



Surface characterisation of thermally modified spruce wood and influence of water vapour sorption

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Licentiate Thesis

Stockholm, September, 2015

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TRITA-BYMA 2015:4

ISSN 0349-5752

Printed in Sweden by USAB, Stockholm, 2015

Akademisk uppsats som med tillstånd av Kungliga Tekniska Högskolan i Stockholm framlägges till offentlig granskning för avläggande av teknologie licentiatexamen fredagen den 25 september 2015 kl. 10:00 i sal B26, KTH, Brinellvägen 23, Stockholm.

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ABSTRACT

Today there is growing interest within the construction sector to increase the proportion of biobased building materials made from renewable resources. By-products or residuals from wood processing could in this case be valuable resources for manufacturing new types of biocomposites. An important research question related to wood-based biocomposites is how to characterise molecular interactions between the different components in the composite. The hygroscopic character of wood and its water sorption properties are also crucial. Thermal modification (or heat treatment) of wood results in a number of enhanced properties such as reduced hygroscopicity and improved dimensional stability as well as increased resistance to microbiological decay.

In this thesis, surface characteristics of thermally modified wood components (often called wood fibres or particles) and influencing effects from moisture sorption have been analysed using a number of material characterisation techniques. The aim is to increase the understanding in how to design efficient material combinations for the use of such wood components in biocomposites. The specific objective was to study surface energy characteristics of thermally modified spruce (*Picea abies* Karst.) under influences of water vapour sorption. An effort was also made to establish a link between surface energy and surface chemical composition. The surface energy of both thermally modified and unmodified wood components were studied at different surface coverages using inverse gas chromatography (IGC), providing information about the heterogeneity of the surface energy. The water vapour sorption behaviour of the wood components was studied using the dynamic vapour sorption (DVS) method, and their surface chemical composition was studied by means of X-ray photoelectron spectroscopy (XPS). Additionally, the morphology of the wood components was studied with scanning electron microscopy (SEM).

The IGC analysis indicated a more heterogeneous surface energy character of the thermally modified wood compared with the unmodified wood. An increase of the dispersive surface energy due to exposure to an increased relative humidity (RH) from 0% to 75% RH at 30 °C was also indicated for the modified samples. The DVS analysis indicated an increase in equilibrium moisture content (EMC) in adsorption due to the exposure to 75% RH. Furthermore, the XPS results indicated a decrease of extractable and a relative increase of non-extractable compounds due to the exposure, valid for both the modified and the unmodified wood. The property changes due to the increased RH condition and also due to the thermal modification are suggested to be related to alterations in the amount of accessible hydroxyl groups in the wood surface. Recommendations for future work and implications of the results could be related to knowledge-based tailoring of new compatible and durable material combinations, for example when using thermally modified wood components in new types of biocomposites for outdoor applications.

Keywords: Thermally modified wood, Norway spruce, inverse gas chromatography (IGC), dynamic vapour sorption (DVS), X-ray photoelectron spectroscopy (XPS), surface energy

SAMMANFATTNING (IN SWEDISH)

Det finns idag ett växande intresse inom byggsektorn för att öka användningen av trä- och biobaserade byggnadsmaterial tillverkade av förnybara råvaror. Biprodukter från olika träbearbetningsprocesser kan i detta fall vara värdefulla resurser för tillverkning av nya typer av biokompositer. En viktig forskningsfråga relaterad till sådana träbaserade biokompositer är hur molekylär interaktion mellan de olika komponenterna i kompositen kan karakteriseras. Träets hygroskopiska karaktär och dess vattensorptionsegenskaper är också avgörande. Termisk modifiering (eller värmebehandling) av trä resulterar i att ett antal av dess egenskaper förbättras, såsom minskad hygroskopicitet och förbättrad dimensionsstabilitet samt ökad motståndskraft mot röta.

I denna avhandling har ytegenskaper för termiskt modifierade träkomponenter (ofta kallade träfibrer eller träspån) och påverkan av fuktsorption analyserats med ett antal metoder för materialkarakterisering. Syftet är att öka förståelsen för hur effektiva materialkombinationer skall designas för användning av sådana träkomponenter i biokompositer. Det specifika målet var att studera ytenergiegenskaper hos termiskt modifierade träkomponenter av gran (*Picea abies* Karst.) under påverkan av vattenånga. Ett ytterligare mål var att upprätta eventuella samband mellan ytenergi och ytornas kemiska sammansättning. Ytenergiegenskaper hos både termiskt modifierade och omodifierade träkomponenter studerades genom omvänd (invers) gaskromatografi (IGC), som också ger information om ytenergins heterogenitet, d.v.s. ytenergi vid olika andelar av ytsorption. Sorptionsbeteendet hos träkomponenterna vid varierad luftfuktighet studerades genom så kallad dynamisk ångsorption (DVS), och deras ytkemiska sammansättning studerades genom röntgenfotoelektron-spektroskopi (XPS). Vidare studerades träkomponenternas mikromorfologi med svepelektronmikroskopi (SEM).

IGC-analysen indikerade en mer heterogen ytenergikaraktär för det termiskt modifierade träet jämfört med det omodifierade. En ökning av den opolära ytenergin på grund av exponering för en ökad relativ fuktighet (RH) från 0% till 75% RH vid 30 °C. indikerades dessutom för de modifierade proverna. DVS-analysen indikerade en ökad jämviktsfuktkvot vid adsorption för de modifierade proverna som en följd av exponeringen för 75% RH. Vidare indikerade XPS-resultat att exponeringen orsakade en minskning av extraherbara och en relativ ökning av icke-extraherbara extraktivämnen för både det modifierade och det omodifierade trämaterialiet. De förändrade ytegenskaperna orsakade av exponeringen för det ökade RH-klimatet och även den termiska modifieringen föreslås bero på variationer av mängden tillgängliga hydroxylgrupper i träytorna. Rekommendationer för framtida arbete och tillämpningar av resultaten kan relateras till kunskapsbaserad design av nya kompatibla och beständiga materialkombinationer, exempelvis för användning av termiskt modifierade träkomponenter i biokompositer för utomhusapplikationer.

Nyckelord: Värmebehandlat trä, gran, omvänd gaskromatografi (IGC), dynamic vapour sorption (DVS), röntgenfotoelektron-spektroskopi (XPS), ytegenskaper, ytenergi

PREFACE

This licentiate thesis has been carried out at KTH Department of Civil and Architectural Engineering, Division of Building Materials, in Stockholm. The thesis is a part of a research program at KTH Building Materials with the aim to develop new biobased building materials. The main financiers are Troëdssons forskningsfond (Projektnr 793/12 Hydro-termo-mekanisk modifiering av trä), the Swedish Research Council Formas (project EnWoBio 2014-172) as well as KTH.

Firstly, I would very much like to thank my main supervisor Prof. Magnus Wålinder, KTH Building Materials, for his contribution to my studies, and his scientific input and great knowledge. Furthermore, I thank my co-supervisors; Dr. Kristoffer Segerholm and Dr. Dennis Jones, both at SP Technical Research Institute of Sweden, for giving me possibilities to expand my network within wood science and for introducing me to life at conferences.

I would like to thank all the people at my department at KTH and at SP, with whom I had the chance to interact and work. I also thank everyone that I met during conferences and international visits for encouragement and inspiration.

The financial support from Stiftelsen Nils och Dorthi Troëdssons forskningsfond and the Swedish Research Council Formas is hereby greatly acknowledged. Support from EcoBuild Institute Excellence Centre is also acknowledged. Through financial support from the COST Action FP0904 I had the possibility to do a Short-Term Scientific Mission (STSM) at Aalto University, Forest Products Department in Espoo, Finland, where I would like to thank Prof. Lauri Rautkari, Dr. Leena-Sisko Johansson and Dr. Joseph Campbell. Lastly, I owe thanks to my friends and family and loved ones.

Stockholm, September 2015

Susanna Källbom

LIST OF PAPERS

This licentiate thesis is based on the following two appended papers (Källbom *et al.*, 2015a and 2015b) which in the text are referred to by their Roman numbers:

- I. Källbom, S., Wålinder, M.E.P., Segerholm, B.K. and Jones, D. (2015a). "Surface energy characterization of thermally modified spruce using inverse gas chromatography under cyclic humidity conditions". *Wood and Fiber Science* 47(4): 1-11.
- II. Källbom, S., Rautkari, L., Wålinder, M.E.P., Johansson, L.-S., Campbell, J., Segerholm, B.K. and Jones, D. (2015b). "Water vapour sorption characteristics and surface chemical composition of thermally modified spruce". Manuscript to be submitted for publication.

Contribution to the appended papers

Paper I: Källbom planned and carried out the experiments, interpreted the results and wrote the manuscript, all with supervision by the co-authors Wålinder, Segerholm and Jones.

Paper II: Källbom, in co-operation with the co-authors Rautkari, Johansson and Campbell, planned and carried out the experiments, interpreted the results and wrote the manuscript, all with supervision by the co-authors Wålinder, Segerholm and Jones.

Other published research contributions related to the topic of this thesis:

Källbom, S., Wålinder, M., Segerholm, K. and Jones, D. (2013). Physico-chemical characterization of THM modified wood using inverse gas chromatography (IGC). Poster and oral presentation. In: Book of Abstracts of the 3rd COST Action FP0904 Conference "Evaluation, processing and prediction of THM treated wood behaviour by experimental and numerical methods". Popescu, C.-M. and Popescu, M.-C. eds., ISBN: 978-973-702-990-4. 2013, April 9–11, Institute of Macromolecular Chemistry of Romanian Academy Iasi, Romania, pp. 35–36.

Källbom, S., Segerholm, K., Jones, D. and Wålinder, M. (2013). Surface energy characterization of thermally modified wood using inverse gas chromatography. Poster presentation. In: Proceedings of the 44th Annual Meeting of the International Research Group on Wood Preservation (IRG). ISSN 2000-8953. IRG/WP 13-20532. 2013, June 16-20, KTH Royal Institute of Technology, Stockholm, Sweden, 6 pp.

- Källbom, S., Segerholm, K., Jones, D. and Wålinder, M. (2013). Surface energy characterization at different moisture levels of thermally modified wood using inverse gas chromatography. Oral presentation. In: Proceedings of the 9th meeting of the Northern European Network for Wood Science and Engineering (WSE). Brischke, C. and Meyer, L. eds., 2013, September 11–12, University of Hannover, Hannover, Germany, pp. 130–135.
- Källbom, S., Segerholm, K., Jones, D. and Wålinder, M. (2014). Surface energy characterization of thermally modified wood particles exposed to humidity cycling using inverse gas chromatography. Poster presentation. In: Book of Abstracts of the Seventh European Conference on Wood Modification (ECWM7). Nunes, L., Jones, D., Hill, C. and Militz, H. eds., ISBN 978-972-49-2267-6. 2014, March 10-12, National Laboratory for Civil Engineering (LNEC), Lisbon, Portugal, pp. 137-138.
- Källbom, S., Rautkari, L., Wålinder, M., Jones, D. and Segerholm, K. (2014). Water vapour sorption properties and surface chemical analysis of thermally modified wood particles. Oral presentation. In: Book of Abstracts of the final meeting of COST Action FP0904 Conference “Recent Advances in the field of TH and THM Wood Treatment”. ISBN 978-91-7439-937-0 (print), ISBN 978-91-7439-937-7 (pdf), 2014, May 19-21, Luleå University of Technology, Skellefteå, Sweden, pp. 89-90.
- Källbom, S., Ormondroyd, G., Segerholm, K., Jones, D. and Wålinder, M. (2014). Surface energy characteristics of refined fibres at different pressures. Oral presentation. In: Proceedings of the 10th Annual Meeting of the Northern European Network for Wood Science & Engineering (WSE). Wilson, P. eds., 2014, October 13-14, Institute for Sustainable Construction, Edinburgh, United Kingdom, pp. 134-138.
- Källbom, S., Rautkari, L., Johansson, L.-S., Wålinder, M.E.P., Segerholm, B.K., Jones, D. and Laine, K. (2015). Surface chemical analysis and water vapour sorption of thermally modified wood exposed to increased relative humidity. In: Proceedings of the Eight European Conference on Wood Modification (ECWM8). Hughes, M., Rautkari, L., Uimonen, T. and Militz, H. eds., [In publication], 2015 October 26-27, Helsinki, Finland.
- Laine, K., Segerholm, B.K., Wålinder, M.E.P., Rautkari, L., Hughes, M., Källbom, S. and Jones, D. (2015). Hardness, set-recovery and micromorphology studies of densified and thermally modified wood. In: Proceedings of the Eight European Conference on Wood Modification (ECWM8). In: Hughes, M., Rautkari, L., Uimonen, T. and Militz, H. eds., [In publication], 2015, October 26-27, Helsinki, Finland.

LIST OF ABBREVIATIONS

BET	BET (Brunauer, Emmet and Teller) specific surface area
DVS	Dynamic vapour sorption
EMC	Equilibrium moisture content
IGC	Inverse gas chromatography
MC	Moisture content
RH	Relative humidity
SEM	Scanning electron microscopy
XPS	X-ray photoelectron spectroscopy

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1. INTRODUCTION

1.1. Context

There is an increased interest and demand within the construction sector to use biobased building materials. Wood has a long history as a building material in Sweden involving mainly solid wood products. In striving to invent new ways to obtain a sustainable development of the built environment, new types of biocomposites manufactured from wood processing by-products or residuals could be implemented into the building material sector (Erlandsson and Sundquist, 2014). Today most of the by-products, *e.g.* saw-dust or wood chips, are not fully exploited at for example sawmills since there are few fields of added value applications, and normally these by-products are solely used for energy or pulp production.

The primary motive for this thesis is to increase the understanding of material characteristics of wood processing by-products, or so-called wood components, to enable knowledge-based design of new types of biocomposites. In this case, the surface properties of the wood components as well as influences of moisture sorption play an important role for the performance of the composite material. This is not only valid for conventional untreated wood but also for wood products that has undergone modifications of various kinds, *e.g.* thermal modification. The focus in this thesis is therefore to research the surface properties of thermally modified wood components and its susceptibility to moisture to acquire more knowledge about how to design efficient uses of such components in composite materials.

1.2. Background

Structure of wood

Wood is composed of porous cells mainly oriented in an axial (or longitudinal) system related to the tree stem. Figure 1 shows the three main sections of a tree trunk, the transverse, radial and tangential sections, as well as the three principal directions in wood, the longitudinal, radial and tangential directions. In softwoods (conifers), such as spruce and pine, the main volume of the trunk constitutes of so-called tracheid cells oriented in the longitudinal direction. The tracheids are attached to each other and structured in a system, wood tissue, and have an inner cavity called lumen. A schematic drawing of a portion of softwood tracheid cells can be seen in Figure 2. The tracheid cells of spruce are about 2-3.5 mm in length and often about 100 times longer than wide (Bergqvist *et al.*, 1997; Bergander *et al.*, 2002). They are at the ends connected to each other by pits enabling longitudinal water transport. The remaining volume mainly consists of radially oriented ray tracheid cells and ray parenchyma cells (Petrić and Šcukanec, 1973). The parenchyma cells are small brick-shaped cells and are about 150-250 μm long and about 10-20 μm in width. The parenchyma cells are forming different biochemicals, called extractives, which are being emitted into nearby cells through pits (Rowell *et al.*, 2013b).

Together with axial tracheids, they can form pits to connect the axial and radial system. Other structures resembling cavities, which are called resin canals, are often present in the axial and the radial direction. Surrounding these cavities are parenchyma cells that produce resins (Rowell *et al.*, 2013b). In softwoods grown in temperate zones, for example in Scandinavia, two main types of wood tissue named earlywood and latewood are formed during one growth season, together forming so-called annual rings (or growth rings).

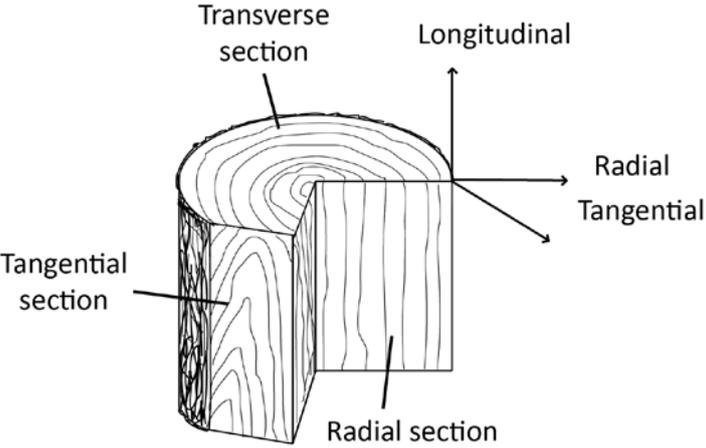


Figure 1. Schematic drawing of a tree trunk showing the three main sections and directions of wood

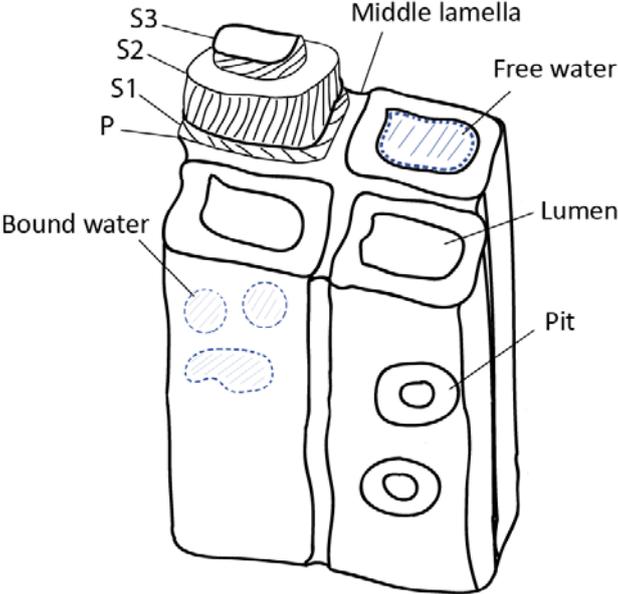


Figure 2. Schematic drawing of softwood tracheid cells showing the cell wall

The earlywood cells are formed during the first part of the growth season, growing rather rapid and forming cells with thinner walls with larger lumina. The latewood on the other hand is formed during the late part of the growth season with slower growing cells resulting in thicker cell walls and smaller lumina. See also the different annual ring patterns for the three typical sections of wood shown in Figure 1. The inner part of the trunk composed of the oldest annual rings is called heartwood, and the outer part with younger annual rings is called sapwood.

The cell wall is the foundation of the wood cell, and it is surrounding the lumen. The major so-called wood polymers building up the cell wall are cellulose, hemicellulose and lignin. Furthermore, pectic substances and proteins (Westermarck *et al.*, 1986), as well as inorganic compounds (Berglund *et al.*, 1999) will be present in smaller amounts. Cellulose is a so-called polysaccharide (built up of glucopyranose units) which appears in wood cells both in crystalline and amorphous form. In wood, cellulose chains are aggregated into longer strings embedded in a matrix of hemicelluloses and lignin, forming so-called microfibrils with high tensile strength (Fengel and Wegener, 1984). Hemicelluloses are also polysaccharides, composed of smaller branched molecules. Lignin is a brittle material with a complex structure of polymeric compounds (Rowell *et al.*, 2013b; Winandy and Rowell, 2013). Furthermore, wood contains two main groups of extractive components; the first group including monoterpenes and resin acids, and the second group including components with a high fat amount (Sjöström, 1993). The extractives can migrate and be redistributed for example during drying of wood (Boutelje, 1990).

The structure of a typical tracheid cell wall is illustrated in Figure 2. The three main regions are the middle lamella, primary cell wall and secondary cell wall, going from the exterior to the interior. The middle lamella is the connecting part between different cells and is rich in lignin. The primary cell wall is composed of randomly oriented microfibrils and pectin. The secondary cell wall consists of three different layers, called the S1, S2 and S3 layers, where the S3 layer is facing the lumen (Fengel and Wegener, 1984). The S1 layer is composed of a thin layer of microfibrils, the S2 layer is composed of lignin and microfibrils and is the thickest layer, which strongly influences the mechanical behaviour of wood. The S3 layer is similar to the S1 layer (Rowell *et al.*, 2013b). The orientation of the microfibrils in the cell wall related to the longitudinal direction of the wood is called microfibrillar angle. An important fact is that both the S1 and S3 layers have their microfibrils oriented more horizontally than vertically related to the direction of the tracheid, whereas the microfibrils in the S2 layer is oriented almost vertically (Kollmann and Côté, 1968).

Moisture sorption in wood

Wood can be considered as a natural bio-polymer composite with a rather hygroscopic nature, *i.e.* a material prone to moisture sorption. This hydrophilic character of wood is mainly due to the hydroxyl groups present in the wood polymers hemicellulose, lignin and cellulose in the cell walls (Fengel and Wegener, 1984).

These groups are creating so-called sorption sites to where the water molecules can interact by the formation of hydrogen bonds (Jeffrey and Saenger, 1991). Hemicelluloses are the wood polymers containing most sorption sites, followed by lignin according to Christensen and Kelsey (1959) and the cellulose microfibrils can attract water molecules only to their surface, according to Engelund (2011).

In their application, all building materials are exposed to moisture. Since wood is both anisotropic and hygroscopic, this may cause in-service problems like poor dimensional stability and cracking due to fluctuating moisture exposure. A high moisture content (MC), (based on the oven-dry weight of wood) normally above 20-30% MC, also increases the risk for decay or discolouration of wood by various fungi. Water can be present in wood in three ways: as water vapour in the lumina or microcavities in the cell wall; as liquid (or free) water in the cell lumina and microcavities in the cell wall; and as water bound by intermolecular forces in the cell wall (Skaar, 1988; Glass and Zelinka, 2010), see Figure 2. Wood strives to reach equilibrium moisture content (EMC) with the surrounding atmosphere, taking up or giving off water, as illustrated in Figure 3 showing an example of a so-called sorption isotherm for wood. Uptake of water occurs through an adsorption process while giving off water occurs through a desorption process. There is a typical difference in EMC between the adsorption and desorption processes called hysteresis, *i.e.* the former results in a lower EMC than the latter, see Figure 3. This implies that sorption isotherm for wood is related to its sorption history. In equilibrium at 100% RH the cell walls are saturated with moisture (fibre saturation point). Above this point the water will be stored in the lumen as free water. As mentioned above, the sorption phenomenon in wood is furthermore related to its dimensional stability (Skaar, 1988).

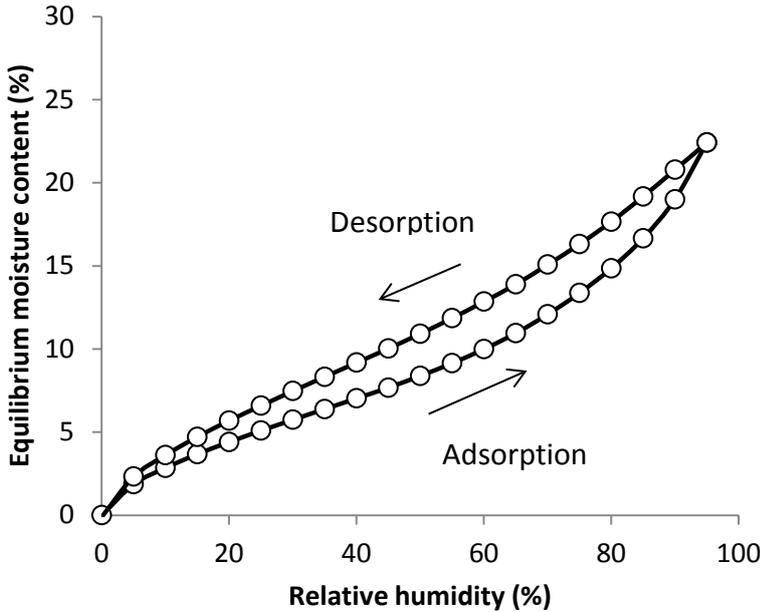


Figure 3. Example of sorption isotherms for wood, including a desorption and an adsorption process

Thermal modification of wood

A number of different methods are today used in the industry to modify wood to make it less hygroscopic and more resistant to decay. The most applied method is thermal treatment, a process where the wood is heated up to temperatures around 200 °C in a low-oxygen environment (Seborg *et al.*, 1953; Stamm, 1956). The treatment leads to chemical and morphological changes of wood, and often results in a significant darkening of its colour. Such thermal modification of wood has during the last decades been claimed to be an efficient modification process resulting in a number of enhanced properties, such as improved dimensional stability and resistance to decay (Hill, 2006; Navi and Sandberg, 2012). This makes thermally modified wood suitable for various outdoor applications, *e.g.* cladding or decking. Disadvantages due to the modification are changes in mechanical properties, such as decreased strength and a more brittle behaviour compared to unmodified wood.

The chemical changes result in a loss of weight in terms of water and also of degradation products and volatiles. Among the wood polymers constituting the cell wall, the hemicelluloses are most hydrophilic polymer and also most sensitive to increased temperatures. Acetic acid will be formed as a degradation product from the hemicelluloses and can lead to a faster degradation of the cell wall polysaccharides in the presence of water or steam. Furthermore, formic acid, methanol and gases like CO₂ will be formed as the temperature increases (Hill, 2006). The degradation of the amorphous parts of cellulose is initiated at about 160-180 °C (Hill, 2006; Rowell *et al.*, 2013a). The presence of water reduces the degradation of cellulose, since the water implies structural changes of the amorphous cellulose regions into a more crystalline structure (Fengel and Wegener, 1984). Lignin is the most stable cell wall polymer even though degradation of lignin can also occur at lower temperatures. Along with the degradation of polysaccharides during thermal treatment there will be an increase of the relative lignin content (Hill, 2006). The wood constituents of unmodified and thermally modified spruce can be seen in Table 1.

Table 1. Wood constituents of unmodified and thermally modified spruce (modification temperature between 180-225 °C)

	Wood constituents (%)			
	Cellulose	Hemicellulose	Lignin	Extractives
Spruce (<i>Picea abies</i> Karst.) ¹	40-46	15-31	27-28	2
	Carbohydrates			
Thermally modified spruce (<i>Picea abies</i>) ²	65-71		28-33	2-3

¹Fengel and Wegener, 1984; ²Alén *et al.*, 2002

One established thermal modification method is the ThermoWood® process, which is an example of a modification process under closed conditions, used for the investigated samples in this study. The ThermoWood®D process consists of three phases, where the first phase involves a drying step using heat and steam. Firstly the temperature is increased to 100 °C and then to 130 °C, where the moisture content at the same time approaches 0%. In the second phase the temperature is increased to 212 °C for 2-3 hours under steam. The third phase implies cooling and re-moisture conditioning, where the temperature is decreased to about 80-90 °C. At the same time the wood is re-moisturised to 4-7% MC (Anonymous, 2003).

The water vapour sorption behaviour of thermally modified wood has earlier been studied (Kollmann and Schneider, 1963; Chirkova *et al.*, 2005; Pfriem *et al.*, 2010; Guo *et al.*, 2015). Results showed a decrease of the moisture content related to an increase of the thermal treatment temperature. Recently, dynamic vapour sorption (DVS) has been used for studying the vapour sorption properties of thermally modified wood (Navi and Girardet, 2000; Kamdem *et al.*, 2002; Kohler *et al.*, 2003; Inari *et al.*, 2006; Boonstra and Blomberg, 2007; Jalaludin *et al.*, 2010a and 2010b; Hill *et al.*, 2012; Olek *et al.*, 2013).

Surface characterisation of wood

A surface is considered as the separation of two phases in an aggregated system, *e.g.* solid-solid, solid-liquid, solid-gas, liquid-liquid and liquid-gas. The energy required to hold up the surface is called the surface energy and is defined as the excess energy required for moving a molecule from the bulk (interior of the material) to the surface (Adamson and Gast, 1997). The molecular interactions are stronger at the surface since there are fewer neighbouring atoms to interact with which implies that they require more energy to hold up the surface.

The total surface energy can be separated into two different parts, a physical part and a chemical part (Berg, 1993; Good, 1993). The physical part is described by Lifshitz-van der Waals interactions (mainly the London dispersion forces which are induced dipole interactions). The physical interaction part is also called non-polar or dispersive interaction. The chemical part constitutes of acid-base interactions, also called polar or specific interaction. They together constitute the total surface energy:

$$\gamma_s = \gamma_s^d + \gamma_s^{ab} \quad (1)$$

where γ_s is the total surface energy, γ_s^d is the dispersive component of the surface energy and γ_s^{ab} is the acid-base, or specific component, of the surface energy. The work of adhesion, defined (Dupré, 1869) as the work required to separate unit area of a solid-liquid interface, can be described in the same way, as the sum of the work of adhesion of the dispersive part and the specific part (Fowkes and Mostafa, 1978):

$$W_A = W_A^d + W_A^{ab} \quad (2)$$

where W_A is the sum of the work of adhesion at the solid-liquid interface, W_A^d is the dispersive part of the work of adhesion, and W_A^{ab} is the acid-base part of the work of adhesion.

Many solid surfaces have a heterogeneous chemical nature, which is related to their chemical composition and different functional groups present at the surface and impurities. This is indeed valid for materials such as wood. In addition, wood has a surface roughness, *i.e.* a varying surface morphology, depending on *e.g.* the applied wood processing method and sharpness of the tools. The surfaces of wood polymers are dependent on temperature, environment and time. The polymer molecules at the surface always strive to reach the lowest energetic state possible and thermodynamics will encourage reorientation of surface components to minimise the surface free energy (Gunnells *et al.*, 1994). Reorientation of the molecules at the surface will, if possible, naturally occur as a result of changes in temperature, environmental conditions or with ageing (time).

Surface characterisation of wood can increase the understanding of its interaction potential with other materials' surfaces, for example between a wood component and a matrix in wood plastic composites (WPCs), as well as in applications involving gluing and coating of wood. It is also likely that the structure and chemical composition of the wood surface will influence its moisture sorption properties. Several methods can be applied to study the surface characteristics of wood, although the most common method is contact angle analysis, *i.e.* involving so-called wetting phenomena, which can be defined as "macroscopic manifestations of molecular interaction between liquids and solids in direct contact at the interface between them" (Berg 1993). Typically, wetting properties, or wettability, of different substrates are determined using thermodynamic wetting parameters such as contact angles, surface energy and work of adhesion (Berg 1993). Determination of wettability of wood (mainly solid wood) and its significance in wood science has recently been extensively reviewed by Petrič and Oven (2015). In this review, the complexity of wood wettability determination based on contact angle measurements and its interpretation was stressed, and it was recommended that great caution must be considered when comparing contact angle data between different laboratories.

Compared with solid wood, it is evident that wetting analyses of wood in particulate or fibrous form (*i.e.* various wood components such as saw dust, wood meal, shavings or pulp fibres) is inherently difficult. Mainly due to the small size and great structural variations of such materials, direct measurements of contact angles using goniometers, or indirect measurements based on Wilhelmy plate principles, are both difficult and tedious. Instead indirect measurements based on so-called wicking techniques may be applied (see *e.g.* Hodgson and Berg 1988; Gardner *et al.*, 1999; Wålinder and Gardner, 1999). However, such techniques involve certain serious uncertainties mainly due to uncontrolled contamination of the probe liquids, and also due to swelling effects when using polar probe liquids (Wålinder and Gardner, 1999).

Other surface characterisation methods applied on wood are for example inverse gas chromatography (IGC), X-ray photoelectron spectroscopy (XPS or ESCA) and atomic force microscopy (AFM). IGC has been used to analyse surface energetics of lignocellulosic materials, mainly in particulate or fibrous form *e.g.* wood pulp fibres, cellulose or lignin (Dorris and Gray, 1980; Matuana *et al.*, 1999; Tze *et al.*, 2006), cotton and linen (Csiszár and Fekete, 2011) and microfibrillated cellulose and cellulose nanofibers (Siddiqui *et al.*, 2011). Also wood particles and fibres, including their interactions with thermoplastics has been analysed using IGC (Kamdem *et al.*, 1993; Tshabalala, 1997; Wålinder and Gardner, 2000 and 2002; Peterlin *et al.*, 2010; Oporto *et al.*, 2011; Cordeiro *et al.*, 2012). These analyses have been performed at low solute concentrations (infinite dilution) with results representing only the highest values of the surface energy, *i.e.* the high-energy sorption sites. A new generation of IGC can, however, be applied to determine the heterogeneity of materials at different surface coverage, including determination of so-called surface energy profiles covering the distribution from the higher to the lower surface energy sites (Ylä-Mäihäniemi *et al.*, 2008). This approach is further described in analysis of the surface energy of alumina and glass, in particulate form, by Ylä-Mäihäniemi *et al.* (2008). XPS analysis has been used to determine the surface chemical composition for paper and refined lignocelluloses already some decades ago (Dorris and Gray, 1978a and 1978b). Lately it has also been applied for analysis of wood surfaces (Nzokou and Kamdem, 2005; Inari *et al.*, 2006; Shchukarev *et al.*, 2002; Johansson *et al.*, 2012; Muguet *et al.*, 2013) and also for chemically or thermally modified wood (Bryne *et al.*, 2010; Tuong and Li, 2011; Wang *et al.*, 2011; Rautkari *et al.*, 2012; Sedighi Moghaddam *et al.*, 2013; Wang *et al.*, 2015).

1.3. Aim and objectives

The aim of this thesis is to gain more insight about the surface characteristics of thermally modified wood components intended to be used in biocomposites. Such information may increase the understanding of molecular interaction ability for uses of the components in composites and how to predict their long-term behaviour and durability. The aim is also to increase the understanding of how the surface characteristics are influenced by water vapour sorption, relevant for *e.g.* outdoor building material applications.

The specific objective was to study the surface energy characteristics of thermally modified spruce wood components. These properties were looked into both at dry and moist states. The focus was on possible influences on the surface properties of thermally modified wood due to exposure to a significant increase in relative humidity (RH). An effort was also made to establish a link between surface energy and surface chemical composition.

The IGC method was applied to study surface energy properties of both thermally modified and unmodified wood components (Paper I). Furthermore, the DVS and the XPS methods were applied to add further insight about influences of water vapour sorption in the wood components and to study the elemental surface chemical composition of smaller solid wood samples (Paper II).

2. MATERIALS

To mimic wood processing by-products, such as saw dust and shavings, from the production of solid thermally modified wood, the wood components in this study were prepared by grinding solid wood boards. The thermally modified wood boards, in the form of planed cladding boards, were prepared by Stora Enso from Norway spruce (*Picea abies* Karst.). The thermal modification method used was the ThermoWood®D process, (Anonymous, 2003). Unmodified sawn and kiln dried solid wood boards were also prepared from Norway spruce from Finland. After the preparation, both the thermally modified and the unmodified boards were stored in a climate of 20 °C and 20-40% RH. For the IGC and the DVS analyses, thermally modified and unmodified wood components were prepared from these solid boards in a two-step grinding procedure (Segerholm *et al.*, 2012). In this process, the solid wood was first cut into thin veneers by the use of a disk flaker. In the second step a knife ring mill was used, converting the veneers into smaller components. These components were then sifted and separated into five different size fractions using a sieve (<0.125 mm; 0.125-0.25 mm; 0.25-0.50 mm; 0.50-1.00 mm; >1.00 mm). The smallest fraction (<0.125 mm) was used for the analyses in this work. Examples of the prepared components of the unmodified and thermally modified wood are shown in Figure 4. For the XPS analysis, solid wood samples were prepared from the sapwood portion of the panels and planks as cubes of about 10 x 10 x 10 mm³, using a saw and a wood chisel.

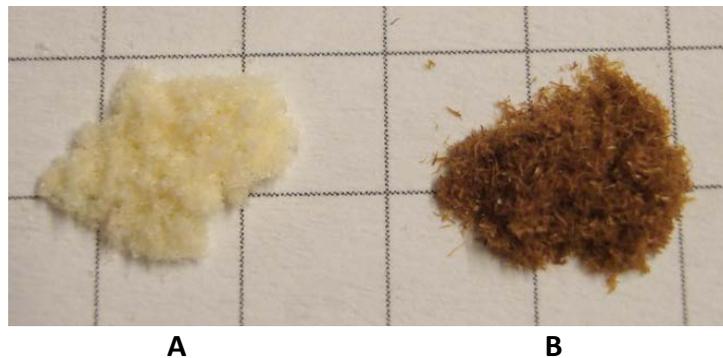


Figure 4. Unmodified wood components (A) and thermally modified wood components (B), sifted through sieve screens of <0.125 mm

3. METHODS

3.1. Component length analysis

Length measurements of the wood component samples were performed using kajaaniFiberLab™ apparatus (Metso automation, Finland). About 2 g of components were mixed with 5000 mL of water and stirred in a tank. For one test, 50 mL was used from this mixture. According to the results, the polarised laser that detected and monitored components passing registered about 15,600 modified and 38,000 unmodified components from four tests respectively.

The lengths of the components, in this study defined as the projected length shown in Figure 5, were obtained by calculations from an image analysis software.

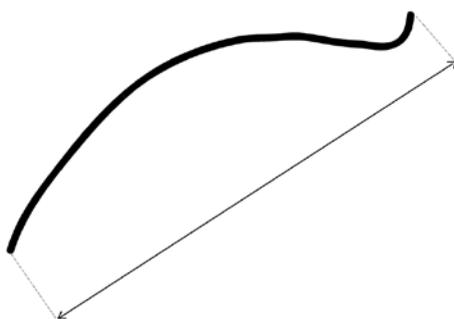


Figure 5. A schematic drawing of an arbitrary wood component where the arrow shows the projected length used as the length measurement in this study

3.2. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was used to observe the overall micromorphology and to analyse specific morphological differences between the unmodified and thermally modified wood components. The samples were analysed uncoated, using a Hitachi TM-1000 scanning electron microscope (SEM). Three replicates of each sample were used for the analysis.

3.3. Inverse gas chromatography (IGC)

3.3.1. IGC theory

Inverse gas chromatography (IGC) was used in Paper I to study the surface area and surface energy of thermally modified and unmodified wood components. It is a useful technique for characterising the physico-chemical properties such as surface area and surface energetics of materials in particle, fibrous or powder form (Lloyd *et al.*, 1989). Knowledge about the surface energy is valuable to better understand and also control the process of interaction between different materials and components.

In Figure 6, a schematic illustration of the process during an experiment using IGC is shown. Helium is used as carrier gas for the transportation of probes through the particulate or fibrous sample packed in a column. The probe is detected after passing through the sample column by a flame ionisation detector (FID). The method is based on the interaction between the sample with unknown surface properties and a set of solvent probes with known properties. The solvent probes can be of both polar and non-polar character. The polar probes are of Lewis acid-base type and the non-polar probes use the Lifshitz-van der Waals interaction (mainly London dispersion forces). The focus in this thesis was on the dispersive surface interactions (using non-polar probes).

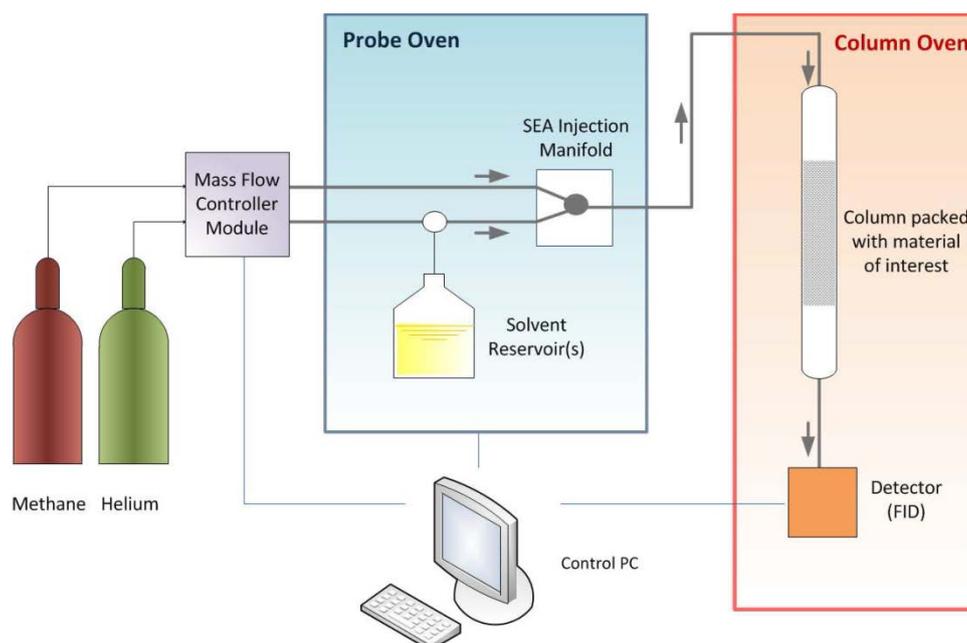


Figure 6. Principles of the inverse gas chromatography (IGC). Helium is used as carrier gas transporting one solvent probe at a time through the sample column. The time of interaction between the probe and the sample is recorded as the retention time. The figure is reproduced with permission from Surface Measurement Systems Ltd., UK

The polar contribution to the surface energy has been shown to be more complex to determine, possibly due to uncontrolled interaction between the polar probe and the wood surface, causing modifications of the latter. This uncertainty and the possible alteration effects of the wood may result in *e.g.* pronounced tailing of the chromatogram, as observed in the initial IGC trials in this study. Such limitations have also been encountered in other studies (Wålinder and Gardner, 1999 and 2000; Tze *et al.*, 2006; Kondor *et al.*, n.d.). The polar interactions are, however, intended to be included in future studies. The solvent probes used in this work are presented in Table 2.

Table 2. Properties of the non-polar IGC probes (supplier: Sigma-Aldrich) used where a represents the surface area that can be occupied by one probe molecule and γ_L^D the surface tension

Solvent probe	a (\AA^2)	γ_L^D (mJ/m^2)
n-heptane	57 ^a	20.3 ^c
n-octane	63 ^b	21.1 ^c
n-nonane	69 ^b	22.4 ^c
n-decane	75 ^b	23.4 ^c
n-undecane	81 ^b	24.2 ^c

^a Schultz *et al.*, 1987; ^b Liu and Rials, 1998

^c the surface tension of the solvent probe at 25°C (Lide, 1995)

The interaction is registered from the detector signal as the retention time which indicates the degree of interaction, where a longer retention time means more interactions and thus higher surface energy. Figure 7 shows a schematic drawing of the probe molecules traveling through the sample column.

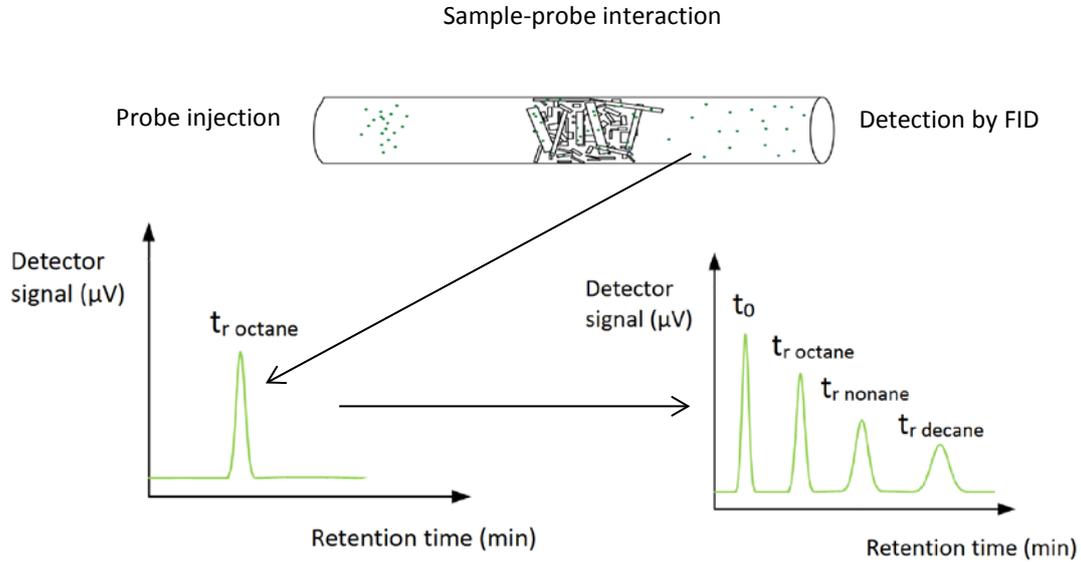


Figure 7. Schematic drawing of sample column in IGC measurements showing the adsorption and surface interaction (adsorption and desorption) between probe and packed wood components. Interaction between sample and sorptive gives the retention times (t_r). t_0 is the time of the methane injection measuring the dead volume

The retention time is determined using the peak com (centre of mass), which means that the integration limits are selected from the start and end time of the peak in the chromatogram for each injection (Surface Measurement Systems Ltd., 2013):

$$t_r = \frac{\int_{t_1}^{t_2} t \cdot I(t) dt}{\int_{t_1}^{t_2} I(t) dt} \quad (3)$$

where t_1 is the start time and t_2 is the end time of the peak, t is the time and $I(t)$ is the detector intensity. To enable analyses of surface properties, the BET (Brunauer, Emmet and Teller) specific surface area of the sample is required. The BET specific surface area is defined as the physical adsorption of gases on solids *e.g.* particulates and fibres, on the external or internal surface. It can be determined by physical adsorption in IGC experiments using an alkane, such as octane. The BET equation is an adsorption isotherm derived from Brunauer *et al.* (1938):

$$\frac{1}{[n(p_1/p)-1]} = \frac{c-1}{n_m \cdot c} \left(\frac{p}{p_1} \right) + \frac{1}{n_m \cdot c} \quad (4)$$

where p_1 and p are the saturation and equilibrium pressures of the adsorbates at the adsorption temperature, n is the amount mole gas adsorbed, n_m is the number of moles for monolayer adsorption and c is the sorption constant based on the heat of adsorption. By plotting the p/p_1 versus $1/n[(p_1/p)-1]$, a linear correlation can be obtained in the range of $0.05 < p/p_1 < 0.35$. The sorption isotherms should form a Type II or IV curve, shown in Figure 8.

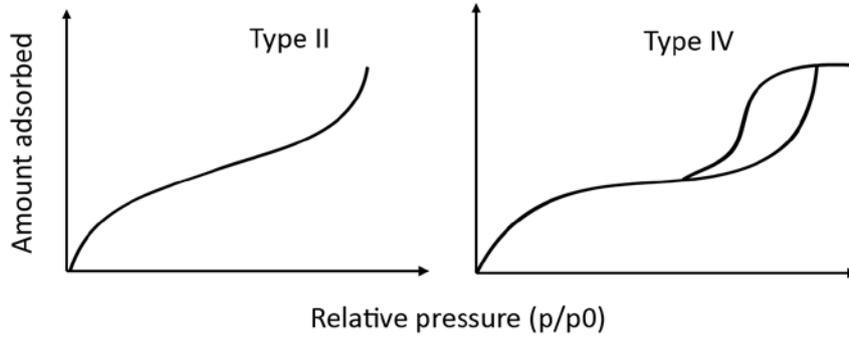


Figure 8. Sorption isotherms of type II and IV

From the slope of the linear correlation in the sorption isotherm, the monolayer capacity (n_m) can be obtained which is the amount of gas needed to create a monolayer. The specific surface area is calculated using the following equation:

$$BET = \frac{(n_m \cdot N \cdot a)}{V \cdot m_a} \quad (5)$$

where N is the Avogadro's number, a is the adsorption cross section of the gas, V is the molar volume adsorbed gas and m_a is the adsorbent mass.

The calculations of the surface properties, in this IGC approach, are based on a net retention volume (V_N), which relates to the interaction between the solid surface of the sample and the probe injected. This will depend on the probe used and the properties and structure of the surface of the solid sample. V_N is described from the following equation:

$$V_N = V_r^0 - V_d^0 \quad (6)$$

where V_r^0 is the measured retention volume of the probe and V_d^0 is the dead volume measured (which is performed with injections before and after the probe injections, using the inert gas methane). The index 0 is connected to a correction for the pressure drop in the column and related to j in Equation 7:

$$V_r^0 = \frac{j}{m} F \cdot t_r \frac{T}{273.15} \quad (7)$$

where m is the mass of the sample, F is the exit flow rate at pressure 1 atm and 273.15 K, T is the column temperature, t_r is the retention time of the probe and the James-Martin correction factor (Halász and Heine, 1967) j is described as:

$$j = \frac{3}{2} \left[\frac{\left(\frac{p_i}{p_0}\right)^2 - 1}{\left(\frac{p_i}{p_0}\right)^3 - 1} \right] \quad (8)$$

where p_i is the inlet pressure of the carrier gas and p_0 is the outlet pressure of the carrier gas.

Many solid surfaces have some kind of heterogeneous character. IGC can be used to determine the surface energy at different surface coverage for a better understanding of the surface heterogeneity. The surface coverage (n/n_m) of each alkane can be determined by the amount of mole adsorbed (n) since the n_m is known, and together with the experimental values of the net retention volume this can describe the surface energy heterogeneity. For the surface energy analysis, sorption isotherms are obtained for each probe. Combining those for different surface coverages, a correlation with the retention volume is obtained (Ylä-Mäihäniemi *et al.* (2008), as exemplified in Figure 9.

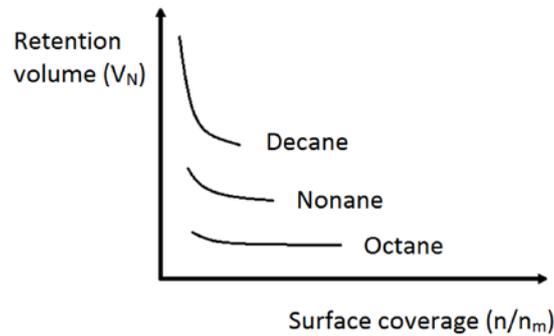


Figure 9. Example plot for determining the dispersive component of the surface energy using IGC showing the retention volume versus surface coverage for different alkanes

Using IGC, there are two possible approaches to determine the dispersive component of the surface energy; the Schultz method (Schultz *et al.*, 1987) or the Dorris-Gray method (Dorris and Gray, 1980). In the Dorris-Gray method the calculations are based on the free energy of adsorption of one methylene group (CH_2) from the probe molecule:

$$\Delta G^{CH_2} = -R \cdot T \cdot \ln \left(\frac{V_{N,n+1}}{V_{N,n}} \right) \quad (9)$$

The dispersive component of the surface energy is obtained from the correlation and slope of the free energy of adsorption of at least three alkanes plotted versus their carbon number:

$$\gamma_s^d = \frac{\text{slope}^2}{4 \cdot N^2 \cdot (a_{CH_2})^2 \cdot \gamma_{CH_2}} \quad (10)$$

Interpolation from Figure 9, gives one value for each alkane at a particular surface coverage as shown in Figure 10. By plotting the free energy of adsorption (Equation 10) versus the alkane carbon number, the dispersive component of the surface energy (γ_s^d) can be obtained to determine the surface energy heterogeneity.

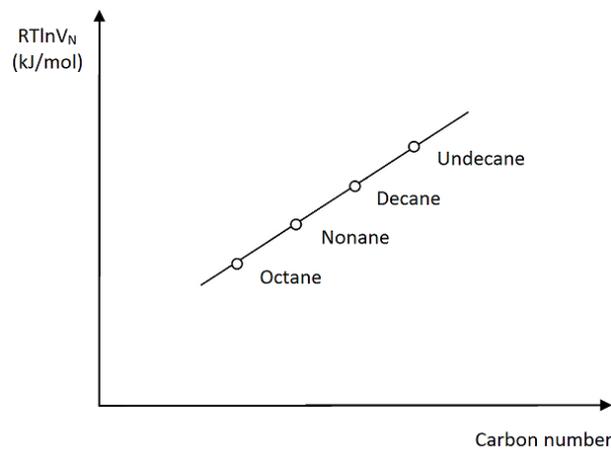


Figure 10. Example plot for determining the dispersive component of the surface energy using IGC (Dorris-Gray method)

The Schultz method is based on the injected probe alkanes, and the free energy of adsorption:

$$\Delta G_A = \Delta G_A^d = R \cdot T \cdot \ln V_N + C \quad (11)$$

where C is a constant depending on the reference state. Combining the free energy of adsorption with the work of adhesion of the alkane probes, the following expression can be achieved:

$$-\Delta G_A = N \cdot a \cdot W_A \quad (12)$$

To calculate the work of adhesion for the alkane probes, a mean of the dispersive surface tension of the alkane probe in liquid form and the dispersive component of the surface energy of the solid is used:

$$W_A = W_A^d = 2\sqrt{\gamma_s^d \cdot \gamma_l^d} \quad (13)$$

where γ_l^d is the dispersive part of the surface tension for the alkane probe in liquid form. Combining Equation 11-13, the following expression is obtained:

$$\gamma_s^d = \frac{1}{4 \cdot \gamma_l^d} \left(\frac{R \cdot T \cdot \ln V_N}{N \cdot a} \right)^2 \quad (14)$$

3.3.2. IGC measurements

The IGC measurements were performed on two replicate columns for each wood sample, placed in the inverse gas chromatograph, an IGC Surface Energy Analyzer developed by Surface Measurement Systems (SMS) Ltd., Alperton, London, UK. The wood components were dried in a conventional oven at 103 °C for 2 h before samples preparation. In a preconditioning step the sample columns, packed with wood components, were further dried at 60 °C for 2 h to obtain the dry mass and to remove volatiles. Purified helium with a flow rate of 10 mL/min was used as carrier gas. The BET specific surface area was determined at finite dilution, in the partial pressure range 5-35% using octane isotherms, before each surface energy measurement. The solvent probes from Table 2 were used in the studies. After injecting a probe it interacted with the sample and the retention time was determined using SMS software. All measurements were performed at 30 °C. The thermally modified samples were first analysed at dry state (0% RH) and then at moist state (75% RH). This was then repeated in two more cycles. Thereafter, three additional cycles were performed, but this time only up to an RH of 25%. For the unmodified components similar results were obtained between the repeating dry and moist cycles, and therefore only one comparing cycle was performed at dry state (0% RH) and then at moist state (75% RH). The IGC data is presented as an average and standard deviation of two replicate columns. It should also be noted here that each replicate consisted of a sample of thousands of wood components.

3.4. Dynamic vapour sorption (DVS)

As mentioned earlier, several studies have been carried out on the vapour sorption behaviour of unmodified and thermally modified wood, using the dynamic vapour sorption (DVS) method. However, limited research has been performed in multiple cycles, where the wood has been exposed to water vapour cycling (Hill *et al.*, 2012). In this study the water vapour sorption behaviour of thermally modified and unmodified wood component samples that previously had been exposed to the increased relative humidity (RH) condition of 75% RH at 30 °C was compared with non-exposed samples.

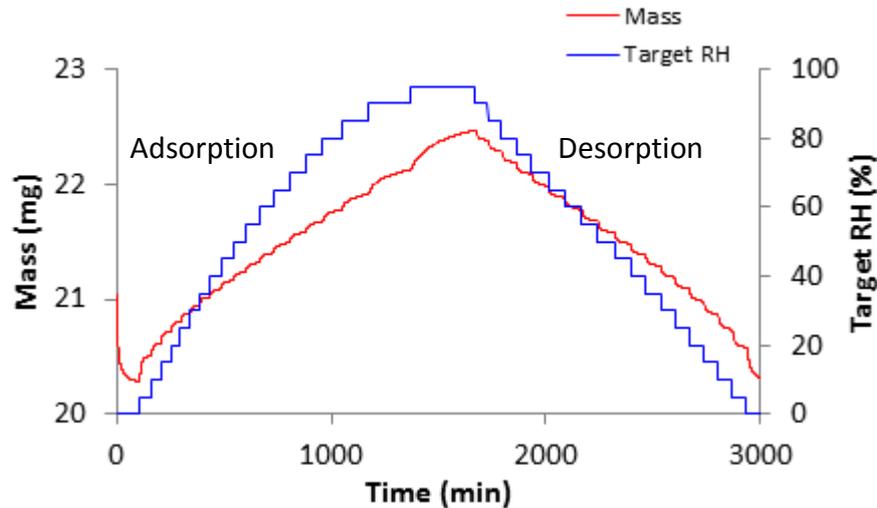


Figure 11. Example plot showing data from a typical DVS isotherm measurement, starting with adsorption. The changes in mass at different RH levels of thermally modified wood previously exposed to high relative humidity conditions

The DVS apparatus used was DVS ET1, Surface Measurement Systems Ltd., London, UK. To enable better comparison with the results from the IGC analyses, the temperature was kept constant at 30°C during the experiments. Each test run was initiated by drying of the sample and then the sorption cycle started at 0% RH and increased stepwise with 5% RH steps, up to 95% RH and then stepwise reversing back to 0% RH, see Figure 11. When the mass change of the sample, sustained for 10 minutes was less than 0.002%/min, the next step in the conditioning process was targeted.

3.5. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS), also called electron spectroscopy for chemical analysis (ESCA), is a very sensitive surface characterisation technique, involving analyses of the outermost surface of a material. This gives information about the surface chemical composition to a depth up to about 10 nm. Several studies have been performed during the last years involving wood and thermally modified wood (Sinn *et al.*, 2001; Bryne *et al.*, 2010; Klarhöfer *et al.*, 2010; Tuong and Li, 2011; Wang *et al.*, 2011; Johansson *et al.*, 2012; Rautkari *et al.*, 2012; Wang *et al.*, 2015). Figure 12 shows a drawing of the principles of the XPS experimental set-up.

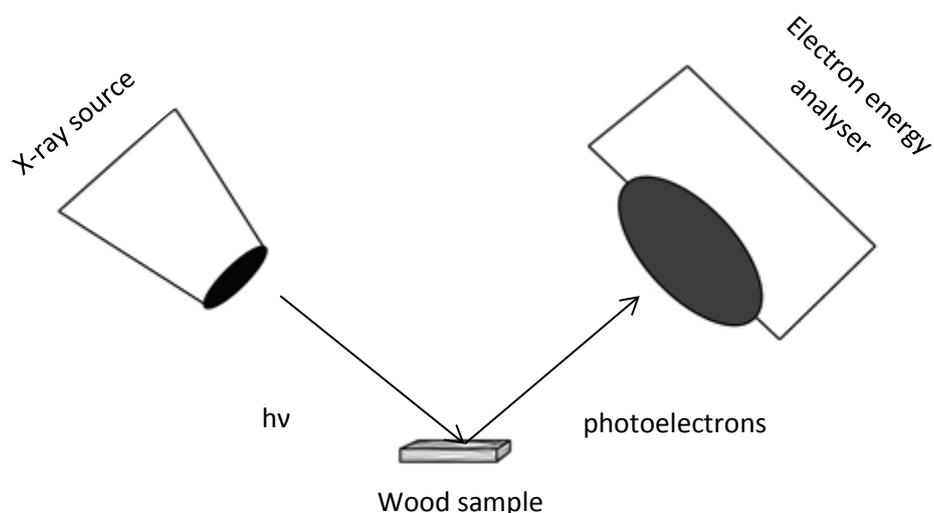


Figure 12. A drawing showing the principles of the XPS experimental set-up where the wood surface is excited sending off photoelectrons that are detected by an electron energy analyser

The chemical surface properties of four freshly cleaved surfaces of the prepared wood samples were analysed using XPS analysis (AXIS Ultra electron spectrometer, Kratos Analytical, UK). Additionally, another set of four matching samples was prepared using acetone extraction, Table 3 shows a compilation of the analysed wood samples. The freshly cleaved/extracted samples were pre-evacuated overnight in order to stabilise analysis conditions in UHV. Data from the analysis was recorded using monochromatic A1 K α x-rays, at 100 W. Survey scans were recorded with 160 eV pass energy with 1 eV step, and the high resolution regions were taken with 20 eV pass energy with 0.1 eV step.

Table 3. Abbreviations for the different non-extracted and extracted thermally modified (TM) and unmodified (UM) wood samples used in the XPS measurements. The abbreviation exp refers to the samples exposed to increased RH of 75% at 30 °C, and extr refers to the acetone extracted samples

	Thermally modified	Unmodified
	TM	UM
Non-extracted	TM exp	UM exp
	TM extr	UM extr
Extracted	TM exp extr	UM exp extr

The carbon chemistry was evaluated from high resolution C1s components, fitted with four Gaussian components (C1-4), which were defined as carbon atoms with 0, 1, 2 or 3 oxygen neighbours (Table 4). The nominal content for lignin, extractives and cellulose were calculated (Koljonen *et al.*, 2003), and furthermore the non-cellulosic C1 component of the high resolution C1s data versus the O/C atomic ratio was plotted (Rautkari *et al.*, 2012).

Table 4. The C1s peak, deconvoluted into four carbon peaks (C1-4) together with the approximate binding energy, functional groups and the percentage distribution of wood constituents from a total of 100%, related to different carbon peaks

C1s	Approximate binding energy (eV)*	Functional groups	Percentage distribution**			
			Cellulose	Lignin	Hemicellulose	Extractives
C1	285.0	C-C, C=C and/or C-H		49		94
C2	286.7	C-O and/or C-O-C	83	49	78	
C3	288	C=O and/or O-C-O	17	2	19	
C4	289.4	O-C=O and/or C(=O)OH			3	6

* Data taken from Beamson and Briggs (1992)

**Approximate percentage distribution of wood constituents based on theoretical values from Laine *et al.* (1994) where arabinoglucuronoxylan was used for hemicellulose and oleic acid for extractives

4. RESULTS AND DISCUSSION

4.1. Morphology (Paper I)

The results from the component length measurements using the kajaaniFiberLab™ are presented in Figure 13. As can be seen, the thermally modified components had a significantly lower frequency of lengths in the range 0.1-0.2 mm, and a significantly higher frequency of lengths in the range 0.3-0.6 mm. In other words, the thermally modified components were in average significantly longer than the unmodified components. It should be remembered that in the sample preparation, the components were sifted through a 120 mesh (>0.125 mm) screen. However, the results showed that the majority of the components were significantly longer and thinner than 0.125 mm, *i.e.* indicating that their aspect ratio could range approximately from 5-20. In other words, the wood components seemed to have an aspect ratio significantly higher than a component with a particulate shape corresponding to an aspect ratio of ca 1. No direct measures of the aspect ratios were however obtained in this case, but in a study by Segerholm *et al.* (2012) it was shown that grinded wood components of thermally modified spruce and unmodified pine had average aspect ratios of about 10 and 5, respectively. The number of the unmodified components registered in this analysis was more than double than that of the thermally modified components. Since the weight of the components was approximately the same in the preparation step, this furthermore confirms that the unmodified components consisted of a larger amount of short-length components (fines).

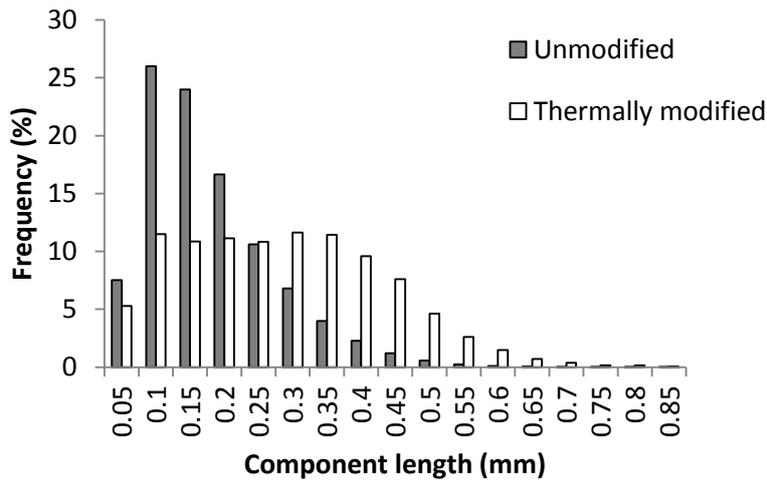


Figure 13. The projected length frequency distribution of thermally modified and unmodified wood components measured by the use of kajaaniFiberLab™ apparatus

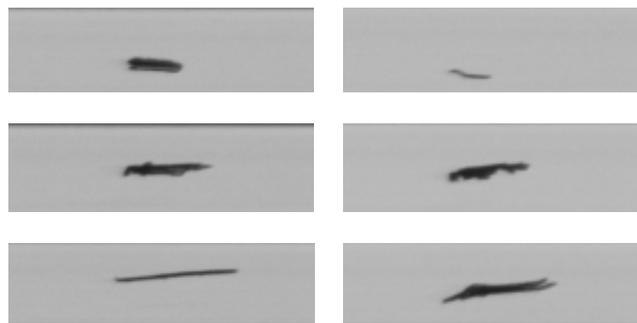


Figure 14. Representative images of wood components obtained from the kajaaniFiberLab™ analysis, showing the difference in length and structure. To the left are thermally modified wood components with lengths: 0.260 mm, 0.430 mm and 0.600 mm; and to the right unmodified wood components with lengths: 0.180 mm, 0.380 mm and 0.560 mm

The structure of different representative components, taken from the kajaaniFiberLab™ analysis, can be seen in Figure 14. All the components show different structure and indicate the morphological heterogeneity and variability on the macroscale of wood components. Figure 15 shows an example of the micromorphology of the unmodified and thermally modified wood components observed using SEM. As indicated in this figure which also confirms the results shown in Figure 13, the unmodified wood sample consists of a higher amount of smaller components and fragments (fines) compared with the modified sample. In addition, the modified components were more splintered and needle-like compared with the unmodified components. This is suggested to be due to changes in the chemical composition of the thermally modified wood influencing the material disintegration during the grinding process to produce the components, which ultimately also would influence the properties of the surfaces created.

It is also important to remember that, as soon as a new wood surface is created an ageing process of the surface will start, for example migration of extractives and/or oxidation effects. Furthermore, the new surfaces created after the milling will also age differently for modified and unmodified wood leading to variations in the surface properties and morphology (Bryne *et al.*, 2010 and Johansson *et al.*, 2012).

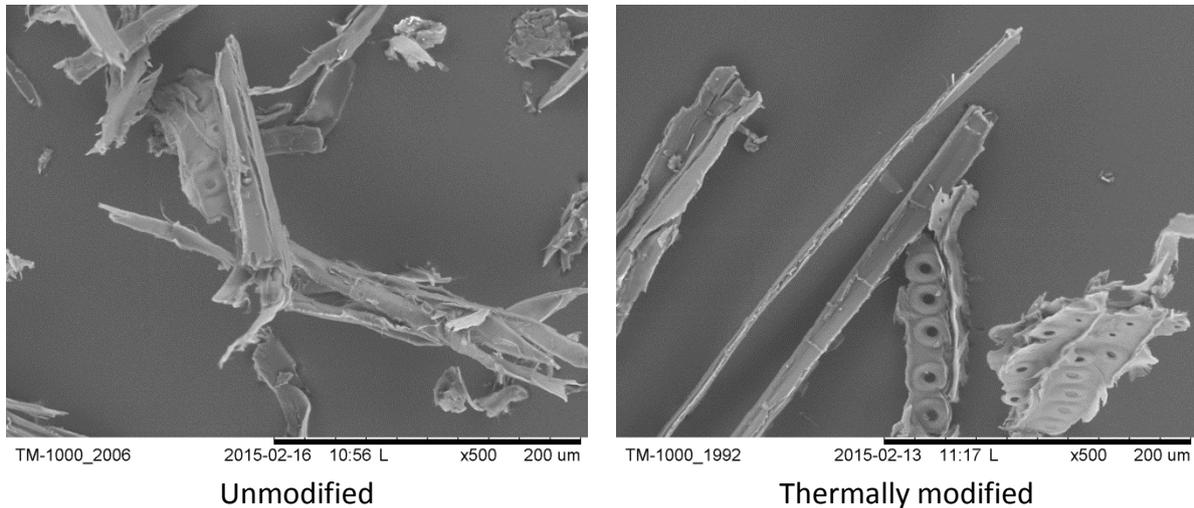


Figure 15. Micrographs of unmodified and thermally modified wood components, respectively, obtained using scanning electron microscopy (SEM)

4.2. Surface area (Paper I)

Figure 16 shows the obtained BET-specific surface areas for the different samples. The surface area was in the range 1.2-1.3 m²/g for the thermally modified wood components which was significantly lower than that for the unmodified wood components which was in the range 1.8-1.9 m²/g. A similar range of BET values have been reported by Lagana *et al.* (2006), Karinkanta *et al.* (2012) and Wiman *et al.* (2012) for sawdust, chips and thermally modified sawdust of Norway spruce using the conventional method with nitrogen as sorptive. Lagana *et al.* (2006) also reported an increase in the surface area with increasing treatment temperature from 20-180°C ranging between 1.3-2.1 m²/g. In BET measurements, using nitrogen or octane as sorptives, it should be remembered that such molecules have limited access to adsorption in the smallest pores, in the wood substance. The BET values are in agreement with the results obtained from morphology studies using the kajaaniFiberLab and SEM, *i.e.* the unmodified component had a higher amount of fines compared with the thermally modified component, resulting in a higher specific surface area of the former.

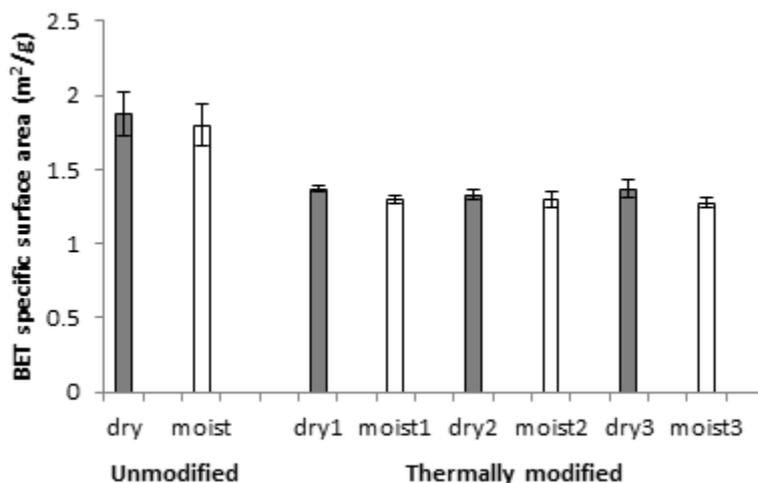


Figure 16. The average BET specific surface area determined using IGC at 30 °C of the unmodified wood components at dry (0% RH) and moist (75% RH) conditions, and the thermally modified wood components exposed to three cycles of dry (0% RH) and moist (75% RH) conditions

Regarding the influence of increased relative humidity on the BET values a trend could be seen indicating a small decrease of the BET specific surface area at the moist state, both for the unmodified and thermally modified wood components. The same trend could be observed both at RH 75% and 25%, with occasional exceptions. It is suggested that this could be attributed to the polar nature of the water molecules which are likely to interact more strongly with the wood surface than the non-polar octane molecules, or perhaps due to swelling effects of the wood cell wall “closing” or changing the morphology and accessibility for sorption of octane.

4.3. Surface energy (Paper I)

Figure 17 presents the obtained dispersive component of the surface energy at 30 °C for the different wood components at dry state and at 25% and 75% RH for the modified wood and at 75% RH for the unmodified wood. The results indicated that the thermally modified components possessed a more heterogeneous surface in terms of the dispersive component of the surface energy compared with the unmodified components. In general, it could be observed that the most pronounced changes of the dispersive component of the surface energy occurred at low fractional surface coverage. Above 5% surface coverage the dispersive component of the surface energy seemed to stabilise with increasing surface coverage for all samples.

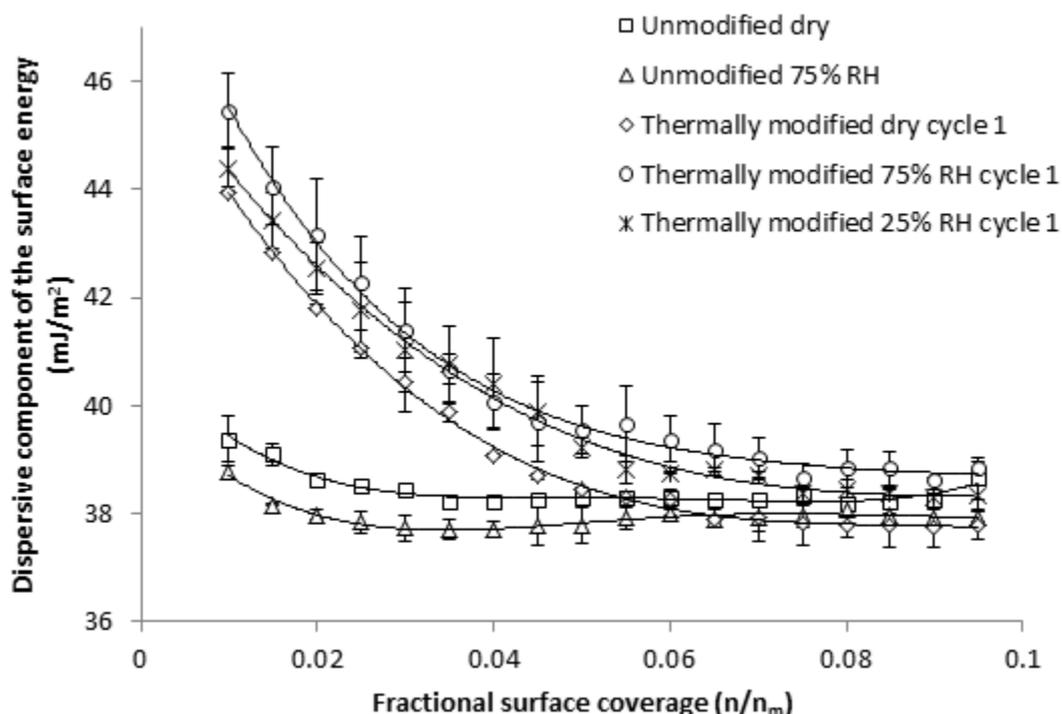


Figure 17. The dispersive component of the surface energy versus different target fractional surface coverage obtained using IGC at 30°C for the unmodified wood components at dry (0% RH) and moist (75% RH) conditions, and for the thermally modified wood component at dry (0% RH) and moist (75% RH and 25% RH) conditions cycle 1. The average of both samples is shown and the error bars represent the standard deviation of the two replicate columns

It should also be noted that the octane, nonane and decane probes appeared to be most suitable for analysing the surface properties of these wood components. The target fractional surface coverage was chosen from 0-10% surface coverage (0-0.1 n/n_m). For heterogeneous samples like wood, this is the most interesting region. A heterogeneous surface implies differences in the distribution of surface energy over the surface. As a result, any changes in surface energy will therefore be visible at lower surface coverage of a heterogeneous material. With increasing surface coverage the probe molecules will target less energetic sites and the values of the surface energy levels out.

As can be seen from Figure 17, a slight increase of the dispersive component of the surface energy was visible for the thermally modified wood due to the exposure to 75% RH. A similar change was observed for all the three cycles which implies that there was no change in the dispersive component of the surface energy due to the repeating cycling. This increase of the dispersive surface energy at the moist state at 75% RH could be related to the adsorption of water vapour leading to breaking of intermolecular bonds, as discussed in the DVS section. As a result of this, the cell wall micropores would be available also creating new high energetic sites. This was also seen in the following three cycles at 25% RH, but to a lesser extent.

The dispersive component of the surface energy for the unmodified components seemed to be of a less heterogeneous character compared with the thermally modified components, as can be seen in Figure 17. In contrast to the modified wood, the exposure to the 75% RH condition in this case seemed to decrease the dispersive component of the surface energy. This observation is in agreement with a study by Laiveniece and Morozovs (2014), which showed that the dispersive part of the surface energy of Norway spruce samples decreased with increasing MC.

An important aspect to take into consideration in IGC analyses is the importance of sample preparation. The components packed in the sample column should be evenly distributed as a prerequisite to obtain good results. This needs to be verified during the packing procedure and also by determining the packing density. One sample contains a large amount of wood components, hence the resulting surface energy for one sample column is an average of the surface energies for all these components. However, to ensure the statistical probability the tests are always performed using two replicate columns, where the packing density must be close to identical.

The dispersive component of the surface energy for thermally modified wood has in other studies, using contact angle measurements, shown to be higher than for unmodified wood of certain wood species: yellow-poplar (Jennings *et al.*, 2006), beech and pine (Gérardin *et al.*, 2007), Norway spruce (Kutnar *et al.*, 2013), and aspen and grey alder (Sansonetti *et al.*, 2013). However, limited research has been carried out analysing the heterogeneity of wood surfaces using IGC at different fractional surface coverage.

4.4. Dynamic water vapour sorption properties (Paper II)

Figure 18 shows the results from the DVS measurements for the thermally modified and the unmodified wood components. The EMC values obtained in the IGC measurements for the conditions of 25 and 75% RH at the same temperature (30°C) are also shown for comparison the moisture content between the two analysing techniques. As can be seen, there is a good correlation between the EMC obtained from the sorption isotherms and the EMC from the IGC measurements, both at 75% and 25% RH. This indicates successful RH conditioning during the IGC analyses. The EMC values obtained from IGC measurements of thermally modified wood at 25% RH seem to be concentrated with a low variation around the desorption curve whereas the corresponding EMC values obtained at 75% RH for both the modified and unmodified wood samples are more concentrated around the adsorption curve, also with a low variation.

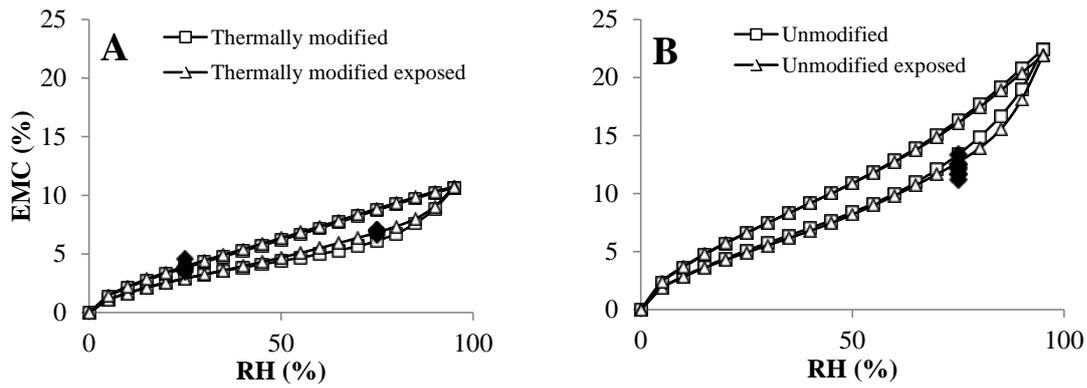


Figure 18. Sorption isotherms for thermally modified (A) and unmodified wood (B), obtained from the DVS measurements. The upper isotherms represent desorption and the lower isotherms represent adsorption. Corresponding EMC values (♦) obtained from the IGC measurements are also included at 25% and 75% RH in A and at 75% RH in B

As can be seen in Figure 18, the thermally modified samples had a significantly lower EMC for all isotherms compared with unmodified samples, which was expected. Figure 18 also presents isotherms for the non-exposed samples compared with the samples previously exposed to the 75% RH condition. For the thermally modified samples a small increase of the EMC was indicated at higher RH as a result of the exposure, whereas for unmodified samples a small decrease was detected. Hence, this resulted in a decrease in hysteresis for modified wood and an increase in hysteresis for unmodified wood due to the earlier exposure to the increased RH condition. The results of the DVS analyses indicate changes in water vapour sorption behaviour in relation to the sorption history. The explanation for this is unclear. As a result of thermal treatment of wood the number of accessible sorption sites is reduced, leading to a decrease in moisture sorption. Additionally, the condition at high temperatures might lead to closing of cell wall micropores through the creation of interstructural bonds. At conditions close to saturated vapour pressure at higher RH, the interstructural bonds are broken which implies that cell wall micropores will be accessible, resulting in a larger surface with accessible sites for water sorption. This results in an increased adsorption curve during a second and third sorption cycle, suggested by Chirkova *et al.* (2005) and also by Hoffmeyer *et al.* (2003). Work presented by Hill *et al.* (2012) also agrees with these observations, *i.e.* that an increase in the EMC for adsorption at the higher RH levels after the first sorption cycle. Hill *et al.* (2012) suggested that this phenomenon could be due to release of built-in stresses caused by the thermal modification.

4.5. Surface chemical composition (Paper II)

In agreement with the IGC and the DVS analyses, the XPS results also indicated differences between the non-exposed and the samples exposed to the 75% RH condition, both for unmodified and thermally modified wood. In this case this was detected as a difference in surface chemistry, or elemental surface chemical composition. A correlation chart for all the analysed samples can be seen in Figure 19, with the amount of C1 in total C (%) as a function of the O/C ratio. At least three data points are presented for the different samples (with exception for UM with only two).

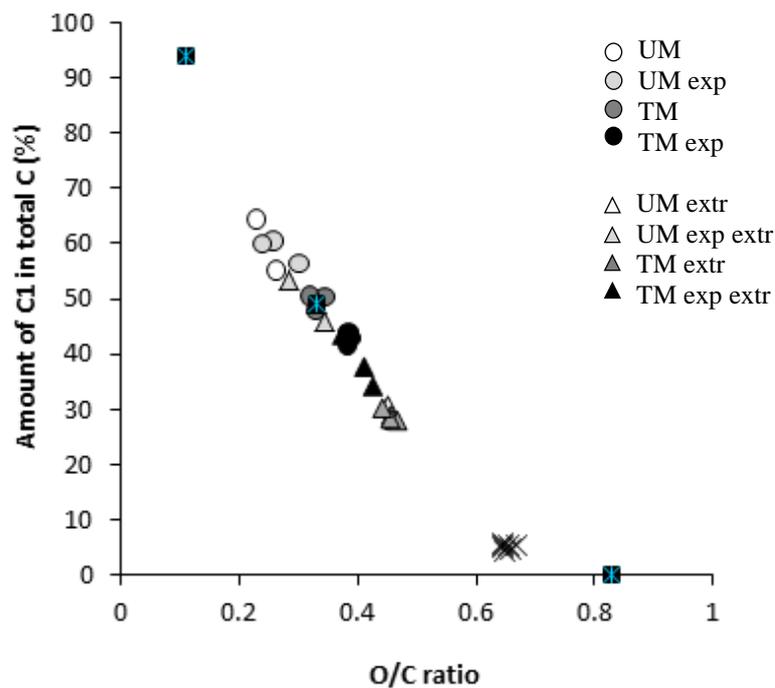


Figure 19. Correlation chart from the XPS analysis showing the amount of C1 in total C (%) versus the O/C ratio for the various wood samples. The theoretical values for cellulose, lignin, extractives (oleic acid) and data from a cellulose reference (X) are shown

In Figure 19, the data points from the non-extracted unmodified wood samples can be seen closest towards the model extractive, indicating that these samples possessed a relatively high amount of certain extractives at the surface. This is furthermore shown by the more scattered data points for the non-extracted unmodified samples, both non-exposed and exposed. The non-extracted thermally modified samples on the other hand, are less scattered which implies a more stable surface. The extracted samples of both thermally modified and unmodified wood shows a higher O/C ratio than the non-extracted samples, in agreement with earlier studies (Liu and Rials, 1998; Johansson *et al.*, 2012; Rautkari *et al.*, 2012).

The previous exposure to the 75% RH condition seemed to indicate a higher amount of extractives for the non-extracted samples, and also a lower amount of extractives for the extracted samples, compared with the non-exposed samples. Extractives include both lipophilic and hydrophilic compounds and a diverse distribution of extractives are present at different locations in wood (Sjöström, 1993). As a result of exposure to the 75% RH condition migration of low-weight compounds and extractives and/or reorientation towards the moist air of certain functional groups in the wood surface may occur. This phenomena may partly also be related to a softening of the wood matrix caused by the increased MC. Additionally, during drying of the wood, water will diffuse towards to surface which may cause reorientation and migration of the low-weight compounds and extractives. This gives different prerequisites for the non-exposed and exposed samples in terms of acetone extraction. The non-exposed samples on the other hand, facing an environment of a dryer and more non-polar character, and hence functional groups in the extractives present in the surface would then be oriented with their non-polar side towards the surroundings. This would result in different conditions for the non-exposed and exposed samples in terms of acetone extraction, where non-exposed samples should be easier to extract using acetone.

4.6. Correlation between surface energy and surface chemical composition

Figure 20 shows a correlation between the dispersive component of the surface energy and the surface chemical composition, and a similar correlation has earlier been made by Liu and Rials (1998). The value of the dispersive component of the surface energy is taken from the highest value obtained, which furthermore also corresponds to the lowest fractional surface coverage ($0.01 n/n_m$) of the non-exposed and exposed samples. The C1/C2 ratio indicates the presence of hydrophobic components, *i.e.* hydrophobic extractives and lignin (Börås and Gatenholm, 1999).

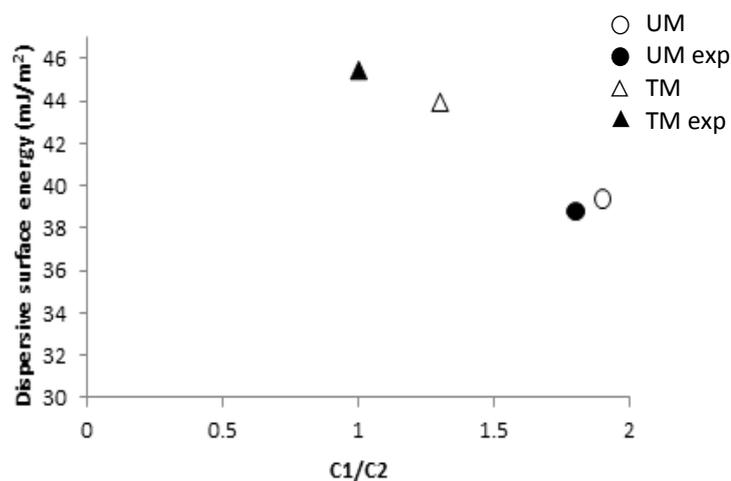


Figure 20. Correlation between the dispersive component of the surface energy and the C1/C2 ratio for the non-exposed and the exposed samples of the thermally modified and unmodified wood

The values for the wood components, theoretically calculated from the neighbouring atoms of carbon (Table 4) are as follow; cellulose 0, hemicellulose 1 and extractives <10. Figure 20 indicates that the unmodified and unmodified exposed samples were most rich in extractives, which seems reasonable. Furthermore, it can be concluded that the thermally modified exposed and unmodified exposed samples showed lower C1/C2 values than their respective non-exposed, TM and UM. This suggests that the exposed samples had a smaller amount of extractives at the surface than the non-exposed.

Above the glass transition point, which is a transition zone of amorphous polymers to change between glassy and rubbery state, dependent on the temperature and the moisture content, the amorphous wood polymers will have higher mobility. The increased relative humidity and thus increased moisture content during the exposure will cause the hemicelluloses to change to a rubbery state, which occurs at around 75% RH at room temperature (Olsson and Salmén, 2004). This will lead to a more ordered structure of the elasticised polymers and furthermore changes in volume. Due to the increased mobility during the rubbery state hemicellulose molecules will change into more energetically favourable configuration if possible. However, as the RH is decreased the hemicellulose will return to its glassy state but might still keep irreversible structural changes from the softening (Engelund, 2011). Cellulose and lignin will not go into their rubbery state during these conditions. The movements of hemicellulose and lignin in the lignocellulosic matrix are limited by the secondary intermolecular bonding with cellulose. This can also restrict the influence of water vapour on the hemicelluloses during the softening (Hon and Shiraishi, 2001).

There are also various chemical reactions taking place during a storage time *e.g.* autooxidative and enzymatic processes (Sjöström, 1993). The effects from storing or ageing of wood will also likely be altered due to a thermal modification. After wood processing the created wood surfaces will change over time, often significantly dependent on the surrounding environment (temperature, humidity, UV radiation *etc.*). A possible ageing effect is that the polymer molecules will reorient into the most favourable position in relation to the current conditions (Gunnells *et al.*, 1994). Hence, during exposure to dry air the non-polar groups of mobile hydrophobic components, or bifunctional components with both polar and non-polar groups (amphiphilic or amphiphilic compounds), at the wood surface will reorient towards the non-polar air. The reorientation may also be enhanced by an increase in temperature. This could result in an increased hydrophobicity of the surface of the non-exposed samples. In contrast to this, during exposure to increased RH condition and temperature (*e.g.* 75% RH and 30 °C), the polar groups of mobile hydrophilic or bifunctional components at the wood surface will reorient towards the moist (polar) surroundings. This could result in an increased hydrophilicity of the surface of the exposed samples. The extraction with acetone might therefore have been less effective for samples previously exposed to the 75% RH condition.

5. CONCLUSIONS

The scanning electron microscopy (SEM) analysis and the component length analysis showed that the unmodified components had a higher fraction of short-length components (fines), compared with the thermally modified components, which showed a more even length distribution. The inverse gas chromatography (IGC) analysis indicated that the thermally modified wood had a rather heterogeneous character in terms of the dispersive component of the surface energy up to about 5% surface coverage. Higher dispersive surface energy values were obtained for the modified than for the unmodified wood, which shows that the former was more hydrophobic. As a result of exposure to the 75% relative humidity (RH) condition a slight increase in the dispersive surface energy was observed for the modified wood. This was more pronounced during exposure to 75% RH than to 25% RH.

The dynamic water vapour sorption (DVS) analysis indicated an increase in equilibrium moisture content (EMC) for the adsorption isotherm at higher RH for the thermally modified wood, corresponding to a decrease in hysteresis, due to the previous exposure to 75% RH. This indicates that an exposure to higher RH conditions (around and above 75%) could result in breaking of intermolecular bonds created during the thermal modification which will reveal surfaces and sorption sites that earlier were blocked for the water molecules. The opposite trend was seen for the unmodified wood. The X-ray photoelectron spectroscopy (XPS) analysis of the surface chemical composition of both the thermally modified and the unmodified wood indicated a decrease of extractable or volatile organic compounds, as a result of the previous exposure to the 75% RH condition. Furthermore, a relative increase of non-extractable compounds could be seen simultaneously. This could be caused by redistribution or migration of remaining extractives towards the surface along with moisture diffusion. It is suggested that the changes in surface chemical composition of the wood is related to structural changes in the wood substance resulting in an increased amount of accessible hydroxyl groups.

6. FUTURE WORK

Recommendations for future work and implications of the results in this thesis can be found in the tailoring of new compatible and durable material combinations, for example when using thermally modified wood components in new types of biocomposites for outdoor applications. Future research is suggested to include further surface characterisation of thermally modified wood including also analyses of the acid-base contribution to the surface energy, given that a reliable methodology could be developed. The influence of extractives on the surface properties of thermally modified wood should also be further investigated. This could include the effects of different solvent extractions, in relation to the surface properties. Additionally, research on the changes in surface properties as an effect of the extractives behaviour during drying is suggested.

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