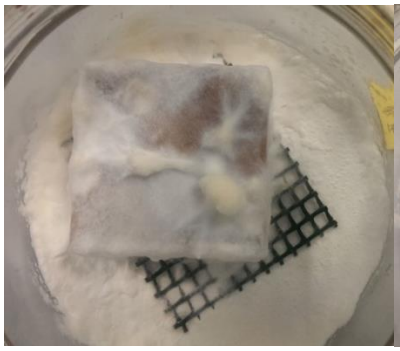
C 10% Walnut shell



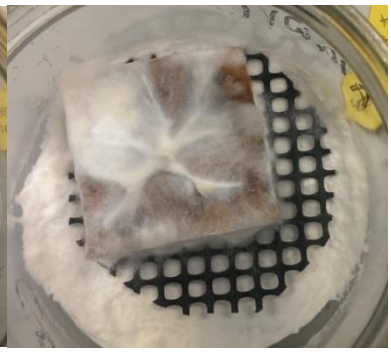
D 15% Walnut shell



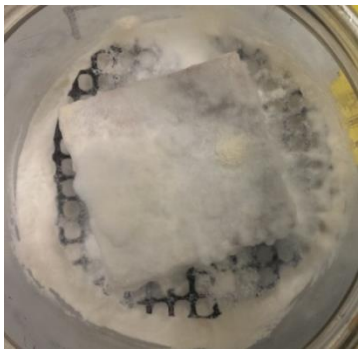
E 5% Peanut shell



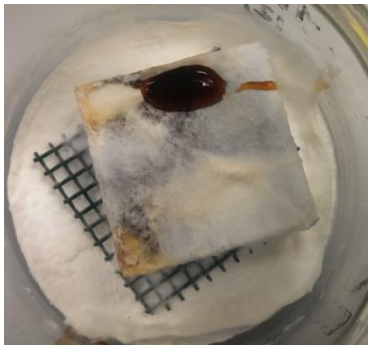
F 10% Peanut shell



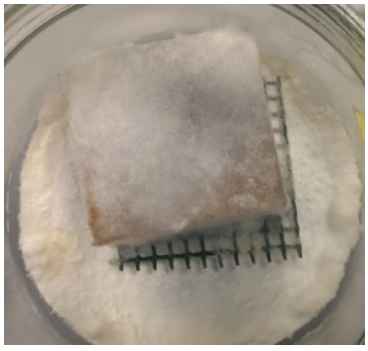
G 15% Peanut shell



H 5% Sunflower seed shell



I 15% Sunflower seed shell



J 10% Sunflower seed shell

Figure 87: Fungal decay by *Coriolus versicolor* after 16 weeks

Figure 88 shows the average mass loss of the control MDF panel and the modified MDF panels after 16-week exposure to the white rot fungus. The greatest mass loss was observed in the control MDF panel at 19.28% and all modified MDF panels had a

lower mass loss than the control. The lowest mass loss was seen in panels modified with 5% peanut shell, 7.38%. This shows that for this fungus, the addition of either lignocellulosic scavenger does reduce the susceptibility of the MDF panel.

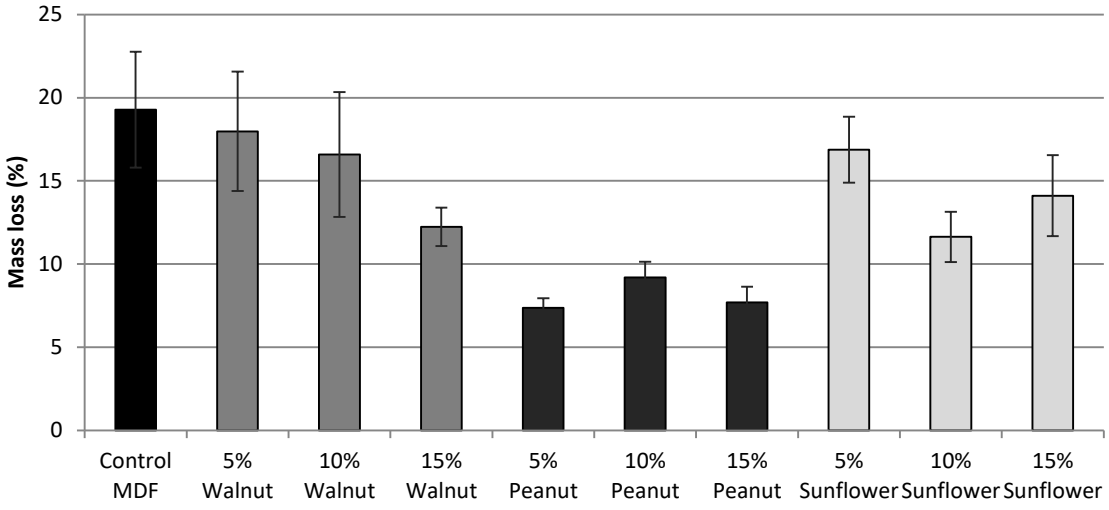


Figure 88: *Coriolus versicolor* decay after 16 weeks

There is a clear relationship between the increasing percentage loading of walnut shell scavenger and decreasing mass loss. Interestingly, the final moisture content is the highest at 5% loading, 125.18% and decreases to 100.62% for the 15% loading. This shows that the MDF samples were at a more optimal condition for fungal decay if modified with 5% walnut shell. However, increasing the percentage loading of walnut shell in the MDF panel, the percent final moisture and mass loss decrease. As the walnut shell was found not to affect the hygric properties of the MDF panel, this reduction in susceptibility could be due to the composition of compounds, such as phenolics, that could be inhibiting the fungal activity. Further investigation could be conducted to determine if compounds could be extracted and used as an antifungal agent. However, as previously mentioned the decay process by fungi also produces water as a by-product. The higher final MC observed could be a result of the high amounts of decay, rather than the modified panel's moisture absorption properties. However, these modified panels have a higher final MC than the MDF panels decayed by white rot fungi.

The addition of the peanut shell pointedly reduces the mass loss of the sample. This is likely a result of the low final moisture content of the samples. The mass loss of the MDF panel modified with 10% peanut shell was slightly higher than those with 5% and 15%, which could be due to the lower density of this panel allowing easier access for the fungal mycelium into the panel. MDF panels modified with 15% peanut shell had the lowest final MC of 60.24%. Again this suggests that the waxy nature of the peanut shells prevent the movement and uptake of moisture and subsequently reducing the panels' susceptibility to decay by this fungus.

The addition of sunflower seed shell also resulted in a lower percentage of mass loss compared to the control MDF panel. However, there does not appear to be a correlation between percent mass loss and percentage shell loading. This could be a result of the spread of the scavenger throughout the panel as described in chapter 4, section 4.1.1. The samples cut for the decay test may have had a higher proportion of sunflower seed shells than 10%, or lower than 15%. The MC of the samples is not likely the cause as the MDF panels modified with 10% sunflower seed shell had a higher MC of 77.61%, compared to panels modified with 5% sunflower seed shell, 75.06%.

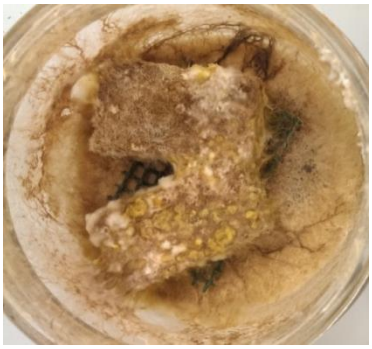
Coniophora puteana

Table 63 shows the final moisture content and average mass loss of the virulence samples, the control MDF panel and the modified MDF panels after 16 weeks exposure to the brown rot fungus, *C. puteana.* Unlike the validity test of *P. ostreatus,* the results showed that the *C. puteana* strain PWB E11 was valid. The mass losses of the pine samples was 33.22%. Therefore the results for the control MDF panel and modified MDF panel are valid for analysis.

Table 63: Final moisture content (MC) (%) and mass loss (%) of samples exposed to *Coniophora puteana* after 16 weeks

Board/sample	Final MC (%)	Standard deviation	Mass loss (%)	Standard deviation
Virulence Pine	61.67	2.93	33.22	2.78
Control MDF	171.89	31.06	53.23	2.09
5% Walnut shell	213.56	13.74	53.95	0.71
10% Walnut shell	198.94	21.71	51.84	1.25
15% Walnut shell	193.20	17.64	51.89	1.39
5% Peanut shell	162.45	11.05	50.81	0.56
10% Peanut shell	135.26	19.27	46.82	1.02
15% Peanut shell	158.64	12.53	47.48	0.51
5% Sunflower seed shell	64.30	3.87	54.06	1.46
10% Sunflower seed shell	155.23	10.68	51.73	1.67
15% Sunflower seed shell	189.03	25.55	49.86	1.90

Figure 90 shows the average mass loss of the control MDF panel and the modified MDF panels after 16-week exposure to the brown rot fungus, *Coniophora puteana*. The greatest mass loss was observed in 5% sunflower seed shell MDF panel, 54.06% and the least mass loss, 46.82%, in 10% peanut MDF panel. The control MDF panel showed a mass loss of 53.23%. All modified MDF panels, except for MDF panels modified with 5% walnut shell and 5% sunflower seed shell had a lower mass loss than the control MDF panel. The results show that addition of peanut shell reduced the mass loss of the MDF panel and with increasing the percentage loading of sunflower seed shell, the susceptibility also decreased. This indicates that the susceptibility of the MDF panel to brown rot is reduced with the addition of the scavengers. However, a greater percentage of sunflower seed shell would need to be added to the MDF panel to decrease the susceptibility to a lower level than the control MDF panel. There does not appear to be significant difference between the mass loss of the control MDF panel and MDF panels containing walnut shell, at any percentage loading.

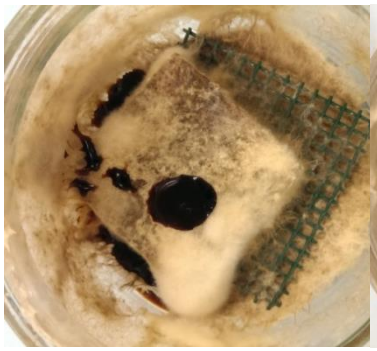


A Pine virulence

C 5% Walnut Shell

D 10% Walnut shell

E 15% Walnut shell

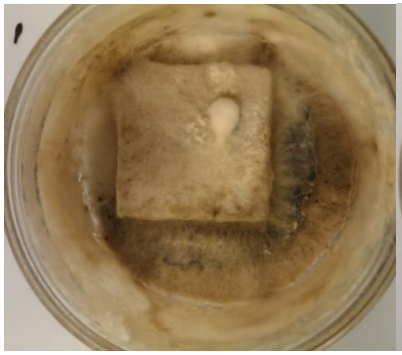


F 5% Peanut shell

G 10% Peanut shell

H 15% Peanut shell

I 5% Sunflower seed shell



J 10% Sunflower seed shell

K 15% Sunflower seed shell

Figure 89: Fungal decay by *Coniophora puteana* after 16 weeks

The high final moisture content of the panels could be a result of the decay process itself. MDF panels modified with walnut shell had an extremely high final MC of almost 200%. Brown rot fungi are not famed for their decomposition of lignin, but

are experts at breaking down sugars. The different composition of the shell compared to the wood fibre, changes the composition of the MDF panel as a whole. If the panels have a greater proportion of accessible sugars, then decay is likely to be greater and more water produced as a by-product. It may that the decay of all the sugars within the MDF panel by condensation reactions is responsible for the higher final MC of the panels observed. This may certainly be true for MDF panels modified with walnut shell exposed to *C. puteana*, which had very high final MC and high amounts of decay. The results how that the mass loss due to decay for the MDF panels were all around 50%.

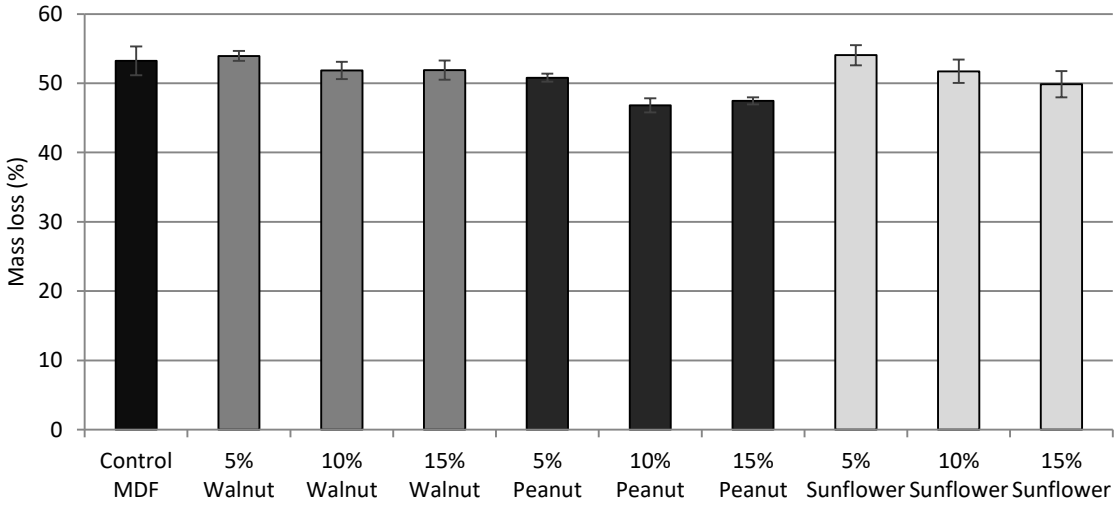


Figure 90: *Coniophora puteana* decay after 16 weeks

Gloeophyllum trabeum

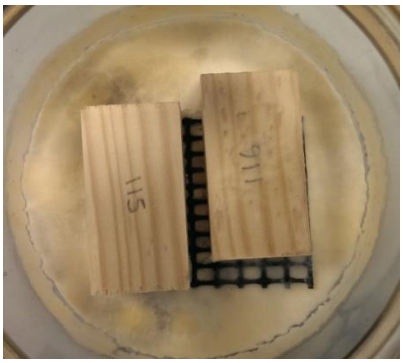
Table 64 shows the final moisture content and average mass loss of the virulence samples, the control MDF panel and the modified MDF panels after 16 weeks exposure to the brown rot fungus, *G. trabeum.* The virulence samples for pine did not meet the required mass loss of 20% the standard required, as the mass losses was 4.97%.

Table 64: Final moisture content (MC) (%) and mass loss (%) of samples exposed to *Gloeophyllum trabeum* after 16 weeks

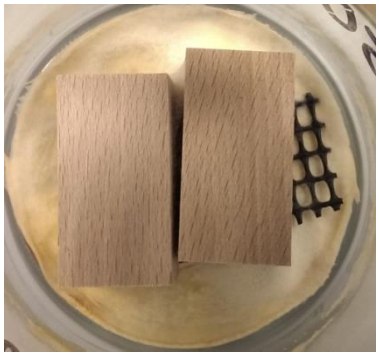
	Final MC (%)	**Standard deviation**	**Mass loss (%)**	**Standard deviation**
Virulence Pine	34.00	1.74	4.97	2.21
Control MDF	70.95	5.06	7.63	4.17
5% Walnut shell	77.85	11.78	5.00	0.54
10% Walnut shell	86.82	7.49	3.34	1.86
15% Walnut shell	79.33	14.80	4.54	1.14
5% Peanut shell	56.60	6.61	3.41	0.86
10% Peanut shell	75.36	2.66	5.84	0.63
15% Peanut shell	71.76	9.15	6.16	1.49
5% Sunflower seed shell	38.33	4.35	6.45	0.21
10% Sunflower seed shell	80.28	7.32	5.45	0.40
15% Sunflower seed shell	87.08	11.27	6.83	0.37

Figure 91 shows the pine and beech virulence samples after the 16 weeks exposure to *G. trabeum.* As is evident there is extremely little growth on the wood samples. The moisture availability may be the cause of the poor growth observed. Table 64 shows the final moisture content of the pine virulence samples at 34% MC. The vessels containing the samples and fungi were stored at 70% ±5 RH humidity and at a temperature of 22±1^{o}C for 16 weeks. Therefore the RH and temperature conditions were not a limiting factor in the growth of the *G. trabeum.* Thus it can be concluded that the lack of growth is likely due to the poor virulence of the strain 108N. As a result the decay data of the control MDF panels and modified MDF panels should be used as indicative only.

However, figure 91 shows that the agar (B) has shrunk and the fungal mycelium growth (A) come away from the edges as the agar has shrunk. This suggests that the relative humidity within the vessels and the conditioning room, in which the samples were stored for the 16 weeks, was not high enough. A low relative humidity would have caused the agar to shrink and reduce the quantity of moisture available for the fungi to grow, reducing its degradation capabilities.



A Pine virulence



B Beech virulence

Figure 91 Fungal decay by *Gloeophyllum trabeum* after 16 weeks

Table 64 shows the mass loss of the control MDF panel and modified MDF panels. The greatest mass loss was observed in the control MDF panel at 7.63% and the least in MDF panels modified with 10% walnut shell, 3.34%. However, as the virulence fungal strain was so low in growth for this experiment, the results will not be further analysed.

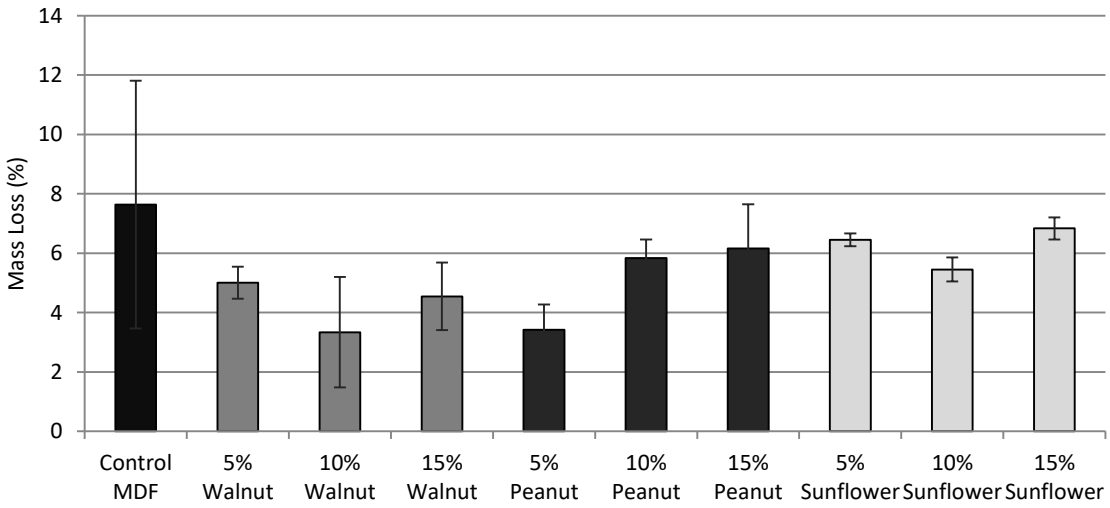


Figure 92: *Gloeophyllum trabeum* decay after 16 weeks

6.1.2 Decay susceptibility index (DSI)

MDF panels must have some resistance to decay when in service. MDF is often used as a construction material in wall cavities and partition walls, therefore its structural integrity must be able to last for its expected service life. The amount of fungal

growth present on a material is dependent on the intrinsic susceptibility of the material to fungal attack (Laks et al., 2002). The decay susceptibility index (DSI) was determined for the modified MDF panels and was used to compare the susceptibility of different materials to basidiomycete decay, irrespective of their thickness and composition. Comparing the decay resistance of the control MDF panel and modified MDF panels is more useful using the DSI calculation as it takes into account the vigour of the fungi. To determine the DSI of each type of the modified MDF panels, the DSI was calculated for each sample and an average was taken, using the following equation:

$$DSI = \frac{T}{S} \; x \; 100 \qquad \text{[Equation 22]}$$

Where

T is the percentage loss in mass of a test specimen

S is the mean percentage loss in mass of the average control MDF specimens

6.1.2.1 Results and discussion

White rot fungi

A decay susceptibility index of 100 means that the modified MDF panel tested has the same decay resistance as the control MDF panel. If the DSI is higher than 100, the fungal growth on the tested sample is greater than the control MDF panel.

Table 65 shows the DSI results for the DSI of the modified MDF panels exposed to white rot decay fungi. The results for MDF panels exposed *P. ostreatus* should be used as indicative only, as the fungal strain used 40C was found to have very low virulence.

Table 65: DSI results of White rot fungi and standard deviation (SD)

Board	*Pleurotus ostreatus*		*Coriolus versicolor*	
	DSI	SD	DSI	SD
5% Walnut shell	116.15	8.33	93.24	18.58
10% Walnut shell	104.92	27.52	86.01	19.45
15% Walnut shell	147.00	14.68	63.45	6.01
5% Peanut shell	120.40	6.28	37.94	3.11
10% Peanut shell	101.38	3.97	51.76	2.22
15% Peanut shell	97.56	9.01	38.64	5.49
5% Sunflower seed shell	110.88	3.28	87.41	7.38
10% Sunflower seed shell	115.45	7.54	60.34	7.86
15% Sunflower seed shell	130.56	10.89	58.29	15.49

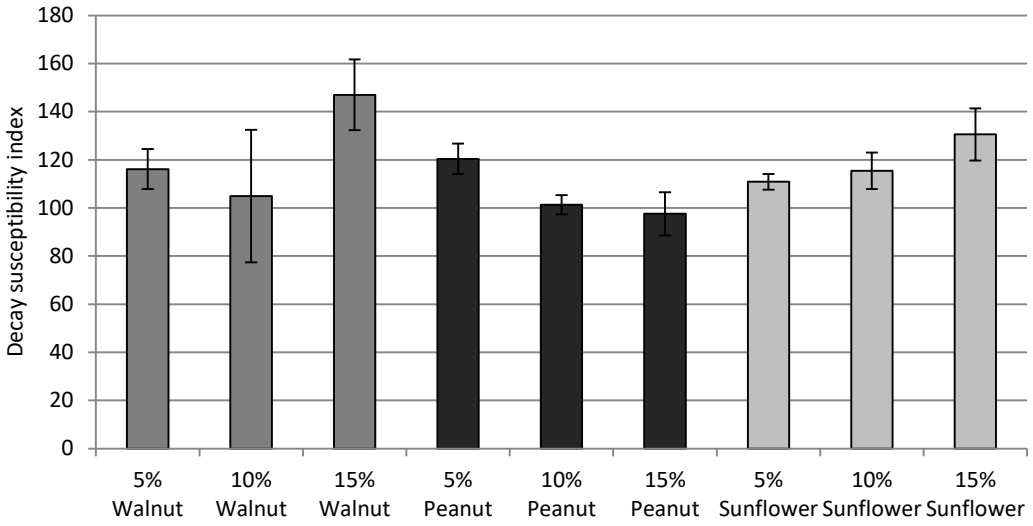


Figure 93: DSI results for *Pleurotus ostreatus*

Figure 93 depicts the DSI of the modified panels exposed to white rot decay by *P. ostreatus*. All the modified MDF panels, except those modified with 15% peanut shell had a DSI greater than 100, showing that MDF panels modified with these lignocellulosic scavengers have are more susceptible to *P. ostreatus* than the control MDF panels. There appears to be a decrease in DSI with increasing peanut shell percentage loading and an increase in DSI with increasing addition of sunflower seed shell.

Figure 94 depicts the DSI of the modified panels exposed to white rot decay by *C. versicolor.* All the modified MDF panels have a DSI lower than 100, showing that MDF panels modified with these lignocellulosic scavengers have are less susceptible to *C. versicolor* than the control MDF panels. Panels modified with 5% peanut shell had the lowest DSI, 37.95 and those modified with 5% walnut shell had the greatest, 93.24. MDF panels modified with10% peanut shell had a higher DSI compared to 5% and 15% peanut shell, this is due to the lower density of the panel, allowing easier access for the fungi and decay.

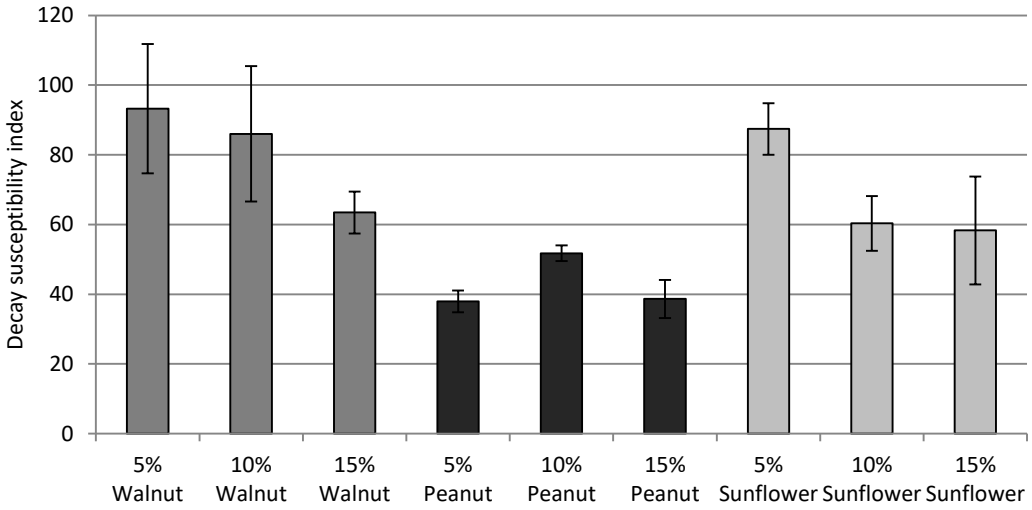


Figure 94: DSI for *Coriolus versicolor*

Statistical analysis

Analysis of variance (ANOVA) was conducted to find the differences in DSI results between the lignocellulosic scavenger modified MDF panels exposed to white rot fungi (Table 66). Table 66 shows that there was a significant difference in the DSI of MDF panels modified with each scavenger at different percentage loadings when exposed to *P. ostreatus.*

Table 66 shows that there was no significant difference in the DSI of MDF panels modified with walnut shell at different percentage loadings, exposed to *C. versicolor* (p-value 0.06). Whereas there was a significant difference found between the DSI of MDF panels modified with peanut shell (p-value 0.004) and sunflower seed shell (p-value 0.02), at difference percentage loadings.

Table 66: Summary of ANOVA results for DSI of white rots (✓ statistical difference and X no statistical difference)

	Pleurotus ostreatus	***Coriolus versicolor***
Walnut shell	✓	X
Peanut shell	✓	✓
Sunflower Seed shell	✓	✓

To determine the source of the variation between the modified MDF panels, T-Test assuming equal variances was performed for each of the scavenger loadings (5%, 10% and 15%) exposed to *P. ostreatus* and *C. versicolor* (Table 67).

Table 67 shows that there is a significant difference in the DSI of panels modified with 5% and 15% walnut shell (p-value 0.0006). This shows that increasing the walnut shell loading, increases the decay susceptibility of the MDF panel to *P. ostreatus.* There was no significant difference in the DSI of panels modified with 5% and 10% walnut shell (p-value 0.18).

The results for peanut shell modified panels show that there is a significant difference in the DSI of MDF panels modified with 5% and 10% (p-value 4.65×10^{-5}) and 5% and 15% (p-value 2.33×10^{-4}) peanut shell, exposed to *P. ostreatus.* This shows that increasing the percentage loading of peanut shell reduces the DSI of the MDF panel. However, there was no significant difference observed in DSI between panels modified with 10% and 15% peanut shell. Therefore, it possible to reduce the susceptibility to *P. ostreatus* (reduce DSI to less than 100) with a higher percentage loading of peanut shell but increasing loading greater than 15% may not significantly reduce MDF panel's susceptibility to *P. ostreatus*. Table 67 also shows that was a significant difference in DSI between panels modified with 5% and 10% peanut shell (p-value 6.46×10^{-4}) and between 10% and 15% peanut shell (p-value 0.006) MDF panels exposed to *C. versicolor*. There was not a significant difference in the DSI of panels modified with 5% and 15% peanut shell (p-value 0.42), exposed to *C. versicolor.*

Table 67 Summary of the T-Test assuming equal variance for DSI of walnut shell MDF panels exposed to *P. ostreatus* (✓ statistical difference and X no statistical difference)

Board		*P. ostreatus*			*C. versicolor*		
		5%	10%	15%	5%	10%	15%
Walnut shell	5%	-	X	✓	-	-	-
	10%	X	-	✓	-	-	-
	15%	✓	✓	-	-	-	-
Peanut shell	5%	-	✓	✓	-	✓	X
	10%	✓	-	X	✓	-	✓
	15%	✓	X	-	X	✓	-
Sunflower seed shell	5%	-	X	✓	-	✓	X
	10%	X	-	✓	✓	-	X
	15%	✓	✓	-	X	X	-

Table 67 shows that there was not a significant difference between the DSI of MDF panels modified with 5% and 10% sunflower seed shell, exposed to *P. ostreatus* (p-value 0.10). However, there was found to be a significant difference in DSI of MDF panels modified with 10% and 15% sunflower seed shell (p-value 0.009) exposed to *P. ostreatus.* This shows that with increasing percentage loading of sunflower seed shell, the susceptibility of the MDF panel to *P. ostreatus* increases. However, there was no significant difference between MDF panel's DSI when modified with 5% and 10% sunflower seed shell. This suggests that up to 10% of sunflower seed shell can be added to the MDF panel before its susceptibility is affected. The T-Test results show that for sunflower seed shell modified panels exposed to *C. versicolor*, the DSI decreases with increasing percentage loading of the scavenger. However, no significant difference was found between MDF panels modified with 10% and 15% sunflower seed shell (p-value 0.053). This suggests that any greater percentage loading of the scavenger would not further decrease the MDF panel's susceptibility to *C. versicolor.*

Brown rot fungi

Table 68 shows the DSI results for the DSI of the modified MDF panels exposed to brown rot decay fungi. The results for MDF panels exposed *G. trabeum* were not included in the DSI analysis as the fungal strain used 108N was found to have very low virulence. The results show that the modified panels with walnut shell and sunflower seed shell have a decay susceptibility the same as the control MDF panel. MDF panels modified with peanut shell were found to have a slightly lower DSI than the control MDF panel.

Table 68: DSI results of Brown rot fungi

Board	***Coniophora puteana***	
	DSI	**Standard deviation**
5% Walnut shell	101.36	1.33
10% Walnut shell	97.39	2.35
15% Walnut shell	97.49	2.61
5% Peanut shell	95.45	1.05
10% Peanut shell	87.96	1.91
15% Peanut shell	89.19	0.96
5% Sunflower seed shell	101.56	2.75
10% Sunflower seed shell	97.19	3.13
15% Sunflower seed shell	93.67	3.57

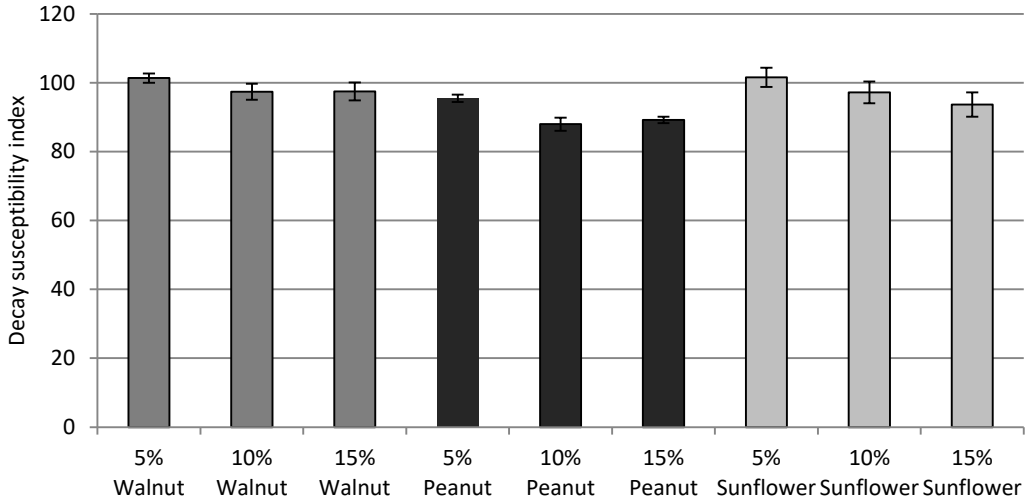


Figure 95: DSI results for *Coniophora puteana*

Statistical analysis

Analysis of variance (ANOVA) was conducted to find the differences in DSI results between the scavenger modified MDF panels exposed to brown rot fungi (Table 69). The results show that there was a statistical difference between the percentage loading of the walnut shell (p-value 0.009), peanut shell (p-value 2.02 x 10^{-7}) and sunflower seed shell (p-value 0.002) and the DSI.

Table 69: Summary of ANOVA results for DSI of brown rots (✓ statistical difference and X no statistical difference)

	Coniophora puteana
Walnut shell	✓
Peanut shell	✓
Sunflower Seed shell	✓

To determine the source of the variation between the modified MDF panels, T-Test assuming equal variances was performed for each of the scavenger loadings (5%, 10% and 15%) exposed to *Coniophora puteana* (table 70).

Table 70: Summary of the T-Test assuming equal variance for DSI of modified MDF panels exposed to *C. puteana* (✓ statistical difference and X no statistical difference)

Scavenger		5%	10%	15%
Walnut shell	5%	-	✓	✓
	10%	✓	-	X
	15%	✓	X	-
Peanut shell	5%	-	✓	✓
	10%	✓	-	X
	15%	✓	X	-
Sunflower seed shell	5%	-	✓	✓
	10%	✓	-	✓
	15%	✓	✓	-

The T-Test results show that there was a significant difference in DSI between MDF panels modified with 5% and 10% walnut shell (p-value 0.002), showing that increasing the percentage loading of this scavenger reduces the DSI to *C. puteana.* However, no significant difference was observed between panels modified with 10% and 15% walnut shell (0.47). This suggests that any further increase in percentage loading of this scavenger would not further reduce DSI to brown rot fungi. MDF panel modified with peanut shell show the same results and that any further increase in percentage loading of peanut shell would not further reduce DSI to *C. puteana.*

The T-Test results for MDF panels modified with sunflower seed shell showed that there was a significant difference between 5% and 10% (p-value 0.012) and 5% and 15% (p-value 0.001) sunflower seed shell, exposed to *C. puteana.* This shows that with increasing percentage loading of the sunflower seed shell scavenger, the susceptibility of the MDF panel to *C. puteana* decreases. This suggests that further percentage loading of the sunflower seed shell may further reduce the DSI of the MDF panel.

Further investigation is required into the DSI of the modified MDF panels exposed to different species of brown rot fungi. This will help identify if the scavengers are

multifunctional and help reduce the susceptibility of the MDF panel to brown rot fungi or only to specific species such as *C. puteana.*

6.2 Microbial loading

The microbiological loading on the MDF panels was evaluated following the dilution plating method that determines the colony forming unit (CFU) as described in chapter 2, section 2.7.2, whereby each sample was left in ambient conditions for a set period of time.

Results and discussion

The purpose of this dilution plating test is to determine the susceptibility of the modified MDF panels to colonising mould species. When the samples were collected, no mould that was visible to the naked eye was found growing on the surface of the modified panels. The samples were removed from ambient conditions and soaked in sterile deionised water. This water was then plated onto nutrient agar and left in a dark chamber at 70% ±5 RH and 22±1 ^{o}C for four weeks. Allowing four weeks of microbial growth enabled for adequate growth of different species, making it easier to differentiate between fungal or bacterial colonies forming on the samples. Each colony forming unit growing on the agar was counted after the four weeks. Table 71 shows the CFU for the control MDF panel and modified MDF panels at three dilutions. Where no number is given, no microbial growth was observed on the agar plates.

Table 71: Colony forming unit (CFU) of control MDF and modified MDF panels and standard deviation (SD)

Board		Sample mass (g)	1 in 10		1 in 100		1 in 1000	
			CFU	SD	**CFU**	SD	**CFU**	SD
Control		2.7496	48.49	1.53	-	-	-	-
Walnut shell	5	3.8274	60.96	1.53	8.71	0.58	-	-
	10	3.5289	18.89	2.08	-		9.45	0.58
	15	3.2859	30.43	1.73	10.14	0.58	-	-
Peanut shell	5	3.3629	49.56	0.58	-	-	-	-
	10	4.3254	23.12	0.58	23.12	1.73	-	-
	15	3.9985	25.01	0.58	-	-	-	-
Sunflower seed shell	5	4.0994	48.79	1.00	-	-	-	-
	10	2.6741	24.93	0.58	12.47	0.58	-	-
	15	5.1207	45.57*	*	13.02	1.16	-	-

Key: - no mould growth observed and * uncountable with bacteria

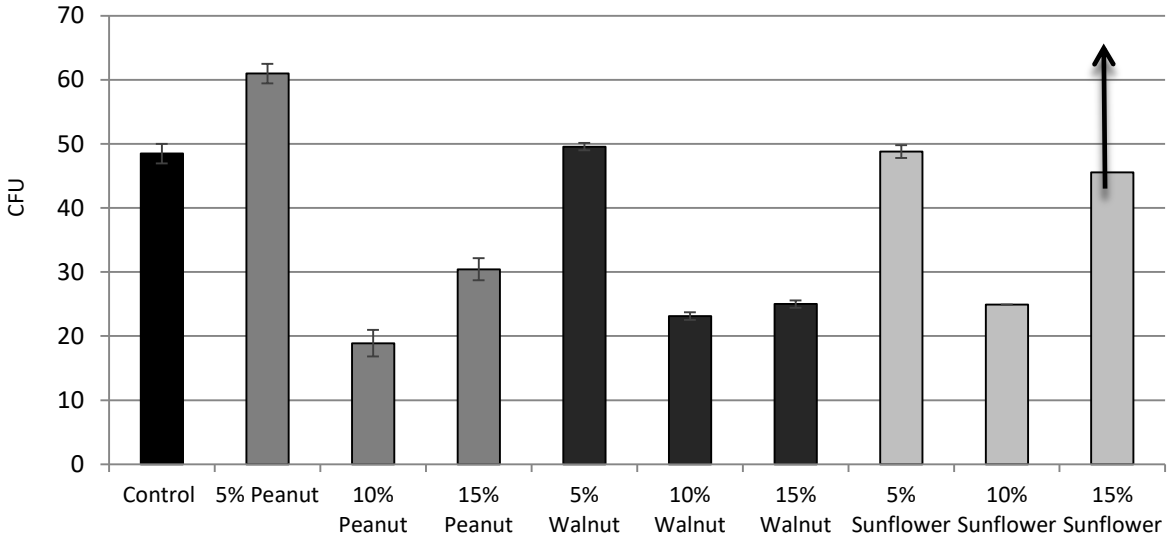
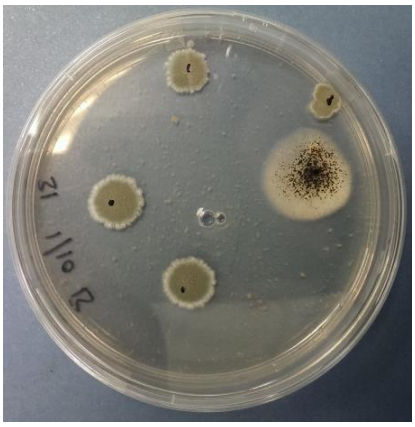


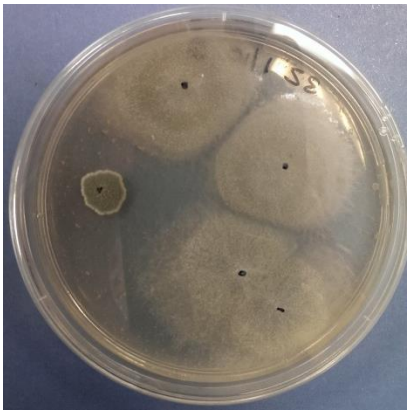
Figure 96: Microbial loading of control MDF and modified MDF panels after 4 weeks

The results show that MDF panels modified with 5% peanut shell, 5% walnut shell, 5% and 10% sunflower seed had a greater number of colony forming units than the control MDF panel. Increasing the percentage loading of peanut shells and walnut

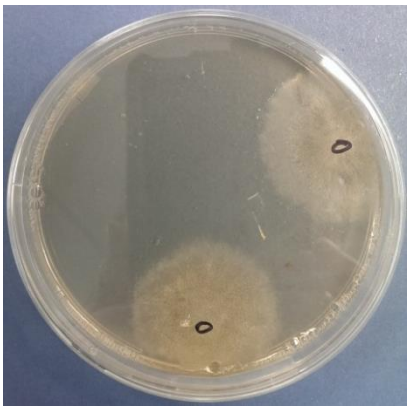
shells to 10% and 15% markedly reduced the number of CFU on the modified panels. Increasing the sunflower loading to 10% resulted in a reduced number of CFU. This suggests that the addition of these lignocellulosic scavengers reduces the susceptibility of the MDF panel to microbial colonisation. However, the CFU results on 15% sunflower seed shows that two of three replicates had an uncountable colony count growth (fig 97D). This could have been a result of contamination of the agar plate during the preparation stage or incubation. However, the results for the modified MDF panel emissions showed that, for only panels modified with sunflower seed, 1-octen-3-ol was detected. According to Markowicz and Larsson, (2014), this VOC suggests the presence of mould growing on the surface of the material. Therefore, it might well be possible that MDF panels modified with sunflower seed are much more susceptible to mould colonisation and growth. Further investigation is required.



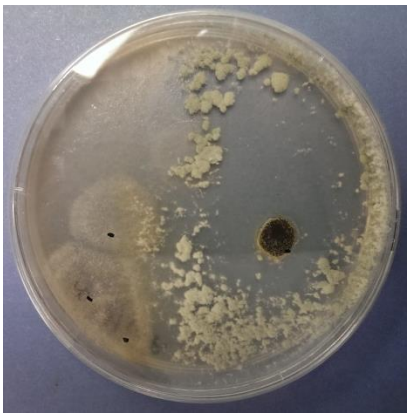
A) Control MDF panel



B) 5% Peanut shell



C) 10% Walnut shell



D 15% Sunflower seed shell

Figure 97: Examples of microbial loading plates after 4 weeks

This test is somewhat subjective and the results are dependent on a great number of environmental factors where the samples have been positioned for the 6 months. These factors include; relative humidity, temperature, room activity and its effects on air velocity, water activity, sunlight (UV) and the mould species spores present in the environment during the testing period. Some mould species have spores that can land on a surface and remain dormant for longer periods than others when environmental conditions are not adequate. These species that can withstand dynamic changes in the environment are phylloplane fungi and can restore growth quickly when conditions are optimal once again (Segers et al., 2016). These species are more likely to be identified as surviving on the surface of the MDF materials. However, the identification of such species is useful as it helps to identify the types of species that are more likely to colonise a material in a certain indoor environment. Wood-inhabiting fungi are capable of becoming dormant if moisture conditions are not adequate to support growth and revive when moisture conditions are favourable again (Carll and Highley, 1999). This is important to consider as some indoor environments such as kitchens, bathroom and to a lesser extent bedrooms, experience extremes in moisture fluctuations throughout the day. When conditions are dry, (pre-cooking, showers and sleeping (respiring humans)) fungal species are dormant but after, such species such as phylloplane fungi will rapidly rejuvenate and continue to grow. However, the capacity of a fungal species to survive periods of dry conditions can often depend on the rate of drying as some species will die if dried rapidly (Carll and Highley, 1999).

Another drawback to this experiment is that it is difficult to determine if the observed mould growth on the agar plates is genuine or results from plate contamination. This could be the case with MDF panels modified with 15% sunflower seed shell and MDF panels modified with 10% walnut shell at 1 in 1000 dilution.

It is highly probable that the lignocellulosic scavengers within the MDF panels are actively absorbing VOCs from the indoor air during the experiment. This absorption of VOCs may well have had an influence on mould colonisation on the MDF panel surface.

6.3 Influence of absorbed VOC on mould growth

This piece of work has been published in the International Wood Products Journal and a reference to the article can be found in Appendix G.

6.3.1 Rationale

This study was developed from the mould colonisation work previously described. The presence of moulds in damp buildings can also contribute to SBS as many mould species' spores are known to cause health problems such as asthma, allergies and bronchitis (Nielsen 2003 and Jarvis and Miller, 2005). The presence of moulds on construction materials can also increase a material's susceptibility to more destructive biological activity, such as decay fungi. It is highly important to study the implications of modifying current products to sequester VOCs on mould growth. It is widely known that the presence of formaldehyde will significantly prevent the growth of fungi on wood-based panels. However, little is known about the effects of absorbed VOCs on the colonisation and growth of moulds. This section of work provides a method developed to evaluate mould growth on the modified MDF panels that were "flooded" with the VOCs formaldehyde, toluene and limonene and then exposed to five different mould species: *Trichoderma virens, Cladosporium sphaerospermum, Chaetomium globosum, Aspergillus niger* and *Penicillium rubens.*

6.3.2 Materials, Mould and Method

Materials

The three chemical solutions used in this experiment were chosen to represent different chemical groups of VOCs. Formaldehyde (F) represents polar VOCs (37% concentration in water), limonene (L) represents nonpolar VOCs (99% concentration) and toluene (T) represents aromatic VOCs (99% concentration). These chemicals were sourced from Sigma-Aldrich without further purification. Sterile de-ionised water (W) was also used as a control.

The materials tested were modified MDF construction materials and solid pine wood (*Pinus sylvestris*) as a control. The MDF panels were produced at pilot scale, using a mix of pine, fir and spruce wood chips and a urea-formaldehyde (UF) resin (12%). Six MDF panels were modified with different VOC scavengers, walnut shells and peanut

shells, at three different loading percentages; 5, 10 and 15% (on a dry weight basis). The peanut shell and walnut shell were milled to a particle size of 5mm. A Control MDF panel without scavengers was also produced. The boards were produced using a formaldehyde-based resin, therefore all the samples were placed into a conditioning room at a temperature of 23^{o}C ±1 and 60 ±3 % relative humidity, for 6 months to allow for de-gassing of free formaldehyde (Curling and Murphy, 1997).

Six replicates of each material were used for the sorption test of each VOC. As the analysis of mould growth was visual, dimensions of the test specimens were not critical but were approximately 50 x 25 mm (±2 mm) at product thickness of 12mm. A further six replicates were used as sorption control specimens. All the test specimens were conditioned in standard conditions at 23^{o}C ±1 and 60 ±3 % RH until a constant mass was reached.

Moulds

All the mould species were purchased from Fungal Biodiversity Centre, Institute of the Royal Netherlands Academy of Arts and Science (KNAW). The mould species selected for use in testing are representative of species commonly found within buildings:

1. *Cladosporium sphaerospermum* (Penz) CBS 122.63
2. *Chaetomium globosum* (Kunze ex Fr.) CBS 107.14
3. *Penicillium rubens* (Biourge) CBS 401.92
4. *Trichoderma virens* (J.H. Mill, Giddens & A.A. Foster) CBS 100946
5. *Aspergillus niger* (M. Frank) CBS 101698

Preparation of spores

Using well sporulated cultures of each of the five moulds, a final mixed spore suspension following EN ISO 846 1997 was produced. 5ml of sterilised water was added to the culture and a sterile needle was used to gently scrape the spores from the surface into the water. The spore suspension was decanted off into a sterile tube and agitated using an orbital shaker and then filtered to remove mycelial fragments. The five spore suspensions were combined together and agitated again.

VOC and water exposure

The VOCs chosen for this work were formaldehyde (F) (37% concentration), toluene (T) (99% concentration) and limonene (L) (99% concentration). Samples were also exposed to water (W) as a control.

To expose the modified boards to VOCs and water, 600ml volume vessels were used. Prior to exposing the samples to the VOCs, the jars and samples were sterilised. This was achieved by spraying the inside of the jars, metal support and samples with 70% ethanol and allowing them to dry in sterile conditions. 60 ml of either water or liquid VOC source was poured into the jars with a sterile supporting metal mesh. The samples were placed on top of the mesh, to ensure that the samples were out of contact with the solvents. Each chamber was sealed with an aluminium lid and wrapped with a wax film to ensure that no solvent was lost through evaporation. The chambers were then stored for seven days at a constant temperature and humidity at 20 ±2 °C and at 70% ±3 RH.

Inoculation and exposure

The setup of vessels in which the "flooded" VOC samples were exposed to mould growth was based on the BSEN 12038 2002 standard procedure using 600ml vessels with ventilated aluminium lids. 80ml of water agar was poured into each vessel and then autoclaved at 121 °C for 50 minutes. Sterile, inert plastic meshes were added to ensure the samples were not in direct contact with the water agar.

Under sterile conditions, two of the board samples were removed from the VOC chambers and placed into 600ml vessels on top of the plastic mesh. Each sample was then inoculated with 0.5ml of the spore suspension. The vessels were then quickly sealed with an aluminium lid. These vessels were then stored in a dark chamber at 20 ±2 °C at 70 ±3% RH for two weeks.

Assessment

For the assessment, the presence or absence of the different mould species was identified and given a score of 1 (present) or 0 (absent) for each of the replicates. A mean value was calculated to show the frequency of growth of all the mould across

all replicates, i.e. the value of 0.5 shows that the mould was present on 3 out of 6 replicates.

The sum of the mean values of frequency of growth was then calculated to show the total frequency of growth of all the moulds collectively. Where possible, the primary, secondary and tertiary colonisers were identified and the dominant mould species identified and recorded.

Figure 72 summarises the sorption, by mass gain, of water, formaldehyde, toluene and limonene by the control MDF panels and modified MDF panels with peanut shells, sunflower seed shell and walnut shells.

Table 72: Shows the average sorption (g kg^{-1}) of VOCs by modified panels

Board	Water	Formaldehyde	Toluene	Limonene
5 % Walnut shell	1.28	1.12	0.94	0.49
10 % Walnut shell	1.53	1.17	0.87	0.74
15 % Walnut shell	1.87	1.35	0.66	0.59
5 % Peanut shell	1.47	1.18	1.20	0.78
10 % Peanut shell	1.37	1.37	1.29	1.17
15 % Peanut shell	1.52	1.10	0.67	0.48
5% Sunflower seed shell	1.63	1.39	0.56	0.31
10% Sunflower seed shell	1.59	1.37	0.67	0.42
15% Sunflower seed shell	1.47	1.48	0.94	0.42
MDF Blank	1.56	1.56	1.00	0.91
Pine	1.43	0.98	1.55	0.35

6.3.2.1 Water and VOC Sorption

Figures 99, 100, 101 and 102 show the results of the sorption of water and the three VOCs by the different modified panels. The boards containing 15% walnut absorbed the most water in the water chamber (1.87 g kg^{-1}) and 5% walnut the least (1.28 g kg^{-1}). Using this data the equilibrium moisture content (EMC) at 20 ±2 ^{O}C and at 70% ±3 RH of the MDF panels and pine wood can be determined (fig 98). The EMC shows

the same relationship as the moisture uptake (fig 99). Panels modified with 15% walnut shell had the highest EMC of 18.75% and MDF panels modified with 5% walnut shell had the lowest EMC of 12.79%.

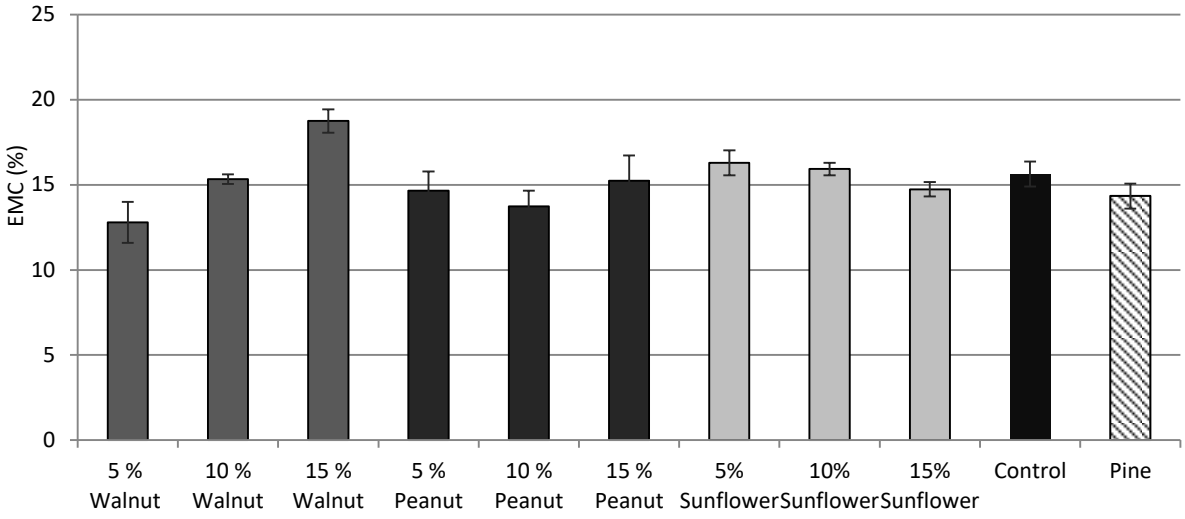


Figure 98: EMC of MDF panel, modified MDF panels and pine wood

Of the samples exposed to formaldehyde VOC (fig 100), the MDF panels modified with 15% sunflower seed shells absorbed the most and solid pine wood the least, 1.48 g kg^{-1} and 0.98 g kg^{-1}, respectively. Of the toluene-exposed samples (fig 101), solid pine absorbed the most (1.55 g kg^{-1}) and boards modified with 5% sunflower seed shell absorbed the least (0.56 g kg^{-1}). Panels containing 10% peanut shell absorbed the most limonene (fig 102) and panels modified with 5% sunflower seed shell absorbed the least limonene, 1.17 g kg^{-1} and 0.31 g kg^{-1} respectively.

As can be seen from the Figure 101, the uncertainty bars are quite large for the toluene sorption results. This is due to toluene being a volatile compound. Once removed from the chamber, the boards de-gassed and the free toluene immediately began to evaporate. It is likely to be the same for limonene sorption, as only some of the VOC will be bound to the scavenger and within MDF boards (fig 102).

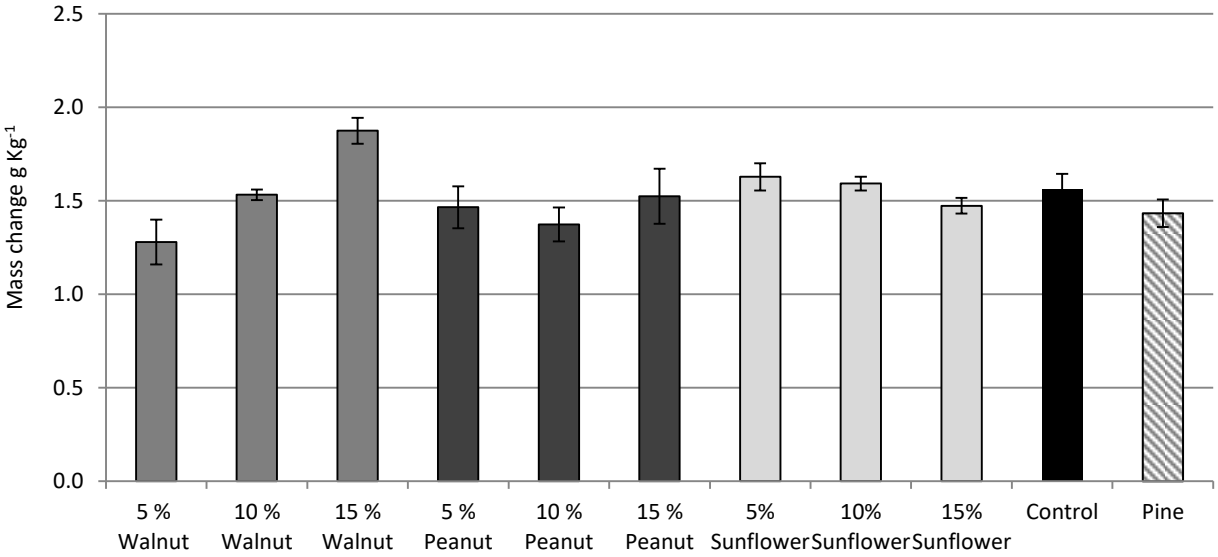


Figure 99: Water sorption of MDF panel, modified MDF panels and pine, after 1 week

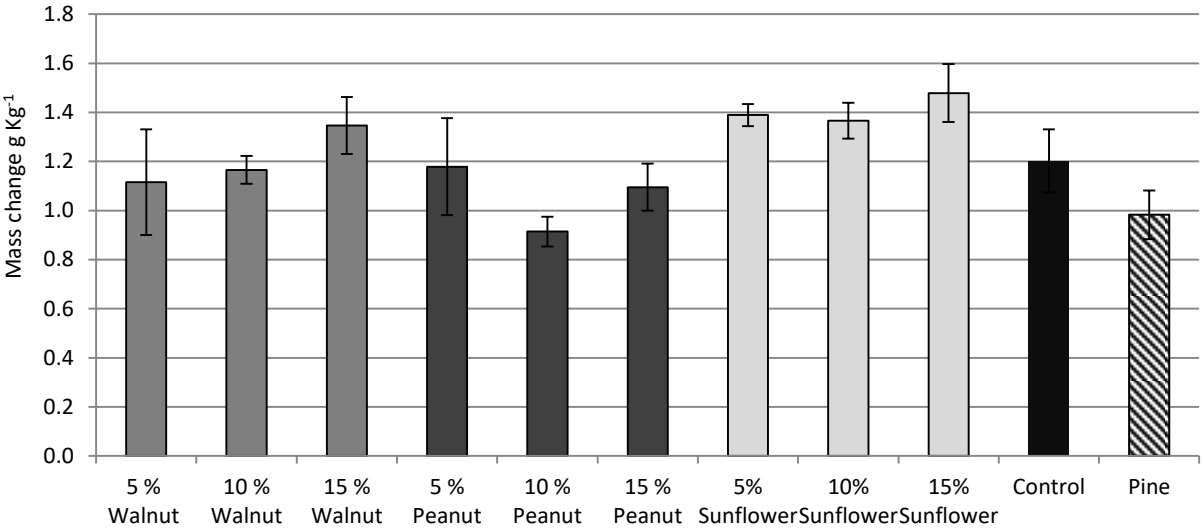


Figure 100: Formaldehyde sorption MDF panel, modified MDF panels and pine, after 1 week

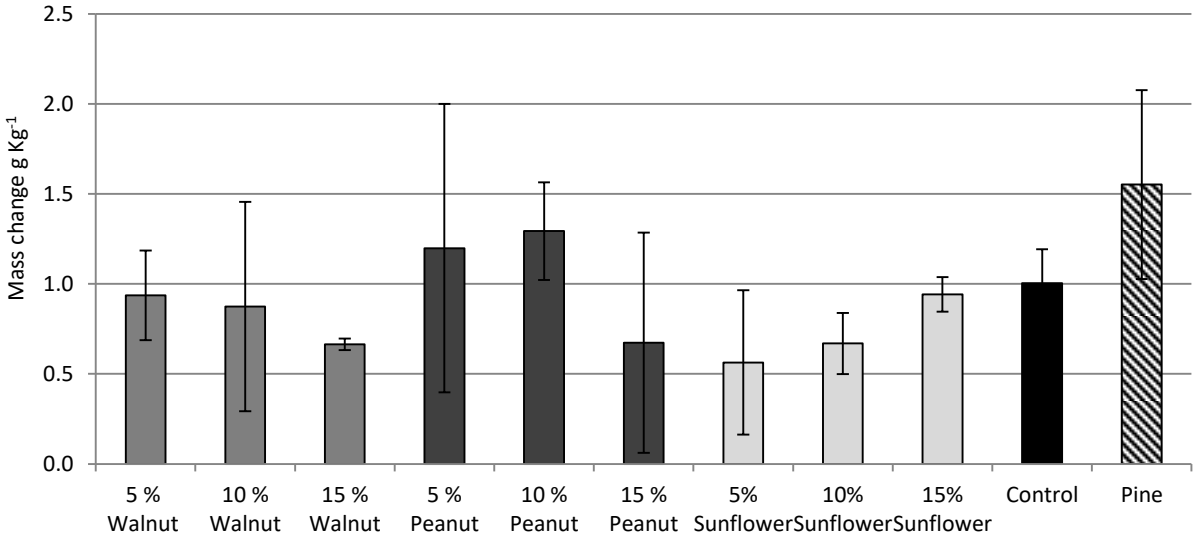


Figure 101: Toluene sorption control MDF panels modified MDF panels and pine, after 1 week

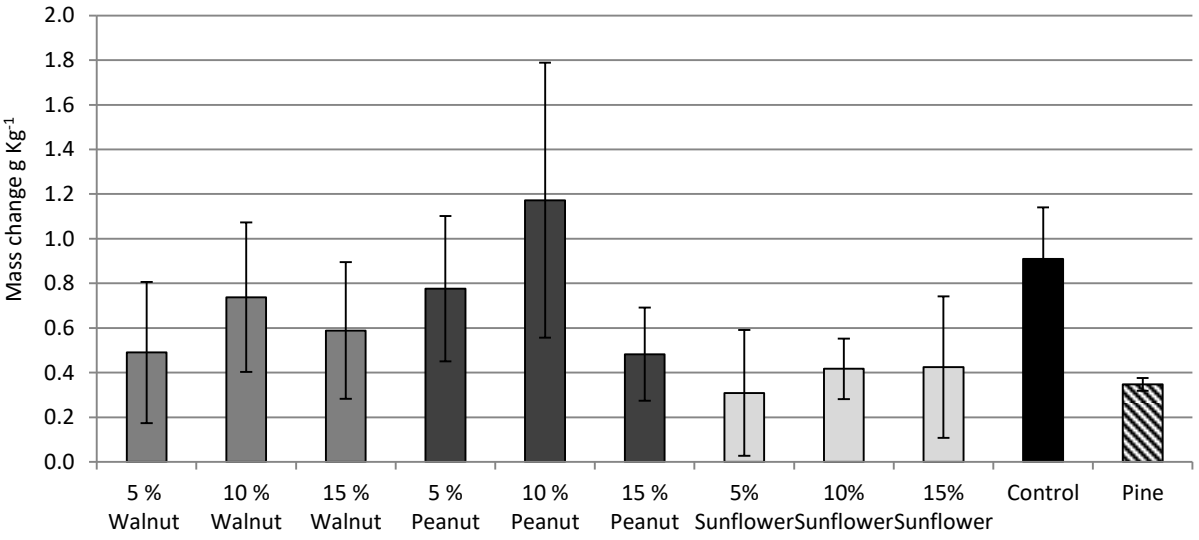


Figure 102: Limonene sorption control MDF panels modified MDF panels and pine, after 1 week

6.3.2.2 Mould growth

Table 73 shows the results for the mean frequency of growth of each mould species across the replicates, exposed to water and the three VOCs. Unfortunately, *Chaetomium globosum* failed to grow across all the samples. The greatest mould growth was, as expected, observed on the modified boards exposed to water.

Table 73: Frequency of species mould growth on samples exposed to water (W), formaldehyde (F), toluene (T) and limonene (L), after 2 weeks

Board	*Trichoderma virens*				*Cladospoirum sphaerospermum*				*Aspergillus niger*				*Penicillium rubens*			
	W	F	T	L	W	F	T	L	W	F	T	L	W	F	T	L
5% Walnut shell	0.83	-	-	-	1	-	-	-	1	-	-	-	0.83	-	-	0.67
10% Walnut shell	1	-	-	-	1	-	-	-	1	-	-	-	1	-	0.33	0.33
15% Walnut shell	1	-	-	-	1	-	-	-	1	-	-	-	1	-	0.17	-
5% Peanut shell	0.83	-	-	-	1	-	-	-	1	-	-	-	0.5	-	-	-
10% Peanut shell	1	-	-	-	1	-	-	-	1	-	0.33	-	-	-	0.33	-
15% Peanut shell	1	-	-	-	1	-	-	-	1	-	0.33	-	0.67	-	0.33	-
5% Sunflower seed shell	1	-	0.17	-	1	-	0.33	0.67	1	-	0.83	0.33	0.5	-	1	0.67
10% sunflower seed shell	0.67	-	0.67	-	1	-	0.83	-	1	-	0.5	0.5	1	-	1	0.5
15% sunflower seed shell	0.17	-	0.67	0.17	1	-	0.67	0.33	1	-	0.67	1	1	-	1	1
MDF Blank	0.83	-	-	-	1	-	-	-	1	-	-	-	0.5	-	0.17	-
Pine	-	-	-	-	0.50	-	0.17	-	1	-	-	-	-	-	-	-

Mould growth post water exposure

Aspergillus niger had successfully developed on all types of modified boards and was observed in all replicates. *Cladosporium sphaerospermum* and *Trichoderma virens* were also seen on all types of modified panels, but not of the same intensity as *Aspergillus niger. Penicillium rubens* was largely observed on all types of boards but showed the least intensity of growth. However, as a primary coloniser, it may have been out-competed by the other secondary and tertiary colonisers over the two weeks.

Table 74 shows the total intensity of mould growth observed on the modified MDF panels and pine wood samples exposed to water. The greatest extent of growth was observed on the 10 and 15% walnut boards. This is likely to be a result of the higher EMC of the boards, due to absorbing more water when in the chamber. Solid pine showed the lowest intensity of mould growth. This is likely to be the result of the lower moisture sorption and EMC, inhibiting the mould growth. However, panels modified with 5% walnut shell had the lowest EMC but did not have the least frequency of mould growth. This shows that measuring EMC is not enough to suggest the quantity of mould growth a modified panel would experience. Panels modified with 5% walnut shell was able to support a greater frequency of mould growth than solid pine despite having a lower EMC. This could be a result of the sugar content of the walnut shells.

Table 74: Total intensity of mould growth on modified MDF, MDF and pine

Board	Water	Formaldehyde	Toluene	Limonene
5 % Walnut shell	3.66	0	0	0.67
10 % Walnut shell	4	0	0.33	0.33
15 % Walnut shell	4	0	0.17	0
5 % Peanut shell	3.33	0	0	0
10 % Peanut shell	3.0	0	0.67	0
15 % Peanut shell	3.67	0	0.83	0
5% Sunflower seed shell	3.5	0	2.33	1.67
10% Sunflower seed shell	3.67	0	3	1
15% Sunflower seed shell	3.17	0	3	2.5
MDF Blank	3.33	0	0.17	0
Pine	1.50	0	0.17	0

Figure 103 shows the differences in the frequency of mould growth of primary, secondary and tertiary colonisers. All primary, secondary and tertiary colonisers were present on all samples tested, except on pine samples, although there is a lower frequency of tertiary colonisers on 15% MDF panels modified with 15% sunflower seed shells. This suggests that, at higher percentage loading of this scavenger, mould colonisation is reduced. On pine samples, only primary and secondary colonisers were observed. This could be a result of the pine having a lower moisture content than MDF samples. There is little difference between the samples, however, there is a difference between the dominating species (Table 75).

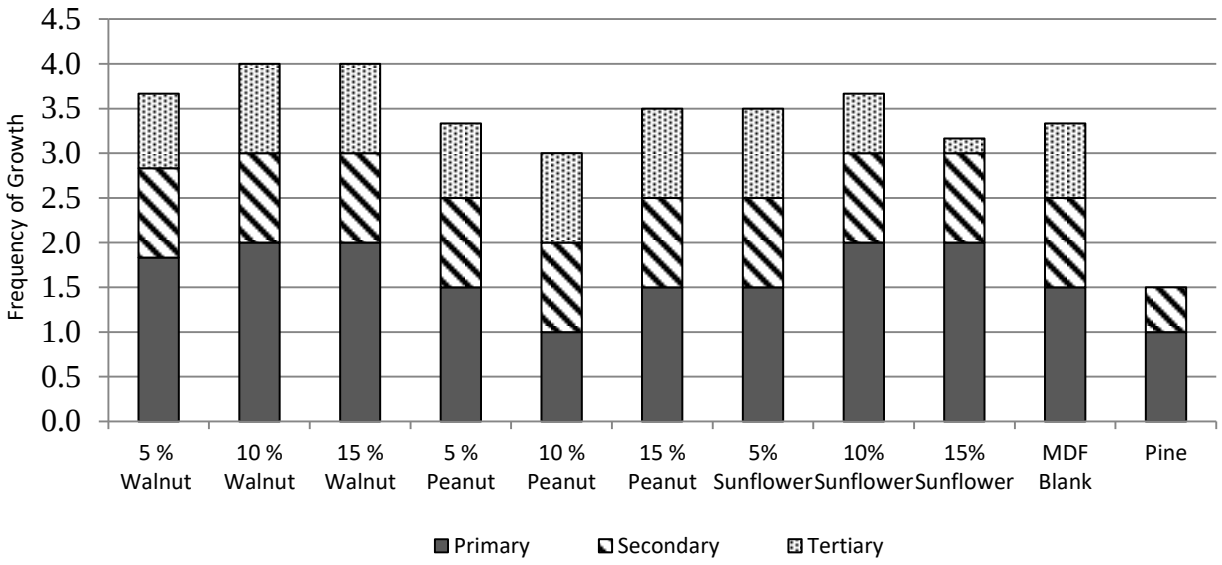


Figure 103: Total frequency of colonising mould species growth and the different colonising species on modified boards after water exposure

Mould growth post formaldehyde exposure

Across all the modified boards and replicates, no mould growth of any mould species was observed (Table 74). Formaldehyde is toxic (Rong et al., 2002b; Rosenkranz, 1972) and therefore the lack of mould growth is not surprising. Of the VOCs tested, formaldehyde was absorbed to the greatest extent by the modified boards, see Table 72. The formaldehyde used was in an aqueous solution at 37%, therefore part of the observed weight gain after absorption is likely to be water as well as formaldehyde. However, there was a total absence of mould growth, compared to samples exposed to water alone. This shows that a sufficient amount of formaldehyde was absorbed to prevent any mould growth. This also shows that the presence of formaldehyde in the resins is not responsible for the lack of mould growth, as all panel samples underwent the same degassing period to remove any free formaldehyde.

As mould growth was not observed on solid pine, this indicates that wood can absorb enough formaldehyde to prevent mould growth too. However, this experiment was not continued after two weeks. Therefore it is possible that the formaldehyde was not trapped within the pine wood chemically and would eventually de-gas and mould would colonise and grow on the wood.

6.3.2.3 Mould growth post toluene sorption

Little growth was observed on the toluene-exposed samples, see Table 73. Only primary colonisers were observed towards the end of the two weeks of the experiment on 10% and 15% walnut shell and peanut shell MDF boards. On MDF panels modified with sunflower seed shell, full colonisation was observed (primary, secondary and tertiary colonisers). Figures 104, 105 and 106 shows that there was no correlation between fungal growth and the amount of toluene absorption on all scavenger modified MDFpanels. It is possible that due to the off-gassing from the sample of free toluene, toluene gas could have accumulated inside the vessels to a toxic level, preventing the growth of mould species. The vessels were all tightly sealed with a plugged hole of non-absorbent cotton wool to allow oxygen ventilation. Therefore, over the two weeks experimental time, the oxygen levels will have increased and the toluene levels decreased inside the vessels. Eventually, this allowed for primary colonisers, *Aspergillus niger* and *Penicillium rubens* to grow and establish on the exposed MDF boards. If allowed more time to grow, it is possible that more growth and further colonisation may occur. This suggests that, although a lot of toluene was not chemically bound within the panel, it can reduce the time for colonisation, growth and succession.

In the case of sunflower seed shell modified MDF panels, 4 of the 5 mould species were found growing on the samples, suggesting that these boards did not absorb a sufficient quantity of toluene to prevent or stunt mould colonisation and growth on this substrate. Compared to water-exposed samples, mould growth on sunflower seed shell modified panels is slightly reduced but not as much as observed on the walnut shell and peanut shell modified MDF panels.

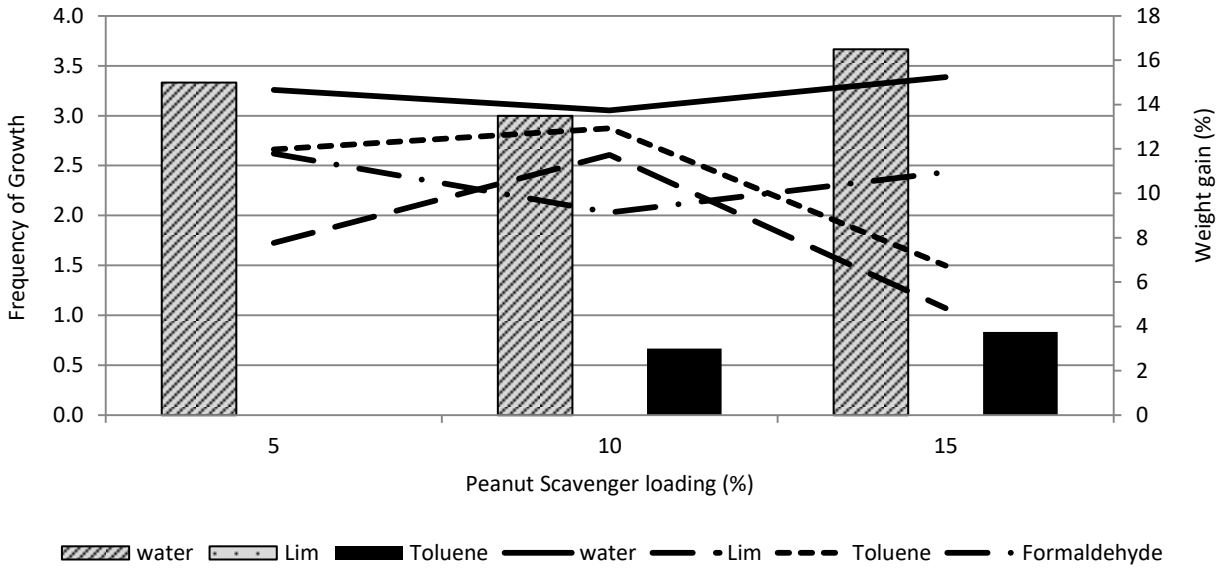


Figure 104: Frequency of mould growth (bars) and sorption weight gain (%) (lines) of MDF panels modified with peanut shell

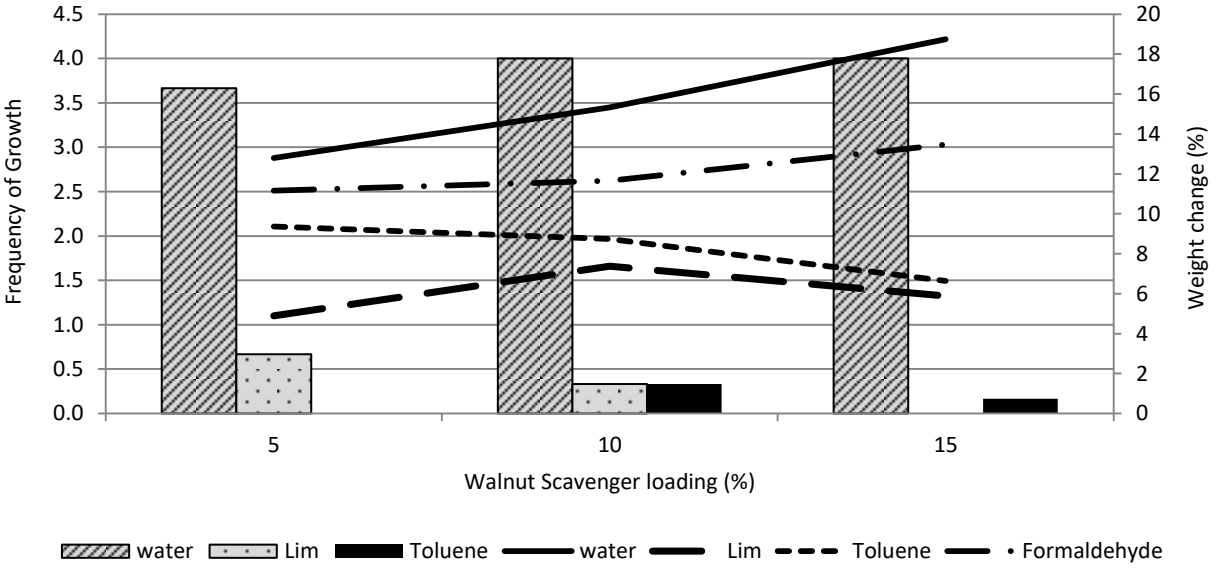


Figure 105: Frequency of mould growth (bars) and sorption weight gain (%) (lines) of MDF panels modified with walnut shell

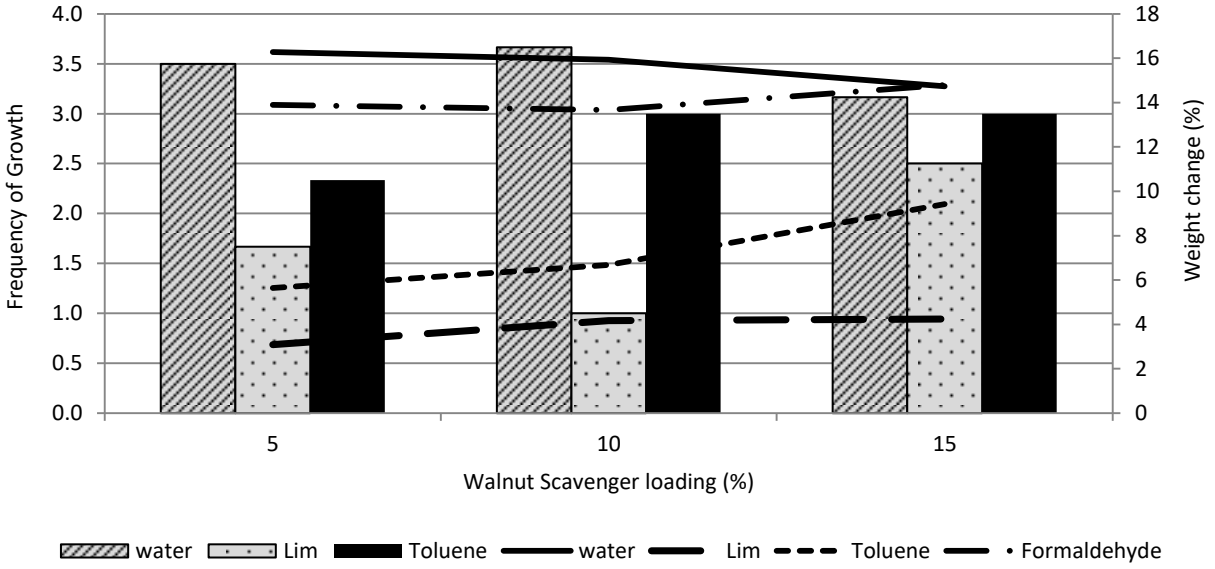


Figure 106: Frequency of mould growth (bars) and sorption weight gain (%) (lines) of MDF panels modified with sunflower seed shell

6.3.2.4 Mould growth post limonene sorption

Table 73 shows the subsequent results of the mould growth on the boards. Minimal growth was observed on the 5% and 10% walnut boards and only of the primary coloniser *Penicillium rubens.* No growth was observed on all other boards modified with walnut shell and peanut shell. This suggests that peanut shell maybe a better scavenger than walnut shell for non-polar compounds. This is important when considering what scavengers to use for target VOCs. However, on MDF panels modified with sunflower seed shell full primary, secondary and tertiary mould species were identified growing. Figures 104, 105 and 106, show that there was no correlation between fungal growth and the amount of limonene absorption on the modified panels. However, when compared to the growth on samples exposed to water, there is a marked reduction in growth, so the presence of limonene is preventing mould growth on the walnut shell and peanut shell modified MDF panels. Mould growth on limonene-exposed samples is slightly reduced but not as much on other modified MDF panels.

6.3.3 Dominating species

Table 75 shows the dominant species found on the different types of modified boards exposed to water, toluene and limonene. Formaldehyde is not included in Table 75, as there was no growth observed for any of the test moulds.

Table 75: Dominant species found on modified boards exposed to water, toluene and limonene

Board	Water	*Toluene*	*Limonene*
5 % Walnut shell	*Aspergillus niger*	-	*Penicillium rubens*
10 % Walnut shell	*Cladiosporum sphaerospermum*	*Penicillium rubens*	*Penicillium rubens*
15 % Walnut shell	*Aspergillus niger*	*Penicillium rubens*	-
5 % Peanut shell	*Cladiosporum sphaerospermum, Aspergillus niger*	-	-
10 % Peanut shell	*Trichoderma virens, Aspergillus niger*	*Penicillium rubens*	-
15 % Peanut shell	*Aspergillus niger*	*Penicillium rubens, Aspergillus niger*	-
5% Sunflower seed shell	*Trichoderma virens*	*Penicillium rubens*	*Penicillium rubens*
10% Sunflower seed shell	*Cladiosporum sphaerospermum*	*Penicillium rubens*	*Penicillium rubens*
15% Sunflower seed shell	*Cladiosporum sphaerospermum*	*Penicillium rubens*	*Penicillium rubens*
Control	*Aspergillus niger, Cladiosporum sphaerospermum*	-	-
Pine	*Aspergillus niger*	-	-

Key: - no mould growth observed

On samples exposed to water, a different succession of growth was observed. On boards containing 5% walnut, although Table 73 shows primary, secondary and tertiary species present, the dominant mould species was a primary coloniser *Aspergillus niger*. *Aspergillus niger* was also a dominant species on the boards

containing 15% walnut. This suggests a slower succession of growth of the mould species grown on boards containing a walnut scavenger.

There was a lower frequency of growth on the boards containing peanut shells when compared against those boards containing walnut shell. There was also a difference in the specific species growing and their prevalence on the peanut samples. Although primary colonisers are still present, the secondary and tertiary colonisers are more dominant. This suggests a difference in the growth rate of the moulds on boards containing peanut shell, compared to boards containing walnut shell.

The mould growth observed on limonene and toluene-exposed samples are by the primary coloniser *Penicillium rubens.* Primary coloniser *Aspergillus niger* was observed only on boards containing 15% peanut exposed to toluene. This shows that the presence of these two VOCs significantly reduced colonisation when compared to samples exposed to water.

On MDF panels containing sunflower seed shells, all colonisers were present but tertiary colonisers were dominant in boards containing 5% and secondary species was dominant in boards containing 10% and 15% shells. This suggests a shift in the dominating species with different percentage loading of sunflower seed shell. This is also reflected in Figure 103, where there is a reduction in the frequency of growth of tertiary colonisers on MDF panels containing 15% sunflower seed shell. Although Table 73 shows that the three colonisers were present on samples exposed to toluene and limonene VOC, the dominating species are still primary coloniser, *Penicillium rubens.* This shows that, despite the lower sorption of toluene and limonene, the rate of colonisation has been reduced.

6.3.4 Conclusion

The aim of this study was to evaluate the addition of organic scavengers on the absorption of VOCs and the effect this has on mould growth. The study conducted suggests that the addition of the walnut shell increases the boards' susceptibility to mould colonisation and growth. This is possibly due to an increased moisture uptake by the walnut. The addition of sunflower seed shell also seems to increase susceptibility to mould growth and this could be a result of its composition, rather than water uptake, which was lower than panels modified with walnut shell. The

presence of peanut scavenger also seems to increase vulnerability but to a lesser extent. It can also be concluded that the boards modified by the addition of walnut shell or peanut shell or sunflower seed shell can absorb formaldehyde, toluene and limonene. The absorption of formaldehyde from the atmosphere by the scavengers prevents colonisation and initial growth. This sorption of VOCs does affect mould growth on boards, reducing the frequency as well as causing a variation in the presence of different mould species and colonisation dynamics.

6.4 Development of a rapid screening method for susceptibility to mould growth

This section describes a rapid screening method that was developed to evaluate and compare the susceptibility of different materials to mould growth and colonisation, taking into consideration their different hygric properties. This piece of work has been published in the International Journal of Biodeterioration and Biodegradation and a copy can be found in Appendix G.

6.4.1 Rationale

During the service life of buildings, bio-based construction materials could be at risk of biodeterioration such as that caused as a result of the biotic processes of microorganisms. In the environment, saprophytic organisms such as mould and decay fungi are the main agents responsible for the decomposition and recycling of organic matter. However, in the built environment they are associated with physical and aesthetic damage and human health problems such as allergic and toxic reactions (Airaksinen et al., 2004; Cooley et al., 1998; Jarvis and Miller, 2004; Mensah-Attipoe et al., 2015; Nielsen, 2003). Modern building practices have, in some cases, exaggerated this problem with increased insulation hindering ventilation, resulting in increased areas of condensation and subsequent mould growth (Schmidt, 2006). Moulds will readily colonise lignocellulosic materials but can also attack synthetic floor coverings, aeroplane fuels, oils, glues, paints and textiles (Pasanen et al., 1992; Schmidt, 2006). This ability to attack a wide variety of materials is enabled by the variety of physiological responses demonstrated by

mould fungi in regards to temperature, water activity, relative humidity and pH (Schmidt, 2006).

Hygroscopic (water sorption) properties are an inherent characteristic of materials that influence both the application and microbiological resistance (Airaksinen et al., 2004; Xie et al., 2010). Natural fibres are hygroscopic because their cell walls contain high amounts of water sorption sites (hydroxyl groups) and can expand to accommodate the water (Xie et al., 2010). Moulds have been shown to appear in succession on a material as the moisture content of the material fluctuates, according to their minimum moisture demands of the mould, (Pasanen et al., 1992). Therefore, although the need for determining a materials' vulnerability to mould growth is obvious, it is clear that not all materials have equal susceptibility (Johansson et al., 2012; Mensah-Attipoe et al., 2015), which adds complexity when considering composite materials. Isopleths have been used to describe relationships between temperature, moisture and fungal growth on nutrient media and although isopleths can be very useful, they are, however, only suitable for predicting growth of known fungi on one material at a time and are time intensive (Johansson et al., 2013b). There have been a number of mathematical models developed and reported in recent years that can be used to evaluate durability and susceptibility of wood and wood-based materials to biological deterioration (Ojanen et al., 2007; Viitanen et al., 2010). Basic models are used to indicate mould germination conditions, such as the isopleth technique, but these do not account for fluctuations in environmental conditions. More advanced models such as the VTT model and the bio-hygrothermal model (Sadovský et al., 2013) can be used but these have also shown significant variations in results due to simplifications and assumptions (Sadovský et al., 2013). There are, however, further disadvantages to using some models to predict microbiological growth, in that most are based on laboratory data, where optimum conditions are used and are therefore often not comparable to construction materials, which are comprised of less nutrient rich materials (Clarke et al., 1999). Very rarely do they take into account species dominance (Gu and Gu, 2005). One key characteristic in predicting the susceptibility of materials requires a knowledge of the organisms' minimum water requirements, that are specific to the individual mould species (Nielsen et al., 2004). Models also do not

consider the materials ability to absorb moisture, in contact or as vapour. It is possible that errors occur, due to a delay in a change in the surface conditions at different relative humidities, when compared to adjacent conditions.

These models may therefore not be the most applicable way of determining a materials' susceptibility to mould growth. As stated above, these models are often developed using the moulds optimal growing conditions and therefore, if materials are destined for use outside of these environmental ranges, such as furniture in a bathroom or kitchen, the level of biological attack may be based on false assumptions. Moulds can still colonise materials and grow in sub-optimal conditions and it has been shown that even at low humidities, where substantive growth may be retarded or prevented, spores and mycotoxins can still be released (Abbott, 2002; Nielsen et al., 2004). This can be detrimental to both the material, as it may enable degradation by other fungal species and in the case of mycotoxins, to human health.

It is highly important to understand how a mould responds to a different substrates and materials susceptibility to microbial attack. Any misunderstanding or poorly informed decisions can have damaging consequences to product industry, economy and human health (Gu, 2016; Gu and Gu, 2005; Mensah-Attipoe et al., 2015). Ultimately the best way to determine a materials' susceptibility to moulds is to physically test the subject material. The aim of this study was the development of a rapid screening method for evaluating the susceptibility of different materials to mould growth under varying conditions and methods of inoculation. The hygric properties of the materials tested were also determined in order to evaluate correlations between mould growth and the material's hygric properties.

6.4.2 Materials and methods

The method described below, is derived from BS EN ISO 846: 1997 Plastics – Evaluation of the action of microorganisms and ASTM D 4445-91 1991 Standard Method for Testing Fungicides for Controlling Sapstain and Mould on Unseasoned Lumber (Laboratory Method).

Construction and Insulation Materials

The materials tested include three commercial grade construction medium density fibreboard (MDF), laminated MDF, chipboard and laminated chipboard and three commercial insulation materials sheep's wool, hemp and wood fibre insulation with solid pine wood (*Pinus sylvestris*) used as a control. The construction panel specimens were prepared to give an upper surface area of 30 mm^2 with the thickness being that of the test material. As the insulation materials were 50 to 60mm thick, a subsample of 5mm thickness was removed from the top surface of the material for use as the test specimen.

Preconditioning

All specimens were conditioned in conditions of 23 ±1 °C and 60 ±3 % RH and once constant mass was reached, the specimens were weighed. The specimens to be inoculated with moulds were sterilised with ethanol and water 70:30 (BSI 1997).

6.4.2.1 Hygric

The sorption dynamics of natural fibres are complex partly due to fibre internal structure and partly due to continuous nanostructural changes, associated with dynamic behaviour of cell walls (Xie et al., 2010). Two methods were used to determine the material's sorption properties; Dynamic Vapour Sorption (DVS) and water absorption coefficient (BSI 2002). Pine (*Pinus sylvestris*) was excluded from the hygric tests.

Water absorption coefficient

The water absorption coefficient (W_{ac}) was determined following the same procedure as described in chapter 2, section 2.6.1.

Dynamic Vapour Sorption (DVS)

DVS is designed to accurately measure weight changes of a sample (less than 10mg), as it absorbs and desorbs moisture at differing relative humidities and temperatures. The sample was suspended in a microbalance within a sealed thermostatically controlled chamber, where a constant flow of dry nitrogen gas was

passed over the sample at a flow rate of 200 cm^3s^{-1} and a temperature of 21 ± 0.2 °C (Popescu et al., 2013). The inert gas carried a controlled quantity of water, maintaining a set RH. The schedule for the DVS was set to start at 0% RH and then increase in 5% steps up to 95% for the adsorption phase and the reverse for the desorption phase (Popescu et al., 2013). The DVS maintained a given RH until the weight change of the sample was less than 0.002 % min^{-1}. Mass change data were acquired every 20 s. Sorption and desorption isotherms were produced for each material by plotting mass change against relative humidity (RH).

6.4.2.2 Mould tests

Moulds

The mould species chosen for this experiment are based on standards used, however, they are also consistently found in indoor environments (Cooley et al., 1998). The mould species were acquired from Fungal Biodiversity Centre, Institute of the Royal Netherlands Academy of Arts and Science (KNAW). The species selected were: *Aspergillus versicolor* (Vuill) CBS 117286, *Cladosporium sphaerospermum* (Penz) CBS 122.63, *Chaetomium globosum* (Kunze ex Fr.) CBS 107.14, *Penicillium rubens* (Biourge) CBS 401.92, *Alternaria alternata* ((Fr.) Keissl) CBS 120829, *Paecilomyces variotii* (Bainier) CBS 108945, *Trichoderma virens* (J.H. Mill, Giddens & A.A. Foster) CBS 100946 and *Aureobasidium pullulans (var. pullulans)* CBS 101160.

On the basis of the minimal requirement of available water for fungal growth on material surfaces, indoor fungi and moulds can be divided into primary (<0.80 a_w), secondary (0.80 – 0.09 a_w) and tertiary colonisers (>0.90 a_w) (WHO, 2009). Using this definition the aforementioned moulds are divided into the appropriate colonisers. Primary colonisers; *Aspergillus versicolor* (Górny, 2004), *Paecilomyces variotii* (Górny, 2004) and *Penicillium rubens* (WHO, 2009). Secondary colonisers; *Cladosporium sphaerospermum* (Górny, 2004) and *Alternaria alternata* (Klarić et al., 2007). Tertiary colonisers; *Chaetomium globosum* (Klarić et al., 2007) and *Trichoderma virens* (Górny, 2004).

Preparation of spores

A mixed spore suspension, containing all of the selected mould species, was produced following the method described in BS EN 846 Plastics – Evaluation of the action of microorganisms 1997

Inoculation and exposure

The three mould tests were conducted using sterile 600ml vessels with aluminium lids.

For direct/indirect contact test, a mineral salt solution agar was used (BSI, 1997), which was autoclaved at 121°C for 15 minutes, cooled and 60ml was poured into each vessel.

To expose samples and moulds to a limited RH, a saturated salt solution was used, mixed with sterilised deionised water, generating a 60% RH within the vessels at 20 ±2 °C. Sterilised supports were added to each vessel to hold the sample in the centre of the vessel. Figure 107 shows a diagram of how the samples were positioned in each of the tests. Two of the 6 replicate samples of each material were placed in one vessel.

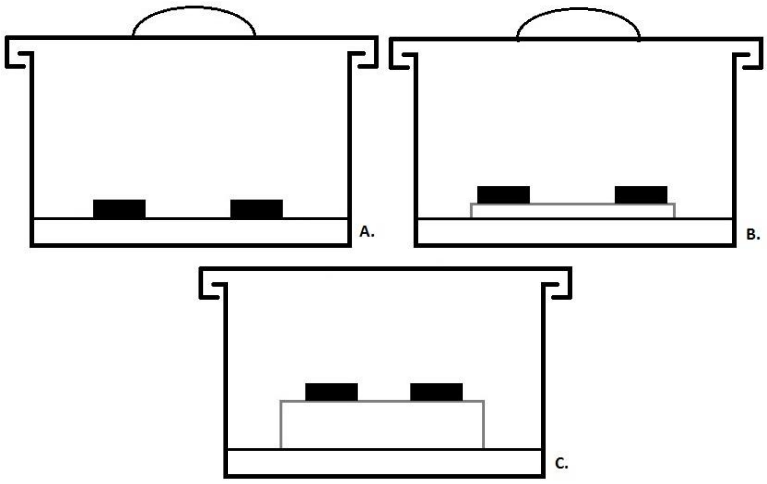


Figure 107: A) Sample in direct contact with agar, (B) Sample indirect contact and (C) Sample raised to the centre of the vessel RH test

Specimens were introduced to the vessel one at a time and placed according to test specifications. Vessel A and B (fig 107) had a ventilated lid, plugged with non-absorbent cotton wool to allow gas exchange. Samples for the relative humidity experiment were securely sealed (fig 107C) to ensure no moisture loss or gain. Each sample for all three experiments was inoculated with 1ml of the mould spore solution. The vessels and sample were then stored in a dark chamber at 20 ±2 °C at 70 ±3 % RH for three weeks.

Each mould underwent a viability test on sterilised 4% malt agar plates (40g malt extract and agar 20g in 1000ml) apart from, for *Chaetomium* and *Trichoderma* moulds, where a 4% oatmeal agar culture was used. 1ml of the spore solution was pipetted onto the agar and spread using a sterile glass rod. The agar plates were then sealed with a wax film and incubated at 20 ±2 °C at 70 ±3 % RH.

6.4.2.3 Assessment

After exposure to mould, the samples were removed from the vessel and visually evaluated for mould growth (Table 76). Where possible, primary, secondary and tertiary colonisers were identified and recorded. A rating of 1 (present) or 0 (absent) was given to the presence or absence of primary, secondary and tertiary colonisers. The occurrence of the colonisers was given as percentage across the replicates.

Table 76: Visual assessment of mould growth (BSI, 1997)

Intensity of growth	**Evaluation**
0	No growth apparent under the microscope
1	No visible growth to the naked eye but visible under a microscope
2	Visible growth, up to 25% coverage
3	Visible growth up to 50% coverage
4	Visible growth up to 75% coverage
5	Heavy growth, covering more than 75% of sample surface

6.4.3 Results and Discussion

6.4.3.1 Wide Range of Moisture Properties

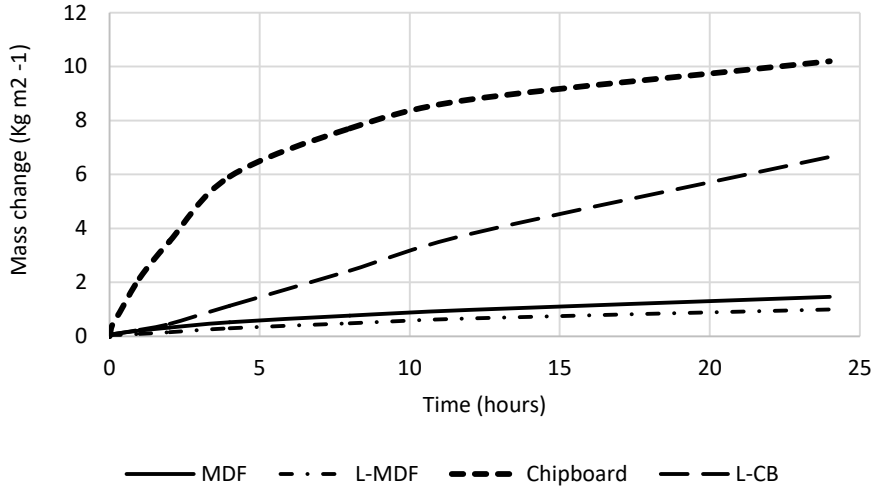
The principle of the water sorption coefficient test was to measure the water absorption by partial immersion in water, by measuring the change in mass over time. Table 77 shows the results for water absorption coefficient. For this test, water absorption relies on the capillary action (uptake) and in natural fibres, this can cause the swelling of the material. As wood fibres can expand to accommodate additional water (Xie et al., 2010), for wood-based construction materials, the results should, therefore, be taken as indicative only.

Table 77: Water absorption coefficient and EMC of test materials at 95% and 60% RH

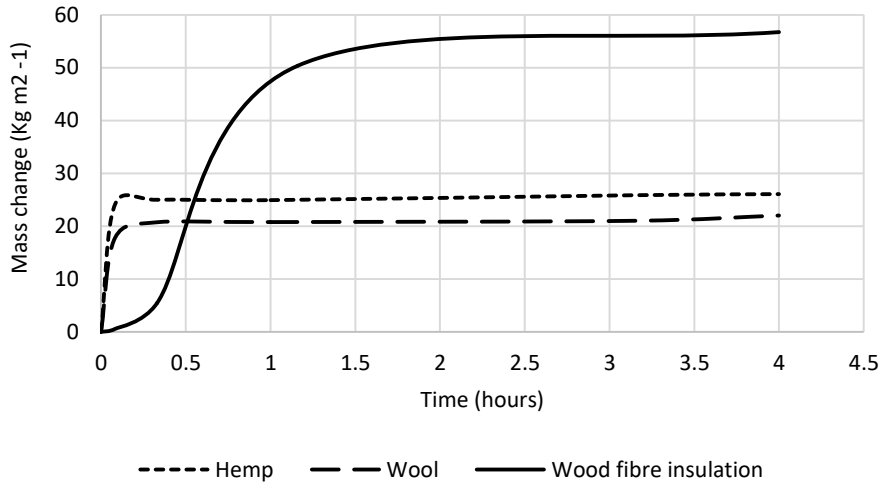
Material	Water absorption coefficient (Kg/(m^2 hr^{-1}))	EMC at 95% RH (%)	EMC at 60% RH (%)
MDF	3.25	17.46	7.92
Laminated MDF	3.38	14.18	7.55
Chipboard	4.65	18.01	9.39
Laminated chipboard	4.25	16.58	9.28
Hemp	5.28	20.92	4.02
Wood fibre insulation	2.50	21.77	4.21
Wool	4.50	19.17	11.78

Figure 108 shows the mass change over time. Chipboard had almost become saturated by the end of the 24 hour period, as the rate of water uptake decreased. In comparison, MDF and laminated MDF showed a slower, steady rate of water absorption. This could be due to a combination of variables between materials such as particle and resin distribution and the density difference between MDF and chipboard, 700 kg m^{-3} and 600 kg m^{-3} respectively. The laminated chipboard showed a slower rate of absorption due to its less permeable melamine coating. Wool and hemp materials became saturated within the first hour as these materials have a low density of 22.64 kg m^{-3} and 43.72 kg m^{-3} and therefore can hold less water proportionally within matrix before becoming saturated. Wood fibre insulation has a density of 205.03 kg m^{-3}, therefore absorption was slower but the sample still

became saturated within 5 hours. The test for all three insulation materials, ceased after four hours, as water was absorbed through to the top surface of the sample.



A



B

Figure 108: Water absorption of construction (A) and insulation (B) materials

The data (fig 109) derived from the DVS shows that all the materials exhibited varying levels of hysteresis (the difference in EMC (equilibrium moisture content) dependent on sorption or desorption) with them all exhibiting IUPAC type 2 sorption and desorption isotherms (Hill et al., 2009). The construction materials all exhibited significant hysteresis effect, though in contrast hemp and wool showed only a small hysteresis effect. This could be related to the materials densities and higher lignin content of the wood-based materials (Hill et al., 2009).

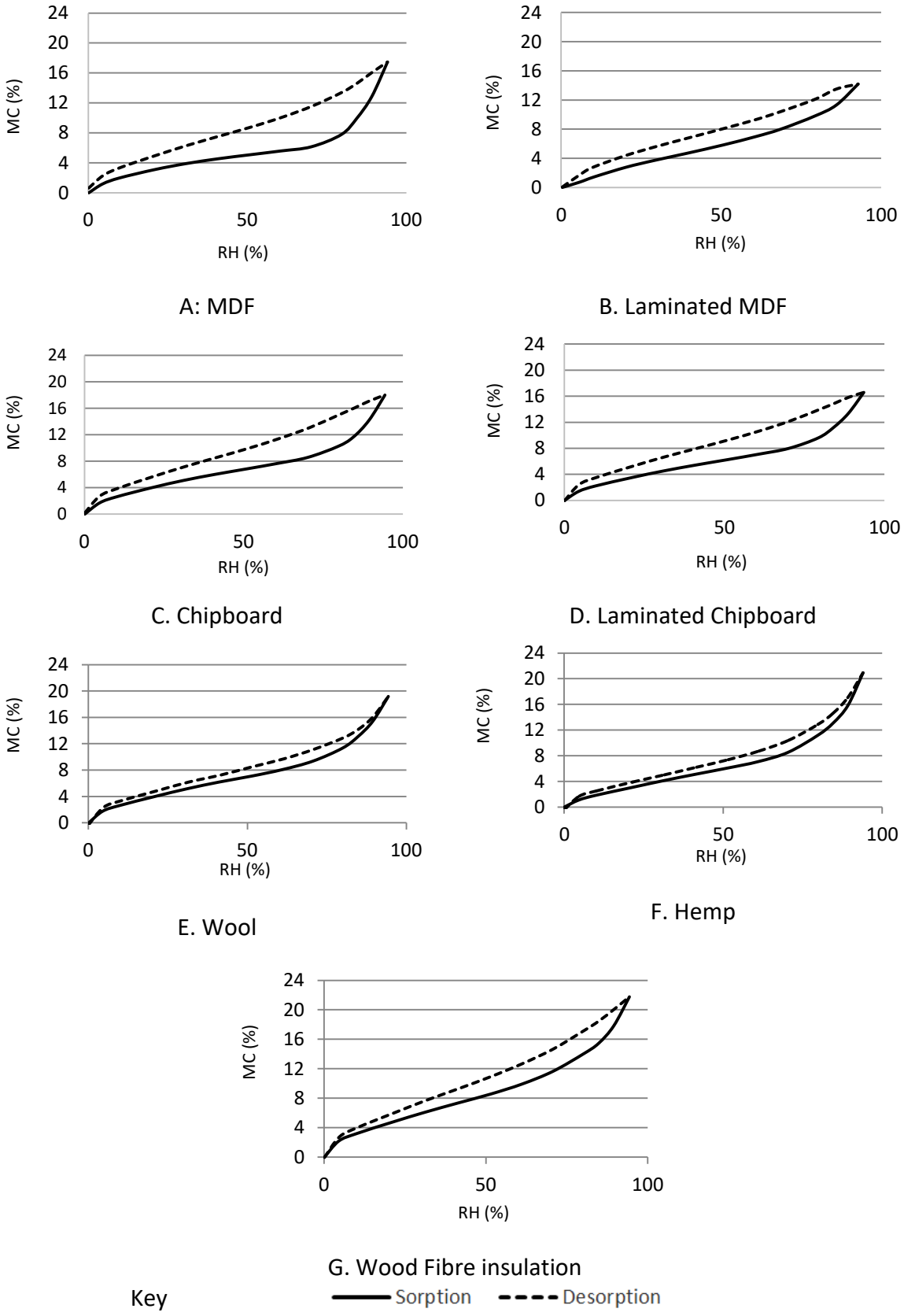


Figure 109: Sorption and desorption curves of insulation and construction materials

Table 77 shows the maximum moisture content (EMC) of the material when exposed to a humidity of 95%. Hemp absorbed the most moisture at 95% RH with 20% of dry weight and laminated MDF the least at 14.18%. Laminated materials have lower EMC values than un-laminated materials due to the presence of the less permeable melamine coating.

6.4.3.2 Material Specific Mould Ecology

Table 78 summarises the intensity of mould growth on samples in contact, indirect contact and samples in sub-optimal conditions at 60% RH.

Table 78: Intensity of mould growth on sample in contact and indirect contact with agar and suboptimal conditions at 60% RH

Material	Intensity of growth		
	Contact	Indirect contact	60% RH
MDF	3	2	1.8
Laminated MDF	3	2	1.6
Chipboard	5	4	2
Laminated chipboard	4	4	1.6
Wool	2	1	0.4
Hemp	4	3	1.6
Wood fibre insulation	3	3	1.2
Pine	4	3	1.6

Observations were made at the end of a three week period to evaluate the mould coverage over the sample (%). Note was taken of the presence of primary, secondary and tertiary species, to give an indication of colonising mould succession and competition. The mineral salt agar was present to act as a moisture source and would not act as a carbon source for growth; therefore the mould fungi had to use carbon derived from the samples i.e. utilisation of the sample material (Gu, 2016). Although moulds had successfully grown in all vessels there were differences depending on the material and exposure method.

For contact samples, the chipboard had the highest intensity of growth, (5 rating). Laminated chipboard, hemp and pine had the second highest, (4 rating). Figure 111 shows that in the vessels containing chipboard and dense wood fibre, all moulds were present, as primary, secondary and tertiary colonisers were observed. This corresponds to previous work where the greater availability of free water in the structure of the chipboard (Górny, 2004) enhanced its susceptibility to moulds. The data derived from the DVS studies also shows that the chipboard and dense wood fibre had higher moisture contents than the other materials at similar relative humidity levels. However, greater intensity of growth was observed on chipboard, showing a greater susceptibility to moulds than the other materials tested which may be due to the availability of nutrients and a preference of the moulds.

In contrast, the least intensity of growth was observed on MDF and wool – with MDF exhibiting lower nutrient availability than chipboard because it is processed wood fibre (Johansson et al., 2013a). This shows that moulds attack materials suited to their chemical and physical capabilities and material composition (Gu, 2003).

For indirect contact, chipboard (both un-laminated and laminated) had the most intense growth, with a rating of 5 and 4 respectively. All materials showed a reduced intensity of growth when not in direct contact with the agar, expect wood fibre insulation and laminated chipboard (Table 78). This may be indicative that the sample's hygric properties enhance mould growth through the sorption of moisture from the agar. However, the presence of primary, secondary and tertiary colonising moulds are similar in both sets of samples.

Figure 110 graphically shows the difference in mould growth between contact and indirect contact samples. All growth on all materials in contact with agar had a higher intensity of mould growth compared to indirect contact samples, although not statistically different, except for chipboard. This shows the influence of the presence of the moisture in the agar on a sample's MC and subsequently, mould growth. However, materials with higher water absorption coefficient and MC values did not necessarily have the highest intensity of growth.

From Figure 111 it can be observed that primary, secondary and tertiary colonisers were present in all vessels on all samples. It should be noted that where tertiary colonisers occurred >80% of replicates, *Trichoderma virens* and *Chaetomium*

globosum were the prevalent moulds. *Trichoderma* sp. were present, had excellent growth, which in other studies has been attributed to its production of antifungal products (Šegvić Klarić et al., 2007) that enable it to outcompete other fungal species (Ghisalberti and Sivasithamparam, 1991; Wiest et al., 2002).

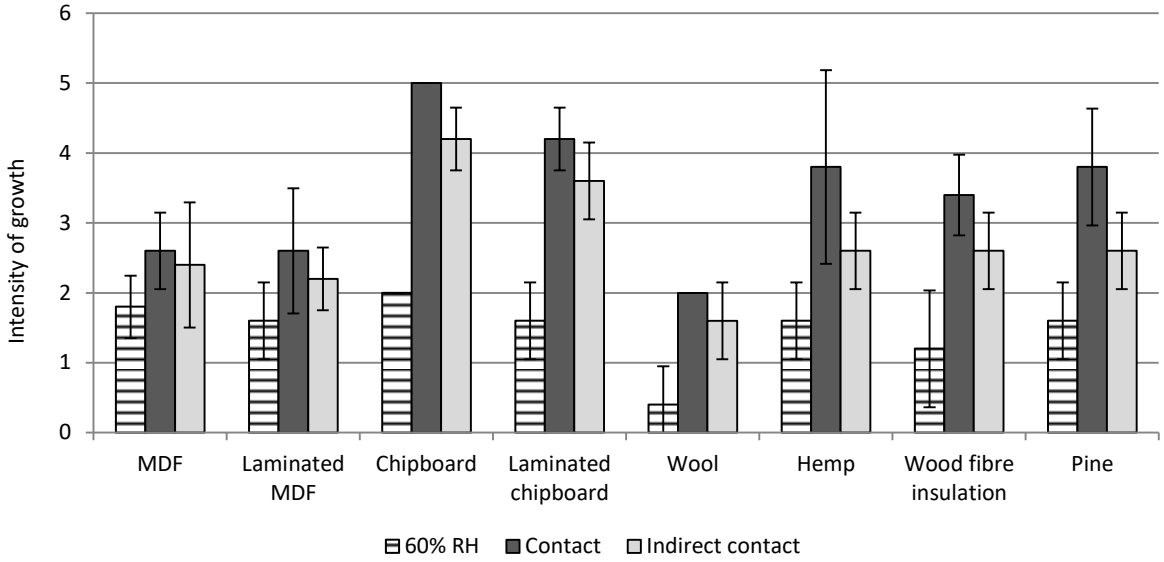


Figure 110: Intensity of growth, in contact, indirect contact and 60% RH conditions

There were no clear correlations between water absorption and mould growth as those materials with high levels of water sorption did not always show the highest levels of colonisation. Hemp had the highest water absorption coefficient but showed lower growth intensity than laminated chipboard. This reduced intensity of growth could be a result of the presence of *T. virens,* which may have colonised quicker on hemp than chipboard and thus prevented other mould growth. Also, wool samples had high hygric values of sorption but the lowest levels of growth. This is due to the limits of the moulds themselves, as they are not capable of decaying such materials.

Using hygric data, materials can be assigned a 'critical moisture level' where moulds can develop on the materials. These results show that moisture environment alone is not enough to model the likelihood of mould growth, as other factors such as material composition and mould species capabilities and preference have a major influence on comparative growth between materials. The hygric data does illustrate

an important point that although some materials may not sustain heavy mould growth, they can easily absorb water. This factor may influence fungal growth on other materials if they are used in conjunction (Curling et al., 2015).

When analysing these results, it was observed that there were differences in the presence of primary, secondary and tertiary colonisers (Figure 111). A value of 1 represents the presence of primary, secondary or tertiary colonisers across all replicates. All samples and replicates had primary species colonising the samples in contact, indirect contact and at 60% RH. No secondary or tertiary colonisers were observed on any material when cultivated at 60% RH. This shows that building materials can form small niches in indoor environments for different organisms (Mensah-Attipoe et al., 2015).

Figure 111A and 111B show the succession of growth on MDF and laminated MDF respectively. The frequency of growth of secondary and tertiary colonisers was significantly reduced when samples were out of contact with agar and at 60% RH. However, on MDF, secondary colonisers were still present even when out of contact with the agar, whereas on Laminated MDF the frequency of growth of secondary colonisers was reduced. This shows that a change in the surface of a material can alter the susceptibility to different mould species. Laminated chipboard and chipboard revealed a similar pattern.

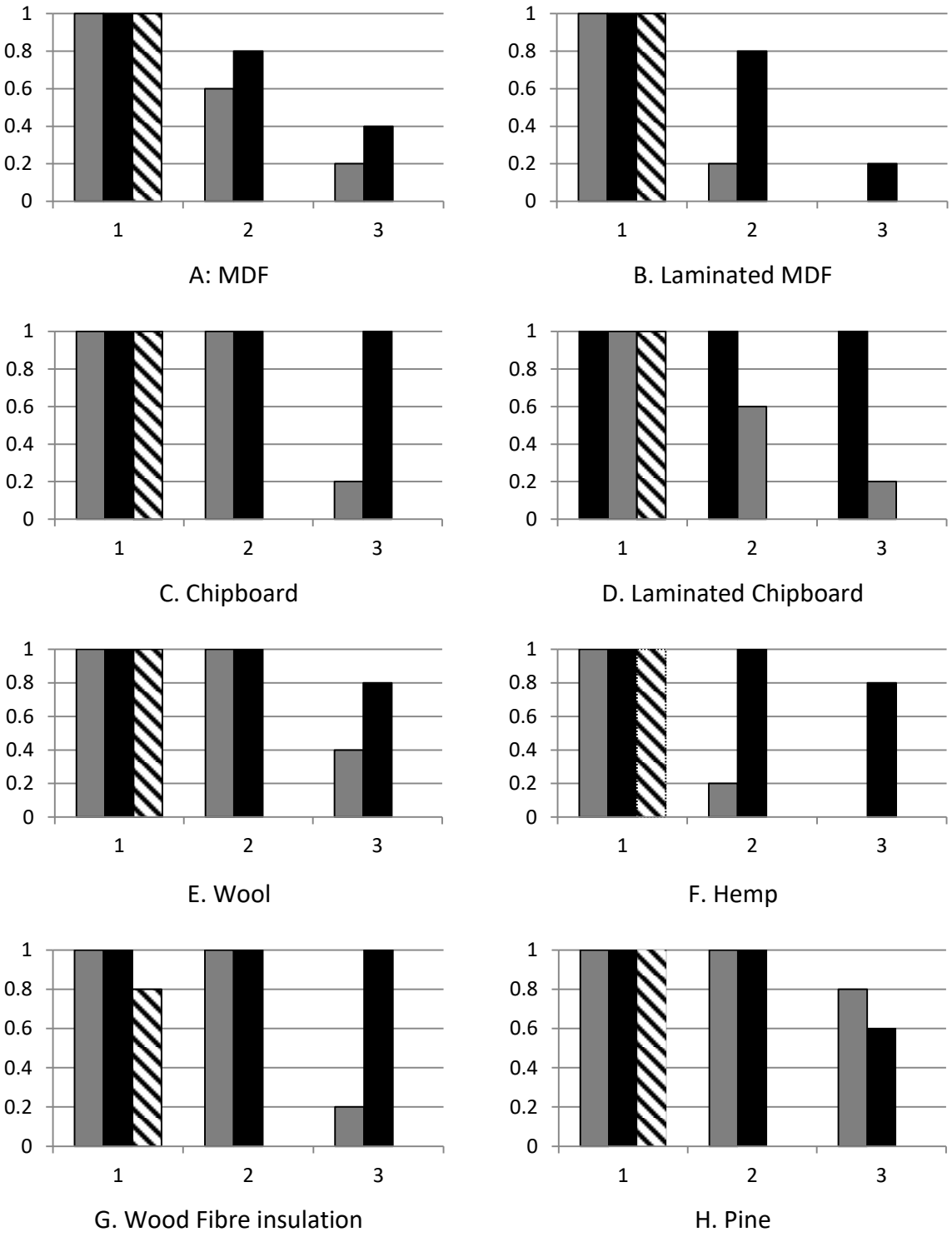


Figure 111: Frequency of growth by primary (1), secondary (2) and tertiary (3) colonisers in contact with agar (black), indirect contact with agar (grey) and at 60% RH (stripe)

Figure 112 shows the combined data of intensity of growth and frequency of colonisers for materials in direct contact with agar. It illustrates that different

materials, exposed to the same moulds under the same conditions, experience differing colonisation patterns.

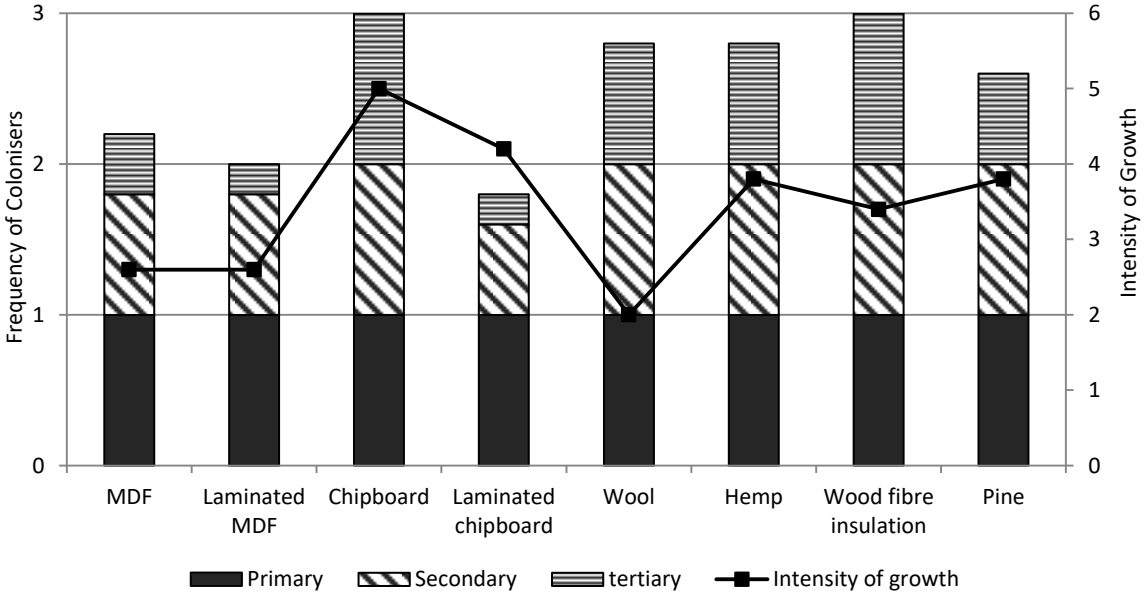


Figure 112: Intensity of growth and frequency of primary, secondary and tertiary colonisers on in contact samples

Chipboard showed that with a high intensity of growth, there is a full succession of colonisers, whereas laminated chipboard while exhibiting a similar intensity of growth, had reduced incidence of tertiary colonisers. Wool samples showed a high, almost full succession of growth but the intensity of growth was the lowest of all materials tested. This is important as it demonstrates the usefulness of the test method in identifying the differing response of the organisms to the different materials. In the case of wool, moulds can colonise and survive on the wool, likely surviving off contaminants in the insulation (Górny, 2004; Johansson et al., 2013a) which, again is highly important when considering real-life scenarios where different materials are used in conjunction.

Many mould growth models rely on known optimum conditions for specific moulds and assume uniform susceptibility of different species of mould spores (Viitanen et al., 2010). However, in real life, environmental conditions in buildings are rarely optimal and fluctuate (Johansson et al., 2013a; Pasanen et al., 2000) so it is crucial

to know the extreme limits for mould growth, as different mould species may be either actively growing or just surviving on a material.

From the DVS isotherms, it can be observed that different materials absorb vapour at different rates at different RH. It is considered that the limit value of relative humidity is between 70-90% for fungal growth on building materials (A. L. Pasanen et al., 2000). However, as mould species have differing limiting conditions, a study was made to determine the effects on colonisation, growth and competition at a lower limit of 60% RH. This showed that only primary colonising moulds were observed growing on construction materials at 60% RH (Figure 111).

Table 78 shows the differences in intensity of growth at 60% on different materials. The highest moisture content observed was that of chipboard, at just under 10% MC and this is generally considered too low for mould growth, although in this study mould growth was obvious on all samples. This could be a result of the initial equilibration period, following inoculation, where water availability was slightly higher. After which time the mould growth rate reduced but primary colonisers were largely established. It was observed that the most intense growth was on the wood-based materials, with chipboard showing the greatest growth (2 rating). This is highly important as there is evidence that *Penicillium* species are strong indoor contaminants and contribute significantly to SBS (Abbott, 2002; Cooley et al., 1998). No secondary or tertiary growth was observed in any vessels. This is due to the MC requirements of the mould species, as only xerophyllic moulds (dry loving) such as *Aspergillus* and *Penicillium* species were observed, which require <0.80 a_w (A.-L. Pasanen et al., 2000). The same was observed by Pasanen et al., 2000 were xerophyllic moulds have great prevalence at low water activity. Secondary and tertiary colonisers are more hydrophyllic moulds and require higher levels of moisture to successfully grow and colonise a material.

Figure 112 graphically depicts the differences between the intensity of growth of mould on sample materials in contact and indirect contact, at optimal conditions and at 60% RH. It highlights the differences between growth at optimal and less than optimal conditions, which is important to understand these relationships as moulds can still produce metabolites and mycotoxins at low RH and temperatures (Nielsen et al., 2004). Statistically, there is a difference between the intensity of

growth between test conditions on materials tested, except for MDF and laminated MDF. This indicates that MDF may have a lower MC requirement to support mould growth.

The results also show that moulds will grow on all materials even at limiting conditions, albeit with reduced growth. This suggests that testing specific material characteristics on a small scale may not be representative of the full product, due to bulk effects, especially when considering composite materials.

6.4.3.3 Fast and Versatile Method

This rapid screening method took only 3 weeks to obtain data on a materials' susceptibility to mould growth. However, consideration must be given to time as an influencing factor for mould growth (Vereecken and Roels, 2012). If a mould species is known to have a slow growth rate, extra time should be provided. It has an advantage over BS EN 846 in that it can be used for a range of materials and not just plastics. The method uses the principle from ASTM D 4445 to use a support, which can be used to evaluate the vulnerability of the material as a "carrier" of moulds. This may be important when considering wall constructs. As with wool for example, although all moulds were present, the intensity of growth on the wool itself was minimal in both situations but the mould growth on wool implies it will not act as a barrier for more vulnerable materials such as MDF. This can result in the spread of moulds and may increase the material's and adjacent material's vulnerability to degradation fungi. Testing materials at lower RH can show which if any species can survive and continue to utilise the material. This is especially important when considering drying materials, particularly after water damage (A.-L. Pasanen et al, 2000).

Although in this study a mixed spore suspension of commonly used test strains was used, the method is equally adaptable for use with specific single mould types or a mix of test or naturally isolated fungal strains. The method is also adaptable for the study of any construction or insulation material and the test environmental conditions can be altered to simulate particular environmental conditions a material is intended for.

Using the 600 ml vessel over thinner agar plates enables the testing of whole thickness samples rather than a thinner sample. This is highly beneficial especially when testing composite materials. At full thickness, the sample is more representative of the product and the interactions with moisture and subsequent mould growth is more comparable with the product in service. It is also beneficial as it tests any bulk effects of the product.

6.4.4 Conclusion

Identification of susceptible materials and mould growth patterns is highly important, especially when considering toxic moulds. This study developed a rapid screening method to enable the determination of the susceptibility of different materials to different mould species. The method provides data enabling identification of more vulnerable materials, materials that may have synergistic with other materials, material responses to varying moisture environments and consequential mould growth dynamics under varying environmental conditions: data which is unlikely to be obtained by modelling alone.

6.5 Chapter Summary

The aim of this chapter was to determine if and how the addition of the lignocellulosic scavengers affected the MDF panels' susceptibility to basidiomycete decay and mould colonisation. This chapter also evaluated the effect of VOC sorption by the scavengers on the mould colonisation and growth. This chapter also described a rapid screening method that was developed to evaluate and compare the susceptibility of different materials to mould growth and colonisation, taking into consideration their different hygric properties.

6.5.1 Basidiomycete decay

The addition of walnut shell to MDF panels reduced the panel's susceptibility to *C. versicolor* and a higher percentage loading of walnut shell could reduce susceptibility further. The addition of this scavenger did not influence the panels' susceptibility to *C. puteana,* positively or adversely. The addition of peanut shell to the MDF panel significantly reduced susceptibility to *C. versicolor.* However, increasing the

percentage loading of the shells did not further reduce susceptibility. The addition of peanut shell was found to reduce the panels susceptibility to *C. puteana.* However, there was no statistical difference between MDF panel modified with 10% and 15% peanut shell, suggesting that the susceptibility could not be further reduced despite increasing loading of peanut shell. The addition of the sunflower seed shell appeared to reduce the susceptibility to *C. versicolor* but 15% loading was found to increase the panel's susceptibility to the white rot fungi. It was found that the addition of this scavenger to the MDF panel initially increased the susceptibility of the MDF panel to *C. puteana,* but increasing the percentage loading over 5% decreased the susceptibility to the brown rot. Therefore, higher percentage loadings of this lignocellulosic scavenger could further improve susceptibility.

6.5.2 Microbial loading

There are many external factors that influence the results of this test. As the samples are left in the open environment, the mould spores landing on the sample surface and able survive is influenced by moulds present, sunlight, temperatures, humidity and air movement. As such, the fungal species found to be surviving on the surface of the MDF panels are likely to be phylloplane fungi that can withstand periods of poorest conditions, dormant and restore growth when conditions are optimal again. Despite the drawbacks of this test, it can be seen that MDF panels containing 15% sunflower seed shell had the highest microbial loading. The lowest microbial loading was found on MDF panels modified with 10% walnut shell.

6.5.3 VOC absorption and mould growth

The aim of this study was to evaluate the addition of lignocellulosic scavengers on the absorption of VOCs and the effect this has on mould growth. A great benefit to this test was that the panels' susceptibility to mould colonisation can be determined in a more controlled environment compared to the microbial loading method, with known mould species and more definite conclusions can be made. This study showed that the addition of the walnut shell and sunflower seed shell increased the MDF panel's susceptibility to mould colonisation and growth. The presence of peanut scavenger also seemed to increase vulnerability but to a lesser extent. This

method also showed that the modified panels with either lignocellulosic scavenger can absorb formaldehyde, limonene and toluene. The absorption of the VOCs markedly reduced mould growth and colonisation on the modified MDF panels compared to the control MDF panel and caused a variation in the presence of mould species and colonisation dynamics.

6.5.4 Rapid screening method for susceptibility to mould growth

This study developed a rapid screening method to enable the determination of the susceptibility of different materials to different mould species, whilst taking into consideration each material's different hygric properties. This method enabled the identification of mould species and evaluation of the intensity of growth of the moulds. The frequency of primary, secondary and tertiary colonisers can also be acknowledged to give an indication of the rate of mould succession and risk of further, more damaging form of biodegradation. This method was proved to be a fast and versatile method. It can easily be modified to cater for the mould species under investigation and can be used for a wide range of materials, regardless of their composition. The main advantages of this method is that the material can be tested at sample thickness, can be used to identify materials that act as a "carrier" to moulds and testing materials in sub-optimal conditions shows which moulds can survive on the material, despite poor environmental conditions.

A further study would be to expose the modified MDF panels to this procedure to determine the interactions of mould growth under difference RH and moisture environments.

6.6 Microbiology - Comparison to commercial MDF panel

6.6.1 Basidiomycete decay

To compare the decay susceptibility of the modified MDF panels and commercial MDF panels, the decay susceptibility index (DSI) was calculated comparing the two. A value of 100, means that the modified MDF panels have the same decay susceptibility as the commercially produced MDF panels. DSI results for *P. ostreatus* and *G. trabeum* was not included as for both sets of experiments the virulence of the strains was not up to standard. Table 79 shows the percentage difference in DSI

of modified MDF panels and commercially produced MDF panel for *Coriolus versicolor* and *Coniophora puteana.*

Table 79: Decay Susceptibility Index of Modified MDF panels compared to commercial MDF

Board	*Coriolus versicolor*	*Coniophora puteana*
5% Walnut	68.38	75.19
10% Walnut	63.07	72.24
15% Walnut	46.53	72.31
5% Peanut	27.82	70.80
10% Peanut	37.96	65.25
15% Peanut	28.33	66.16
5% Sunflower	64.10	75.34
10% Sunflower	31.18	72.09
15% Sunflower	42.75	69.48

The results for DSI of MDF panels exposed to *C. versicolor* shows that all the modified panels had a DSI of less than 100. This shows that the modified MDF panels have a lower susceptibility to *C. versicolor* than commercial MDF panels. Panels modified with peanut shell have the lowest DSI. The results for MDF panels exposed to *C. puteana* also had a DSI lower than 100. Panels modified with peanut shell had the lowest DSI result. These, results suggest that industrially produce MDF panels modified with lignocellulosic scavengers would have a lower susceptibility to *C. versicolor* and *C. puteana.* However, these results should be used as only be used as indicative. Even though the same strains of fungi were used for both basidiomycete decay tests, different generations were used, as the modified MDF panels and commercial MDF panels were not tested at the same time.

The DSI was calculated for the commercial MDF panel and modified MDF panel using solid timber as the reference material (Table 80). The results show that there is a marked difference in the DSI results between the strains used for the commercial MDF panel and modified MDF panels. All the MDF panels had a DSI of less 100, showing that the decay susceptibility to *C. versicolor* was lower than the solid

reference timber. The DSI for commercial panel exposed to *C. versicolor* was only 12.14, whereas modified MDF panels had DSI much greater. Panels modified with 5% peanut shell had the lowest DSI exposed to *C. versicolor* of 30.43. The highest DSI was observed on control MDF panels. This shows that modifying MDF panels with lignocellulosic scavenger reduced the decay susceptibility of the MDF panel to *C. versicolor.*

There is an observed difference in the DSI of modified MDF panels and control MDF panel and commercial MDF panel. This is due to the final moisture content of the control MDF panel which was almost double that of commercial MDF panel. The lower MC of the commercial MDF panel is due to the addition of the other additives such as waxes and the production parameters when upscaling MDF panels. Therefore it is hard to make a direct comparison of the two different DSI results.

Table 80: DSI of commercial and modified MDF panels compared to solid timber

Board	***Coriolus versicolor***	***Coniophora puteana***
Control MDF	79.52	130.93
5% Walnut	74.16	132.69
10% Walnut	34.20	127.49
15% Walnut	50.47	127.63
5% Peanut	30.43	124.96
10% Peanut	37.97	115.16
15% Peanut	31.75	116.76
5% Sunflower	69.63	132.96
10% Sunflower	47.99	127.24
15% Sunflower	58.19	122.62
Commercial MDF	12.14	66.45

MDF panels modified with lignocellulosic scavengers had a DSI at least double that of commercial MDF panels, when exposed to *C. puteana*. Lowest DSI of the modified MDF panel was observed in panels containing 10% peanut shell, 115.16. The highest DSI was observed on panels modified with 5% sunflower seed shell, 132.96. Table 79 showed that physically modified MDF panels had a lower DSI lower than 100, when

compared to the control MDF panel produced for comparisons. Table 80 shows that the DSI when compared to the solid reference timber (pine) the modified panels and control MDF panels are more susceptible to the decay by *C. puteana* than solid pine.

6.6.2 Microbial loading

Table 81 shows the results for the percentage difference in microbial loading of the modified MDF panel and commercial MDF panel at 1 in 10 dilution.

Table 81: Percentage difference of Colony Forming Unit

Board	CFU
5% Walnut shell	40.09
10% Walnut shell	81.43
15% Walnut shell	70.09
5% Peanut shell	51.29
10% Peanut shell	77.28
15% Peanut shell	75.42
5% Sunflower seed shell	52.05
10% Sunflower seed shell	75.50
15% Sunflower seed shell	*

The results show that the panels modified with lignocellulosic scavenger had a lower number of CFU than the commercially produced MDF panel. Panels modified with 10% walnut shell were found to have a CFU count 81% lower than commercial MDF panel. The results for MDF panels modified with 15% sunflower seed shell was not recorded as the CFU count was uncountable. This suggests that the boards produced with lignocellulosic scavenger would reduce the microbial loading on the MDF panel.

7 Conclusions

The purpose of this study was to identify modifications that could be applied to existing construction material generating a multi-functional material that actively and passively absorbs indoor air pollutants, to improve indoor air quality.
This work identified a mechanical modification and a physical modification that was applied to medium density fibreboard (MDF). The mechanical modification was to change the pressure at which woodchip was refined to produce fibre for panel production. The results found that the by changing the refiner pressure, the wood fibres possessed different capabilities of formaldehyde absorption. For optimal formaldehyde absorption in a MDF panel, the fibre should be refined at medium refiner pressure of 8 bar (116 psi). The physical modification was to apply a scavenger to the MDF panel that will actively absorb formaldehyde and VOCs from the atmosphere. Of the nine different scavengers tested for formaldehyde absorption, lignocellulosic scavengers walnut shell, peanut shell and sunflower seed shell were found to be the most effective absorbers of formaldehyde.

Pilot scale MDF panels were produced with 8 bar refined fibre and the lignocellulosic scavengers at three different loading percentages. Despite being exposed to high temperatures and pressures during panel production, the three scavengers were found to remain active within the MDF panel and actively absorb formaldehyde. MDF panels modified with 5% sunflower seed shell was found to absorb the most formaldehyde. However, the average formaldehyde absorption of the modified MDF panels was found to be lower than MDF panel that was only mechanically modified. In terms of VOC absorption, there was found to be change in the scavenger's ability to absorb representative VOCs after MDF panel production. Walnut shell in its raw state was found to absorb the most toluene, limonene and dodecane out of the three scavengers. However, the walnut shell scavenger's ability to absorb VOCs significant reduced when used in the MDF panel. This change requires further investigation to determine why the ability of the shell to absorb VOC is so reduced. In an MDF panel, sunflower seed shell absorbed the most toluene, limonene, dodecane and formaldehyde. Therefore, it can be concluded that the addition of sunflower seed as the physical modification combined with mechanical modification

improves the MDF panel ability to absorbed VOCs from external sources. If produced and used in service, then these panels would act as a sink to formaldehyde emissions and absorb VOCs, improving indoor air quality. MDF panels modified with peanut shell were found to absorb lower amounts of formaldehyde than the control MDF panel. Although, panels modified with peanut shell absorbed more toluene and dodecane than the control MDF panel. This shows that this panel, although relatively poor at absorbing formaldehyde, could still be a useful multifunctional product that actively absorbs aromatic compounds, straight chain and non-polar compounds and therefore, improving indoor air quality.

The primary purpose of an MDF panel is its use in construction and it is important that the modifications do not significantly impair the properties of the MDF panel. Panels modified with lignocellulosic scavenger, at either percentage loading, exhibited no significant change in internal bond strength. However, the effect of the scavenger addition on the MOR and MOE properties of the MDF panel is a different story. Panels modified with sunflower seed shell, were found to have a reduced MOE with increasing percentage loading. Therefore, if produced in service no more than 5% of sunflower seed shell should be added to the MDF panel. The addition of peanut shell reduced the MOE and MOR with increasing percentage loading but only to the same values as the control MDF panel. Therefore, if MDF panels were produced with peanut shell additions, the mechanical properties would not be impaired but at the sacrifice of formaldehyde absorption.

The third part of this investigation was to determine the susceptibility of the modified MDF panels to microbiological activity. Wood-based materials such as MDF are expected to have low levels of susceptibility to basidiomycete decay and mould growth and colonisation. The addition of walnut shell to the MDF panel was found to decrease susceptibility to white rot fungi but not brown rot. The microbial loading on walnut shell modified MDF panels was found to be greater than that of control MDF panels, but the absorption of VOCs was found to reduce mould growth and colonisation. Panels modified with peanut shell reduced susceptibility to white rot fungi and brown rot fungi. However, mould growth was found to be reduced with

the absorption of VOCs. Sunflower seed shell addition to MDF panels was found to increase the panel's susceptibility to mould colonisation and growth, however, the absorption of VOCs by the scavenger reduced this. White rot and brown rot susceptibility was also found to decrease with sunflower seed shell addition.

7.1 Future Work

Mechanical modification

- Evaluate fibre resonated in a blow line, to simulate commercially produced fibres and investigate if this method of fibre resination affects the formaldehyde and VOC absorption capabilities and emissions of the fibre.
- Modify the resin used in production with a protein scavenger and/or replace the formaldehyde based resins with a protein based resin to reduce initial free formaldehyde emissions. This resin could then be used in conjunction with lignocellulosic scavengers and mechanical modifications to produce a better MDF panel that has low emissions and actively absorbs external air pollutants.
- A further investigation in understanding the physical effects of refining wood fibre at different pressures on the surface area of the fibres, pore structure and porosity when loose before being pressed into a MDF panel.
- Study the effects of long press times and different press temperatures on refined fibre and the influence the change in schedule has on a panel's capabilities of formaldehyde absorption.

Physical modification

- Investigate the effects of varying relative humidity on the modified MDF panels' ability to absorb VOCs. This study has shown that the lignocellulosic scavengers can absorb formaldehyde which is a polar compound. If the MDF panel is used in service, the relative humidity is not constant, such as in bathrooms. At higher RH, VOC absorption may be reduced as polar VOCs compete with water, also polar, with absorption sites within the MDF panel.
- Determine the phenolic content of the scavengers and identify individual compounds that could be isolated for formaldehyde scavenging. This

phenolic or other compound could be used to chemically modify a resin to scavenge free formaldehyde and reduce panel emissions.

- Investigate if increasing the percentage loading of sunflower seed shell would increase the formaldehyde absorption capabilities of the MDF panel.
- Concerning the walnut shell and sunflower seed scavengers, longer DVS formaldehyde sorption cycles should be run to determine the working life-span of these scavengers and if they become permanently saturated with formaldehyde.
- Deeper investigation into VOCs reacting with the surface chemistry of the modified MDF panel and secondary VOCs are emitted would be important. This data could be combined with mVOC analysis of moulds and fungi growing on construction materials to identify any decay present on walls panels that are hard to access, such as stud wall cavities.
- Further investigation is required into how peanut shell and walnut shell could be added to the MDF panel without impairing the strength properties. This could be achieved by simply using smaller sized pieces of the scavenger in the MDF panel, or if their structure is better suited to be used in a different wood-based panel such as particle board.

Microbial investigation

- Investigate the effects of drying (material's moisture desorption) properties and the effects on colonising moulds and fungal species ability to rejuvenate and grow.
- Carll and Highley, (1999) highlights that competition of mould species can be a restricting factor to species of decay fungi. Further investigation could be conducted to better simulate microbial competition between moulds and decay fungi in real-life scenarios and see if/how the modifications to MDF panels influence the amount and outcome of surface competition.

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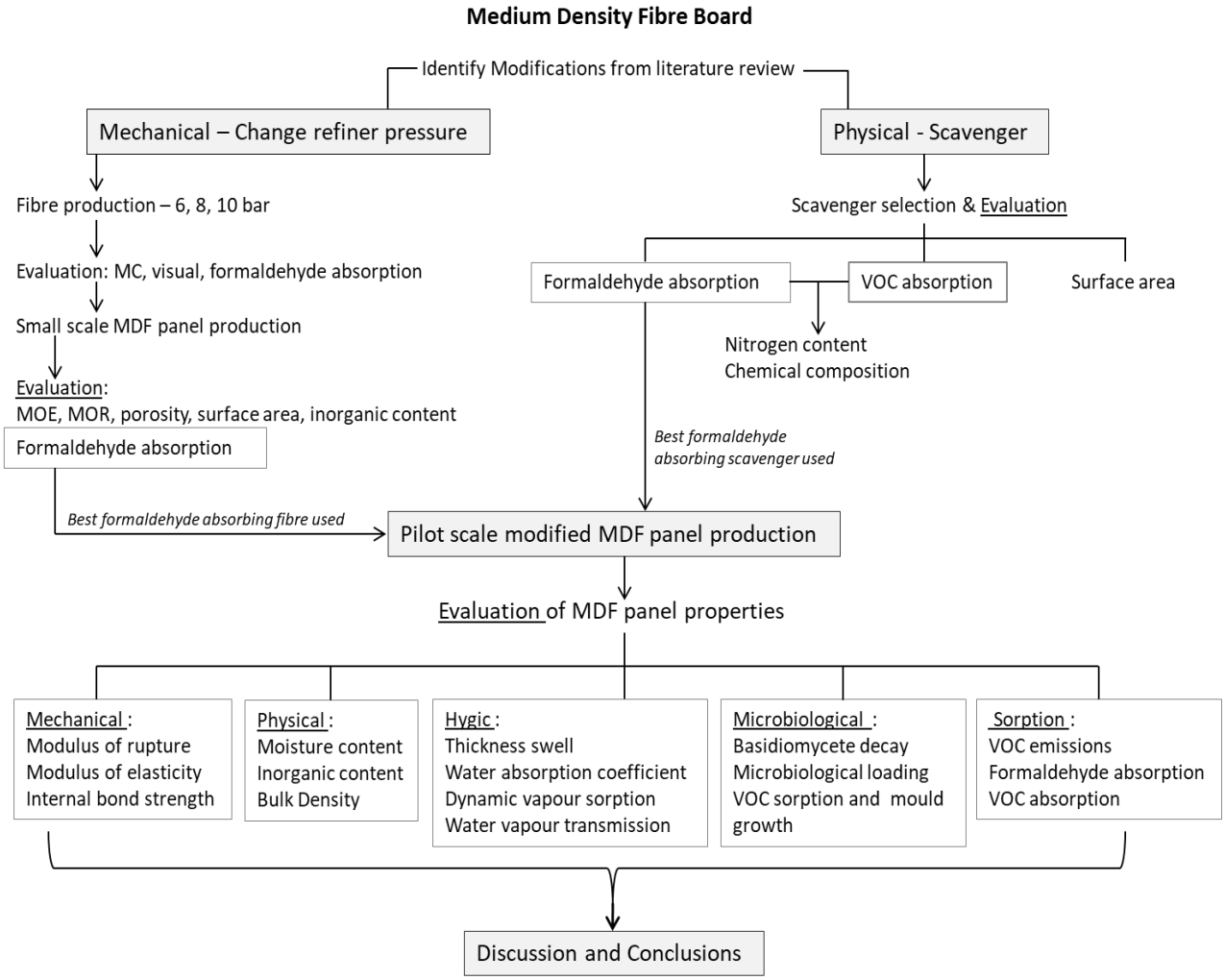
Appendices

Appendix A: Flow chart of thesis plan



Appendix B: Source of experimental scavengers

- The walnut shell and almond shell were obtained from Just Ingredients http://www.justingredients.co.uk/
- Pistachio shells were obtained from Amazon and de-shelled by hand (https://www.amazon.co.uk/d/Pistachios/Jalpur-Salted-Pistachio-1kg/B00B69OQXQ/ref=sr_1_fkmr0_3_a_it?ie=UTF8&qid=1486636883&sr=8-3-fkmr0&keywords=maltbys+stores+pistachio+shell)
- Peanut shells were obtained from Amazon and de-shelled by hand (https://www.amazon.co.uk/11-3KG-MALTBYS-STORES-PEANUTS-SHELLS/dp/B00BJ667L0/ref=sr_1_1?ie=UTF8&qid=1486636262&sr=8-1&keywords=maltbys+stores+peanut+in+shell)
- Coconut husk fibre was obtained from whole coconut bought at ASDA stores, Bangor.
- Sunflower seed shells were obtained from ASDA stores, Bangor and deshelled
- Paper sludge was sourced through ECO-SEE project
- Wool was sourced through ECO-SEE project
- Nanoclay was sourced through ECO-SEE project
- Wood fibre used was derived from the work conducted in section 3.2.2

Appendix C: Modified MDF panels

Table 82: Description of MDF panels

Board	Press schedule	Description					Resin (%)	Resin (g)	Resinated Fibre MC (%)
		Scavenger	Loading (%)	Scavenger mass (kg)	Board Density (kg m^{-3})	Wood fibre mass (kg) +10%			
(31) Control	12MDF180.reg	0	0	0	750	9.1	12 UF	2069	10.2
32		Peanut	5	0.5		8.9			8.86
33			10	0.9		8.4			7.81
34			15	1.4		7.9			7.96
35		Walnut	5	0.5		8.9			7.87
36			10	0.9		8.4			7.59
37			15	1.4		7.9			7.55
38		Sunflower	5	0.5		8.9			8.35
39			10	0.9		8.4			9.29
40			15	1.4		7.9			8.96

Appendix D: Cutting pattern for 1m² MDF panels

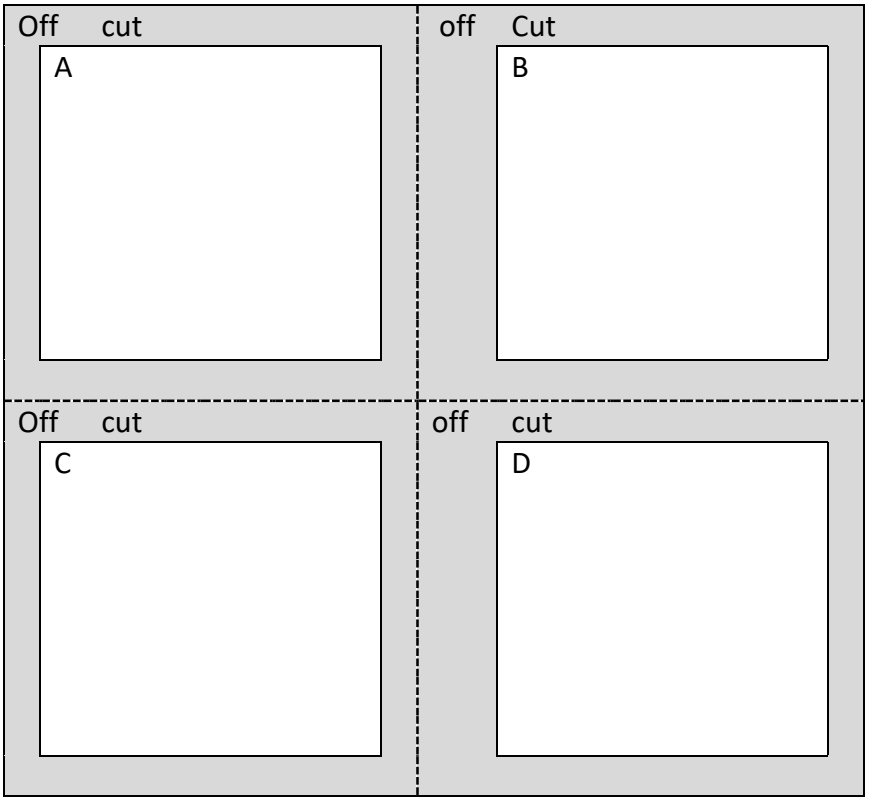


Figure 113: 1m MDF panel cutting pattern

Key	Purpose
*	Centre corner of MDF panel
MOE MOR	Modulus of rupture and elasticity
IB	Internal bond strength
TS	Thickness swell
D	Density profile
WA	Water absorption coefficient
VT	Water vapour transmission
F	Formaldehyde
A	Ash Content
P	Porosity and surface area
DVS	Moisture Isotherm
VOC	VOC adsorption (Micro-chamber)
E	Emissions test (GC-MS)
M	Microbiological Tests (Basidiomycete testing and Dilution plating)

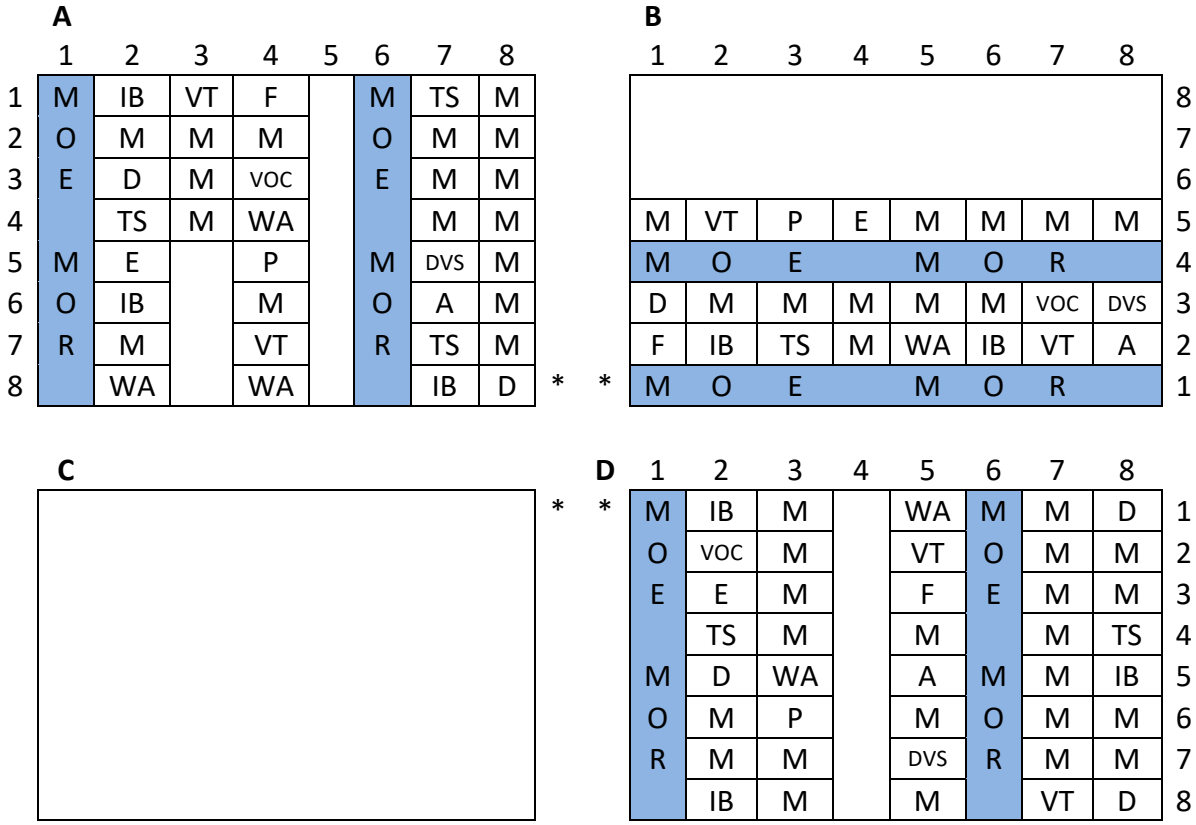


Figure 114: Cutting pattern for experimental samples

Appendix E: Chromatographs of modified MDF panels

Figure 115: GC-MS chromatogram of blank (empty) vessel

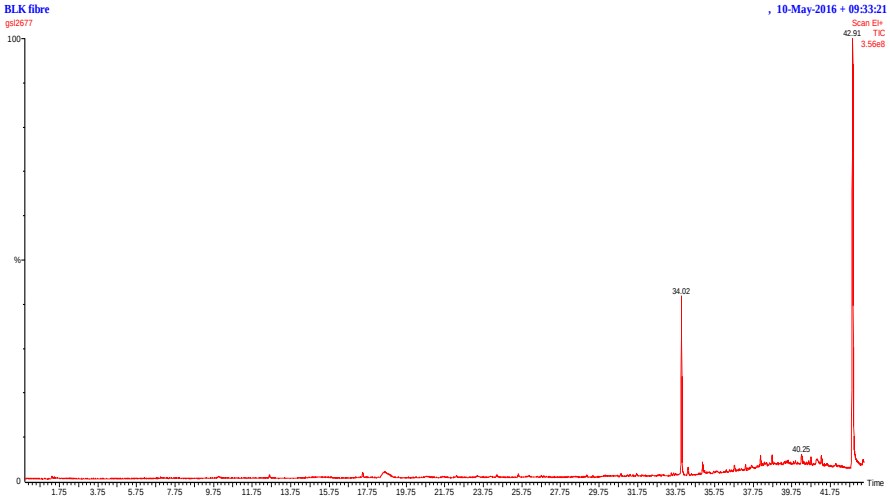


Figure 116: GC-MS chromatogram of MDF fibre

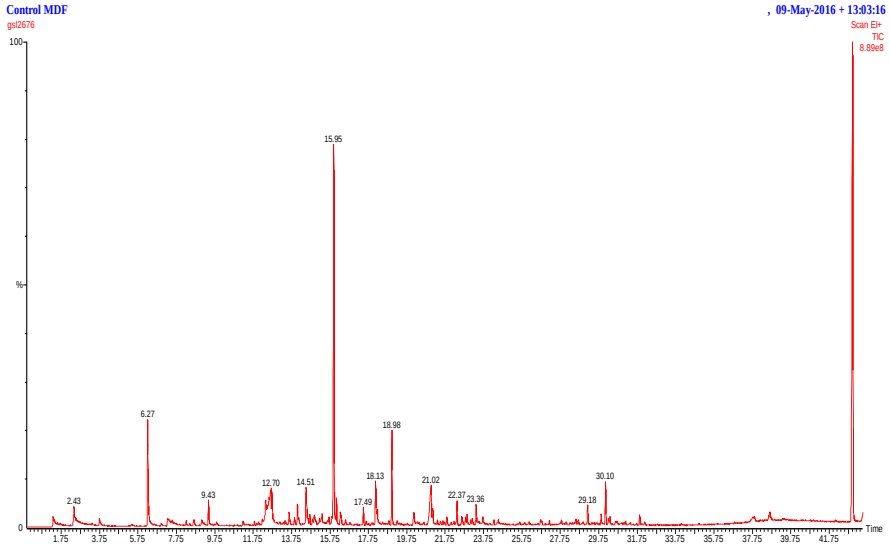


Figure 117: GC-MS chromatogram of control MDF board

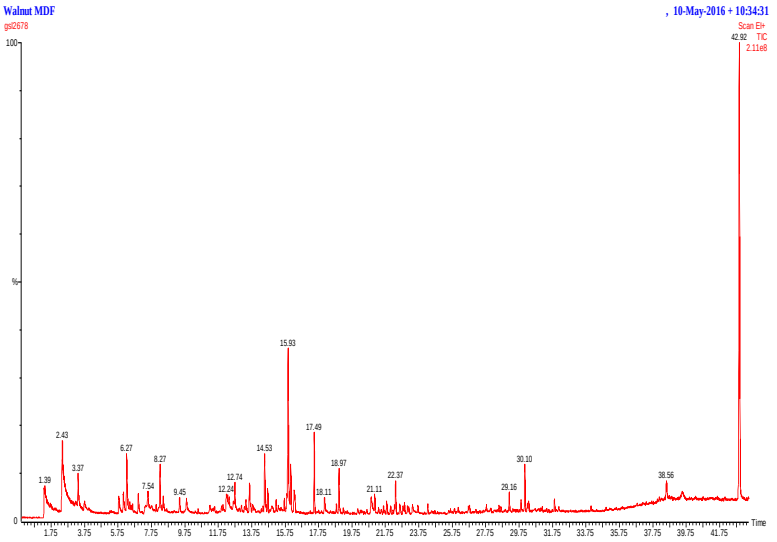


Figure 118: GC-MS chromatogram of walnut shell modified MDF board

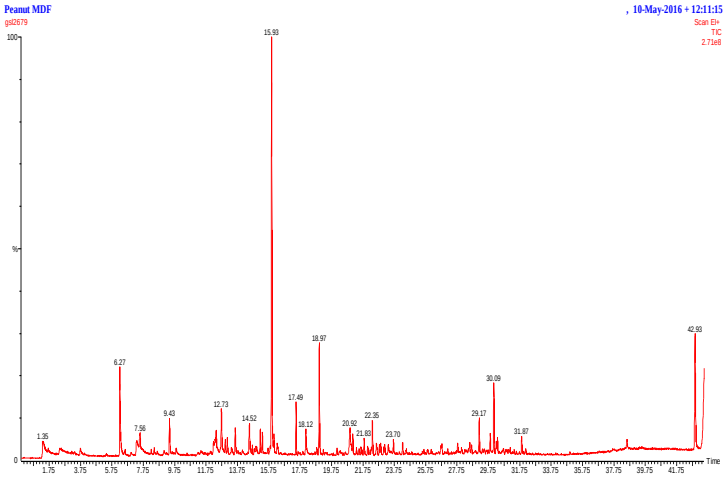


Figure 119: GC-MS chromatogram of peanut shell modified MDF board

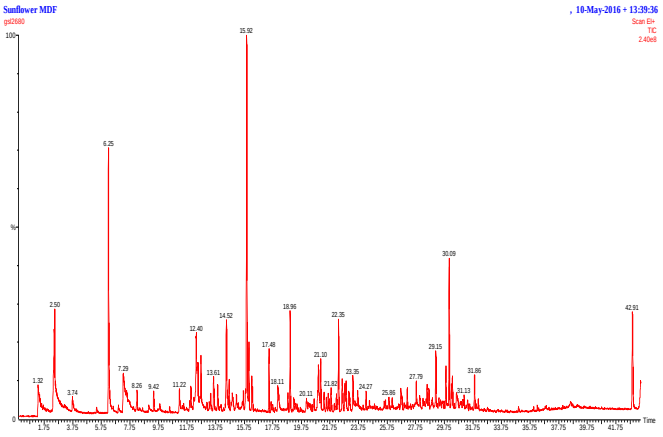
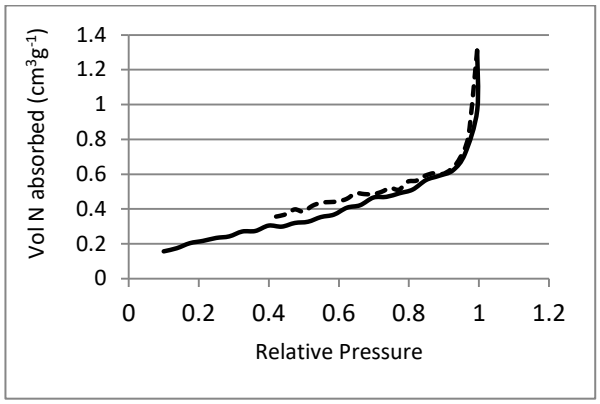
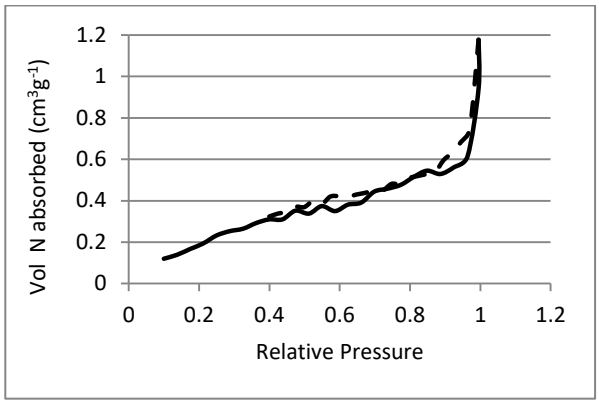


Figure 120: GC-MS chromatogram of sunflower shell modified MDF board

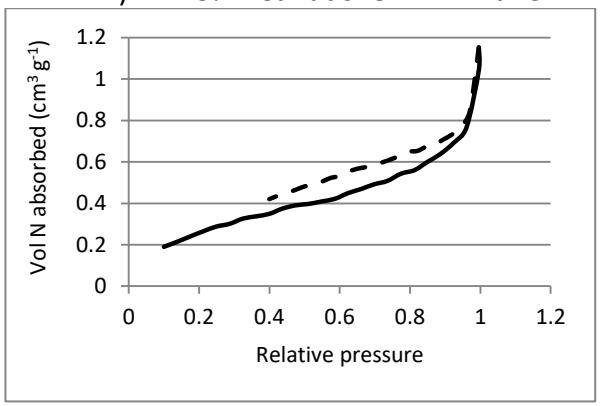
Appendix F. Porosity Data of modified MDF panels



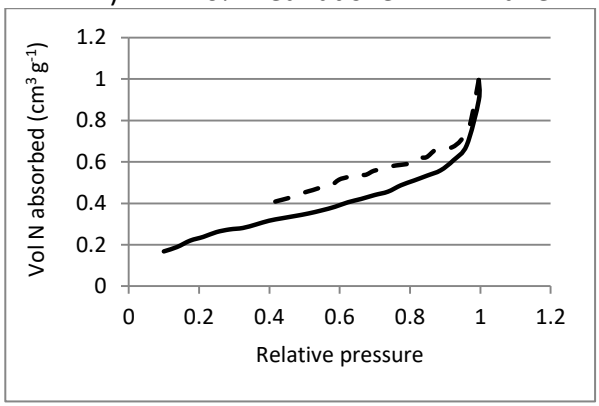
A) 5% Peanut shell MDF Panel



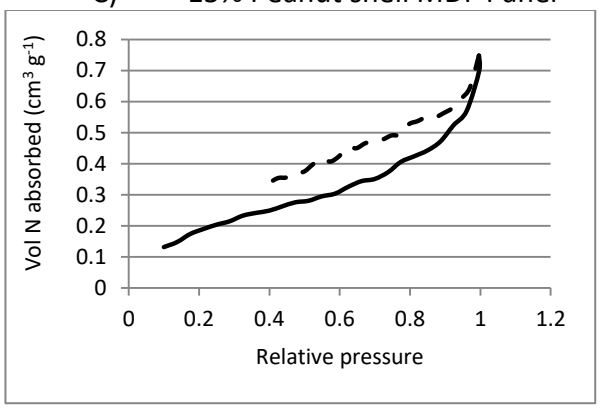
B) 10% Peanut shell MDF Panel



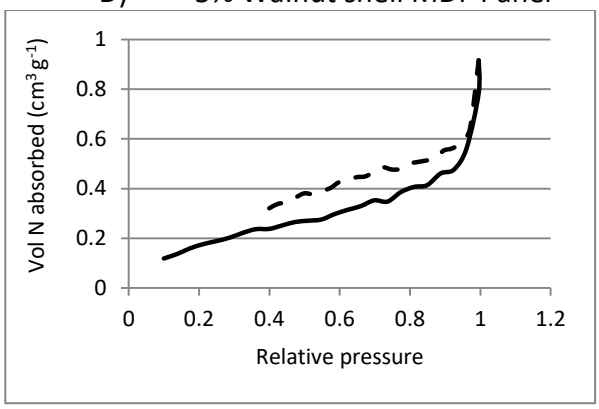
C) 15% Peanut shell MDF Panel



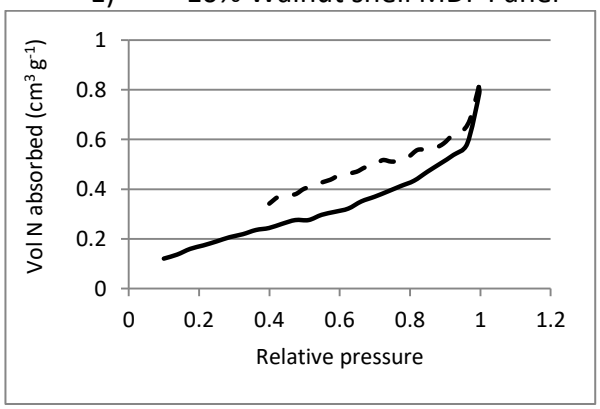
D) 5% Walnut shell MDF Panel



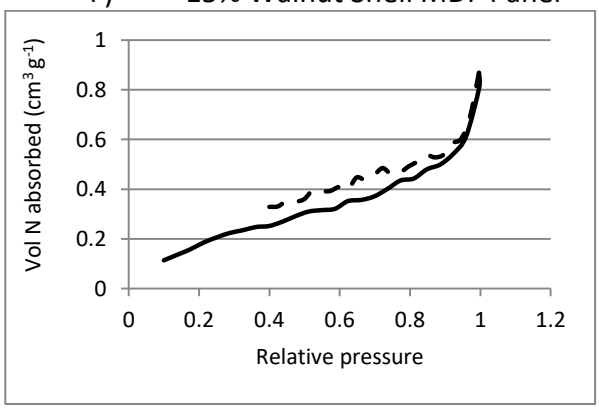
E) 10% Walnut shell MDF Panel



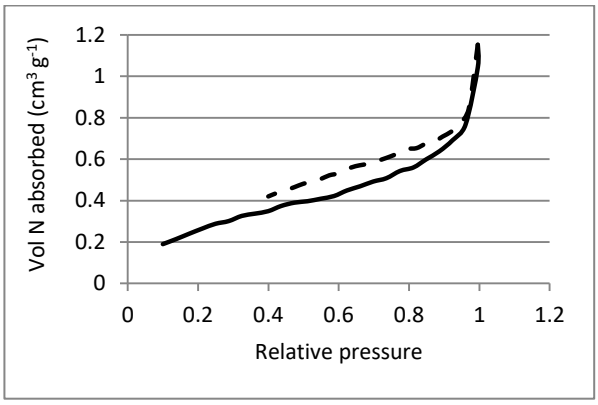
F) 15% Walnut Shell MDF Panel



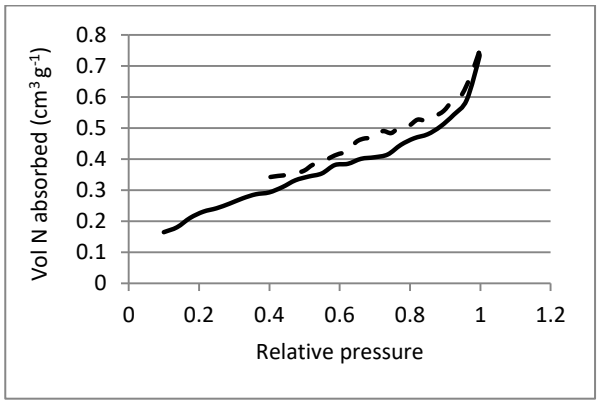
G) 5% Sunflower shell MDF Panel



H) 10% Sunflower shell MDF Panel

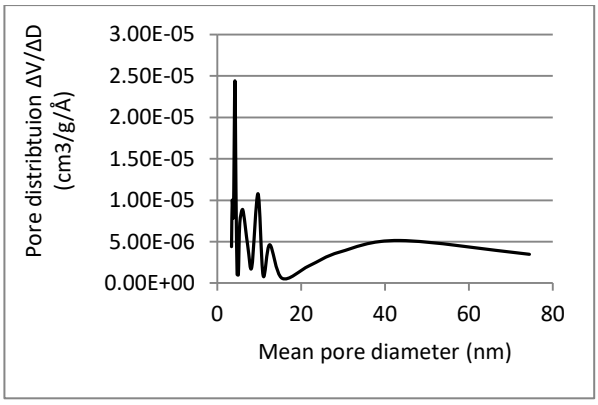


I) 15% Sunflower shell MDF Panel

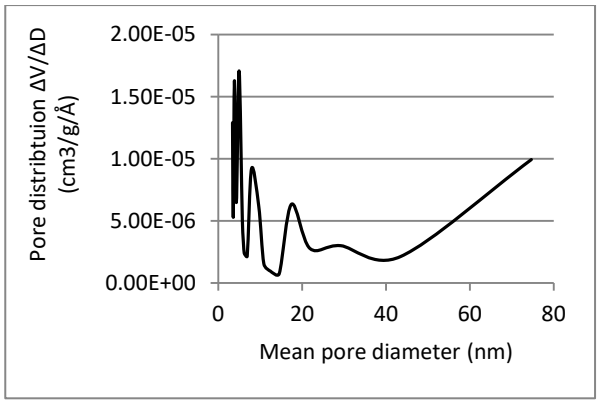


J) Control MDF Panel

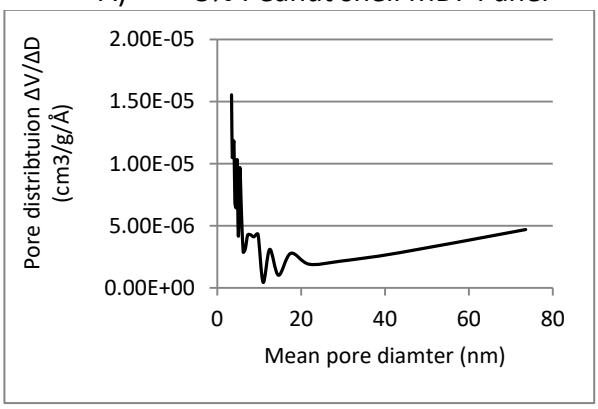
Figure 121: Porosity isotherm of the modified MDF panels and 8 Bar control MDF panel



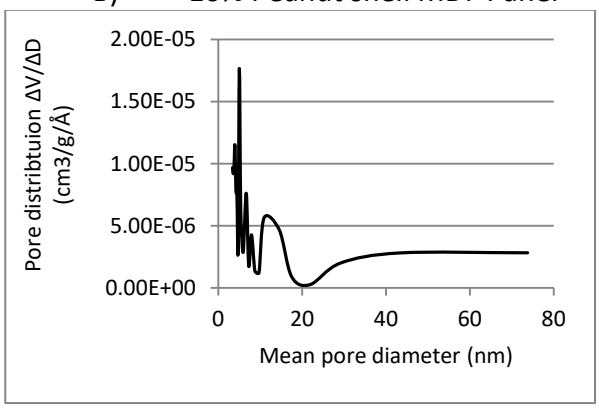
A) 5% Peanut shell MDF Panel



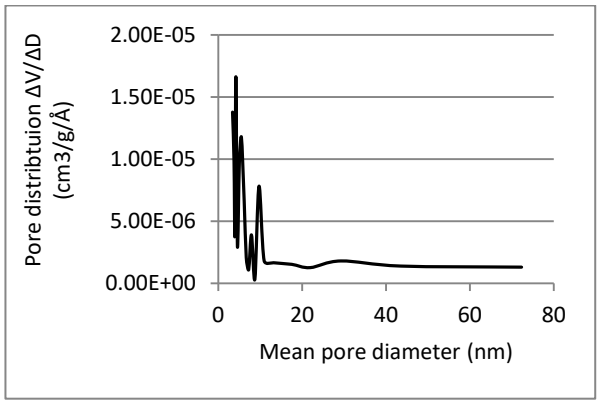
B) 10% Peanut shell MDF Panel



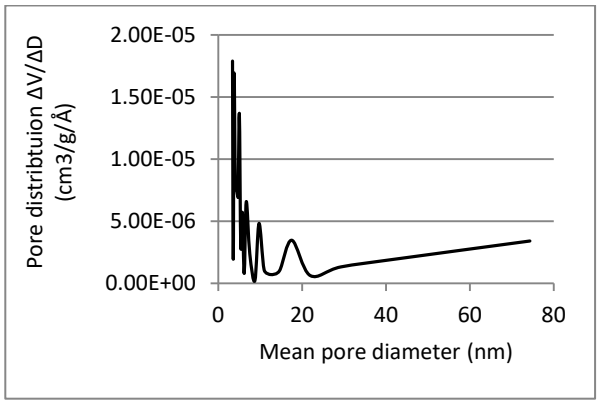
C) 15% Peanut shell MDF Panel



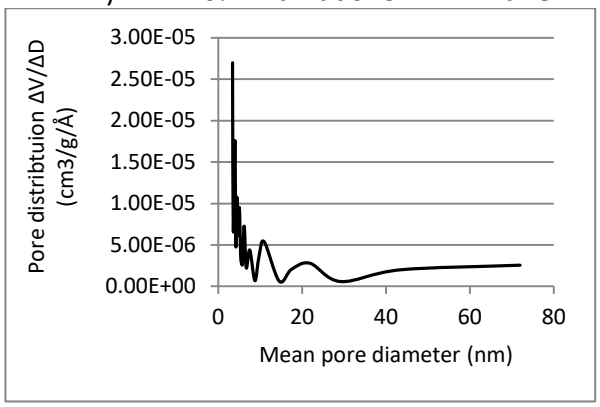
D) 5% Walnut shell MDF Panel



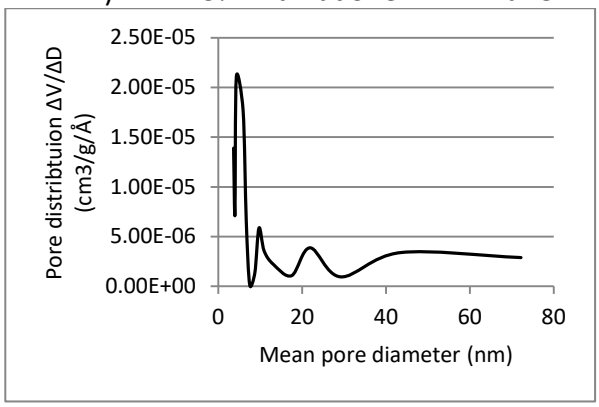
E) 10% Walnut shell MDF Panel



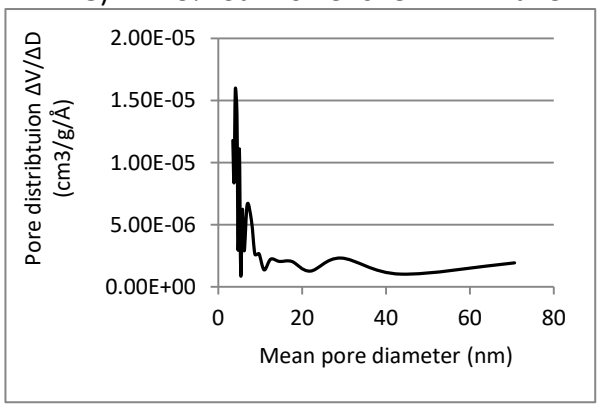
F) 15% Walnut Shell MDF Panel



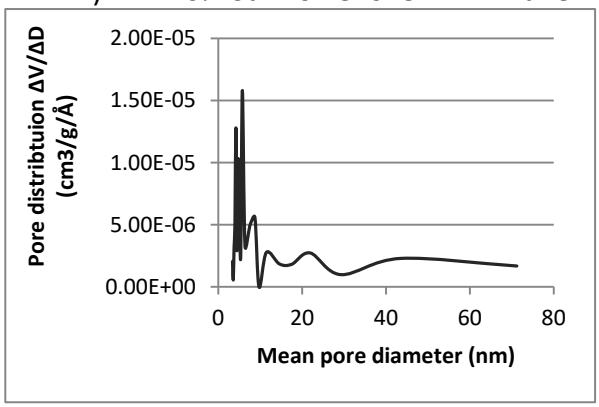
G) 5% Sunflower shell MDF Panel



H) 10% Sunflower shell MDF Panel

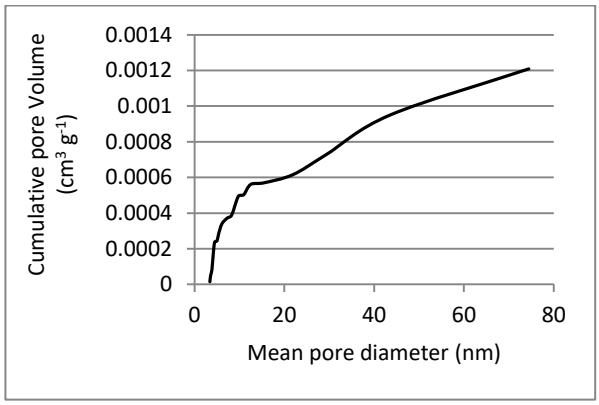


I) 15% Sunflower shell MDF Panel

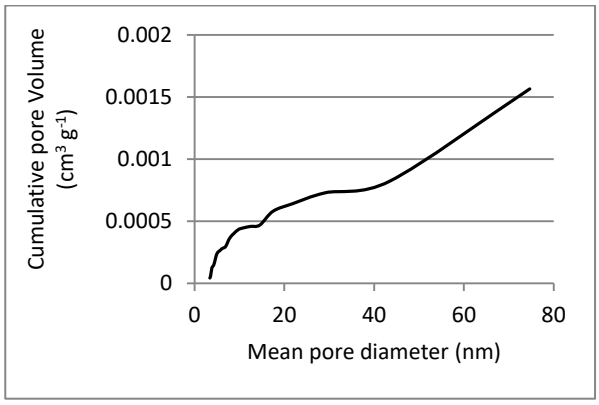


J) Control MDF Panel

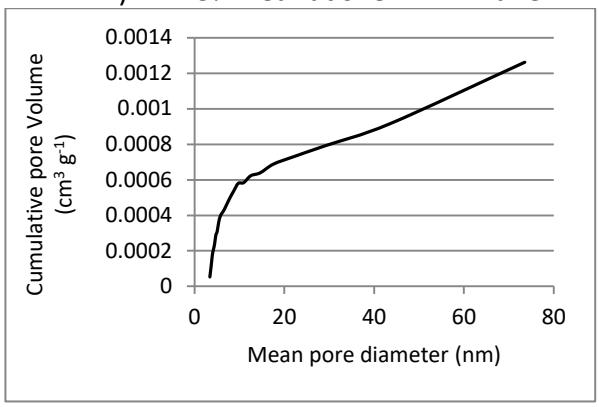
Figure 122: Pore size distribution of the modified MDF panels and 8 Bar control MDF panel



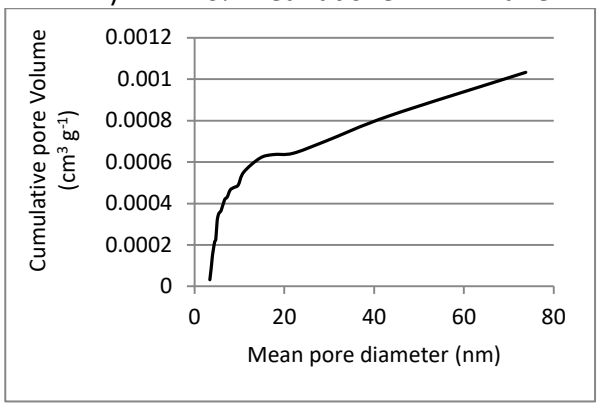
A) 5% Peanut shell MDF Panel



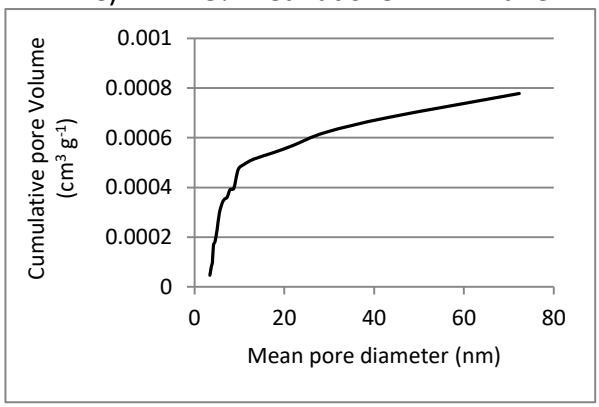
B) 10% Peanut shell MDF Panel



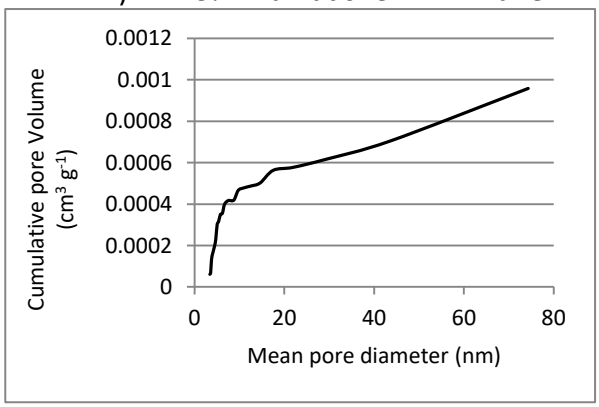
C) 15% Peanut shell MDF Panel



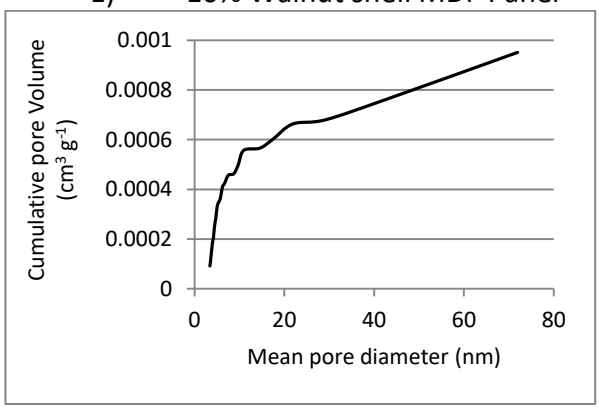
D) 5% Walnut shell MDF Panel



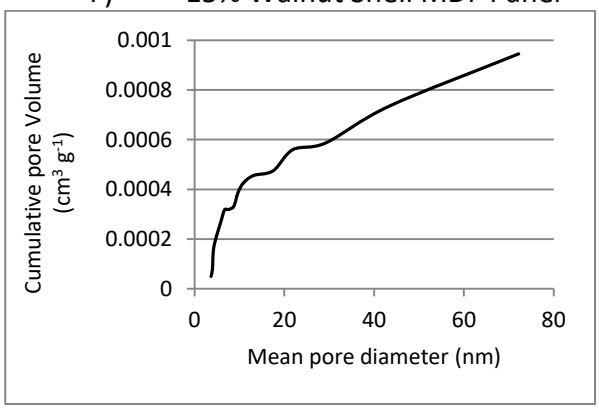
E) 10% Walnut shell MDF Panel



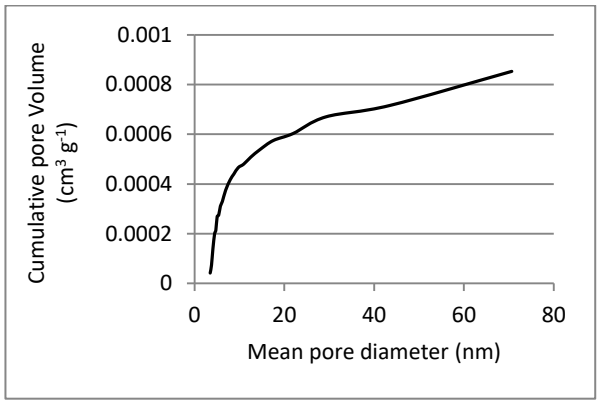
F) 15% Walnut Shell MDF Panel



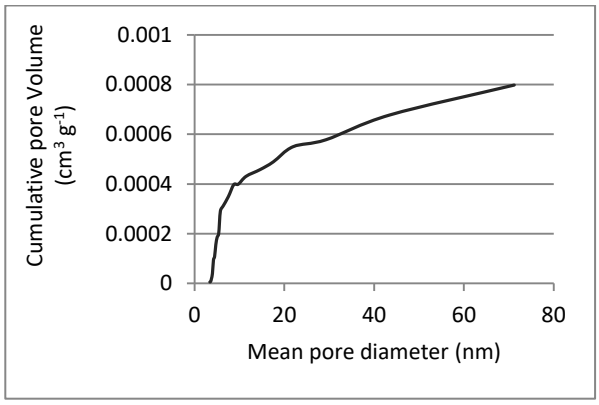
G) 5% Sunflower shell MDF Panel



H) 10% Sunflower shell MDF Panel



I) 15% Sunflower shell MDF Panel



J) Control MDF Panel

Figure 123: Cumulative pore volume of the modified MDF panels and 8 Bar control MDF panel

Appendix G: Published Articles

Journal Articles

1. Stefanowski, B.K., Curling, S., F., Ormondroyd, G.A., 2017. Assessment of lignocellulosic nut wastes as an absorbent for gaseous formaldehyde. Ind. Crops Prod. 98, 25–28.
2. Stefanowski, B. K, Curling, S., F., Ormondroyd, G.A., 2016. Evaluating mould colonisation and growth on MDF panels modified to sequester volatile organic compounds: International Wood Products Journal: Vol 7, No 4. Int. Wood Prod. J. 7, 188–194.
3. Stefanowski, B. K., Curling, S.F., Ormondroyd, G.A., 2016. A rapid screening method to determine the susceptibility of bio-based construction and insulation products to mould growth. Int. Biodeterior. Biodegrad. 116, 124–132. doi:10.1016/j.ibiod.2016.10.025
4. da Silva, C.F., Stefanowski, B., Maskell, D., Ormondroyd, G., Ansell, M.P., Dengel, A., Ball, R.J., 2017. Improvement of indoor air quality by MDF panels containing walnut shells. Build. Environ. doi:10.1016/j.buildenv.2017.07.015
5. Skinner, C., Stefanowski, B.K., Heathcote, D., Charlton, A., Ormondroyd, G.A., 2016. Life cycle assessment of pilot-scale wood fibre production using mechanical disc refining at different pressures. Int. Wood Prod. J. 7, 149–155. doi:10.1080/20426445.2016.1200825
6. Ormondroyd, G.A., Källbom, S.K., Curling, S.F., Stefanowski, B.K., Segerholm, B.K., Wålinder, M.E.P., Jones, D., 2016. Water sorption, surface structure and surface energy characteristics of wood composite fibres refined at different pressures. Wood Mater. Sci. Eng. 0, 1–8. doi:10.1080/17480272.2016.1150343

In press;

1. Ormondroyd, G.A.[1,2]* Stefanowski, B.K.[1] & Curling, S.F (2017) Variation in Formaldehyde absorption by wood fibre refined at different pressures,

Published Book Chapters

1. Stefanowski, B.K. and Ormondroyd G.A, (2015) *Wood Composites – Chapter 5: Fibreboards and their applications Elsevier and Woodhead Publishing Series in Composites Science and Engineering* Edited by Martin P. Ansell, 2015
2. Stefanowski, B.K., Curling, S.F. and Ormondroyd G.A (2017) *Performance of Biobased building materials - Chapter 6 Performance of Buildings,* Woodhead Publishing Series in Civil and Structural Engineering. Edited by Dennis Jones and Christian Brischke