Moisture sorption properties and fungal degradation of torrefied wood in storage

Maija Kymäläinen

Department of Forest Sciences
Faculty of Agriculture and Forestry
University of Helsinki

Academic dissertation

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Author: Maija Kymäläinen

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Thesis supervisors:
Prof. Marketta Sipi
Department of Forest Sciences, University of Helsinki, Finland

Dr.Mikko Havimo
Department of Forest Sciences, University of Helsinki, Finland

Prof. Lauri Rautkari
Department of Forest products Technology, Aalto University, Finland

Pre-examiners:
Prof. Nasko Terziev
Department of Forest Products, Swedish University of Agricultural Sciences
Dr. Erik Larnøy
Norwegian Institute of Bioeconomy Research (NIBIO), Norway

Opponent:
Prof. Holger Militz
Department of Wood Biology and Wood Products, Georg-August-Universität
Göttingen, Germany

ABSTRACT

Replacing fossil fuels with renewable energy sources is an increasingly important research subject in order to combat the global climate change. Wood is a well utilised source of energy that has some problematic characteristics common to all lignocellulosic biomass. Moisture affects the supply chain of wood fuels negatively by complicating logistics and combustion. Hygroscopicity of stored wood leads to fungal deterioration and consequent losses in heating value. The problem has been addressed by reducing the hygroscopicity through the thermal pre-treatment process of torrefaction. The torrefied material is said to be resistant to fungal degradation and subsequent dry matter losses. However, only few studies exist, and the material's performance in storage has been pointed out as an important research area. This thesis aims to provide much needed answers related to the storage properties of torrefied wood and charcoal, most importantly the effect of moisture.

This thesis is made up of four studies, in which the sorption properties and fungal degradation of torrefied spruce and birch, as well as charcoal produced from the same feedstock, were investigated. In one part study, torrefied and steam exploded pellets were compared with the undensified material. The material adsorbed only minor amounts of water vapour, and the hydroxyl group accessibility and particle size were reduced. Although the capillary absorption became slower, the capacity for water uptake increased. This led to high moisture contents during the storage trials. It was also shown that the material is degraded by fungi. The degradation was slow, but dry matter losses were recorded in laboratory conditions. Furthermore, the fungal activity increased the material's moisture content. The torrefied material hosted abundant fungal flora following outside storage trials, and many of the identified genera were known allergens. It was shown that torrefied pellets do not tolerate contact with water and should be stored covered.

Keywords: Biological degradation, Solid biofuels, Thermal pre-treatment, Water, Wood.

PREFACE

The birth of this thesis was a bit of an accident. I finished my master's degree in 2011 and after a few months of nothing worth mentioning landed a spot in PaPSaT – the International Doctoral Programme in Bioproducts Technology. I have to say it was a life changing opportunity! I've always had the desire to learn, so being able to focus on research on the very up-to-date subject of torrefaction was something to celebrate. So, first and foremost, I have to thank my supervisors Mikko Havimo and Marketta Sipi for helping me start out in PaPSaT, to begin my journey as a PhD candidate, and especially to Mikko for introducing me into the exciting world of torrefaction!

I owe a lot to Lauri Rautkari for stepping in when I needed the most help. It was interesting, and slightly scary to enter the world of engineers, but I think it was worth it. Also, a big hand to the other good people at Aalto, who helped me out with my experiments. The financial support of PaPSaT, the Department of Forest Sciences, Niemi-säätiö, Walter Ahlströmin säätiö and AGFOREE is much appreciated! And now that I'm almost done, I'm grateful to the pre-examiners Erik Larnøy and Nasko Terziev, who gave their time to help substantially improve this thesis.

I wish to express my sincere gratitude to Juha Solio and the rest of the personnel in Anjala for help and though-provoking discussions. Your enthusiasm in all things related to bioenergy is truly inspiring. A very warm thank you to my co-writers, especially Miia, who introduced me to the fascinating world of fungal DNA. Seriously, who knew pipetting could be so much fun? And of course Juha Rikala, for always being right next door to read my texts and replying to my silly questions. I'd also like to thank Marjut Wallner for always being positive and helping me out with whatever problems I had, and Pekka Oivanen for providing his expertise related to fungi – I would not have got far without your tips and advice! I also want to thank the people at Koetila for the research material, as well as Jussi Kukkonen and Kiira Happonen at HelEn for sharing their expertise of the Real World of Biofuels – and of course for showering me with pellets! A warm hug to Raimo Alén for being the nice guy, writing me letters to ask how I was doing, sharing interesting research, and helping me get much needed contacts.

Thank you, Titta, for going through the PhD process before me, it was very educational to watch! And Minna, for countless lunch hour conversations, mostly unrelated to work which were blessings in the middle of stressful and tiresome days. Also to all the other people in the coffee room, whom I had a chance to discuss with about all the matters between here and there, you made my days!

Mum, Dad, yes it's true. You have a doctor in the family! And Matti, Sara, Mikko, Sanni, Mimmi… And all the other people who have made my life better by belonging to it! I could have not done it – well, anything – without you!

And, finally to Janne for listening to my ranting, complaining, excitement, sadness, anger, happiness, and all the other feelings that went by during these four years, even though you always remembered to emphasize how you had no idea what I was talking about. It doesn't matter; you still listened! And of course to Reino, who made a lot of miserable days into wonderfully funny ones!

Helsinki, October 2015

Maija Kymäläinen

LIST OF ORIGINAL ARTICLES

The present thesis is based on the following original articles, which will be referred to by Roman numerals in the text (I–IV). The articles are reprinted with the kind permission from the publishers.

I.   Kymäläinen M., Havimo M., Louhelainen J. (2014). Sorption properties of torrefied wood and charcoal. Wood Material Science and Engineering 9(3): 170–178.
http://dx.doi.org/10.1080/17480272.2014.916348

II.   Kymäläinen M., Havimo M., Keriö S., Kemell M., Solio J. (2014). Biological degradation of torrefied wood and charcoal. Biomass & Bioenergy 71: 170–177. http://dx.doi.org/10.1016/j.biombioe.2014.10.009

III.   Kymäläinen M., Mäkelä M.R., Hildén K., Kukkonen J. (2015). Fungal colonisation and moisture uptake of torrefied wood, charcoal, and thermally treated pellets during storage. European Journal of Wood and Wood Products.
http://dx.doi.org/10.1007/s00107-015-0950-9

IV.   Kymäläinen M., Rautkari L., Hill, C.A.S. (2015). Sorption behaviour of torrefied wood and charcoal determined by dynamic vapour sorption. Journal of Materials Science 50: 7673–7680.
http://dx.doi.org/10.1007/s10853-015-9332-2
Erratum to study IV (2015):
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AUTHOR'S CONTRIBUTION

Maija Kymäläinen designed the experimental setup in all the papers (in co-operation with Mikko Havimo (I, II) and Lauri Rautkari (IV)). She was responsible for realising the experiments (in co-operation with Susanna Keriö and Marianna Kemell (II), Miia Mäkelä and Kristiina Hildén (III), and Lauri Rautkari (IV)). Maija Kymäläinen was the main author of all the papers.

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ABBREVIATIONS

ATR FT-IR = Attenuated Total Reflectance Fourier Transform Infrared spectroscopy
BET = Brunauer-Emmett-Teller- method
BLASTn = Basic Local Alignment Search Tool (nucleotide)
BNM = Benomyl-Novobiosin-Malt agar
C/N = Carbon/Nitrogen
DB = Dry Basis
EMC = Equilibrium Moisture Content
FE-SEM = Field Emission Scanning Electron Microscope
FSP = Fibre Saturation Point
GHG = Greenhouse Gas
ITS-PCR = Internal Transcribed Spacer – Polymerase Chain Reaction
MC = Moisture Content
MEA = Malt Extract agar
MY = Mass Yield
NCBI = National Center for Biotechnology Information
OH = Hydroxyl group
RH = Relative Humidity
TGY = Tryptone-Glucose-Yeast agar
WB = Wet Basis

1 INTRODUCTION

1.1 The use of biomass for energy

In order to slow the rate of global warming and to meet the goals set by the European Union, there is a need to increase the use of renewable energy sources, increase energy efficiency, and reduce greenhouse gas (GHG) emissions. It has been estimated that by 2040 the global energy demand would have increased by nearly 40% and, during the same year, the internationally agreed limit for temperature increase (maximum 2 °C) will be surpassed (IEA 2014a). There is no question that rapid solutions are needed. The simplest solution would be to cut down emissions from the energy sector, which was globally the largest source of GHG's in 2010, producing more than 2/3 of total emissions, of which about 90% was carbon dioxide (IEA 2013). Increasing the share of sustainable renewable energy sources would reduce the total CO_2 emissions, but it also has other advantages. Biomass production and consumption is often local, which is beneficial in terms of employment as well as energy and national security, as dependency on imported fossil fuels can be reduced. Biomass also contributes to a major carbon sink, for example in 1990–2005 the European forests absorbed 10% of the region's CO_2 emissions. This sink could be further increased by active forest management (Bellassen and Luyssaert 2014).

Biomass is essentially solar energy converted into solid form. Carbon dioxide and water turn into carbonaceous compounds in photosynthesis. Bioenergy is often stated to be carbon neutral, as after harvest new biomass will replace the old and absorb the CO_2 released in combustion, creating a closed circle. However, in the short term, harvesting and combusting biomass produces cumulative emissions, as the released CO_2 takes time to reabsorb into the renewing vegetation. The benefits are nonetheless evident, as for example reported by Repo et al. (2012) where after only 20 years the emissions from using Finnish branch bioenergy were up to 57% smaller compared to those emitted by fossil fuels. Naturally, the growth site, age and size of removed biomass, as well as the management choices have an effect on the overall reduction (McKechnie et al. 2011, Repo et al. 2012). Maximising the sink with diligent forest management practices makes biomass a far more sustainable option than fossil fuels.

When producing biomass for energy, woody biomass has several advantages over agricultural crops. Growing energy crops easily conflicts with food production, whether or not edible crops are grown, as they require extensive land areas. According to Zah et al. (2007), the largest percentage of GHG emissions in biofuel production originates from agricultural cultivation; other environmental impacts include the use of machinery and fertilizers, nutrient leaching, loss of biodiversity and soil acidification. In short rotation forestry the use of inorganic fertilizers accounts for a large fraction of the energy input as well, but it is possible to utilize waste streams to improve the system (Heller et al. 2003). In conventional forestry the use of fertilizers is very low and the ash remaining after processing and combustion of forest biomass can be recycled for that purpose (Huotari 2012). Also, trees do not require fertile agricultural lands to be productive.

Using wood for energy has a very long history and still over 2 billion people depend on wood energy for cooking and/or heating in their daily lives (FAO 2012). This kind of traditional utilisation accounts for 1/3 of global consumption of renewable energy sources and takes place mainly in the developing countries (FAO 2012). Wood can be used as is, or it can be converted into charcoal with larger energy content and easier handling properties.

The downside of charcoal production is its inefficiency. It is considered a major source of environmental degradation in tropical rural areas (Antal and Grønli 2003; Kammen and Lew 2005). Adding to the traditional utilisation, the use of wood energy has increased also in the developed countries. In 2014, around 90 million people in Europe and North America used wood – firewood, chips and pellets – as the main source of domestic heating (FAO 2014). In Finland, wood constitutes 79% of the total consumption of renewable energy sources (Metsätilastollinen vuosikirja 2014). During the last few years the growth of Finnish forests has been about 33 million m^3 higher than the removals (Metsätilastollinen vuosikirja 2014) and the use of forest fuels could therefore be increased easily. However, certain aspects hinder the use of wood fuel – most importantly the fluctuation of coal prices – but wood fuels also present certain problems associated with their efficient use. The harvesting, storage, transport, and combustion of wood suffer from problems inherent to biomass fuels: low heating value, low bulk density, heterogeneity, high moisture content, and substances that may be harmful for the machinery and combustion equipment. Certain steps can be taken to reduce the effect of unfavourable properties. The biomass can be pre-treated after harvesting, which can lead to savings throughout the logistic chain and improve the performance of the fuel compared to fossil fuels. One such pre-treatment option is torrefaction, or mild pyrolysis, which has been generating interest due to the beneficial properties of the end product, such as low moisture content and increased heating value. Especially the hydrophobicity is considered a very useful characteristic, and therefore the torrefaction of wood could present an interesting option to improve wood fuel properties especially in terms of transport, storage, and combustion.

1.2 Wood as a raw material

1.2.1 The components of wood

Wood is composed of carbon, oxygen and hydrogen, which together account for approximately 95% of its dry mass (Nurmi 1997). About 50% is carbon, usually more than 40% oxygen, 6% hydrogen, and the rest is made up of nitrogen and mineral elements (Hakkila 1989; Ragland et al. 1991). The amount of ash in temperate and boreal zone woods is generally below 0.5% but the bark and foliage contain much more inorganic elements. The elements are found as cellulose, lignin and the hemicelluloses. In addition, there are some non-structural carbohydrates and low molecular weight extractives. In temperate and boreal woods the amount of extractives is quite small (less than 5–10% of total dry weight) (Hakkila 1989), but they have an effect on the physical properties of wood (Siau 1995).

The structure of wood cells is layered. The middle lamellae separate the cells from each other as well as bind them together. The cells have primary walls and three-layered secondary walls. The walls enclose a cavity, the lumen, through which the transportation of fluids takes place. The fluids move from one cell to another through pit pairs.

Wood is a porous but not very permeable material. As a tree grows, earlywood (springwood) and latewood (summerwood) cells are formed, of which earlywood is more permeable due to its thin cell walls and large inner cavities. As the transition to latewood takes place, the cell walls become relatively thicker and the cavities smaller. The heartwood of a tree is less permeable than the outer sapwood with its active conduction of nutrients and

water. Wood material is also anisotropic in three directions: radial, tangential and longitudinal. This influences the physical properties such as permeability, thermal conductivity and diffusion of moisture (Siau 1995). In certain parts such as in leaning stems and branches, the wood cells develop abnormally into reaction wood: compression wood in softwoods and tension wood in hardwoods. In addition to the cell dimensions, the chemical composition varies in respect to normal wood.

Cellulose

Cellulose is the most abundant organic material in the world. It constitutes about half of the wood material and its function is to provide mechanical strength for xylem cell walls. The cellulose molecule is linear and composed of repeating cellobiose segments, each of which consists of two glucose units. The unit cell consists of four glucose anhydride units, because the two pairs are mirror images, and it is therefore the smallest perfectly repeating unit (Figure 1). In wood the cellulose chain length is about 5,000 nm, which corresponds to about 10,000 glucose units (Sjöström 1973; Siau 1995). The amount of glucose units is also known as the degree of polymerisation. The smallest building block is the elementary fibril, in which there are about 36 parallel cellulose molecules, held together by hydrogen bonds (Sjöström 1973). The high degree of order in the fibrils makes up a crystalline structure, but the crystallites are shorter than the fibrils. Therefore, the cellulose molecule contains several crystallites and also disordered, amorphous areas. As much as 65% of wood may be crystalline (Joly et al. 1996; Rowell et al. 2005), and the rest is amorphous. The elementary fibrils are combined into microfibrils, which combine to form greater fibrils, and finally lamellae. The disordered cellulose molecules, hemicellulose, and lignin are located in the spaces between the microfibrils (Sjöström 1973). The fibrils are oriented in the cell wall layers in ways that have a major effect on the physical properties of wood.

The crystallinity greatly affects the moisture adsorption properties of cellulose. This will be discussed further in Chapter 1.2.4.

Lignin

Lignin is a very complex amorphous material, consisting of phenylpropane units. In wood it acts as glue binding the cells together. Normal softwood contains 26–32% of lignin, and hardwood 10–25% (Sjöström 1973). The lignin of hardwoods is slightly more chemically reactive than that of softwoods (Stamm 1964). The lignin precursors are generated from D-glucose through complex reactions and the resulting phenylpropane units are linked together by ether linkages, or to a minor extent by carbon-carbon linkages. The lignin-carbohydrate complex (LCC) features covalent bonds between lignin and the polysaccharides (Sjöström1973). The exact form of lignin is not known, since it lacks clear repeating units and the composition varies between wood species. Generally wood lignins are composed of three monolignol monomers (Figure 2) that appear as phenylpropanoids: syringyl and guaiacyl are the common propane units in hardwoods, and softwoods are most often built up of guaiacyl with minor amounts of syringyl and 4-hydroxyphenyl propane units (Fengel and Wegener 1984).

Hemicellulose

Hemicelluloses are heterogeneous, side-chained polysaccharides of relatively low molecular weight. They provide the matrix in which lignin and cellulose are embedded, serving as strengthening elements in the cell walls. Wood hemicelluloses are most often composed of the following monosaccharides: D-glucose, D-mannose, D-galactose, D-xylose, and L-

arabinose. The softwood hemicelluloses are principally galactoglucomannans (Figure 3) (around 20% of dry weight), with some arabinoglucuronoxylan, while the hardwood hemicelluloses are mostly glucuronoxylan (15–30% of dry weight) and glucomannan (Sjöström 1973). The pectic substances found e.g. in the middle lamellae and pit membranes, are not usually classified as hemicelluloses though the distinction is somewhat arbitrary. Pectin has a backbone of polyuronides with uronic acid (Sjöström 1973).
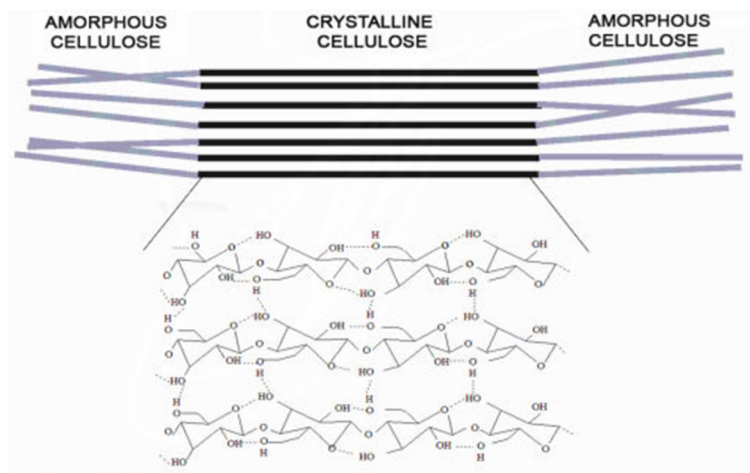
Figure 1. A graphic representation of a cellulose microfibril segment, showing the amorphous and crystalline regions, as well as the constituting glucose units of cellulose molecules. Image from Quiroz-Castañeda & Folch-Mallol (2013), CC BY 3.0. Modified from original.
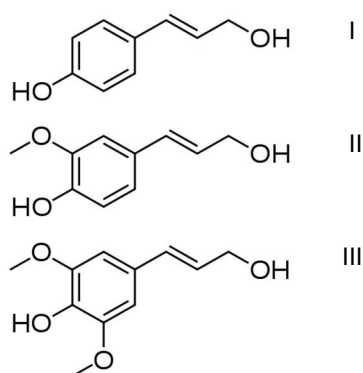
Figure 2. Monolignol monomers *p*-coumaryl alcohol (I), coniferyl alcohol (II) and sinapyl alcohol (III) are the primary building units of lignins. Wikimedia commons (PD-self). Modified from original.

Figure 3. Structure of galactoglucomannan hemicellulose typical for softwoods. Wikimedia commons (PF-self).

1.2.2 Softwoods

Trees are divided into coniferous softwoods (gymnosperms) and broad-leaved hardwoods (angiosperms). Generally softwoods consist of tracheids (90–95% of stem volume) and parenchyma ray cells (5–10%) (Sjöström 1973). The softwood tracheids are long, pitted, and tapered at the ends. The amount of bordered pits is about 200 per tracheid in the earlywood and the number decreases to 10–50 pits per latewood tracheid. Buksnowitz et al. (2010) found the length of a Norway spruce (*Picea abies*) tracheid to be on average 4.6 mm. The width of Norway spruce tracheids is 10–40 μm (Johansson 2008) and the thickness of cell walls is approximately 3 μm (Havimo et al. 2008). In spruce wood, the resin canals are smallish and evenly distributed throughout the structure (Sjöström 1973). The wood of conifers is generally more uniform than the wood of broad-leaved species (Figure 4 a).

In softwoods the fluids travel from one cell to the next most often through bordered pits, but some transportation also takes place through simple pit pairs and half-bordered pits. The bordered pit is formed as a gap or a recess in the secondary wall and the pit membrane, composed of the middle lamella, is wedged between the primary walls of two cells (Siau 1995). In the middle is a thickened portion, torus, suspended by the margo. The pit membrane is essentially non-permeable, but the transportation takes place through the minute openings in the microfibrillar structure of the margo.
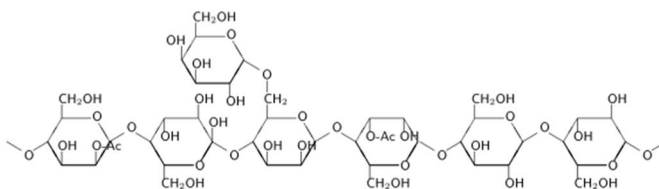

1.2.3 Hardwoods

Hardwoods, or angiosperms, have greater variation in their physical properties when compared to softwoods. They have a wider variety of cells – libriform cells and fibre tracheids for support (65–70% of stem volume), vessels for conduction purposes (~25%), and parenchyma cells for storage. The ray cells are more numerous than in softwoods and account for 5–30% of stem volume (Sjöström 1973). The vessels are short, e.g. the length of downy birch (*Betula pubescens*) fibres varies between 0.47 and 1.3 mm (Kujala 1946). The fibre length varies according to position and the fibres and vessels of Finnish birches are shorter in branches and roots than in stems (Bhat and Kärkkäinen 1981). The vessels are larger than softwood tracheids and the cross section in most common European hardwoods is on average 70 μm (Süss and Müller-Stoll 1970).

The structure of hardwoods may be diffuse-porous, ring-porous, or a combination of the two. In diffuse-porous wood, vessels are scattered relatively uniformly throughout the wood (Figure 4 b). Scalariform perforation plates and extensive intervessel pitting are characteristic. In ring-porous wood the earlywood vessels are large and simple perforation
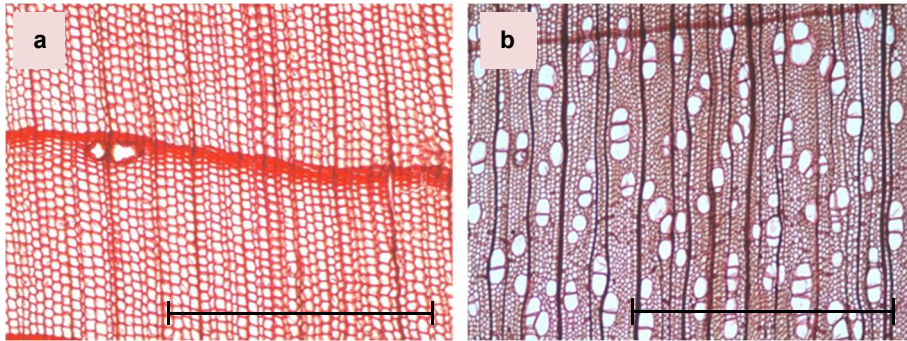
Figure 4 a–b. Cross section of safranin stained **a**) softwood (*Picea abies*) and **b**) hardwood (*Betula pubescens*). Magnified 35X, bar indicates 1 mm. Images courtesy of J. Rikala.

plates are located between the vessels. The flow resistance in both plate types is low and the vessels can therefore be considered as long tubes, unless they are blocked with cellular membranes known as tyloses (Siau 1995). Hardwood pits are usually bordered or simple. The pit structures differ from softwood pits, as the pit membrane is continuous with no torus or margo (Siau 1995).

1.2.4 Wood-water relationships

The phenomenon of sorption

When a tree is felled, it immediately starts losing moisture. Wood retains equilibrium with the relative humidity (RH) of the surrounding atmosphere, taking in moisture when the RH increases and releasing moisture when the RH decreases. Moisture content (MC) is the mass of moisture in the wood, expressed as a fraction. In wood technological and chemical applications it is usually presented as the mass of water per dry wood, dry basis (DB; as presented in this chapter),

$$MC\% \ (DB) = \frac{M1 - M0}{M0} * 100 \qquad (1),$$

where M_1 is the mass of wet wood and M_0 the mass of completely dry wood. Within the field of bioenergy the MC is usually stated as the mass of water per wood and water combined, or wet basis (WB),

$$MC\% \ (WB) = \frac{M1 - M0}{M1} * 100 \qquad (2)$$

Equilibrium moisture content (EMC) is reached at a certain RH where the wood is neither losing nor gaining moisture. At about 98% RH the EMC is 30–40% and the fibre saturation point (FSP) is reached. At this point, the cell walls of wood become saturated without there being any free water in the voids (Tiemann 1951). The point cannot be precisely determined since the capillary absorption of liquid water and adsorption of water vapour overlap and merge (Tiemann 1951). It has been pointed out by Engelund et al. (2013) that the FSP should not be regarded as a point, but more a gradual transition from one state to the next.

Moisture in wood exists as bound water and free (capillary) water (Siau 1995), also referred to as non-freezing bound water and (freezing) free water (Engelund et al. 2013). The most firmly held water in wood is the water of constitution that can only be extracted by heating the wood up to the point of structural degradation (Stamm 1964) and is therefore not considered as "pure" water. The bound water is adsorbed in the cell walls with physical hydrogen bonds that form between the water molecules and the hydroxyl (OH) groups. Hemicelluloses are the most hydrophilic constituents of wood, followed by amorphous cellulose. Lignin also has OH groups, but it is generally less hydrophilic than the two, and important in reducing dimensional changes that occur during sorption (Hakkila 1989). The crystallinity of cellulose has a great effect on water sorption. Water molecules enter freely into the amorphous zones of cellulose but cannot enter the crystallites, where they only attach on to available sites on the surface (Stamm 1964). This is due to the mutually satisfied nature of the OH groups in crystalline cellulose, where they are connected to adjacent OH groups instead of possible water molecules. Part of the amorphous cellulose is also covered with other elements, hemicelluloses and lignin (Rowell et al. 2005). As a result, about two thirds of cellulose is inaccessible. Each glucose unit contains three OH groups that are theoretically capable of bonding with water and the oxygen of the glucose ring provides a fourth site (Joly et al. 1996).

The sorption sites may attract water molecules with differing energies, which has an effect on the positioning of the water molecules. The molecules exhibit a fluid-fluid cooperative effect that allows them to cluster and bridge across free sites depending on the position of the sites (Müller et al. 1996). In wood, clustering of water molecules is suggested to begin around 55% RH, before which the dominant process is the chemical attraction between binding sites and water molecules, i.e. formation of a monolayer (Hartley et al. 1992).

It is important to distinguish between the terms absorption and adsorption. According to Stamm (1964) "**absorption** is the mechanical take up of a liquid by a porous solid within its gross capillary structure as a result of surface tension forces". **Adsorption**, on the other hand, is "the intimate take up of a gas, liquid from the vapour phase, or a solute from solution by a fine powder, a porous substance, or a swelling gel substance". Absorption can occur in quite large capillaries and only a limited reduction in vapour pressure takes place. Adsorbed water affects all the wood properties, whereas free water only plays a role in structural collapse during rapid drying (Tiemann 1951).

The capillary rise of water is based on the strong attractive forces between water and the cell wall. The free water in the cell cavities is therefore subject to capillary forces (Skaar 1972), essentially surface tension and adhesive forces. Not much energy is needed for capillary absorption, and the heat of wetting above the fibre saturation point is very small compared to the heat of adsorption (Skaar 1972). Capillary condensation occurs as the water vapour turns to liquid when entering small pores and the preconditions can be described by the Kelvin equation (Wang 2014); based on the equation it can be calculated that the required relative vapour pressure increases as pore size decreases. True capillary condensation can theoretically occur in pre-existing capillaries down to molecular dimensions. In addition, lignocellulosic material hosts a transient microcapillary structure in the presence of water. True capillary condensation within the cell walls is restricted to 2% of cell wall volume but the majority will occur in the microscopically visible capillary structure after cell wall saturation – on average the lumen can take up to 150% of water beyond the 30–40% of the cell wall (Stamm 1964). Capillary condensation in wood, as noted by Thygesen et al. (2010), does not have a significant role until the RH nears 100%.

EMC at a certain RH is plotted into a sorption isotherm. The types of adsorption are classified into different isotherms (Figure 5) (Stamm 1964; Sing et al. 1985):

Type I or Langmuir isotherm depicts adsorption which is always one molecule thick (monomolecular);

Type II or sigmoid isotherm is always polymolecular and it portrays the formation of solid solutions, such as adsorption of water vapour by cellulose. Considerable heat of adsorption is released. The upward bend in the Type II isotherm was previously attributed to capillary condensation, but a more recent explanation suggests that it may be due to the softening of amorphous polymers (Vrentas and Vrentas 1991; Engelund et al. 2013);

Type III occurs with a very small heat of adsorption as the attractive force of the adsorbent for the adsorbate is almost the same as of the adsorbate for itself;

Type IV is a special case of Type II isotherm, in which final adsorption is limited due to rigid nonswelling porous solids that contain permanent capillaries so small that the vapour pressure condensed therein is significantly reduced and polymolecular adsorption is limited by the size of the pores;

Type V is a special case of Type III isotherm, where like in Type IV isotherm the final adsorption is limited due to rigid nonswelling pores that tend to fill considerably before saturation vapour pressure is reached. The adsorption of water vapour by charcoal follows the Type V isotherm.
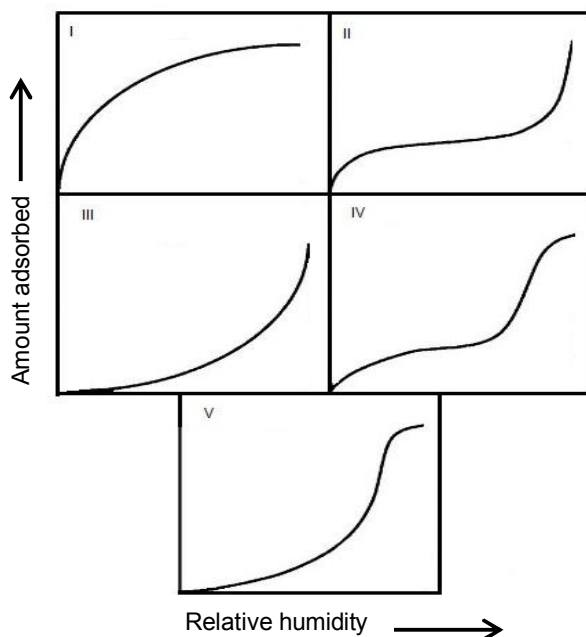

Figure 5. Types of adsorption isotherms. Wikimedia commons (CC0 1.0). Modified from the original.

Porosity

Wood voids can be classified into three categories (Griffin 1977; Thygesen et al. 2010):

1. Cell lumina (fibre cavities) are macrovoids with a radius of approximately 5–200 μm or greater;

2. The pointed ends of lumina, pit apertures, pit-membrane pores, and other small voids excluding the cell lumina are known as microvoids with a radius of approximately 0.005–5 μm;

3. Transient voids, or nanovoids, within the cell walls, with a maximum radius of approximately 0.005 μm.

The void volume (porosity) of most commercial dry woods is 45–80% of the total volume. However, voids other than the cell lumina are largely discreet in nature and have little communication between each other (Stamm 1964). These transient voids are probably in the form of very small spaces between cellulose chains in the amorphous regions (Stamm 1964). In the dry state, the voids and pores are absent from the wood cell wall (Griffin 1977), but as water is introduced, the cell wall swells and pores are created between the microfibrils.

In wood, vapour and bound water move through the void structure by diffusion. The diffusion characteristics of bound water are difficult to determine experimentally (Engelund et al. 2013). Bound water diffusion is controlled by vapour pressure of water, and is often referred to as "random molecular walk or jump", where the molecules will jump from one site to the next as a result of differing attractive forces and cell wall swelling (Stamm 1964). If a molecule is bound to another water molecule instead of the actual binding site, the jump requires less energy, and at a certain point a moisture gradient is set. Diffusion increases rapidly with the degree of MC as polymolecularity increases (Stamm 1964). In contrast to wood, which is a swelling material, charcoal contains lots of rigid permanent submicroscopic voids. The adsorption of gases and vapours is very fast as there is no need for diffusive action as there is in normal wood material (Stamm 1964).

Hysteresis

Hysteresis is linked to the history of the sample. As wood is dried for the first time, the initial desorption curve of an isotherm is always higher than subsequent desorption curves above 50–60% RH. After that, the amount of water adsorbed from the dry condition is always less than that retained on desorption at any fixed RH, but the curves are usually reproducible (Stamm 1964; Siau 1995). There have been many attempts to explain hysteresis, but no generally accepted model exists (Keating et al. 2013).

According to Stamm (1964) and Siau (1995), the changing availability of OH groups may have some effect in hysteresis: in drying they become mutually satisfied due to shrinkage and some of them are not freed when the wood is again wetted. According to a more recent explanation, hysteresis follows from hygro-expansion (Engelund et al. 2013): the cellulose molecules are very stiff in length direction, but their layered structure allows deformation against the length. This deformation, or slippage, is facilitated by breaking and rebonding of hydrogen bonds (Grossman 1976; Engelund et al. 2013), and the EMC of wood will consequently change along the stress state depending on the stress relaxation. As was explained by Hill et al. (2010a; 2010b), the thermal motion of water molecules causes the expansion of the structure and the creation of nanopores, where new internal surfaces are created. As the moisture desorbs, a time lag occurs as a result of the matrix stiffness that fails to respond instantaneously. Therefore, adsorption and desorption take place in a material that is at different states (Lu and Pignatello 2002). Lignin also appears to have a role in the extent of hysteresis, as it may be able to deform in order to accommodate water – in a study by Hill

et al. (2009) lignin-rich fibres exhibited a larger hysteresis loop than cellulose-rich fibres. This finding is consistent with that of Christensen and Kelsey (1959), who reported isolated lignin exhibiting higher hysteresis than other wood constituents.

Water and logistics

The hygroscopic nature of wood is considered a major problem from the point of view of the forest products industry. The MC of freshly felled wood is around 50–60% WB (Hakkila 1989; Gigler et al. 2004), which means that large amounts of unnecessary water are transported, handled, and in many cases, combusted. Transportation costs, energy and fuel consumption and emissions are consequently increased (Gigler et al. 2004). In combustion, variable MC can result in operating problems (Nurmi 1997) and the effective heating value is lowered as MC increases (Hakkila 1989), because additional energy is required to evaporate the water. If wood is not processed in the green state, it can be left to dry, but problems arise also during storage. Moisture facilitates biological degradation that may have severe consequences in terms of spoilage, loss of heating value, and worker health problems during storage and handling. These moisture-related problems are addressed in the following sections of Chapter 1.3.

1.3 Storage of solid biofuels

1.3.1 Storage of wood fuels

Energy wood is usually collected as forest residues (branches, tops), small diameter wood (stems, whole wood), large diameter wood (low quality wood or pulp wood) and stumps. Also by-products from the industry (chips, sawdust, and bark) as well as recycled wood are used for energy (Metsätilastollinen vuosikirja 2013). In Nordic countries it is beneficial to utilise logging residues due to their low price and lack of conflicting uses (Filbakk et al 2011). As the need for energy fluctuates between seasons, storage is required when the supply and demand do not coincide. Buffer storages are important during the winter months (Nurmi 1999), when the need for energy is highest. Forest residues and energy wood can be stored at the site of harvest, transported and stored at or near the landings, bundled and transported to or near the landings, or directly chipped at harvest (Johansson et al. 2006; Van Loo and Koppejan 2008). Most often storage takes place uncovered outside (Noll et al. 2010; Barontini et al. 2014).

Biomass is a challenging energy source. The material is characterized by low energy density, heterogeneity, low bulk density, hydrophilicity, and tenacity due to its fibrous nature. These properties are crucial for the economics of biomass use. Due to the low energy density, transport costs are higher than those for fossil fuels (Van Loo and Koppejan 2008) and therefore critical for profitability (Johansson et al. 2006). Thus, distances should be kept as short and transported volumes as large as possible.

Sawdust, fine wood waste and pellets are usually stored in silos to avoid dust emissions and wetting of the material (van Loo and Koppejan 2008). Forest residue bales and bundles can easily be stored uncovered, as they are not very sensitive to moisture (Johansson et al. 2006; van Loo and Koppejan 2008) as long as the storage site location is carefully positioned to promote drying. Wood chips are often stored at landings uncovered in large piles outdoors.

However, the quality of wood chips suffers from storage and they should be used as soon as possible. Especially the system where chipping takes place at the harvesting site is considered "hot" as it decreases the available time window within which the material should be used to avoid loss of energy content (Forsberg 2000). The problems associated with storage of biofuels are connected to wood-water interactions and the consequent biological degradation.

1.3.2 Biological degradation of wood

Lignocellulosic biomasses, such as wood, are used as an energy source by many organisms. Here, the main focus is on wood degrading micro-organisms, essentially rot and mould fungi.

The wood decaying organisms are generally divided into white-, brown-, and soft-rot causing fungi. White and brown rot are caused mainly by fungi in the division Basidiomycotina, while soft rot is usually caused by various members of Ascomycotina. What is common with all types of decay causing fungi is their requirement for certain environmental and nutritional preconditions. A carbon source, sufficient mineral availability, moisture, and oxygen are essential for growth and reproduction. Nitrogen is a very important nutrient in protein synthesis and is needed for example for the construction of degrading enzymes (Noll and Jirjis 2012). The stress tolerance for nitrogen starvation varies among fungal species.

Generally wood decay fungi are mesophilic, i.e. active at 0–45 °C, with an average optimum of 20–30 °C (Rayner and Boddy 1988). Thermotolerant and thermophilic species thrive at higher temperatures, at about 20–50 °C (Cooney and Emerson 1964; Bergman 1985). All decay fungi are known to use readily accessible substrates, such as soluble sugars, lipids, and peptides, for sustenance. The carbon sources can be extracted directly from the substrate, but to access polymeric substances, extracellular enzymes are needed; cellulases for solubilisation of cellulose, and ligninolytic enzymes for lignin (Rayner and Boddy 1988). There are a great number of fungal species that are specialised in using certain exclusive substrates, such as charred wood generated in forest fires.

During wood decay the fungal hyphae preferentially travel via passages of least resistance. They enter through the cell lumina of axial elements – fibres and vessels – and move from cell to cell through pits. As cell walls are eroded progressively, bore holes are formed, and movement between cells becomes easier (Cowling 1961). The hyphae of several fungi are also able to grow within the compound middle lamellae or within the secondary walls (Fengel and Wegener 1984).

White rot
Decay fungi causing white rot can degrade all the major structural components of wood, although lignin is usually removed in preference to cellulose (Rayner and Boddy 1988). These fungi prefer hardwoods, which may be related to the more refractory nature of softwood lignin (Rayner and Boddy 1988). During decay, the wood substance presents a bleached appearance and it becomes fibrous and elastic (Cowling 1961). The fungal hyphae lie predominantly on the inner surfaces of cell walls, where lysis zones are formed next to the hyphae by secretion of exoenzymes, such as laccase and peroxidases (Fengel and Wegener 1984; Tang and Diehl 2014). The utilisation of carbohydrates as energy sources is a necessary precondition for lignin degradation, but they are also used for synthesis of the ligninolytic enzymes. The carbohydrates are often removed preferentially and it appears that

nitrogen starvation triggers the actual ligninolytic system (Rayner and Boddy 1988; Shimada and Higuchi 1991).

Brown rot

Brown rot type decay causes extensive degradation of the cellulose and hemicellulose fractions, but lignin is not removed although it is altered to an extent depending on the fungus and wood species in question. The characteristic brown colour of decayed wood is caused by the lignin-rich residue left behind. The wood tends to shrink abnormally when dried and is extremely brittle. Brown rot is usually associated with softwoods, but the preference is not as pronounced as it is for white rot for hardwoods (Cowling 1961). The amorphous carbohydrates are preferentially hydrolysed and the less accessible crystalline part of cellulose is degraded more in the later stages (Cowling 1961). The alteration of lignin is characterised by loss of methoxyl groups and increased content of carbonyl and carboxyl groups (Fengel and Wegener 1984). The solubilisation of cellulose and lignin modification is initiated by highly destructive free radicals, such as hydrogen peroxide; the enzymatic saccharification of polysaccharides is a secondary process (Rayner and Boddy 1988; Arantes et al. 2012). The cellulosic S2 and S1 layers become extensively hollowed out, while the lignin rich S1 layer and the middle lamella alter very little (Rayner and Boddy 1988). It is agreed that the ligninolytic capability is greater than previously thought, but the exact mechanism through which the brown rot fungi solubilise wood is very complex and yet to be fully understood (Arantes et al. 2012).

Soft rot

Following colonisation by soft rot fungi, wood is (superficially) softened. Many genera and species can be read under the vague class of soft rot fungi, and the environmental requirements are vast. They can often be found in circumstances where both white and brown rot fungi are inhibited (Rayner and Boddy 1988). In a study by Eslyn et al. (1975), six studied soft rot fungi preferred hardwoods to softwoods, and cellulose to the major hemicellulose (xylan). In addition, lignin was depleted in all samples, though the rate was slow. According to Rayner and Boddy (1988), type 1 and type 2 attacks are produced, where type 2 is similar to a white rot attack with hyphae growth outward from the lumen and eroded grooves around the hyphae. Type 1 attack results in microfibril-oriented cavities in the S2 layer of the secondary wall.

Bacteria

Actinomycetes, but also bacteria, are likely to be the most common wood-inhabiting micro-organisms and the initial colonisers of wood (Greaves 1971; Clausen 1996). The important aspect of bacterial degradation is that they can affect the permeability of wood quite quickly, and many species also thrive in harsh conditions too hostile for wood-decay fungi. During wood storage bacteria are regarded harmless, because they degrade wood at very slow rates (Assarsson et al. 1970). Still, it is noteworthy that through the structural changes caused by bacteria, further attacks by decay fungi are facilitated, and that dead bacterial cell mass may provide a valuable nitrogen source to support subsequent fungal growth (Clausen 1996).

1.3.3 Degradation of wood in storage

Moisture is the most important environmental factor affecting wood storage. It is essential for different types of fungi in metabolic actions, growth, and cell functions. According to Rayner and Boddy (1988), adsorption from the air is a minor but important factor. Input from precipitation, capillary rise, translocation via fungal mycelia, and production of metabolic water as a result of fungal respiration during degradative actions also provide moisture. Free water in cell cavities suits the microbes best, but they also have the ability to utilise some cell wall bound moisture. The microbes are forced into dormancy when they experience drought, but they are revived once the material is rewetted (Kubler 1987). The role of metabolic water may be a significant one: in case of a certain brown rot fungus, *Serpula lacrymans*, over 50% of cellulose is converted to water if decay is complete (Rayner and Boddy 1988), so fungi are also able to produce some of the necessary water through their own actions. Differing estimates of the required decay facilitating MC have been reported. The most commonly cited growth limiting values are in the range of 18 to 21% (Lindgren and Eslyn 1961; Boonstra and Tjeerdsma 1998; Wihersaari 2005), but MCs as low as 15% have also been reported (Jirjis 1995). For most relevant fungi, the area for most rapid growth is between 25 and 60% MC (Bergman 1985). As the higher heating values for lignin and cellulose are directly related to their carbon content, microbial degradation of these compounds can change the energy contents of stored biomass, as well as cause dry matter losses (Noll and Jirjis 2012).

The comminution of wood into chips facilitates microbial colonisation by increasing the available surface area. As the chipped material is piled for storage, the subsequent development of an ecosystem is dependent on many environmental factors. Depending on the moisture content, chip size, the amount of fines, the extent of compaction, the freshness of the material, the amount of bark and foliage, the size of the pile, and the season and length of storage, varying dry matter and heating value losses can be expected. Biotic and abiotic factors lead to oxidation, hydrolysation, and heat release. If the conduction of heat is hindered by dense-packed layers, which is often the case in the inner parts of storage piles, self-heating takes place. This process can be detrimental for the stored material, but it also creates a hazard for the working environment.

Self-heating
Self-heating often occurs in large piles of wood chips, bark, pulp chips and sawdust, but also in stacks of wood-based panels and in enclosed spaces (Kubler 1987). Piles of charcoal and different types of coal also self-heat frequently (Monazam 1998; Kaymacki and Didari 2002) through the adsorption of gases such as oxygen and CO_2, though oxidation proceeds slowly (Lowry and Hulett 1920, as cited by Kubler 1987). Generally forest products containing less than 20% of moisture do not self-heat (Kubler 1987). The biotic factors influencing self-heating are those presented by the wood cells and micro-organisms. The living parenchyma cells respire, and the respiration continues for some time after the wood is felled and comminuted. Temperature increase is recorded also with dead cells and Thörnqvist (1983) reported that temperature development is independent of whether or not fresh residue is used. Torrefied material could therefore also self-heat quite easily if it is wetted. The mechanism may be related to the one taking place in peat piles, where heat is generated through equalisation of different MCs in separate particles (heat of wetting). An increase in the amount of fines reduces aeration and leads to heat accumulation (Niggermann 1968, as cited by Thörnqvist 1983). Spontaneous ignition can take place in compacted piles already at 80

°C (Assarsson et al. 1970). Temperatures of 45 °C (Ferrero et al. 2011), 60 °C (Jirjis 2005), and even up to 75 °C (Jirjis 1995) are frequently recorded from wood chip piles.

As the storage pile warms up, a "chimney effect" is created where hot air starts flowing upwards to be replaced by cooler air from outside (Assarsson 1969). This ventilation, though momentarily cooling the interior, supplies oxygen to the microorganisms inside the pile and promotes their growth. The cooling effect also favours mesophilic fungi over thermophilic ones and maintains temperatures in which growth and sporulation are possible. Compacted sections retard the dissipation and cause the temperature to rise. The air current translocates moisture to the outer parts, where it condenses and as a consequence the outer parts may have an MC of over 70% (Thörnqvist 1983).

If self-heating proceeds to the stage of pyrolysis, a slowly smouldering fire is created. It is only revealed once the pile is broken and oxygen is let in, at which point extinguishing it can be time-consuming and dangerous. Further problems may arise if a fire occurs e.g. in a pellet silo where water cannot be used, since pellets absorb water and swell rapidly. In the worst case the expansion can cause the entire silo to collapse (Stelte 2012).

The large size of comminuted material (chunks instead of chips) reduces self-heating by influencing the heat and air flow inside the pile and increasing ventilation (Jirjis 2005). After two months of storage willow chips exhibited a small decrease in calorific value (Jirjis 2005), which is partly offset by the increase caused by drying. Small particle size is also a factor in coal self-heating (Monazam 1998; Kaymacki and Didari 2002). The length of the storage period is also critical, as self-heating does not usually continue to pyrolysis temperatures in less than six months, but many factors contribute (Assarsson et al. 1970). According to Jirjis (2005), only marginal changes in the fuel quality can be recorded if storage lasts for under two months.

The occupational hazards caused by fungal degradation
There is a known risk associated with handling wood, wood chips, and other biomass fuels in biofuel plants (Madsen 2006). Unloading, piling and moving large quantities of wood materials releases high concentrations of fungal spores that may be deposited onto and inhaled by the workers (Barontini et al. 2014). Large scale storage sites represent reservoirs of fungal spores. Jirjis (2005) recorded 8 and 20-fold increase in the spore count of two experimental wood chip piles during the first months of storage. The sites of, and the tasks associated with largest spore concentrations vary.

The fungal community in wood storage ecosystems consists usually of opportunistic moulds, many of which are capable of causing allergic reactions even in healthy people (Washburn 1996; Barontini et al 2014); in immunologically compromised persons the infections can be fatal (Washburn 1996). The most common respiratory disease among wood workers is the organic dust toxic syndrome – other diseases include hypersensitivity pneumonitis, allergic rhinitis, and allergic asthma (Diehl 1998). Organic particles that contribute to these problems include actinomycete spores, fungal spores, endotoxins, mycotoxins and certain wood dusts (Diehl 1998).

Storage of wood in piles also produces emissions, the most common being CO_2 and methane (Wihersaari 2005). When the storage takes place in silos, closed storage rooms or transport vessels, the emissions become a more serious problem. As oxidation consumes oxygen, closed spaces may become dangerous to enter due to unhealthy levels of volatiles, especially carbon monoxide and hexanal (Svedberg et al. 2004). Inhalation of accumulated volatile organic compounds and the resulting irritation, as well as suffocation due to oxygen

deprivation have been reported in cases especially related to pellet handling (Svedberg et al. 2004; Stelte 2012). Dust explosions are also possible with material containing a lot of fines.

1.4 Torrefaction

1.4.1 Thermal pre-treatment of wood by torrefaction

Coal is the primary material for energy production in many countries. In 2014, it represented 29% of the global total primary energy supply, and accounted for 44% of the global CO_2 emissions (IEA 2014b). The large share of emissions from coal combustion is sought to be reduced by co-combustion of biomass. Co-combustion represents an attractive option for utilisation of biomass since it requires relatively small capital investments considering the existing plant infrastructure and the required equipment (van Loo and Koppejan 2008). However, biomass remains a difficult feedstock compared to coal and it can only be combusted within certain limits in plants designed for coal, usually only up to 5–10% of total mass (Maciejewska et al. 2006). The major problems when considering combustion are the high MC, low heating value, and low bulk density compared to coal. Important properties, such as ash, nitrogen, and chlorine contents may vary greatly between different biomasses and can lead to problems in large concentrations. Wood is generally considered to be less problematic than herbaceous biomass fuels due to its smaller concentrations of harmful substances, such as corrosion-inducing chlorine.

Torrefaction, also known as slow or mild pyrolysis, has been introduced to overcome some of the unfavourable properties of biomass. It is a carefully controlled thermochemical degradation process, where the components of the feedstock decompose according to the treatment temperature and residence time. Any type of biomass, including demolition and waste wood, can be torrefied. The process is executed at ambient pressure, in the absence of oxygen, and with a relatively long residence time. The feedstock is essentially "roasted" at mild temperatures; the most often cited range is 200–300 °C and the reactor residence time can range from a few minutes to few hours (Bourgois and Guyonnet 1988; Bergman et al. 2005; Prins et al. 2006b; Medic et al. 2012). Torrefaction is basically a similar process as the one that produces charcoal, only the peak temperatures and holding times are different. Charcoal is usually manufactured above 400 ºC (Antal and Grønli 2003) and the mass yields are small compared to those obtained through torrefaction, where yields of 60–90%, depending greatly on the feedstock, peak temperature, and residence time, have been reported (Bergman et al. 2005, Prins et al. 2006b; Yan et al. 2009). While longer residence times promote structural degradation, temperature has been shown to be the most important parameter in respect to the properties of the end-product as well as the economics of the process (Bridgeman et al. 2010; Medic 2012). In addition to dry torrefaction, a process of hydrothermal torrefaction has been introduced. The material is treated in hot pressurized water and slightly differing mass and energy yields are obtained (Yan et al. 2009; Acharjee et al. 2011), but the focus in this paper is solely on "conventional" dry torrefaction as it continues to be more promising in large-scale production systems.

During torrefaction, limited devolatilisation of the wood constituent takes place and, especially when treated at the more severe temperatures, the end-product resembles coal. The solid product consists of the original and modified sugar structures, newly formed polymeric

structures, char and ash (Bergman et al. 2005). The oxygen-to-carbon (O:C) and hydrogen-to-carbon (H:C) atomic ratios decrease, therefore the heating value of the product improves (Bergman et al. 2005). Hygroscopicity is reduced while homogeneity increases. With increasing treatment temperatures, the product is also increasingly brittle and the energy required for crushing it into a powder decreases (Bergman et al. 2005; Svoboda et al. 2009). This is an important improvement compared to traditional biomasses such as chips or pellets when we consider the co-combustion properties, because very small particles are required in coal-fired plants and gasifiers (Verhoeff et al. 2011). When biomass is co-combusted with coal, problems may also arise from parasitic losses associated with more energy intensive handling and high moisture content, as well as the larger cost of transport, storage, and on-site handling of biomass (Baxter 2005). Pre-treating the material by torrefaction could help to reduce those losses. According to the results of Li et al. (2012), torrefaction is able to provide a technical option for high substitutions of biomass in co-firing systems.

Bergman et al. (2005) have described the torrefaction process as follows:
1) Initial heating, where the material is heated up to 100 ºC until the stage of drying;
2) Pre-drying, where the free water evaporates at a constant rate;
3) Post-drying and intermediate heating, where the temperature is increased to 200 ºC. Water of constitution is released through thermal degradation processes, after which the material is practically free of water;
4) Torrefaction, where the process continues from 200 ºC up to the desired peak temperature, where it remains for a chosen residence time. This stage contains a heating period and a cooling period in addition to the period of constant temperature;
5) Solids cooling, where the product cools from 200 ºC down to the desired final temperature.

There is no single optimal torrefaction condition, and each feedstock will require a different recipe aiming for the desired end result. This means compromising between overall energy efficiency, heating value, grindability and hydrophobicity (Verhoeff et al. 2011). To facilitate higher energy density and easier handling, torrefed biomass has to be densified into pellets. Several demonstration technologies for combined torrefaction and pelletisation exist, such as the BO_2-pellets developed by Energy Research Centre of the Netherlands (ECN) (Verhoeff et al. 2011), but at the moment no commercial scale production exists. According to Deutmeyer et al. (2012) the current trajectory of development indicates the technologies will become available in the next 10 years.

Due to the lack of commercial scale production and utilisation, the costs are difficult to calculate and only theoretical results exist. The production of torrefied wood requires more energy than the production of conventional wood fuels. It has been pointed out that the lower logistical and handling costs almost fully compensate for the higher conversion costs (Deutmeyer et al. 2012), but to reach this end densification is essential. The energy requirement for densification is controversial (Adams et al. 2015), and is strongly dependent on the torrefaction recipe and the feedstock. Drying of the material prior to torrefaction is important, but the actual energy requirements create uncertainties to the economics. As the volatiles (torgas) can be combusted for drying, its heating value is crucial to the overall balance and dictates the need for a utility fuel, therefore also affecting the GHG emissions of the process (Adams et al. 2015). The torgas consists mostly of water and CO_2 (about 60%) and lesser amounts of CO and methane, and requires high flame temperatures for combustion (Bergman et al. 2005). The condensable fraction consists, among others, of acids, methanol, acetone, and ammonia.

1.4.2 Effect of torrefaction on the wood components

Hemicellulose
Torrefaction of wood is mainly characterised by the degradation of the hemicellulosic fraction, as hemicelluloses are the most reactive components. They undergo depolymerisation and recondensation reactions at lower temperatures than the other components of wood. Deterioration begins at 180–200 ˚C (Sivonen et al. 2002; Werner et al. 2014) and maximum mass loss is experienced in the range of 243–332 ˚C (Werner et al. 2014). Due to the differences between coniferous glucomannan- and deciduous xylan-based hemicelluloses, the reactivity of hardwoods is higher and they lose more mass during torrefaction (Bergman et al. 2005; Prins et al. 2006a; Verhoeff et al. 2011). The degradation products of hemicellulose pyrolysis are mainly water, acetic and formic acids, esters, aldehydes, and ketones (Stamm 1964; Prins et al. 2006b).

Cellulose
Cellulose has a more resilient structure than hemicelluloses and in the torrefaction range of 200–300 ˚C its decomposition is slow (Prins et al. 2006a). Cellulose decomposes at 250–380 ˚C (Gasparovic et al. 2010) by two pathways: the first dominates below 300 ˚C and involves the evaporation of moisture, reduction of the degree of polymerization, evolution of gases, formation of different chemical components such as free radicals and carbonyl groups, as well as the formation of reactive carbonaceous char. The second pathway is indicated by an exothermic reaction that dominates above 300 ˚C: molecular cleavage, fission and disproportionation reactions provide a mixture of tarry anhydrosugars and lower molecular weight volatile compounds (Shafizadeh 1984; Elder 1991). Depolymerisation decreases fibre lengths and contributes to the increasingly brittle structure of the end product (Bergman and Kiel 2005). At the beginning of the exothermic reactions just above 300 ˚C, fast thermal cracking of cellulose may cause tar formation, which is considered one reason for keeping torrefaction process temperatures below 300 ˚C (Prins et al. 2006b).

   Cellulose crystallinity changes due to thermal treatment. The amorphous regions degrade faster than the crystalline ones, and therefore the relative proportion of crystalline cellulose increases at least at the lower end of the torrefaction range (Sivonen et al. 2002). Reorientation and rearrangements may explain some of the increase, and hemicelluloses can also crystallize following pyrolysis (Bhuiyan at el. 2000).

Lignin
The degradation of lignin takes place over a wide range of 180 to 900 ˚C (Gasparovic et al. 2010). Lignin softens, i.e. undergoes glass transition, at approximately 100–150 ºC (Bergman et al. 2005). The softened lignin acts as glue and is a very good binder when manufacturing pellets. Although the lignin structure begins to modify at rather low temperatures, the major changes do not happen until higher temperatures. During torrefaction, the proportion of lignin increases in relation to the carbohydrate fraction (Sivonen et al. 2002). Demethoxylation reactions increase cross-linking within the lignin complex (Tjeerdsma et al. 1998; Sivonen et al. 2002).

1.4.3 Changes in sorption properties after torrefaction

The uptake of moisture changes due to torrefaction. Because of extensive degradation of the hemicelluloses and the destruction of OH groups, the water adsorption potential of wood material decreases. This is considered to be the main reason for the increased hydrophobicity. Formation of non-polar substances has also been suggested to contribute to the reduced moisture uptake (Bergman et al. 2005). The preferential degradation of amorphous carbohydrates increases the crystalline portion of cellulose, further reducing the adsorption potential. Also the cross-linking reactions provide for an increasingly stable structure. There are many studies dealing with the reduced EMC of materials subjected to torrefaction: The EMC of different woody feedstock materials treated between 260 and 300 °C has been reported to fall between 1 and 6% (Bourgois and Guyonnet 1988; Bergman et al. 2005; Pach et al. 2002; Acharjee et al. 2010; Patel et al. 2011). At room conditions the EMC of the materials in these studies was reported to fall between 5 and 11% prior to heat treatment. Hopes or easier and cheaper logistics and combustion have been raised, as the material could be stored without the risk of degradation (Bergman et al. 2005; Yan et al 2009; Medic et al. 2012). It is an established practice to store coal in very large, open piles subjected to weathering and moisture. Usually the storage of coal is easy and only minor losses related to quality are encountered if certain preconditions are met to ensure adequate stockpile management (Speight 2013). Since the chemical composition of torrefied material resembles that of coal, outside storage has been suggested as a cost-effective and easy option. If the material stays dry biological degradation does not occur and its favourable properties are preserved during transport, handling, storage, and most importantly when combusted.

2 AIMS OF THE STUDY

For torrefied biomass to present a viable option for the energy sector, the characteristics of the material need to be carefully examined. Although techno-economic assessments also covering the entire logistic chain have recently been published (Svanberg and Halldórsson 2013; Svanberg et al. 2013), a large number of research articles leave the storage issues unaddressed by simply stating that the material is hydrophobic and can therefore be stored outside. It is an attractive option, because it would reduce costs associated with utilisation, obviating the need for separate storage buildings and silos (Bergman et al 2005; Uslu et al. 2008; Ciolkosz and Wallace 2011; Deutmeyer 2012). The storage of fuel, whether torrefied or not, is necessary to meet the operational requirements of plants and ensure continuous operation. However, no peer-reviewed studies have been published concerning the effects of outside storage on the properties of torrefied wood. Sorption properties should be proven to facilitate outside storage. Therefore, storage issues have been raised as a subject area that needs to be studied further (Svanberg and Halldórsson 2013). These issues include hydrophobicity (Deutmeyer et al. 2012; Batidzirai et al. 2013) as well as health and safety issues (Ciolkosz and Wallace 2011)

   In order to verify the claims of cheap and easy storage, the sorption properties and fungal degradation of torrefied Norway spruce (*Picea abies* Karst.) and downy birch (*Betula pubescens* Ehrh.) were assessed with regard to the possibility of outside storage. As pellets

are the form in which large-scale utilisation would most likely take place, torrefied pellets were compared in one of the part-studies (III).

The specific aims of this thesis were:

- To study the changes in sorption properties induced by torrefaction. Both absorption (I) and adsorption (I, IV) of water were studied. The torrefaction-induced chemical and physical changes associated with sorption, such as porosity and hydroxyl group accessibility, were also studied (I, IV).
- To investigate the fungal degradation of torrefied material. Several decomposing fungi were tested for their abilities to degrade wood components and cause dry matter loss in the laboratory (II). Naturally occurring fungi and the threat they may present towards the material were identified after an outside storage trial (III), where working safety matters were also addressed.
- To determine the mass loss (II) and moisture content changes (II, III) caused by fungi.

3 MATERIALS AND METHODS

3.1 Raw material

Norway spruce and downy birch were chosen to be used in the part-studies. These species represent a common hardwood and softwood species with different chemical compositions. Especially the tops and branches of Norway spruce present a large, underutilised raw material source in Finland.

The material consisted of one large mature spruce, and several smaller birches. The trees were cut down in Helsinki (approximate location 60.216 N, 25.024 E). The spruce grew in a closed-canopy site near the forest edge and was identified as a typical specimen of a mature spruce. The birches grew next to a ditch by an agricultural field and represented the average downy birches. The stems and thick branches (with a diameter of minimum 5 cm) were manually cut into blocks of approximately 5 x 5 x 5 cm and dried in a large cold-air drier to an average MC of 6% (DB).

3.2 Pyrolysis of raw material

Pyrolysis is used in the text to describe the torrefaction and the charring processes in combination. The material was pyrolysed in a pilot scale indirectly heated reactor managed by the Biosampo-project of Kouvola Region Vocational College (KSAO) (Figure 6). The reactor was separated from a heated airspace by a wall. Wood is often torrefied as chips but here the reactor set special requirements for the size, and the material was pyrolysed as blocks, described more closely in chapter 3.1.

Batches of 25 kg were used and the chosen temperatures were 220 °C, 260 °C and 300 °C (torrefaction), as well as 450 °C (charring). The pyrolysis was executed in steps: 60 min at 110 °C, 60 min at 170 °C, and three hours at the peak temperature. After three hours the

Figure 6. Biosampo's torrefaction apparatus. Photo by the author.

heating was switched off and the reactor was left to cool for several hours. Treatments at 450 °C required an extra 60 min step at 290 °C to prevent damage to the reactor. The pyrolysis time was long, but thorough conduction within the large blocks was essential. The effect of the long residence time on the level of degradation of the more reactive birch was tested with a shorter comparative run at 300 °C, with a halved residence time of 30 x 30 x 90 min (II).

The mass yield was determined after the solids had cooled. In studies II and III the material underwent a carbon-nitrogen (C/N) analysis where samples were extracted from each block and ground into a fine powder by a ball mill or a knife mill. To obtain the carbon and nitrogen contents (percentages of mass), 100–200 μg of the powder was analysed with VarioMAX (Elementar Analysensysteme GmbH, Germany).

3.3 Sorption properties of torrefied wood and charcoal

3.3.1 Adsorption of water vapour (I)

To study the adsorption of water vapour into the material treated at different temperatures, an experiment was designed where small bark-free cubes (3 x 3 x 3 cm) cut from the original pyrolysed blocks were placed into a climate chamber (Weiss WK11 340, Germany). The chamber allowed for manipulation of RH at a constant temperature. The sample cubes (ten

cubes per treatment) were placed in at 30–95% RH and the adsorbed moisture was measured as increase in mass. The measurements were repeated.

3.3.2 Absorption of liquid water (I)

Capillary absorption of liquid water was measured from similar cubes as described in chapter 3.3.1 through partial immersion. Two cubes per treatment were suspended from a scale (Precisa 2200, Switzerland), with their axial elements exposed to water. The absorbed moisture was measured as change in mass, and the rate of absorption was recorded at 5-min intervals for a period of one hour.

3.3.3 Theoretical maximum moisture content (I)

In order to investigate the effect of pyrolysis on the water uptake capacity, the samples (similar samples as described in Ch. 3.3.1; 3 cubes per treatment) were boiled for approx. 1.5 hours to estimate the inner volume and the capacity for water absorption. Boiling removed air from the voids, and theoretically only water was left in the voids. The uptake of water was measured as change in mass.

3.3.4 ATR-FTIR spectroscopy (I)

Small samples extracted from representative original blocks of pyrolysed (and untreated) wood underwent ATR-FTIR (Attenuated Total Reflectance Fourier Transform InfraRed) spectroscopy in order to assess the chemical changes induced by the different treatments and the effect of those changes on the water sorption properties. The samples were ground into a fine powder from which the measurements were made directly with a FT-IR spectroscopic device (Bruker ALPHA, Germany) fitted with a Platinum ATR single reflection diamond ATR module that measured the spectra in the wavenumber range of 4000–400 cm^{-1}.

3.3.5 Sorption isotherms determined with dynamic vapour sorption (IV)

To gain more thorough information on the sorption properties, a dynamic vapour sorption (DVS) apparatus (DVS ET, Surface Measurement Systems Ltd, UK) was used. The DVS allows for collection of highly accurate information on adsorption, desorption, and hysteresis. A more detailed description of the apparatus can be found in paper IV, as well as in Hill et al. (2010a) and Hill et al. (2010b). Representative samples were chosen from the original pyrolysed (and untreated) blocks. The samples were ground to a fine powder of which 20 ± 1 mg was weighted onto the sample pan. One adsorption-desorption cycle composed of a stepwise increase (5% steps) of RH from 0 to 95% at constant temperature, after which the RH was again lowered to zero. Two cycles were run for each sample, with three repeats. Absolute hysteresis was calculated from the difference between EMC at desorption and EMC at adsorption at a certain RH.

3.3.6 Accessibility of torrefied wood and charcoal (IV)

Accessibility of the samples (same material was used as described in Ch. 3.3.4) was measured with the DVS. The water vapour used in the adsorption-desorption experiment was switched to deuterium vapour (D_2O). Adsorption of deuterium oxide (heavy water) into available OH groups is directly measurable through the increase in mass. Eight cycles in the RH range of 0–95% were conducted with three repeats, and the amount of accessible OH groups was calculated as presented in paper IV, equation 1.

3.3.7 Specific surface area and particle size measurements

The Brunauer-Emmett-Teller theory (BET) (Brunauer et al. 1938) was formulated for estimation of the specific surface area of a solid material of interest. It is based on the adsorption of nitrogen on the surface of the solid and calculation of the amount of adsorbate corresponding to a monomolecular layer on the surface. The BET method requires special circumstances because liquid nitrogen is used, but the DVS provides a function for surface area calculation at room temperature with water vapour.

Because the particle size affects the sorption properties, changes in the particle size distribution were investigated with Mastersizer 2000 (Ver. 5.60; Malvern Instruments LTD, UK).

3.4 Storage properties of pyrolysed materials

3.4.1 Preliminary storage experiment (II)

To facilitate a following experiment, a preliminary field trial was set up. The original pyrolysed wood blocks and untreated reference blocks were put into mesh bags and placed outside on compact sandy gravel for natural weathering. The bags were left out for four months, from the beginning of July to the beginning of November. Oven dry mass loss and MC were determined after the trial.

3.4.2 Comparison of covered and uncovered storage (III)

After the first storage trial, another one was set up with more variables. In addition to the pyrolysed and untreated wood, the following material were used:
- wood chips from forest residues, torrefied at 250 °C;
- torrefied wood pellets made from the wood chips described above;
- untreated wood pellets from softwood;
- steam-explosion wood pellets from mixed hard- and softwood

The samples were measured to determine the MC and C/N content, packed into mesh bags as in the preliminary trial (Ch. 3.5.1), weighed, and placed outside. Each treatment used four bags, two of which were left outside and two placed inside a roofed building with wood

Figure 7. Uncovered storage area on compact gravel bottom and covered storage area in an open-walled, roofed building with board tables. Photo by the author.

board tables and open walls (Figure 7). The bags were left untouched for five months, from June to October.

After five months, the bags were weighed and the MC and C/N content were determined. The pellets were subjected to a durability test according to standard CEN/TS 15210-1 (2010). The statistical significance of changes in carbon and nitrogen contents, as well as the significance of storage area location and position of the blocks in the test piles regarding possible fungal degradation were studied through the paired t-test, univariate ANOVA, and crosstabs (IBM SPSS Statistics 22, USA).

3.5 Fungal degradation of pyrolysed material

3.5.1 Evaluation of the degradative abilities of selected fungi (II)

Because of hydrophobicity, torrefied material should be stable with regards to biological degradation. Therefore, the possibility of fungal degradation was investigated. The pyrolysed and untreated materials were inoculated with:

- *Phanerochaete chrysosporium* Burds. F1767 (FBCC283), basidiomycete, white rot;
- *Pycnoporus cinnabarinus* (Jaqc.) P. Karst 331 (FBCC130), basidiomycete, white rot;
- *Gloeophyllum sepiarium* (Wulfen) P. Karst PO121 (FBCC 190), basidiomycete, brown rot;

- *Trichoderma* spp. (Pers.) (FBCC1529), ascomycete, specific species unknown (the genus contains several species with varying wood decaying abilities (Mathew et al. 2008; Albert et al. 2011; Wang et al. 2015)).

The original strains were obtained from the Fungal Biotechnology Culture Collection (FBCC) maintained at the Department of Food and Environmental Sciences, Division of Microbiology, University of Helsinki. The fungi were chosen because of their relative abundance (all fungi), their occurrence in forest fire areas and thus their presumed capabilities to decay charred wood (*P. cinnabarinus*, *G. sepiarium*), and their frequent occurrence in wood fuel storage areas (*P. chrysosporium*, *Trichoderma* spp.). The aim of the particular study was to find out, whether torrefied and charred wood could be used as a substrate by rot and mould fungi.

A water agar medium (2%; wt/vol) was chosen to minimise any carbon source from the medium. Small plugs of fungi were inoculated on the plates. Samples split from the pyrolysed and untreated blocks and the growth medium were sterilised in an autoclave and the MC of the wood pieces were measured. Four parallel groups were established. The dishes were sealed with Parafilm M (SPI Supplies, USA) to allow gas exchange, and placed inside the climate chamber (25 °C, 80% RH) for incubation of 30 to 60 days.

After 30 days one of the groups was removed. The dishes were weighed, the MC of the wood pieces was measured and the plates were photographed. Due to aerial contamination, the plates were discarded. After 60 days the measurements were repeated for the remaining three groups. A visual assessment matrix was used to evaluate the advance of fungal growth:
1) very sparse growth, i.e. growth sustained by the medium (~0% coverage);
2) sparse growth clearly emanating from the wood pieces (0–10%);
3) mediate growth with some visible mycelia on the wood piece(s) (11–30%);
4) considerable growth on the wood pieces (31–90%);
5) abundant growth with discolouration of the medium (91–100%).

Small pieces were cut from the inner surface of spruce and birch samples with signs of fungal growth. Four sample pieces were cut after 30 days and four after 60 days of incubation. The pieces were inspected with field emission scanning electron microscopy (FE-SEM; Hitachi S-4800 FE-SEM, Japan) to find out, whether the fungal hyphae had penetrated the wood instead of merely growing on the surface.

Sample pieces of every temperature-fungus combination, with visible fungal mycelia scraped off, were ground for C/N-analysis. The changes in carbon and nitrogen contents, as well as the change in mass following incubation were analysed with one-sample and paired samples t-test (IBM SPSS Statistics 22, USA).

3.5.2 Fungal contamination during outside storage (III)

Several fungi are known to utilise charred wood generated in forest fires and therefore pose a threat for stored pyrolysed material. These kinds of agents were of primary interest in the storage experiment (Ch. 3.5.2). After storage, samples were taken from the top, middle, and bottom of each bag. Similar samples of pellets and chips were taken from only one bag stored outside and one inside. The blocks were broken aseptically and specimens were extracted from the inner surface to avoid aerial contamination and gain access to possible wood-inhabiting fungi. The pellet and chip samples were not broken open and contained the surface that had been in contact with the outside air. Three specimens from each wood block and

chip were placed on one agar plate; one pellet was used for one dish. Malt extract agar (MEA), tryptone-glucose-yeast agar (TGY) and benomyl-novobiosin-malt (BNM) media were used. The plates were sealed with Parafilm M and incubated for one to four weeks. The dishes were grouped according to their visual appearance. A few representatives of each group were aseptically re-inoculated on new MEA dishes and incubated for two more weeks to obtain pure cultures for identification.

3.5.3 Identification of fungal genera after outside storage (III)

Altogether 36 visually different fungi were prepared for identification with internal transcribed spacer polymerase chain reaction (ITS-PCR). Genomic DNA was extracted and the ribosomal DNA ITS region (ITS1 + 5.8S + ITS2) was amplified with ITS1 and ITS4 primer pairs (White et al. 1990). The amplified PCR products were run on agarose gels and sequenced (Macrogen Corp., The Netherlands). The nucleotide sequences were analysed with BLASTn against the NCBI database (https://blast.ncbi.nlm.nih.gov/) for identification. Only the highest identity matches were used.

4 RESULTS AND DISCUSSION

4.1 Pyrolysis

The mass yield (MY) of spruce and birch after pyrolysis was 46–27%. The carbon content increased with increasing temperature and the nitrogen content decreased with increasing temperature for spruce and increased for birch. The carbon and nitrogen values in Table 1 are averages between two measurements made in studies II and III. The comparative run executed for birch at 300 °C with half the residence time resulted in a slightly lower carbon content and larger mass yield and nitrogen content compared to the original long run (Table 1).

The mass yields generally reported in the literature are greater than the ones reported here. Though the effect of time on mass yield is considered relatively small, the holding time was still above the ones frequently reported in peer-reviewed literature (see Ch. 1.4.1). The material, "blocks", was also different from those often used in small laboratory scale equipment. These kinds of reactors usually only hold a few grams of powdered material, while 25 kg of blocks provide a much larger array of potential error sources. One significant error source was the pyrolysis of spruce at 260 °C, which produced an uneven result. Some of the pieces were left charred only on the surface, while the ones in contact with the reactor walls were thoroughly charred, which can easily be seen in the carbon content deviating from the other results. When it came to samples treated at 260 °C, pieces that represented the average pyrolysis result were carefully selected for all the experiments other than the larger scale storage trials.

There are some differences in the effect of pyrolysis on wood constituents depending on the conditions used. Torrefaction can be implemented in vacuum, which is the case with

Table 1. The effect of pyrolysis at 220–450 °C on mass yield (MY; %) and carbon (C) and nitrogen (N) contents (mass %) of spruce (S) and birch (B).

Material	MY, %	C, %	N, %	Material	MY, %	C, %	N, %
Spruce, untreated	100	49	0.3	Birch, untreated	100	52	0.6
S, 220	54	63	0.4	B, 220	46	70	0.5
S, 260	50	60	0.3	B, 260	39	71	0.6
S, 300	33	77	0.3	B, 300	32	78	0.7
S, 450	27	88	0.1	B, 450	26	85	0.5
				B, 300 ½	35	75	0.8

indirectly heated reactors, or by using inert gases, such as nitrogen, as heat carriers. Many small laboratory scale reactors are operated under nitrogen flow and thus the research papers report results from pyrolysis under nitrogen. According to Candelier et al. (2013), thermal treatment under vacuum yields slightly lower extractives and lignin content than under nitrogen. The volatile compounds, such as acetic acid and furfural are progressively removed under vacuum, which hinders their re-condensation and the subsequent catalysing effect on polysaccharide degradation. Nitrogen pyrolysis also promotes an increase of carbon content more than a vacuum (Candelier et al. 2013). However, in this paper the cited studies dealing with pyrolysis both in vacuum and in nitrogen are considered of equal relevance, because the general magnitudes of, for example, carbon content and EMC are similar. Studies dealing with the thermal treatment of wood meant as construction materials, such as the Thermowood® process, have been used as reference material only with caution. Thermal treatment is often conducted in the presence of air and involves the use of water vapour as a shielding gas (Jämsä and Viitaniemi 2001). The degradation processes of wood are much greater under these conditions – as stated by Stamm (1956), the degradation is at least ten times more severe under steam than under dry heat.

4.2 Sorption behaviour of torrefied wood and charcoal

4.2.1 Adsorption

The most relevant property of torrefied wood, with respect to logistics, is the reduced hygroscopicity. The motivation for the part-studies of this thesis dealing with adsorption stemmed from the absence of data on the moisture adsorption behaviour of pyrolysed Finnish tree species and the results obtained from studies I and IV were seen as an important addition. Sorption hysteresis and OH accessibility have not been reported for torrefied material before. Figure 8 compares the adsorption isotherms obtained from the climate chamber (I) and DVS (IV). The adsorption behaviour of the samples was in line with those reported previously (Bourgois and Guyonnet 1988; Bergman et al. 2005; Pach et al. 2002; Patel et al. 2011; Acharjee et al. 2010). As a general rule, higher treatment temperatures produce more hydrophobic material. The adsorption isotherms of spruce and birch differ at 220 °C due to faster degradation of hardwood hemicelluloses. The isotherm of spruce at 220 °C still
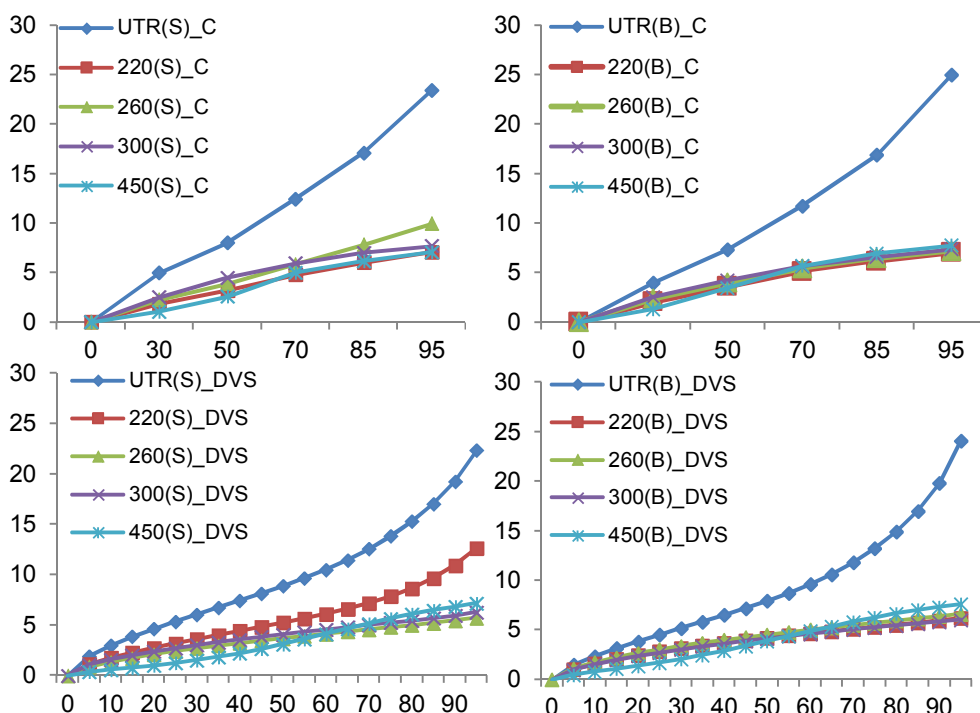
Figure 8. Adsorption isotherms measured in the climate chamber (C) and DVS; UTR = untreated reference, S = spruce, B = birch.

exhibits the sigmoid shape, but as treatment temperature increases, the isotherms resemble more Type I and Type V (Figure 5). The characteristic Type V isotherm is evident for both charcoal samples in both experiments. The isotherms for samples in the torrefaction range can be compared to Type I, although unlike the true Type I isotherm, the adsorption does not continue in a monomolecular fashion (horizontal) but increases slowly with increasing RH. The upward bend observed in the Type II isotherm of the untreated references is missing and the final adsorption is most likely limited, as in Type V isotherm. The Type I isotherm indicates microporosity, and the Type V one the presence of small rigid pores (nano- and micropores) that are not able to swell and fill up before any condensation can occur.

The results from the two experiments are very similar, although the isotherms obtained by DVS are clearer because of a larger number of measuring points. Because the physical size of the samples was much larger in the climate chamber experiment, the uneven pyrolysis result of spruce at 260 °C is clearly visible (the shape resembles Type II isotherm); in the DVS, the bias was successfully eliminated by powdering a small uniform piece. In the climate chamber, the spruce sample treated at 220 °C shows a different curve from the one measured in DVS. It is possible that the equilibrium time was not sufficient in the climate chamber, where the sample was deemed to have reached EMC when the mass was unchanged after two consecutive weightings.

After the climate chamber experiment, it was concluded that sample pieces from more severe treatments obtained equilibrium faster than untreated samples and samples treated at

lower temperatures. The standard deviation between two repetitions was below 0.94 (1.57 for spruce treated at 260 °C). Basically, adsorption should depend on accessibility: the more available sites for water molecules to occupy, the more water should be adsorbed. This may be evident in the faster establishment of equilibrium of the samples treated at higher temperatures, as accessibility was reduced for both species, from 9.2 to 1.5 mol/kg for birch, and from 11.1 to 1.3 for spruce. However, accessibility is not very well correlated with EMC, as noted by Rautkari et al. (2013). The reasons for this were discussed in paper IV, where it was concluded that accessibility and EMC are dependent on complex interactions between available sites, changes in porosity, particle size, as well as the clustering and bridging behaviours of water molecules.

The degradation of OH's due to volatilisation of the amorphous polysaccharides is an obvious explanation for reduced adsorption. In Figure 8, this is most visible in the isotherms of samples treated at lower temperatures (i.e. 220–260 °C), where birch undergoes more drastic changes. These changes can be attributed to the more reactive hemicelluloses that volatilise more extensively than those of spruce. But, as was stated previously, the sorption of pyrolysed wood is a more complex phenomenon and depends on more variables than just the accessible sites in hemicelluloses and amorphous cellulose. There is increase in cross-linking of the lignin fraction that leads to higher dimensional stability of the wood (Tjeerdsma et al. 1998; Hill et al. 2009) by increasing the rigidity of the matrix. The cross-linking further reduces hygroscopicity (Acharjee et al. 2011), and increases hysteresis (Lu and Pignatello 2002). This may also affect the isotherms of birch, as lignin starts to react and is modified already at low temperatures. The lignin of hardwoods is more reactive than that of softwoods, which indicates structural modifications at lower temperatures than softwood lignin. However, according to Bergman et al. (2005), the main decomposition reactions taking place below 250 °C can be attributed to the degradation of hemicelluloses. The condensation of carbons of the aromatic ring and the increase of crystallinity also negatively affect the hygroscopicity (Tjeerdsma et al. 1998). Surface complexity, which negatively affects sorption through accessibility, also increases and becomes an important factor above 250 °C (Nakano and Miyazaki 2003).

Pyrolysis caused a reduction in sorption hysteresis, although hysteresis should increase with increasing matrix stiffness. This has to do with the time lag between the creation of nanopores as water molecules enter the matrix with increasing EMC, and the collapse of those nanopores as the molecules exit the matrix with reducing EMC. With a more elastic material, the response is faster, and the extent of hysteresis is smaller (Keating et al. 2013). With pyrolysed material, however, the increased cross-linking creates a stiffer matrix that resists deformation and prevents a fast response to the movement of water molecules, as swelling is reduced (Kamdem et al. 2002; Nakano and Miyazaki 2003). The reduction in hysteresis is most likely associated with the overall reduction in hygroscopicity (Popescu et al. 2015), as well as the formation of pores inaccessible to water or blockage of pores. It was also speculated that the collapse of the matrix following adsorption and desorption has some effect on the diminishing hysteresis. At higher RH, the access to pores may be further hindered by the slowing down of diffusion as a result of the increasing cluster size of water molecules (Harding et al. 1998; Davis and Elabd 2013).

4.2.2 Absorption

Water absorbs in the capillaries through a combination of adhesion and surface tension forces, when a concave meniscus that wets the walls of capillaries is formed. The absorption of water is often neglected in the literature dealing with the moisture properties of torrefied wood, where the focus is on the adsorption of water vapour. It is therefore important to address this matter. When studying the sorption properties of thermally modified wood, Kamdem et al. (2002) noted that the heat-treatment does not limit the absorption of water, and while Pfriem (2011) agreed saying that longitudinal absorption is increased, opposing views exist. Metsä-Kortelainen et al. (2006) and Kekkonen et al. (2013) both stated that thermally modified wood absorbs less water. Johansson (2008) claims that thermal modification reduced the water transport capacity, but increased the capacity to store free water at low absorption heights.

The absorption measured in paper I did indeed slow down, but the capacity for water uptake was larger than for untreated wood. This could easily be discerned by approximating the free volume inside the samples by boiling. During boiling the pieces of wood may sink before being fully saturated, and also aspiration of spruce pits caused most of the spruce samples to not sink at all. Nonetheless the method was still seen perfectly adequate in estimating the general magnitude of the sorption capacity. It was interesting to note the initial reduction in the volume available for absorption (paper I, Fig. 5). This result is in line with the results obtained in the experiments of Metsä-Kortelainen et al. (2006), Kekkonen et al. (2013), and Johansson (2008). As pyrolysis temperature increases, the amount of absorbed water increases. With spruce, the capacity is above that of the untreated reference, while for birch, it stays slightly lower. Spruce pits aspirate during drying, and mild thermal treatment has not been shown to cause much damage to the pit membranes. However, the membranes do become more permeable (Zauer et al. 2014) and severe temperatures must also damage the pits as the constituting materials volatilise. This causes an increase in the absorption capacity.

Porosity plays a major role in increased absorption. The FT-IR measurements (paper I) confirmed earlier results of increased microporosity. According to Blankenhorn et al. (1978), total porosity measured by mercury porosimetry increased up to 600 °C and it was said the pore size distribution stays fairly uniform after its formation, possibly below 320 °C which corresponds to exotherm of cellulose pyrolysis. Pfriem et al. (2009) measured porosity using helium pycnometry and found an increase. Also, the existing pores widen, which at first leads to reduction in the relative share of micro- and nanopores (Zauer et al. 2014) as well as a reduction in surface area, but microporosity increases rapidly above 300 °C (Rutherford et al. 2005). Larger pores are also created due to the coalescence of existing pores.

Increased microporosity leads to increased surface area but the results from the measurements in paper IV were not very consistent, as the surface area values decreased with increasing treatment temperature. It has been claimed that the BET method is not a very good estimator of surface area of pyrolysed wood, as it is not recommended for microporous materials (Sing et al. 1985). As microporosity does not develop until more severe temperatures, other issues affecting the decreased surface area such as the particle size should also be considered. As particle size decreases due to thermal treatment, accessibility and surface area increase. However, small particles agglomerate easily in the presence of water, and may block access to the pores. Particle size therefore creates two contradicting effects by both increasing and decreasing accessibility. The pores may also be blocked because of re-condensation of degradation products, as well as the plastic flow and subsequent solidifying

of lignin into pore openings. Matrix collapse and restricted diffusion due to water molecule clustering may also play a role, as noted in Ch. 4.2.1. If the material has very large pores due to coalescence, the surface area may decrease. The BET method remains widely used also in wood technology and the results were added for comparison purposes.

4.3 Effect of storage on torrefied and charred wood

4.3.1 Moisture sorption and dry matter losses during storage

The outside storage clearly affected the MC of samples in both experiments. In the first experiment the material took in enough water to account for a mass increase of up to 200%. Mould and fungal mycelia were also clearly seen on the pieces treated at less severe temperatures, but neither the species nor genera were identified. The MCs of samples following outside storage in papers II and III were 16–69% and 25–59%, respectively. The effect of the direct contact with water from precipitation and ground contact was evident, as in covered storage, the samples took in moisture only to a maximum of 16% MC (Figure 9). In addition to the blocks of torrefied and charred spruce and birch, different types of refined materials were examined in paper III. Wood pellets, torrefied pellets, steam-explosion pellets, and torrefied chips exhibited more varying responses to the storage period. In uncovered storage, the MC of untreated pellets rose to 64%, while in covered storage it remained at 10%. Pelletisation of torrefied material had a clear effect on the moisture adsorption in covered storage, as the feedstock chips torrefied at 250 °C adsorbed moisture to a MC of 20%, while the pellets only took in moisture to an MC of 5%. This could be related to the slowing down of diffusion within the dense pellets. Also the increased rigidity following from cross-linking reduces swelling under moderate humidity. However, in uncovered storage the contact with liquid water caused swelling and pellet disintegration following extensive wetting (Figure 10 a–c), and both the chips and torrefied pellets had a MC of around 44%. The steam-explosion pellets, on the other hand, resisted disintegration remarkably well (Figure 10 c). Even after uncovered outside storage, the pellets were intact and the durability was above 90%. The high quality may be related to the behaviour of lignin: as the fibres are exploded, lignin is released from the matrix. It plasticises easily during densification and hardens on the pellet surface during cooling (Anglés et al. 2001; Biswas et al. 2011). The same phenomenon should apply for torrefied pellets but somehow the durability is far from that of steam exploded pellets. Li et al. (2012) wrote that the parts of lignin responsible for binding the particles together are mostly of low molecular weight, and volatilise early in the torrefaction process. It could be that the lignin does not volatilise as easily in water, and also that more lignin is retained inside the matrix during torrefaction, and does not provide as extensive hardening as in steam-explosion pellets. The torrefied chips took in more moisture than the blocks. This is likely related to the increased surface area of smaller, chipped particles. In covered storage, the MC fell naturally between the MC of blocks treated at 200 and 300 °C. In wood fuel storage, larger chunks are usually considered better than smaller sized chips in terms of moisture uptake, but also in terms of agglomeration of fine particles in the pile, that may lead to self-heating and have destructive consequences (Gigler et al. 2004; Jirjis 2005).
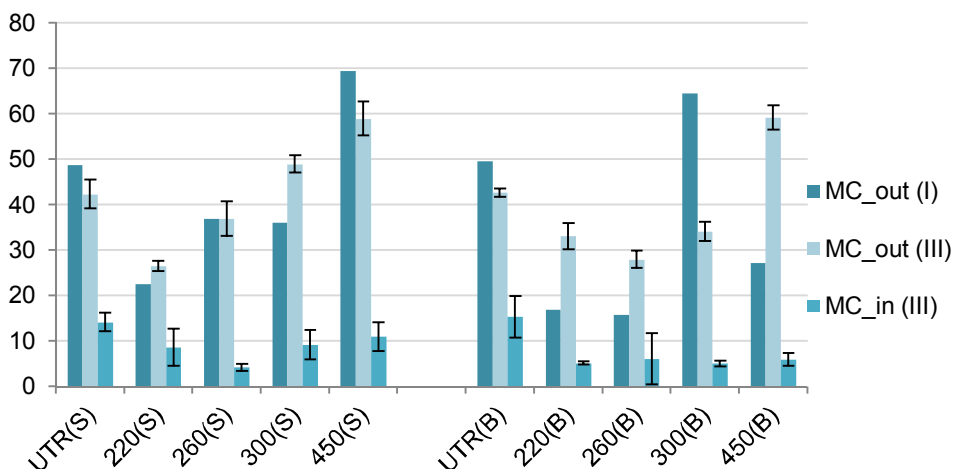
Figure 9. Moisture contents (MC, WB) of samples after covered and uncovered storage. MC_out (I) is the moisture content of samples after uncovered outside storage for 4 months (paper I; Jul-Oct; only one bag per treatment), MC_out (III) and MC_in (III) are the moisture contents of samples after uncovered and covered storage for 5 months (paper III; Jun-Oct; the standard deviations between the two repeats are shown). UTR = untreated reference, S = spruce, B = birch.

The results show that the adsorption of water vapour is not a major problem for torrefied and charred blocks, chips, and pellets, as the MC of all these samples was moderate in covered storage. Torrefied pellets exhibited poor adhesion, although their durability was better than that of untreated wood pellets following storage. The durability of torrefied pellets was below standards (min 97.5% durability) even before the storage experiment. Absorption created more issues. If the material is in touch with bare ground, capillary uptake can be quite large. For untreated and torrefied pellets this was detrimental. For chips, blocks, and chunks the increased MC may prove troublesome as additional handling steps, such as drying, are required. Drying increases the associated costs, but if no drying is used, heating value is lost due to the need to evaporate water in combustion or further refining. The increased MC also has a direct effect on the extent of fungal colonisation, discussed in the next section, as the absorption of water can increase the MC to a level suitable for biological degradation.

4.3.2 Degradation of pyrolysed material under controlled environmental conditions

The degradation of the material was studied in a climate chamber with four selected fungi, growing at a temperature and humidity that simulated optimal conditions. Mass loss was recorded for all samples. After 30 and 60 days the losses were below 3%. The decrease is small, but still in line with dry matter losses recorded from outside storage piles, as for example the loss of 1–3% per month recorded by Thörnqvist (1983). The mass loss was statistically significant ($p < 0.05$) for all the samples compared to the starting point. It is
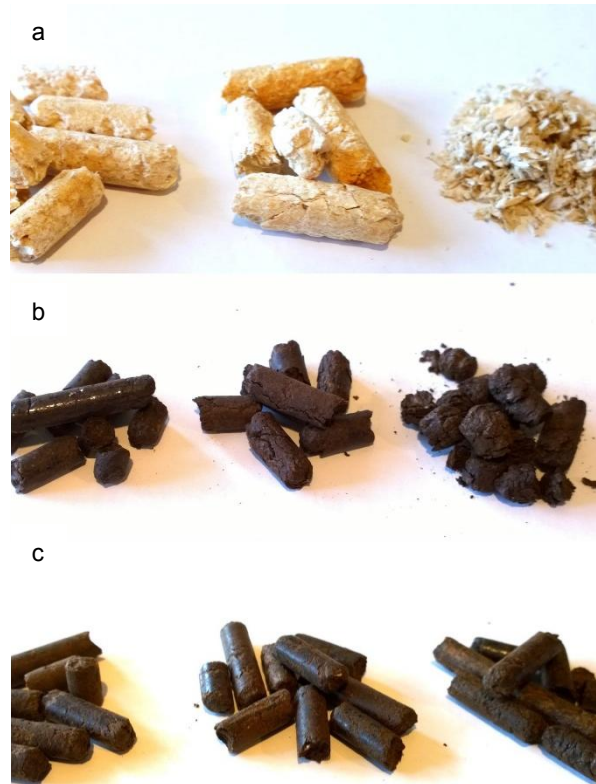
Figure 10 a–c. From left: pellets before storage, following covered outside storage, and following uncovered outside storage; **a**) wood pellets, **b**) torrefied pellets, **c**) steam-explosion pellets. Photo by author.

possible that with longer exposure times, higher losses would have occurred, as the experiment only lasted for 60 days. The mass loss was slightly higher for the birch samples, which was speculated to be related to the nitrogen content that increased during pyrolysis. The same possibility was discussed in paper III, where birch wood samples, when assessed visually, hosted more fungal growth than spruce wood samples.

The growth of fungi was reduced according to the visual evaluation matrix: untreated reference samples were evaluated as 4–5, or abundant growth, whereas pyrolysed samples were mainly between 1 and 3 (no growth to mediate growth). The more severely treated charcoal samples had clearly less fungal growth compared to the less severely treated ones. Loss of carbon and nitrogen were significant for all the samples except for the birch samples removed after 30 days.

The ability of fungi to utilise seemingly inhospitable materials has economic importance in e.g. bioremediation of contaminated soils (e.g. Covino et al. 2015). As noted, the relative share of lignin increases in pyrolysis, and the elemental composition of char from lignin has been compared to lignite coal (Elder 1991), which is known to be degraded by both brown and white rot fungi. Apparently lignite can serve as a principal nutrient source (Cohen and Gabriele 1982) and therefore it seems plausible that also pyrolysed wood can host fungal

growth. However, in absence of essential nutrients the processes are generally very slow. Certain degradation products formed in pyrolysis are thought to further inhibit fungal growth, but according to Kamdem et al (2000), the proportions of such polynuclear aromatic hydrocarbons are quite low. In paper II it was suggested the breaking of the polysaccharidic components into smaller compounds early in the pyrolysis process could promote fungal growth, as the nutrients would become more accessible. However, the simultaneous thermal modification of these compounds may have the opposite effect. Theander et al. (1993) and Sehlstedt-Persson (1995) reported the translocation of nutrients on wood surface during drying, but in the latter the high temperature induced caramelisation was suspected to inhibit the growth of mould fungi. In the paper in question only the effect of one *Penicillium* species was examined and other species could well tolerate the conditions. In paper II the growth of the selected fungi was not totally inhibited even after treatment at 450 °C. This finding contradicts the results of Hakkou et al. (2005) and Singh et al. (2013), who reported that fungal growth was inhibited at 280 and 300 °C, respectively. According to Hakkou et al. (2005), the extractives generated during heat treatment do not play a role in the increased biological durability of wood, but the modification of the lignin network does, as it inhibits the ligninolytic system. Singh et al. (2013) attributed the increased durability to loss of hemicelluloses and also to changes in lignin. These matters must be of importance, but it seems that the choice of fungi is the most relevant matter. The fungi used in study II were all capable of utilising pyrolysed material. This can also be seen in Figure 11, where fungi selected for the experiment were found to produce clearly visible hyphae on both moderately and severely pyrolysed samples.

The importance of MC has been emphasized throughout this thesis, and the effect can also be seen in the controlled experiment of paper II. The reference samples that hosted no inoculated fungi had taken in moisture to a MC of 28–37% (untreated) and 10–26% (pyrolysed) during the storage period of 30 to 60 days at 80% RH. The samples with inoculated fungi had MCs ranging from 16 to 66%, which were not as high as those of the untreated references with inoculated fungi (45– 72%), but very close (paper II, Fig. 2). The increase could in part be attributed to the absorption of the condensed water from the bottom of the dishes, but since the reference samples were stored in a similar way, the absorption
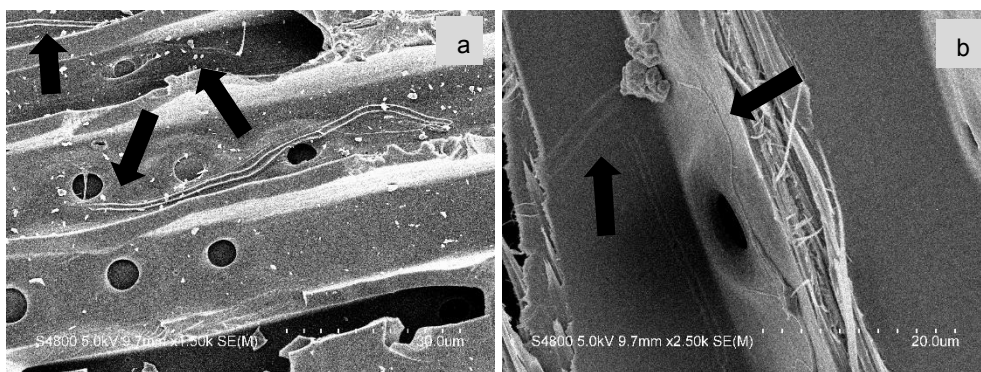

Figure 11. FE-SEM images showing fungal hyphae of **a**) *G. sepiarium* in spruce treated at 450 °C, and **b**) *P. chrysosporium* in spruce treated at 260 °C. Images courtesy of M. Kemell.

can be regarded as proof of fungal activity. Wood constituents are degraded to CO_2 and metabolic water, which also helps to sustain the growth and metabolism of the decaying agent. As noted by Kubler (1987), self-heating may also occur when MC exceeds 20%.

4.3.3 Degradation in storage under uncontrolled environmental conditions

After the outside storage experiment in paper III, the possibility of natural contamination of torrefied and charred material became evident. The material hosted abundant fungal flora, and representatives of both basidiomycetes and ascomycetes were found. The most common genera identified from the samples were *Aureobasidium* sp., *Epicoccum* sp., *Cladosporium* sp., *Fusarium* sp., and *Penicillium* sp., but also genera such as *Trichoderma* sp., *Mucor* sp., *Fomitopsis* sp., and *Bjerkandera* sp. were found (Figure 12). Specialist species requiring charred wood were not found. In the experiment, no additional carbon source was available (compared to the agar plates in the climate chamber experiment) and the sole carbon source was the stored material. Similar to the results of paper II, more growth was visually detected on birch samples, which may be related to the increased nitrogen content. Although most wood decay fungi are adapted to low nitrogen contents, many opportunistic ascomycetes may better utilise the material provided it contains more than the minimum amount required. After storage the content of nitrogen had decreased in all samples, but statistical significance was only found in the pellets and chips. Changes in the nitrogen content may be difficult to detect, because the fungi recycle it very effectively. Compared to the starting point the change in carbon content was significant ($p < 0.01$) in all samples, and the treatment temperature as well as the location of the storage area (covered/uncovered) affected the content significantly. The measured values were very small, and most likely will not affect the combustion properties of the material, but it was noted that to verify this, calorimetric measurements should be conducted. The fungal growth was significantly affected by only the location of storage area (covered/uncovered), which leads back to the importance of increased MC and the role of capillary water in uncovered storage.

Mass loss was recorded following outside storage described in paper II. Unfortunately, in the second storage experiment the mass loss determination was not successful. The results would have provided important information on the physical aspect of outside storage. In paper II up to 22% of mass was lost following outside storage, but the range was wide (0–22%). The effect of leaching is difficult to estimate and was therefore left out from the experiment. Leaching may have had an effect on the losses, as it was shown in paper II that the dry matter losses increased with increasing temperature. The particle size decreases with increasing temperature and thus it is possible that more fine material is washed away by rain.

The decreased particle size also increases fungal susceptibility due to increased surface area available for colonisation. The fines resulting from the disintegration of pellets may also increase the risks of workers having health problems by creating a source of organic dust. A more serious risk is associated with the identified fungal species, since well-known allergens were isolated. There are no internationally accepted limit values or exposure limits for microorganisms and endotoxins for people working with biomass fuels (Madsen 2006) and the threshold values are difficult to establish, as the health impact of all microbes, as well as the combined effects of allergens are not known (Ajanko-Laurikko 2009). However, for agricultural and waste management environments the limit values for most common fungal
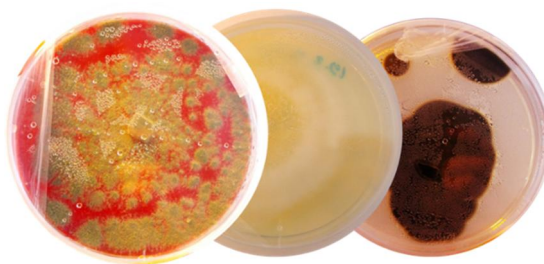
Figure 12. From left: pure cultures of *Penicillium* sp. (Ascomycota), *Fomitopsis* sp. (Basidiomycota) and *Cladosporium* sp. (Ascomycota); identified with BLAST. Photo by the author.

species are known and could easily be applied to the biofuel industry as similar species are found in both cases.

Although changes in carbon content were discovered, it was concluded in paper III that the pyrolysed and steam-exploded material do not provide a very good growth medium for fungi, as the actual measured losses were very small. Based on this result, silos do not seem to be a mandatory storage option for torrefied and charred material as long as the material is protected from direct contact with liquid water. The MC of torrefied pellets after covered storage was a very moderate 5%, but their durability was low. However, the durability was almost the same even before the experiment and is more a question of tuning the pellet manufacturing process. In terms of MC it may be acceptable also to store torrefied pellets in a covered storage instead of a silo. The problems related to durability are another matter, as any type of handling regardless of storage type increases the abrasive stress, and dusting is to be expected. Storage of pellets in closed spaces increases the risk of of e.g. carbon monoxide emissions that may cause suffocation if safety regulations and appropriate ventilation are not taken into consideration. Partly open storage areas could be safer in practice, although fungal contamination is to be expected. Roofed areas and covers could also be cheaper than silos, but it does not obviate the need to add in the costs associated with storage when planning the material's logistic chain. The protective measures required to prevent fungal spores being inhaled by the personnel also need to be carefully considered.

4.4 Future perspectives

Finland is dependent on imported fossil fuels (Weckroth 2011), though steps have been taken to increase the share of domestic renewable sources. As 78% of Finland is forested (Weckroth 2011), forest based energy is a promising raw material source that could also promote local economies. However, renewable energy sources remain underutilised as long as fossil energy sources are favoured. In 2013, fossil fuels were globally subsidised by 550 billion dollars, while renewable fuels by only 120 billion dollars (IEA 2014). Political decisions play a key role.

In this thesis, torrefaction has mainly been introduced as an option for heat generation and coal co-combustion, or as a replacement fuel for coal, but there are more possibilities.

Torrefied material can also be used as a feedstock in enzymatic hydrolysis, when treated at mild temperature, as it significantly reduces the energy required for grinding (Chiaramonti et al. 2011). Grinding presents a major energy sink also in biomass gasification, and in addition torrefaction may be used to improve the quality of the produced gas (Prins et al. 2006c).

If the use of torrefied material as an energy source is to increase, certain storage related issues should be addressed. Occupational safety guidelines should be set to prevent illnesses and allergies. The durability issues related to torrefied pellets should be investigated further to facilitate handling during storage so as to avoid dusting and disintegration that may further cause safety issues for personnel. It would be interesting to discern the separate effect of precipitation and capillary water to clarify the effect of both paths contributing to the moisture content of the material. Also, investigating the effect of length of storage would be useful. Torrefied pellets have been shown to perform poorly after short-term exposure to water (Järvinen and Agar 2014), but the performance of chips and chunks have not been widely reported. There may be a threshold period of outside storage without loss of quality. The effects of leaching, mass loss, and changes in heating value should also be carefully investigated to fully understand how storage changes the properties of torrefied and charred material.

5 CONCLUSIONS

Storage is an important issue in the logistics of all fuels, as the continuous operation of plants need to be ensured. The part-studies of this thesis considered the sorption behaviour of torrefied and charred material, as moisture is the most important variable affecting the properties of the fuel during the logistic chain. Moisture promotes fungal degradation, which changes the properties of the stored material, and poses a threat for working safety. The hydrophobicity of pyrolysed wood increased with increasing treatment temperature, but porosity also increased, which led to increased absorption capacity. The material should therefore not be stored uncovered, as the sorbed moisture can increase the MC up to a level suitable for fungal degradation. The material was degraded by fungi both in a controlled environment with selected species, and in outside storage with naturally occurring fungi. Loss of carbon was detected, but the magnitude of the loss was small and should be thoroughly established to find out the effect on the heating value of the material. The degradation is most likely too slow to cause noticeable loss in the heating value, but metabolic water resulting from fungal activity wets the material and thus the combustion properties suffer. The handling of the material becomes more hazardous due to the fungal activity especially without proper occupational guidelines and threshold values for spores to protect the personnel. Thus issues related to storage of torrefied and charred material should be carefully considered when establishing supply chains, and the added costs of covered storage need to be taken into account to provide a realistic picture of the advantages of using this type of material.

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