U.Porto Journal of Engineering, 4:1 (2018) 9-26
ISSN: 2183-6493
DOI: 10.24840/2183-6493_004.001_0002

Received: 24 November, 2017
Revised: 29 December, 2017
Published: 27 April, 2018

Structural Characterization of Heat Treated Poplar Wood

Gonçalo Monteiro
Faculty of Engineering of the University of Porto, Porto, Portugal; LGPM, CentraleSupélec, Université Paris-Saclay, Gif-sur-Yvette, France (bio11049@fe.up.pt)

Abstract

Wood has been very useful in many fields due to its excellent properties. However, it also has less attractive characteristics, like high hygroscopicity and low bioconversion efficiencies. Heat treatment has been proved to improve these properties making lignocellulosic materials a stronger alternative to non-renewable sources to produce energy and other products. This study focused on the structural changes of heat treated poplar (*populus*) wood specimens treated under different temperature conditions. Nitrogen adsorption, pore size distribution and specific surface area of heat treated wood were studied. Increasing the temperature of treatment leads to a change on the characteristics of the nitrogen adsorption isotherms. The volume of pores for samples treated at higher temperatures is much greater comparing with samples below 400 ºC BET specific surface areas were generally low for samples at temperatures until 400 ºC, after this a great increase occurred while increasing temperatures up to 500 ºC (413,06 m^2/g).

Author Keywords. Biomass, Heat Treatment, Nitrogen Adsorption, Porosity, BET

Type: Research Article
Open Access Peer Reviewed CC BY

1. Introduction

As wood continues to be very useful for many fields and applications, mainly because of its many excellent material properties (such as an incredible strength to weight ratio, appearance etc.), it also has some disadvantages. Dimensional changes in response to different atmospheric conditions and susceptibility to biological attack are examples of this (Green, Winandy, and Kretschmann 1999). The genesis of the wood properties can be better understood by studying its structural characteristics at the macroscopic, microscopic and molecular levels.

Wood is a natural material, and because of that it exhibits great range of variation in its properties. Variations occur between tree species, between trees of the same species and within the tree itself. This can lead to problems for any study of the material, making it difficult to obtain comparable results. In the great majority of reviews related with wood sciences (or indeed any other kind of science), it is easily detected that, sometimes, disagreements appear between different studies, and it is not always possible to reach a consensus.

Since a great number of properties of wood are defined by its chemical constituents, wood treatment often tries to promote changes at this level, in order to produce a material with improved properties. However, there are also some wood treatments that do not lead to an alteration of the chemical composition of the material. Wood treatment works as a mean of changing the material to overcome or improve one or more of its disadvantages (Esteves and Pereira 2009; Rowell 2006).

The objective of a treatment may focus on the dimensional stability or decay resistance, to reduce water sorption and so on. The term 'wood treatment' can be applied when using a process that alters the properties of the material such that during its lifetime, there is no loss of the enhanced properties.

Particularly, the heat treatments on wood result in degradation associated with chemical changes in the material. However, if carefully controlled, the properties that are obtained due to thermal treatment can be valuable for certain fields. There has been a major research and commercial activity in this sector, mainly in France (Vernois 2001).

The main studies on heat treatment of wood focus mainly on the dimensional stability, equilibrium moisture, durability and mechanical properties. Although, wettability, mass loss, wood color and chemical transformations have also been extensively studied, while more recent works try to highlight the quality control, modeling and investigate the reasons for the improvements.

2. Using Wood: the Biorefinery Approach

The mankind's strong dependence on fossil fuels comes from the intensive use and consumption of petroleum derivatives which, combined with diminishing petroleum resources, leads to environmental and political concerns. Emissions of greenhouse gases (GHG), such as carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O), arising from fossil fuel combustion and land-use change as a result of human activities, have been scientifically proven to be responsible for perturbations on the Earth's climate (Cherubini 2010).

It is increasingly acknowledged globally that plant-based raw materials (i.e. biomass) have the potential to act as substitutes of a large fraction of fossil resources as feedstock for industrial productions, addressing both the energy and non-energy (i.e. chemicals and materials) sectors. Recently, society started to acknowledge alternatives given by a future sustainable economy based on renewable sources and has been starting to finance R&D activities for its implementation. The production of liquid biofuels from biorenewable feedstock has been regarded as a promising method for the future (Demirbas 2009). Currently, fuels obtained from biomass (i.e. biofuels) are identified as 1st and 2nd generation biofuels (Jansen 2013). First generation biofuels usually refer to biofuels produced from raw materials that with compete with food and feed industries. Because of this competition, these biofuels give rise to ethical, political and environmental concerns. In order to overcome these issues, production of second generation biofuels, from raw materials based essentially on waste, residues or non-food crop biomass, gained an increasing global interest in the last few years as a possible ''greener" alternative to fossil fuels and conventional biofuels. As a way to improve the 2nd generation biofuel production, using biomass within a biorefinery concept is expected to guarantee additional environmental benefits and implement national energy security, thanks to the co-production of both bioenergy and high value chemicals (Naik et al. 2010). Among several definitions of biorefinery, the most exhaustive was recently performed by the IEA (Kamm 2008): "Biorefining is the sustainable processing of biomass into a spectrum of marketable products and energy". The biorefinery concept is capable of embracing a wide range of technologies able to separate biomass resources (wood, grasses, corn) into their building blocks (carbohydrates, proteins, triglycerides) which can be converted to value added products, biofuels and chemicals. A biorefinery works as a facility (or network of facilities) that promotes the integration of biomass conversion processes and equipment to produce biofuels, power, and chemicals from biomass. This concept is analogous to today's petroleum refinery, which produces multiple fuels and products from petroleum (Cherubini 2010). The most important biobased products are today obtained from conversion of biomass to basic products like starch, oil, and cellulose. In addition, chemicals like lactic acid and amino acids are produced and used in the food industry. Other already commercially available biobased products include detergents, cleaning compounds, dielectric fluids, dyes, inks, lubricants, packaging materials, paints and coatings, plastic fillers, polymers, solvents, and sorbents. Some examples of biorefinery and non-conventional biomass industries which are already competitive in the market are listed in Cherubini et al. (2009), along with some existing pilot and demo plant. The majority of the existing biofuels and biochemicals are currently being produced by single production chains and not within a biorefinery concept, and usually require raw materials competing with the food and feed industries. Their interest is thereby limited. By contrast, lignocellulosic crops can reduce the competition for fertile land, since they can be grown on land which is not suitable for agricultural crops. Moreover, in comparison with conventional crops that can only give a small contribution to the above standing biomass, biorefineries based on lignocellulosic feedstocks can have access to larger quantities of biomass per hectare yields, since the whole crop is available as feedstock (Kamm, Gruber, and Kamm 2006).

The development of biorefinery industries as industrial complexes is expected to occur over next few years. Unlike oil refinery, which almost invariably requires plants with great dimensions, biorefineries will most probably be able to work on a wide range of installations with different-sizes. In this context, several bio-industries promote the combination of material flows in order to guarantee a complete utilization of all biomass components: the residue from one bio-industry becomes an input for other industries, leading to an integrated bio-industrial system (Naik et al. 2010). Although the applications of biobased products are raising rapidly, there are yet some limitations on their success and efficiency, mostly due to high non-competitive costs, poor technology reliability and limited resource availability (Chen, Peng, and Bi 2015). Among these products and alternative fuels being developed, the produced energy from biomass is one of the most attractive resources to fill the requirements of substituted fossil energy.

Contrarily to fossil fuels, biomass is considered a renewable resource because it requires a reduced period of time to replace what is used as an energy resource. If this resource is used in a sustainable way, the net carbon emissions over the time frame of a cycle of biomass production should be reduced close to zero (Sriram and Shahidehpour 2005). However, some studies had shown an increase in greenhouse gas (GHG) emissions for some cases of biomass utilization for biofuels. This happens due to GHG emissions resulted by use of fossil energy during several steps of the operation involved in supply-chain logistics showing that, there is a long way yet until reaching the desired success and efficiency on these processes (Jin, Singh, and Zondlo 2013). Apart from the process, there are also several less attractive characteristics that limit its application like high moisture content, low calorific value, hygroscopic nature and low bulk density, which leads to a low conversion efficiency as well as difficulties in its collection, grinding, storage and transportation (Chen, Peng, and Bi 2015). Therefore, its use as raw material is not viable, by which is necessary a treatment before its utilization.

For a long time, there has been done a lot of studies in order to improve the digestibility of lignocellulosic biomass, mainly promoting an increase on the efficiency of conversion of its components to ethanol, methane and, in the last years, also to hydrogen. However, it is not perfectly clear yet, which are the most important characteristics of the lignocellulosic biomass to determine a successful pretreatment. Additional problems, like production of recalcitrant or inhibitory products, are yet to be studied (Hendriks and Zeeman 2009). A lot of literature is written about different pretreatment methods to enhance the digestibility of lignocellulosic material. The objective of this thesis is to study the structural changes of poplar wood after thermal treatment, in order to assess the effect of different temperature conditions on the characteristics of the lignocellulosic biomass studied.

3. Thermal Treatment in Lignocellulose

During treatment the lignocellulosic biomass is heated. When the temperature increases above 150–180 °C, components of the lignocellulosic biomass, firstly the hemicelluloses and shortly after that lignin, will start to solubilize (Bobleter 1994; Garrote, Domínguez, and Parajó 1999). The composition of the hemicellulose backbone and the branching groups can determine the thermal, acid and alkali stability of the hemicellulose. From the two dominant components of hemicelluloses (xylan and glucomannan), the xylans are thermally the least stable, but the difference comparing with the glucomannans is small. Above 180 °C, an exothermal reaction (probably solubilization) of the hemicellulose starts (Beall and Eickner 1969). This temperature of 180 °C is probably just an indication of the temperature at which an exothermal reaction of the hemicellulose starts, because the thermal reactivity of lignocellulosic biomass depends largely on its composition (Fengel and Wegener 1983; Hon and Shiraishi 2000).

During thermal processes occurs the hydrolysis of a part of the hemicellulose and forms acids. These acids are assumed to catalyze the further hydrolysis of the hemicellulose (Gregg and Saddler 1996). Some studies concluded that other, so far unknown, factors than the catalyzing effect of formed acids play a role in the solubilization of hemicellulose (Liu and Wyman 2003; Zhu, Lee, and Elander 2004, 2005).

Thermal pretreatment with temperatures of 160 °C and higher, causes, besides the solubilization of hemicellulose, also the solubilization of lignin. The compounds produced are almost always phenolic compounds and have in many cases an inhibitory or toxic effect on bacteria, yeast and methanogens/archae (Gossett et al. 1982). These soluble lignin compounds are very reactive and will, if not removed quickly, condensate and precipitate on the biomass (Liu and Wyman 2003). Especially too severe pretreatment conditions promote the condensation and precipitation of soluble lignin compounds, sometimes even with soluble hemicellulosic compounds like furfural and HMF (Bobleter and Concin 1979; Lora and Wayman 1978; Negro et al. 2003).

Heat pretreatments in which soluble (hemi) cellulose and lignin compounds are formed, have a risk of formation of phenolic and heterocyclic compounds, like vanillin, vanillin alcohol, furfural and HMF, especially in acidic environments (Ramos 2003). These formed compounds can promote the inhibition of the process (Brownell, Yu, and Saddler 1986).

According to Weimer, Hackney, and French (1995) thermal pretreatment can also cause an increase of the Crystallinity Index (CrI) of cellulose, though no increase was observed when the CrI was already high.

4. Physiochemical Changes in Wood due to Pretreatments

The heating of wood will lead to a variety of processes occurring (Figure 1), which depend upon the heating treatment employed. It is accepted that hemicelluloses are degraded to a greater extent than the other macromolecular components, but the relative stability of the cellulose and lignin is harder to determine (Shafizadeh and Chin 1977). Generally, loss of polysaccharide material becomes particularly significant at temperatures above 180 °C, but this depends very much upon the treatment conditions. The precise relative rates of degradation of the different components depend upon the experimental methods employed, and as a consequence the literature on this subject is complex and apparently sometimes contradictory.

Biomass heat treatment products are a complex combination of the products from the individual treatment of cellulose, hemicellulose and remaining components, each of which has its own kinetic characteristics. In addition, secondary reaction products result from cross-reactions of primary treatment products and between products and the original feedstock molecules. Various chemicals derived from biomass have been discussed by Elliott (2001, 2004). The heat treatment of each constituent is itself a complex process that is dependent on many factors. However, the major changes on the chemical components of plant biomass are discussed below.

Typically, cellulose degradation occurs at 240-350 °C to produce anhydrocellulose and levoglucosan. When cellulose is treated at a heating rate of 12 °C/min under helium in DTA experiments, an endotherm is observed at 335 °C (temperature of maximum weight loss). The reaction is complete at 360 °C (Tang and Neill 1964).

Hemicellulose decomposes at temperatures of 200-260 °C, giving rise to more volatiles, less tars, and less chars than cellulose (Weiland and Guyonnet 2003). Most hemicelluloses do not yield significant amounts of levoglucosan. Much of the acetic acid liberated from wood during treatment is attributed to deacetylation of the hemicellulose.

Regarding lignin, its physical and chemical properties differ, depending on the extraction or isolation technology used to isolate them. Because lignin is inevitably modified and partially degraded during isolation, thermal decomposition studies on separated lignin will not necessarily match the pyrolysis behavior of this component when it is present in the original biomass. Lignin starts decomposing when heated at 280-500 °C (Brebu and Vasile 2010). Lignin pyrolysis yields phenols via the cleavage of ether and carbon-carbon linkages. Lignin is more difficult to dehydrate than cellulose or hemicelluloses. Lignin pyrolysis produces more residual char than does the pyrolysis of cellulose. Lignin decomposition in wood was proposed to begin at 280 °C and continues to 450-500 °C, with a maximum rate being observed at 350-450 °C (Brebu and Vasile 2010).

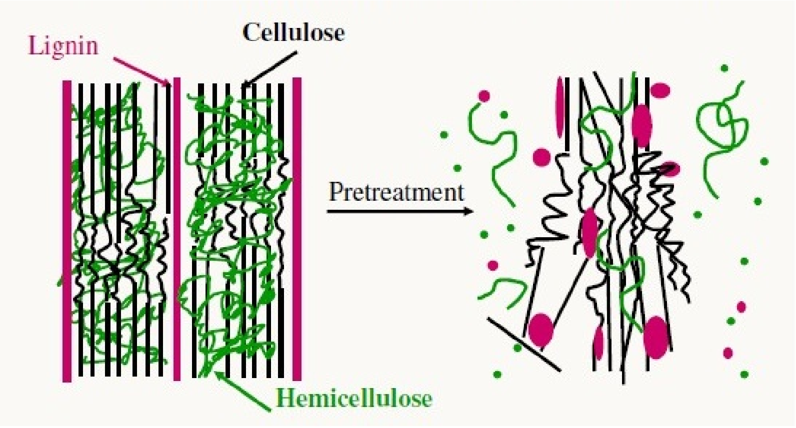

Figure 1: Simplified impact of pretreatment on biomass. Adapted from Mosier et al. (2005)

Much of the work in this area relies upon standard gravimetric methods to determine the relative proportions of the macromolecular components, and whilst such studies have an undoubted value, they need to be treated with some caution, since material loss is not the sole factor indicating that degradation has occurred. There have been many studies that have attempted to elucidate the chemistry of thermolysis of wood by examining the thermal behavior of isolated wood components, and much of the early work in this respect has been reviewed (Beall and Eickner 1969).

The use of thermal analysis techniques has shown that the results obtained are quite variable and heavily dependent upon the method of preparation of the materials as well as the experimental parameters, particularly heating rate and atmosphere. It is also undoubtedly the case that the chemistry of the thermal degradation of the isolated wood components is different from the one taking place within the cell wall, where the various reactions can act synergistically within the wood material. There are also competing processes occurring during heating that can result in simultaneous endothermic and exothermic events, making it difficult to determine the onset temperature for the different processes.

As wood is progressively heated to higher temperatures, production of condensable fractions occurs, with loss of water and volatile extractives at temperatures below about 140 °C. Above this temperature, the production of cellular breakdown products derived from the more labile species attached to the cell wall polymers assumes greater significance. This results in the production particularly of acetic acid derived from the hemicelluloses; but additionally, formic acid and methanol, as well the production of non-condensable gases (mainly CO_2) as the temperature is raised further. Above about 140°C dehydration reactions also begin to occur, as so-called “water of constitution” is lost, leading to a decrease in OH content, and these assume greater importance as the temperature is raised (Bourgois and Guyonnet 1988).

As the temperature is further increased, CO and CO_2 are also increasingly detected in the gases produced. At around 270 °C, there is a significant change in the reaction kinetics due to the onset of an exothermic reaction (Stamm, Burr, and Kline 1946).

Although the chemistry of thermal modification is complex and far from fully understood, it can be readily verified that there are nonetheless distinct changes in the nature of the reactions taking place as the temperature is increased. What is less certain is the exact points at which the different reactions become dominant. As noted, the treatment atmosphere has a significant influence upon the reaction chemistry occurring. Heating under oxidizing conditions results in an increase in carbonyl-containing groups, whilst heating in a reducing or inert atmosphere leads to a loss of oxygen-containing species, although a decrease in OH groups may be associated with a small increase in carbonyl functionality.

Heating of wood in the presence of oxygen has been shown to result in an initial decrease followed by an increase in carbonyl content (as determined from the IR spectrum) at extended heating times (Chow 1971). The decrease was attributed to loss of ester-bonded and carboxylic-containing groups, with the subsequent increase being due to oxidative carboxylation. A decrease in carbonyl band intensity was found with heating in nitrogen, although a slight increase was noted for longer treatment times. Results were strongly influenced by the temperature of treatment and by the presence of wood extractives.

The presence of water also affects the reaction chemistry, although this depends upon the amount of water present and whether or not it is lost from the treatment system. The heating of wood in the presence of water or steam results in the accelerated formation of organic acids (primarily acetic acid) that catalyze the hydrolysis of hemicelluloses, and to a lesser extent the amorphous cellulose (Mitchell 1988). The generation of these acids is also enhanced in the presence of air (wet oxidation). It should, however, be noted that the continued presence of water as steam during the treatment process can prevent oxidative processes from occurring.

Hydrothermal processing results in the hydrolysis of polysaccharide due to the action of hydronium ions generated by auto-ionization of the water, although the formation of hydronium ions from acetic acid is more important (Garrote, Domínguez, and Parajó 1999). Temperature ranges from 150 °C to 230 °C are generally used, because hydrolysis is very slow at lower temperatures, whereas cellulose degradation begins to occur in the region 210–220 °C. Cellulose degradation becomes predominant at 270 °C.

Effects on the Surface Characteristics of Wood

4.1. Torrefaction

Particle size distribution curves, sphericity, and surface area are important parameters for understanding flowability and combustion behavior during the process. Researchers observed that ground, torrefied biomass produced narrower, more uniform particle sizes compared to untreated biomass due to its brittle nature, which is similar to coal.

Phanphanich and Mani (2011) study on torrefied pine chips and logging residues found that smaller particle sizes are produced compared to untreated biomass. They have also observed that the particle distribution curve was skewed towards smaller particle sizes with increased torrefaction temperatures.

Torrefaction also significantly influences the sphericity and particle surface area. Phanphanich and Mani (2011) results also indicated that sphericity and particle surface area increase as the torrefaction temperature was increased to 300 °C. For ground, torrefied chips, they found that the sphericity increased from 0,48 to 0,62%, concluding that an increase in particle surface area or decrease in particle size of torrefied biomass can be desirable properties for efficient cofiring and combustion applications. Also, the bulk and particle densities of ground torrefied biomass increases as it reduces the inter and intra particle voids generated after milling (Esteban and Carrasco 2006). Studies have indicated that ground torrefied material results in a powder with a favorable size distribution and sphericity, allowing it to meet the smooth fluidization regime required for feeding it to entrained-flow processes (gasifier and pulverized coal).

4.2. Pyrolysis

Studying the structural effects of the treatment and the influence of the particle size are important parameters for understanding material's behaviour during the process of combustion. The fluid residence times for particles with bigger dimensions are long enough to allow secondary reactions of the volatiles produced by primary reactions (Bamford, Crank, and Malan 1946; Chan, Kelbon, and Krieger 1985). Large particle size also leads to large thermal gradient. If particles of the material have moisture, it escapes violently promoting cracking of the surface. Condensation of compounds and moisture can also take place. This aspect of pyrolysis requires further investigation. Despite reaction models being able to predict the general tar formation, the tar that results from condensation occurring locally is not considered.

Cracking of the wood surface during pyrolysis has been reported by many researchers (Kansa, Perlee, and Chaiken 1977; Pyle and Zaror 1984). Research has shown that serious structural failures, such as longitudinal channeling and surface cracking, occur. The surface cracking alters the heating characteristics. Despite the total heat transfer remaining the same, heat is transferred faster due to the presence of cracks on the surface. Internal failures result in changed local porosity and permeability, promoting the development of pores with smaller dimensions and leading to major changes on the surface area of material (Tinney 1965).

5. Materials and Methods

5.1. Feedstock preparation

Poplar (genus *populus*) was used in the form of powder. For powder preparation was used an IKA M 20 Universal grinding mill (IKA), the powder was then sieved through a mesh with 0,63 mm of diameter to obtain particles with less than that size.

5.2. Surface structure characterization

The specific surface area and pore size distribution of untreated and treated poplar samples at temperatures of 250 ^{o}C, 300 ^{o}C, 350 ^{o}C, 400 ^{o}C, 450 ^{o}C and 500 ^{o}C were determined by nitrogen adsorption. Nitrogen isotherms were performed on a Micromeritics 3FLEX accelerated surface area and porosimetry system. Nitrogen adsorption was performed at -196.15 ^{o}C with 5 s equilibration intervals using manufacturers settings. Data were collected from a relative pressure (P/P0) of 0.0001 to 0.995. For all samples, the degassing step was done overnight at 80 ^{o}C, to guarantee an efficient cleaning of the surface of the samples.

BET Model: Total specific surface area was calculated using the Brunauer, Emmett and Teller (BET) adsorption isotherm model (Sing 2001) for the nitrogen isotherm data. Specific surface area was calculated from the slope and y-intercept of the linear region of the BET transformation versus relative pressure plot.

Density functional theory: Density functional theory (DFT) model predictions of pore size distributions were calculated using the DFT Plus Models Library. The model assumed a slit pore geometry (Balbuena and Gubbins 1993). Model DFT nitrogen isotherms were fit to the experimental isotherms using a deconvolution technique by a non-negative least squares method, as described in previous studies, (Olivier, Conklin, and Szombathely 1994) to calculate the pore size distribution. The DFT model isotherms ranged from 10 to 2000 Å in a 70-step geometric progression.

6. Results and Discussion

The Nitrogen adsorption isotherms for the untreated and heat-treated poplar samples obtained at different temperatures were determined. Figure 2 shows the adsorption isotherms of all samples. As can be seen from the figure with the increasing of the temperature treatment the characteristics of the isotherms change. Until reaching the 400 ^{o}C, these isotherms show, at low relative pressures, a lower and less pronounced increase in the quantity of nitrogen adsorbed. Following this occurs a plateau at higher relative pressures that would end with a huge increase at relative pressures close to 1 due to the condensation of the adsorptive, indicating a type II isotherm according to the IUPAC classification (Rouquerol, Rouquerol, and Sing 1999). The type II isotherm represents a material with low porosity having its pores a bigger diameter, being in the range of meso and macropores.

However, above this temperature treatment, the isotherms start gradually to change their shape, becoming the initial increasing bigger with the increasing of temperature treatment. When the temperature of treatment is 450 ^{o}C, it is already possible to see a different type of isotherm. As can be seen from Figure 2, the major uptake of nitrogen occurs at very low relative pressures (lower than 0.001), for this kind of adsorption isotherm, which is followed by a plateau at higher relative pressures, indicating a type I isotherm according to the IUPAC classification (Rouquerol, Rouquerol, and Sing 1999). The type I isotherm represents a material with meso and microporous structure. The major uptake occurs at low relative pressures indicating the formation of highly porous materials with narrow pore size distribution.

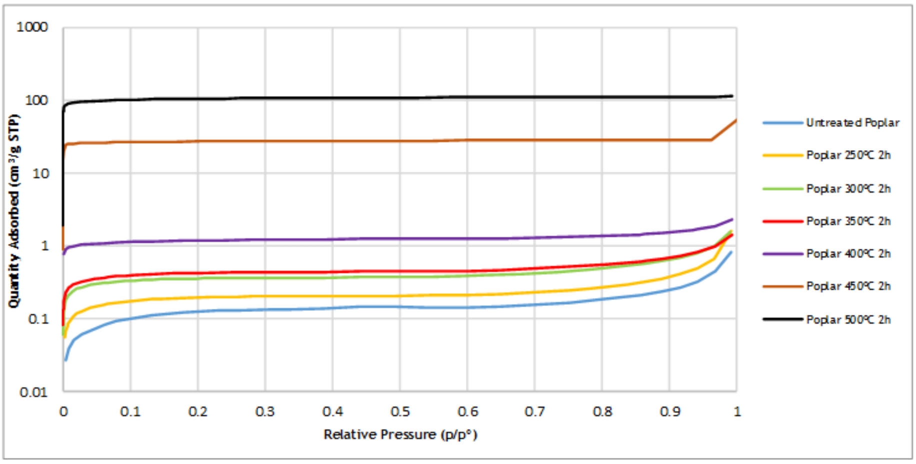

Figure 2: N2 adsorption isotherms at 77K of Untreated and Heat-Treated Poplar samples produced at different temperatures

Looking at these two different types of isotherm, it can be concluded that the increasing of the temperature for the same time of treatment led to a change on the meso and microporous structure of the material what promoted a great increase on the surface area, as can be seen in Table 1.

Micropores have molecular dimensions, the effective radii being less than 20 Å. The adsorption in these pores occurs through volume filling, and there is no capillary condensation taking place. The adsorption energy in these pores is much larger compared to larger mesopores or to the nonporous surface because of the overlapping of adsorption forces from the opposite walls of the micropores. In other hand, the mesopores, also called transitional pores, have effective dimensions in the 20 to 500 Å range and these pores are characterized by capillary condensation of the adsorbent with the formation of a meniscus of the liquefied adsorbate. Besides contributing significantly to the adsorption of the adsorbate, these pores act as conduits leading the adsorbate molecules to the micropore cavity.

From the results obtained, it was possible to explore and determine the pore size distribution of each sample.

Firstly, the choice fell on the classical macroscopic, thermo-dynamic concepts which are based on the assumption of a certain pore filling mechanism. Methods resulting on the application of Kelvin equation linked to the pore condensation phenomena (Barrett, Joyner, and Halenda 1951). Further studies led to conclude that these methods are only viable for mesopore size analysis, failing to correctly describe the pore filling of micropores and even narrow mesopores.

Other classical theories, like for example the Dubinin-Radushkevich approach (Dubinin and Stoeckli 1980), and semi empirical treatments such those of Horváth and Kawazoe (1983), and Saito and Foley (1991) are focused on describing micropore filling but cannot be applied for mesopore size analysis. Hence, in case a material contains both, micro- and mesopores, at least two different methods had to be used to obtain the pore size distribution from such an adsorption isotherm.

Furthermore, the accuracy of such thermodynamic, macroscopic methods is limited, because of the assumption that the pore fluid has similar thermophysical properties as the bulk fluid (Madani et al. 2015).

Contrasting with these macroscopic approaches, methods like the Density Functional Theory (DFT) or methods of molecular simulation (Monte Carlo simulation methods (MC), Molecular Dynamics methods (MD)) are capable of providing not only a microscopic model of adsorption but also a more realistic description of the thermodynamic properties of the pore fluid.

These theories, which are based on statistical mechanics, establish a connection between macroscopic properties and the molecular behavior. Therefore, to achieve a more realistic description of adsorption phenomena and an accurate and comprehensive pore size analysis, methods such as the DFT of inhomogeneous fluids and Monte Carlo simulations, which bridge the gap between the molecular level and macroscopic approaches, are taking a major role (Landers, Gor, and Neimark 2013).

Ultimately, and taking in account the characteristics of samples, the method used to determine the pore size distribution was the Density Functional Theory (DFT). This way, Figure 3 and Figure 4 present DFT pore size distributions of the samples.

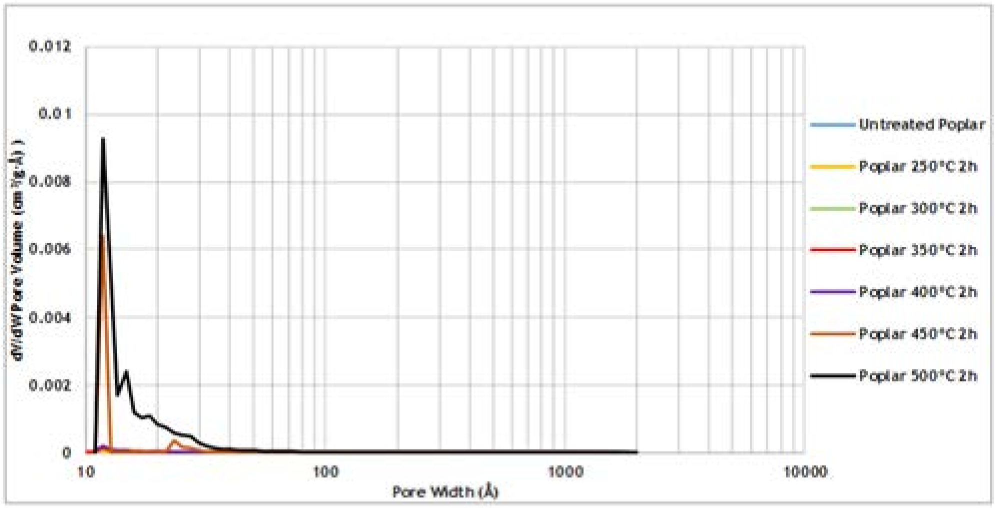

Figure 3: DFT (Density Functional Theory) pore size distribution for Untreated and Heat-Treated Poplar Samples

Due to the great differences between volume of pores on the micropores region, particularly between 450 ºC and 500 ºC and the rest of the samples, in Figure 4, the 450 ºC and 500 ºC samples were not plotted, to allow the better evaluation of lower temperatures pore size distributions.

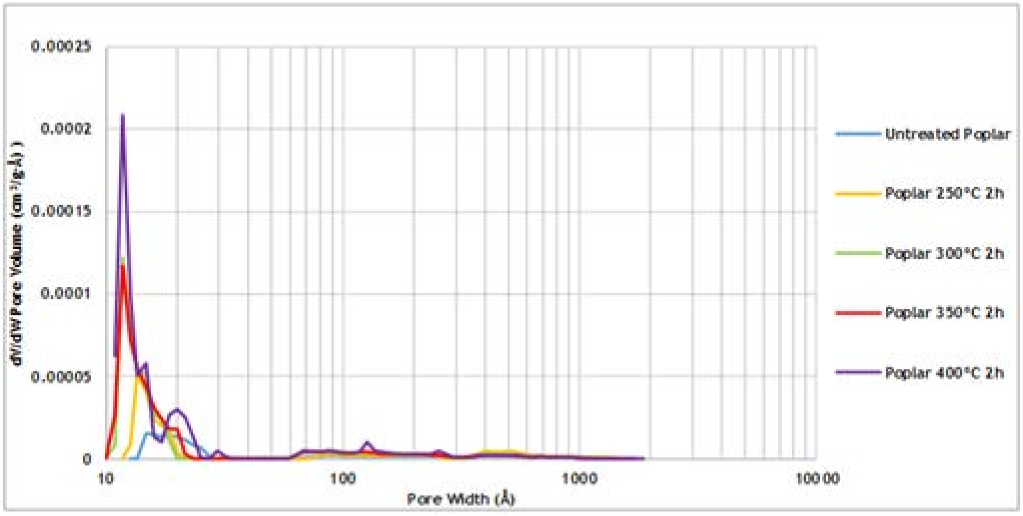

Figure 4 : DFT (Density Functional Theory) pore size distribution for Untreated and Heat-Treated Poplar Samples until 400 ^{o}C

One interesting thing to regard in Figure 4 is the differences between volume of pores on the micropores region and on the meso and macropores regions. This way, in Figure 5, all the samples are plotted but zooming only the meso and macropores regions, to better assess the pore size distributions only on this range.

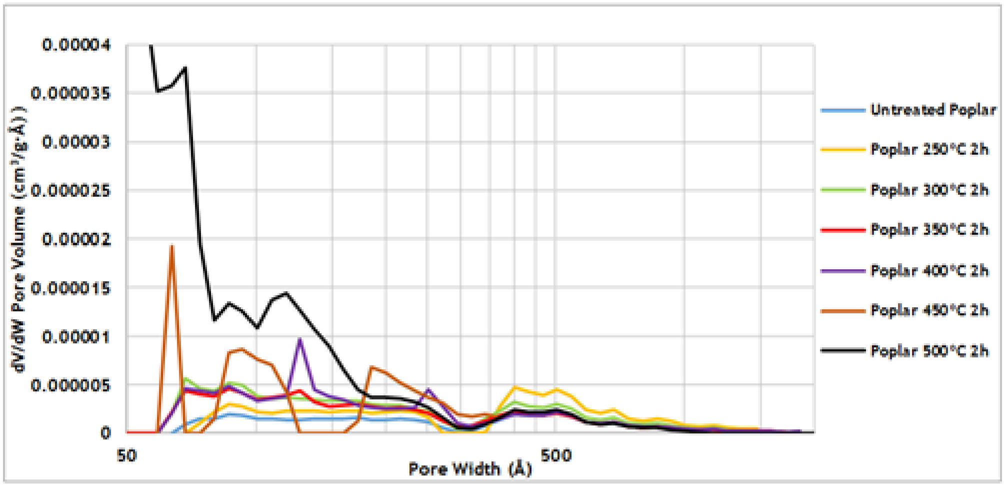

Figure 5: DFT (Density Functional Theory) pore size distribution for Untreated and Heat-Treated Poplar Samples (Zoom of the Meso and Macropores Region)

As can be seen comparing the results presented, the volume of pores on the micropores region for samples treated at higher temperatures is much greater compared with the volume of pores for samples below 400 ^{o}C. There are three mechanisms that occur during high-temperature treatment: thermal degradation, hornification and microscopic cell wall damage that affect the physical and mechanical properties of wood. These three mechanisms also can affect its porosity. In the first case, thermal degradation of wood components after exposure to elevated temperatures (Esteves and Pereira 2009) can lead to the formation of cavities within the cell wall. It has been reported that the removal of hemicelluloses and lignin during pulping created new pores within the fibre cell wall (Maloney and Paulapuro 1999). In the second case, as water exits the pores during drying, the pore walls start to collapse, eventually evolving into pore closure by irreversible hydrogen bonding called the process of hornification (Diniz, Gil, and Castro 2004). In the third and final case, anisotropic drying shrinkage of cell wall layers promotes internal drying stresses, which can be large enough to damage the wood cell walls (Thuvander et al. 2001).

Drying damage is manifested as microcracks irregularly distributed within the cell wall (Wallström and Lindberg 1999).

Looking at the figures, it is possible to see that during the process of heat treatment occurs a development of porosity which increases with the intensity of the treatment, this development of pores in the structure of poplar can be mainly due to the thermal degradation of the main components of the material, which promotes the appearance of micropores, as explained before.

Furthermore, this thermal degradation leads to a reduction on the oxygen and hydrogen molecules on the sample, which leads to the formation of a great quantity of micropores inside the carbon structures.

In the meso and macropores regions, it is possible to see that for pores with bigger dimensions, between 400 and 500 Å, the volume of pores increases for the lowest temperature treatment and then starts to decrease. This can occur because for lower temperatures the treatment will only lead to the formation of bigger cavities due to the process of drying. Higher temperatures, in contrast, will lead to the formation of smaller pores, occurring a conversion of bigger pores in smaller ones due to processes of condensation inside the material that promote the collapse of these macrostructures, being this increase visible for pores under 250 Å.

Sample	*Untreated Poplar*	*Poplar 250ºC 2h*	*Poplar 300ºC 2h*	*Poplar 350ºC 2h*	*Poplar 400ºC 2h*	*Poplar 450ºC 2h*	*Poplar 500ºC 2h*
S_{BET} (m^2/g)	0,50	0,75	1,38	1,64	4,42	111,36	413,06

Table 1: Untreated and Heat-Treated Coconut Shell Samples Mass before and after analysis and Specific Surface areas

The effect of pyrolysis temperature on the BET surface areas of samples are shown in Table 1. BET surface areas were generally low for samples produced at all pyrolysis temperatures until 400 ºC, but after this temperature there was a great increase while increasing pyrolysis temperature up to 500 ºC (413,06 m^2/g).

The specific surface area tends to increase with pyrolysis temperature, as seen in Table 1, being this increasing most often associated with both physical and chemical changes in the material, namely the appearance of microporous structures. At temperatures between 300 ºC and 400 ºC, it is possible that, despite the degradation of the material, the existing tars block the formed microporous structures; thus, yielding a lower surface area biochar compared to higher temperature samples where these same tars are volatilized leading to an increase in surface area.

The relation between temperature and specific surface area is presented in Figure 6 in order to understand its behavior. It was not detected any obvious relation, which reproduced a good correlation coefficient, despite that it is possible to see that the experimental points show an exponential behavior.

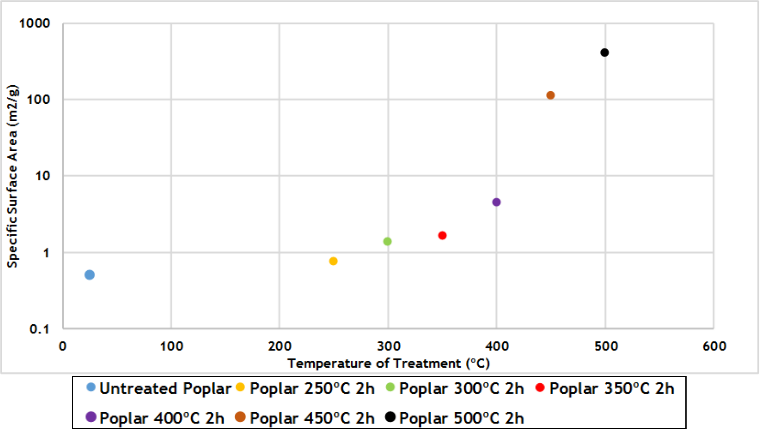

Figure 6: Comparison between specific surface area and temperature of treatment

7. Conclusions

In this study, heat treatments on poplar (genus *populus*) wood specimens were conducted under different temperature conditions. The structural characteristics of the heat-treated wood were then studied.

Firstly, it was developed a study of the effects of different heat treatments on the adsorption isotherms of poplar wood using nitrogen as the adsorptive gas and applying the Density Functional Theory for determination of the pore size distribution of each sample. The results showed that the volume of pores on the micropores region for samples treated at higher temperatures is much greater compared with the volume of pores for samples below 400 ^{o}C. Three mechanisms occurring during high-temperature treatments were studied in order to explain this phenomenon. Thermal degradation, hornification and microscopic cell wall damage can both three affect the physical and mechanical properties of wood. In the meso and macropores regions, especially for pores with bigger dimensions, between 400 and 500 Å, the volume of pores increases for the lowest temperature treatment and then starts to decrease, resulting this from the formation of bigger cavities due to the process of drying and volatilization. In opposition, higher temperatures promote the formation of smaller pores, occurring a conversion of bigger pores in smaller ones due to processes of drying and structure degradation inside the material that promote the collapse of these macrostructures (hornification), being this increase visible for pores under 250 Å.

Furthermore, with the results from adsorption isotherms of heat treated poplar wood using nitrogen as the adsorptive gas and applying the BET theory, it was possible to determine the specific surface area of each sample. The results obtained were in accordance with the results of the pore size distribution showing that, until 400 ^{o}C, there isn’t a major increasing on the surface area of the samples, however, after that temperature, the specific surface area starts to increase exponentially.

References

Balbuena, Perla B., and Keith E. Gubbins. 1993. "Theoretical interpretation of adsorption behavior of simple fluids in slit pores". *Langmuir* 9 (7): 1801–14. DOI: 10.1021/la00031a031.

Bamford, C. H., J. Crank, and D. H. Malan. 1946. "The combustion of wood. Part I". *Mathematical Proceedings of the Cambridge Philosophical Society* 42 (2): 166-82. DOI: 10.1017/S030500410002288X.

Barrett, Elliott P., Leslie G. Joyner, and Paul P. Halenda. 1951. "The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms". *Journal of the American Chemical Society* 73 (1): 373–80. DOI: 10.1021/ja01145a126.

Beall, F. C., and H. W. Eickner. 1969. "Thermal degradation of wood components: A review of the literature". U.S. Forest Products Laboratory. http://www.researchgate.net/publication/236367987_Thermal_Degradation_of_Wood_Components_A_Review_of_the_Literature.

Bobleter, O., and R. Concin. 1979. "Degradation of poplar lignin by hydrothermal treatment". *Cellulose Chemistry and Technology* 13 (5): 583-93. http://agris.fao.org/agris-search/search.do?recordID=US201302808092.

Bobleter, Ortwin. 1994. "Hydrothermal degradation of polymers derived from plants". *Progress in Polymer Science* 19 (5): 797–841. DOI: 10.1016/0079-6700(94)90033-7.

Bourgois, J., and R. Guyonnet. 1988. "Characterization and analysis of torrefied wood". *Wood Science and Technology* 22 (2): 143–55. DOI: 10.1007/BF00355850.

Brebu, Mihai, and Cornelia Vasile. 2010. "Thermal degradation of lignin - A review". *Cellulose Chemistry and Technology* 44 (9): 353–63. https://www.researchgate.net/publication/237090542_Thermal_degradation_of_lignin_-_A_Review.

Brownell, H. H., E. K. C. Yu, and J. N. Saddler. 1986. "Steam-explosion pretreatment of wood: Effect of chip size, acid, moisture content and pressure drop". *Biotechnology and Bioengineering* 28 (6): 792–801. DOI: 10.1002/bit.260280604.

Chan, Wai-Chun R., Marcia Kelbon, and Barbara B. Krieger. 1985. "Modelling and experimental verification of physical and chemical processes during pyrolysis of a large biomass particle". *Fuel* 64 (11): 1505–13. DOI: 10.1016/0016-2361(85)90364-3.

Chen, Wei-Hsin, Jianghong Peng, and Xiaotao T. Bi. 2015. "A state-of-the-art review of biomass torrefaction, densification and applications". *Renewable and Sustainable Energy Reviews* 44: 847-66. DOI: 10.1016/j.rser.2014.12.039.

Cherubini, Francesco, Gerfried Jungmeier, Maria Wellisch, Thomas Willke, Ioannis Skiadas, René Van Ree, and Ed de Jong. 2009. "Toward a common classification approach for biorefinery systems". *Biofuels, Bioproducts and Biorefining* 6 (3): 246–56. DOI: 10.1002/bbb.172.

Cherubini, Francesco. 2010. "The biorefinery concept: Using biomass instead of oil for producing energy and chemicals". *Energy Conversion and Management* 51 (7): 1412–21. DOI: 10.1016/j.enconman.2010.01.015.

Chow, S.-Z. 1971. "Infrared spectral characteristics and surface inactivation of wood at high temperatures". *Wood Science and Technology* 5 (1): 27–39. DOI: 10.1007/BF00363118.

Demirbas, M. Fatih. 2009. "Biorefineries for biofuel upgrading: A critical review". *Applied Energy* 86: S151–61. DOI: 10.1016/j.apenergy.2009.04.043.

Dubinin, M. M., and H. F. Stoeckli. 1980. "Homogeneous and heterogeneous micropore structures in carbonaceous adsorbents". *Journal of Colloid And Interface Science* 75 (1): 34-42. DOI: 10.1016/0021-9797(80)90346-X.

Elliott, Douglas C. 2001. "Issues in value-added products from biomass". In *Progress in Thermochemical Biomass Conversion*. Wiley Online Library, 1186–96. DOI: 10.1002/9780470694954.ch96.

Elliott, Douglas C. 2004. "Biomass, Chemicals from". In *Encyclopedia of Energy*. New York: Elsevier. DOI: 10.1016/B0-12-176480-X/00358-2.

Esteban, Luis S., and Juan E. Carrasco. 2006. "Evaluation of different strategies for pulverization of forest biomasses". *Powder Technology* 166 (3): 139–51. DOI: 10.1016/j.powtec.2006.05.018.

Esteves, Bruno M., and Helena M. Pereira. 2009. "Wood modification by heat treatment: A review". *BioResources* 4 (1): 370–404. http://ojs.cnr.ncsu.edu/index.php/BioRes/article/view/BioRes_04_1_%23%23%23%23_Esteves_P_Wood_Mod_Heat_Treatment.

Fengel, Dietrich, and Gerd Wegener. 1983. *Wood: Chemistry, Ultrastructure, Reactions*. Berlin: Walter de Gruyter. https://books.google.com/books?hl=pt-PT&lr=&id=x1B4uITKnt0C&pgis=1.

Diniz, J. M. B. F., M. H. Gil, and J. A. A. M. Castro. 2004. "Hornification - its origin and interpretation in wood pulps". *Wood Science and Technology* 37 (6): 489–94. DOI: 10.1007/s00226-003-0216-2.

Garrote, G., H. Domínguez, and J. C. Parajó. 1999. "Hydrothermal processing of lignocellulosic materials". *Holz Als Roh- Und Werkstoff* 57 (3): 191–202. DOI: 10.1007/s001070050039.

Gossett, J. M., D. C. Stuckey, W. F. Owen, and P. L. McCarty. 1982. "Heat treatment and anaerobic digestion of refuse". *Journal - Environmental Engineering Division* (108): 437-54. http://www.researchgate.net/publication/255116302_Heat_treatment_and_anaerobic_digestion_of_refuse.

Green, David W., Jerrold E. Winandy, and David E. Kretschmann. 1999. *Mechanical properties of wood*. General technical report FPL; GTR-113. WI: USDA Forest Service, Forest Products Laboratory.

Gregg, David, and John N. Saddler. 1996. "A techno-economic assessment of the pretreatment and fractionation steps of a biomass-to-ethanol process". *Applied Biochemistry and Biotechnology* 57–58 (1): 711–27. DOI: 10.1007/BF02941753.

Hendriks, A. T. W. M., and G. Zeeman. 2009. "Pretreatments to enhance the digestibility of lignocellulosic biomass". *Bioresource Technology* 100 (1): 10–8. DOI: 10.1016/j.biortech.2008.05.027.

Hon, David N. S., and Nobuo Shiraishi. 2000. *Wood and Cellulosic Chemistry.* CRC Press. https://books.google.com/books?hl=pt-PT&lr=&id=pKiTzbEDy1QC&pgis=1.

Horváth, Géza, and Kunitaro Kawazoe. 1983. "Method for the calculation of effective pore size distribution in molecular sieve carbon". *Journal of Chemical Engineering of Japan* 16 (6): 470–75. DOI: 10.1252/jcej.16.470.

Jansen, Roland A. 2013. *Second generation biofuels and biomass: Essential guide for investors, scientists and decision makers*. Wiley-VCH Verlag GmbH & Co. KGaA. DOI: 10.1002/9783527652976.

Jin, Wenjia, Kaushlendra Singh, and John Zondlo. 2013. "Pyrolysis kinetics of physical components of wood and wood-polymers using isoconversion method". *Agriculture* 3 (1): 12–32. DOI: 10.3390/agriculture3010012.

Kamm, Birgit, Patrick R. Gruber, and Michael Kamm. 2006. *Biorefineries - Industrial processes and products: Status quo and future directions*. Vol. 1-2. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA.

Kamm, Birgit. 2008. "Definition and technical status of biorefineries". Accessed November 24, 2017. http://www.biorefinery.nl/fileadmin/biorefinery/BioreFuture_2008/Definition_and_Technical_status_of_biorefineries1.pdf.

Kansa, Edward J., Henry E. Perlee, and Robert F. Chaiken. 1977. "Mathematical model of wood pyrolysis including internal forced convection". *Combustion and Flame* 29 (3): 311–24. DOI: 10.1016/0010-2180(77)90121-3.

Landers, John, Gennady Yu Gor, and Alexander V. Neimark. 2013. "Density functional theory methods for characterization of porous materials". *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 437: 3–32. DOI: 10.1016/j.colsurfa.2013.01.007.

Liu, Chaogang, and Charles E. Wyman. 2003. "The effect of flow rate of compressed hot water on xylan, lignin, and total mass removal from corn stover". *Industrial & Engineering Chemistry Research* 42 (21): 5409–16. DOI: 10.1021/ie030458k.

Lora, Jairo H., and Morris Wayman. 1978. "Delignification of hardwoods by autohydrolysis and extraction". *TAPPI Journal* 61: 47-50. https://www.researchgate.net/publication/245859704_Delignification_of_hardwoods_by_autohydrolysis_and_extraction_TAPPI_J_61_47-50.

Madani, S. Hadi, Alexander Badalyan, Mark J. Biggs, and Phillip Pendleton. 2015. "Uncertainty in pore size distribution derived from adsorption isotherms: I. Classical methods". *Microporous and Mesoporous Materials* 214: 210–16. DOI: 10.1016/j.micromeso.2015.04.026.

Maloney, T. C., and H. Paulapuro. 1999. "The formation of pores in the cell wall". *Journal of Pulp and Paper Science* 25 (12): 430-36.

Mitchell, P. H. 1988. "Irreversible property changes of small loblolly pine specimens heated in air, nitrogen, or oxygen". *Wood and Fiber Science : Journal of the Society of Wood Science and Technology* (3): 320-35. https://wfs.swst.org/index.php/wfs/article/view/956.

Mosier, Nathan, Charles Wyman, Bruce Dale, Richard Elander, Y. Y. Lee, Mark Holtzapple, and Michael Ladisch. 2005. "Features of promising technologies for pretreatment of lignocellulosic biomass". *Bioresource Technology* 96 (6): 673–86. DOI: 10.1016/j.biortech.2004.06.025.

Naik, S. N., Vaibhav V. Goud, Prasant K. Rout, and Ajay K. Dalai. 2010. "Production of first and second generation biofuels: A comprehensive review". *Renewable and Sustainable Energy Reviews* 14 (2): 578–97. DOI: 10.1016/j.rser.2009.10.003.

Negro, M. J., P. Manzanares, J. M. Oliva, I. Ballesteros, and M. Ballesteros. 2003. "Changes in various physical/chemical parameters of Pinus pinaster wood after steam explosion pretreatment". *Biomass and Bioenergy* 25 (3): 301–8. DOI: 10.1016/S0961-9534(03)00017-5.

Olivier, J. P., W. B. Conklin, and M. v. Szombathely. 1994. "Determination of pore size distribution from density functional theory: A comparison of nitrogen and argon results". *Studies in Surface Science and Catalysis* 87: 81–9. DOI: 10.1016/S0167-2991(08)63067-0.

Phanphanich, Manunya, and Sudhagar Mani. 2011. "Impact of torrefaction on the grindability and fuel characteristics of forest biomass". *Bioresource Technology* 102 (2): 1246–53. DOI: 10.1016/j.biortech.2010.08.028.

Pyle, D. L., and C. A. Zaror. 1984. "Heat transfer and kinetics in the low temperature pyrolysis of solids". *Chemical Engineering Science* 39 (1): 147–58. DOI: 10.1016/0009-2509(84)80140-2.

Ramos, Luiz Pereira. 2003. "The chemistry involved in the steam treatment of lignocellulosic materials". *Química Nova* 26 (6): 863–71. DOI: 10.1590/S0100-40422003000600015.

Rouquerol, Françoise, Jean Rouquerol, and Kenneth Sing. 1999. *Adsorption by powders and porous solids: Principles, methodology and applications.* London: Academic Press. DOI: 10.1016/B978-0-12-598920-6.50017-8.

Rowell, Roger M. 2006. "Chemical modification of wood: A short review". *Wood Material Science and Engineering* 1 (1): 29–33. DOI: 10.1080/17480270600670923.

Saito, A., and H. C. Foley. 1991. "Curvature and parametric sensitivity in models for adsorption in micropores". *AIChE Journal* 37 (3): 429–36. DOI: 10.1002/aic.690370312.

Shafizadeh, Fred, and Peter P. S. Chin. 1977. "Thermal deterioration of wood". In *Wood Technology: Chemical Aspects*, 57-81. ACS Symposium Series, Vol. 43. DOI: 10.1021/bk-1977-0043.ch005.

Sing, Kenneth. 2001. "The use of nitrogen adsorption for the characterisation of porous materials". *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 187–188: 3-9. DOI: 10.1016/S0927-7757(01)00612-4.

Sriram, N., and M. Shahidehpour. 2005. "Renewable biomass energy". *IEEE Power Engineering Society General Meeting, 2005*, 1–6. DOI: 10.1109/PES.2005.1489459.

Stamm, Alfred J., Horace K. Burr, and Albert A. Kline. 1946. "Staybwood - Heat-stabilized wood". *Industrial & Engineering Chemistry* 38 (6): 630-4. DOI: 10.1021/ie50438a027.

Tang, Walter K., and Wayne K. Neill. 1964. "Effect of flame retardants on pyrolysis and combustion of α-cellulose". *Journal of Polymer Science Part C: Polymer Symposia* 6 (1): 65–81. DOI: 10.1002/polc.5070060109.

Thuvander, F., L. Wallström, L. A. Berglund, and K. A. H. Lindberg. 2001. "Effects of an impregnation procedure for prevention of wood cell wall damage due to drying". *Wood Science and Technology* 34 (6): 473–80. DOI: 10.1007/s002260000065.

Tinney, E. Roy. 1965. "The combustion of wooden dowels in heated air". *Symposium (International) on Combustion* 10 (1): 925–30. DOI: 10.1016/S0082-0784(65)80235-1.

Vernois, Michel. 2001. "Heat treatment of wood in France - State of the art". *Review on heat treatment of wood. Proceedings of Special Seminar of Cost Action E22: Environmental Optimization of Wood Protection*, 37-44.

Wallström, L., and K. A. H. Lindberg. 1999. "Measurement of cell wall penetration in wood of water-based chemicals using SEM/EDS and STEM/EDS technique". *Wood Science and Technology* 33 (2): 111–22. DOI: 10.1007/s002260050103.

Weiland, J. J., and R. Guyonnet. 2003. "Study of chemical modifications and fungi degradation of thermally modified wood using DRIFT spectroscopy". *Holz Als Roh- Und Werkstoff* 61 (3): 216–20. DOI: 10.1007/s00107-003-0364-y.

Weimer, P. J., J. M. Hackney, and A. D. French. 1995. "Effects of chemical treatments and heating on the crystallinity of celluloses and their implications for evaluating the effect of crystallinity on cellulose biodegradation". *Biotechnology and Bioengineering* 48 (2): 169–78. DOI: 10.1002/bit.260480211.

Zhu, Yongming, Y. Y. Lee, and Richard T. Elander. 2004. "Dilute-acid pretreatment of corn stover using a high-solids percolation reactor". *Applied Biochemistry and Biotechnology* 117 (2): 103–14. http://www.ncbi.nlm.nih.gov/pubmed/15159554.

Zhu, Yongming, Y. Y. Lee, and Richard T. Elander. 2005. "Optimization of dilute-acid pretreatment of corn stover using a high-solids percolation reactor". *Applied Biochemistry and Biotechnology* 121–124: 1045–54. http://www.ncbi.nlm.nih.gov/pubmed/15930580.