PYROLYSIS AND THERMOGRAVIMETRIC ANALYSIS OF WOOD AND ITS COMPONENTS

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PYROLYSIS AND THERMOGRAVIMETRIC ANALYSIS OF WOOD AND ITS COMPONENTS

by

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SWEDEN
Abstract

The present study investigates the thermochemical conversion of spruce wood and its extracted components by thermogravimetric analysis. The extracted components are two pulps, three xylan-lignin samples and one lignin sample; they were produced by the kraft cooking method with different cooking times. The study involves characterization of the biomass through proximate analysis and pyrolysis. A qualitative comparison between the thermal behaviours of the extracted components and wood is also performed.

The study showed that the thermal behaviour of the biomass was highly influenced by the content of cellulose and lignin in the samples. Compounds rich in cellulose produced large quantities of volatiles and had a higher rate of pyrolysis compared to compounds rich in lignin, which produced more char and had a slower rate of pyrolysis. It was also shown that, the amount of char is not solely depending on the amount of the lignin; the structure of the compound also plays a role. On the other hand, the original wood sample showed some deviations regarding the trends in volatile and char production and these deviations were attributed to component interactions.

Both cellulose and lignin rich compounds had an increase in thermal stability with increasing cooking time. For the pulps the increase in thermal stability is believed to be caused by increase in crystallinity, while for the lignin rich samples is believed to be caused by the increase in lignin content and structural changes in the compounds.

The results also show that although changes are introduced in the cooking process, the extracted component still retain properties exhibited by the source biomass.
Acknowledgements

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1 INTRODUCTION

1.1 Background

The concern over the possible depletion of fossil fuels added to their negative impact on the environment has increased in the last decades. Actions to counteract this negative impact call for the use of alternative energy sources [1]. The rapid growth in countries like India and China, the search for energy security are additional reasons contributing for the growing interest in investments and research on alternative renewable energy [2]. Biomass has been identified as a potential source of energy that could replace fossil fuels. Biomass is a term for all organic material that stems from plants with wood as the main representative [3, 4].

The use of biomass as energy source has significant benefits for the environment: biomass is carbon neutral, it captures carbon dioxide through photosynthesis while growing; it is renewable; it has low content of sulphur and nitrogen which makes it less polluting than fossil fuels. On the other hand, biomass is low in energy density compared to fossil fuels, due to low carbon and high oxygen content [1, 5].

Despite its low energy density, it can be upgraded into higher energy density fuels through thermochemical and bio-chemical/biological processes. Thermochemical processes include four processes: combustion, pyrolysis, gasification and liquefaction. Bio-chemical processes comprise: digestion (production of biogas, a mixture of mainly methane and carbon dioxide) and fermentation to produce ethanol. The main products of biomass conversion are: power and heat generation, transportation fuels and chemical feedstock [6].

Sweden is one of the leading countries in the use of renewable energy; the country’s share of renewable energy has been continuously increasing from 33% in 1990 to 48% in 2010. The increase is attributed to greater use of biofuels for the production of electricity and heat, and in the forest industry. Furthermore, the country has set a target to have 50% of its energy usage from renewable sources by 2020 [7]. The GoBiGas project in Göteborg, is an example of the commitment of the Swedish government to increase the production of renewable energy. The project expects to deliver biogas equivalent of 1 TWh to the city of Göteborg; the biogas will be produced from the gasification of forest residues such as branches, roots and tops [8].

For large scale design and optimization of thermochemical conversion systems, the pyrolysis behaviour of the biomass must be known; since the kinetic parameters that are required for reactor design and optimization are obtained from the pyrolysis studies. Additionally, pyrolysis is present as first step in both gasification and combustion [9, 10].

It is mentioned in the literature that the pyrolysis of biomass can be described as the sum of the pyrolysis of its main components, i.e. hemicellulose, cellulose and lignin. In the studies of Zhou et al. [11] the pyrolysis of five biomass species was simulated from the pyrolysis of each of the main biomass components. Yang et al. [12] also conducted a study using the three major components of biomass; they synthesized biomass by mixing biomass
components using a simplex-lattice approach. The thermal degradation of the synthesized biomass was studied with different ratios of biomass components. The results were later used to develop a computing approach to predict the proportions of the three components in biomass. Commercial biomass components were used in both studies and, both studies reported that the pyrolysis of biomass could be described by the sum of the pyrolysis of its components.

It is known from literature that biomass is a complex matter and it can vary depending on factors such as species, for the case of same sample, geographical origin, age or part of the plant [4]. Therefore, the use of commercial biomass components in pyrolysis studies might not reflect those of the original biomass whose pyrolysis characteristics are intended to study. The study performed by Antal et al. [13] is a good example to illustrate the effect of biomass variety and complexity. In this study, the pyrolysis of eight samples of pure cellulose from different origin was performed under the same experimental conditions; the results showed different range of decomposition temperatures, different yields of char and activation energy. It is acknowledged in the study that the crystallization and degree of polymerization influence the different pyrolysis behaviours exhibited, however, not such extent; this led them to conclude that each cellulose is a unique material.

Despite numerous studies on biomass and its constituents, most studies opt for commercially available biomass constituents; studies were the biomass constituents are isolated from the biomass being study were not found. Hence, in the present study instead of using commercial biomass components, the components are extracted from the same biomass (spruce wood). By using the extracted biomass components it is also possible to evaluate the effects of the extraction method on the resulting compounds.

The present study does not serve to take away the merit of the studies using commercial biomass components, but to give additional insights on the biomass pyrolysis process which is crucial for the advancement of thermochemical process design and optimization.
1.2 Aim of the project

The project aims to investigate the thermochemical conversion of a certain type of wood, namely spruce, by means of thermo-gravimmetrical analysis. The analysis includes proximate analysis and pyrolysis at 7K/min. The results are compared to find out whether the pyrolysis of wood can be described by the sum of the pyrolysis of its extracted components.

1.3 Scope

The study presents an experimental exploration of the pyrolysis of wood and extracted components. The analysis includes:

i. Basic characterization of the fuel properties of wood and its constituents by means proximate analysis and thermal stability.

ii. Investigation of the pyrolysis behaviour of the wood and its extracted components and finally a comparison between the two.
WOODY BIOMASS AND PYROLYSIS

2.1 Woody biomass

Wood is composed mainly by cellulose, hemicellulose and lignin. For the case of Norway spruce (*Picea abies*), the predominant spruce in Scandinavia, cellulose accounts for 40.5%, hemicellulose 24.3% and lignin 28% on weight basis. The other 6.2% is made up by acetyl groups (1.4%), resin, mineral substances, proteins and undetermined substances (4.8%) [14].

2.1.1 Cellulose

Cellulose is the main component in the cell walls of true plants. It occurs either in pure form as in the seed hair of cotton, or mixed with other polysaccharides and lignin, as in wood. The role of cellulose in this composite is to work as an enforcing fibre [15].

The cellulose molecule is a linear polymer of D-anhydroglucopyranose units linked together by $\beta$-1,4-glucosidic bonds. The average molecular weight is around 100 000 and the degree of polymerization is often very high; making cellulose the longest of all known polysaccharides [3, 15, 16].

2.1.2 Hemicellulose

Hemicellulose is a complex of polymeric carbohydrates consisting of polymers of pentoses (xylose, arabinose), hexoses (mannose, glucose, galactose), and sugar acids [17, 18]. The composition of hemicellulose varies and is dependent on the plant source. In softwoods, like spruce, glucomannans are the most common type of hemicellulose, whereas hardwoods contain mostly xylans [17]. Together with cellulose, it forms the bulk of the supporting structure of the plant cell – the cell wall [15].

Unlike cellulose, hemicellulose is a heterogeneous branched polysaccharide that binds tightly, but non-covalently to the surface of each cellulose microfibril. The molecular weight is lower than cellulose with an average of $< 30 000$ [3].

2.1.3 Lignin

Lignin is a hydrophobic polymer that fills up between the cellulose microfibrils and hemicellulose fixating them towards each other and thus giving the cell wall its “woody” properties. It also serves as protection against microbial degradation of wood [15].

Lignin has the most complex structure among natural polymers. Unlike cellulose or hemicellulose, the lignin structure is a three-dimensional web with monomers (i.e., building blocks) connected with a number of different ether (C-O-C)- and carbon-carbon (C-C) bonds
that are randomly distributed [15]. The lignin building blocks are made up of mainly three monomers (monolignols): $p$-coumaryl alcohol, coniferyl and sinapyl alcohol. These phenylpropanes differ in the number of methoxyl groups attached to them. For softwoods like Norway spruce, the lignin consists almost exclusively of coniferyl alcohol and may contain small amounts of $p$-coumaryl alcohol but no or only traces of synapyl alcohol [3, 15].

2.2 Kraft Cooking

The objective of pulping is to remove lignin, in order to liberate the fibres in the wood that are “glued” by lignin. Kraft cooking is the dominant chemical pulping method employed globally. In kraft cooking, also called sulphate cooking, delignification is achieved by cooking wood chips in a solution of sodium hydroxide, NaOH, and sodium sulphide, Na$_2$S. In the solution, also called white liquor, the active cooking species are OH$^-$ and HS$. The hydrogen sulphide ion is the main delignifying agent and the hydroxide ion keeps the lignin fragments in the solution. Typical cooking temperatures are 150-160 °C for hardwoods and 160-170 °C for softwoods such as Norway spruce. As for the cooking time, it can vary according to desired degree of delignification [19, 20].

Since the cooking chemicals are not entirely selective to lignin, the delignification process is terminated with some lignin remaining in the pulp; total delignification would imply further losses of carbohydrates, consequently reducing the quality and strength of the pulp. The amount of lignin left in the pulp is expressed by the kappa number, a high kappa number means less delignification and vice-versa [19].

2.3 Proximate Analysis

The characterization of biomass is of vital importance to determine the most suitable conversion technology and to anticipate possible processing problems and/or handling strategies. Proximate analysis provides information such as moisture content (M), volatile matter content (VM), fixed carbon (FC) and ash.

The quantity of moisture contained in biomass is an important factor for the case of thermochemical conversion since it determines how much energy must be spent to dry the material [3].

The volatile matter content which is the portion that is released as vapour upon heating the solid fuel (to 950 °C for 7 minutes) in inert atmosphere, tells how much fuel gas can be produced [3, 21].
The fixed carbon content is the remaining mass of solid after the release of volatiles excluding ash. Both volatile matter content and fixed carbon provide a measure of how easy the biomass can be ignited and subsequently oxidised, depending on how the biomass is to be utilized as an energy source [3].

Ash is the residue left after combustion of the biomass; potassium, calcium, sodium, silicon, phosphorus and magnesium are the main constituents [4]. The amount of ash affects both handling and processing costs and, depending on the magnitude, it can reduce the available energy of the fuel; just like with moisture, the higher the ash content the lower the energy density. Another problem with ash in thermochemical conversion processes is the formation of slag and corrosive chemical species; these reduce plant throughput and result in increased operating costs [3, 21].

### 2.4 Pyrolysis

Pyrolysis is the thermochemical decomposition of organic matter at high temperatures (see Table 1) in an inert atmosphere which results in the production of char and volatile products [1, 22]. Pyrolysis is not just a process on its own; it takes part as first step in gasification and combustion. When a particle is subjected to the high temperatures encountered in gasification and combustion (more than 800 °C), it quickly starts to decompose into volatiles and char. The volatiles leaving the particle, keep oxygen from diffusing into the particle and therefore, creating conditions for decomposition in inert atmosphere. Only when the devolatilization is over the oxygen is able to diffuse into the particle and the heterogeneous combustion of the remaining char takes place [9, 23].

The pyrolysis process can be divided into three subclasses: conventional pyrolysis, fast pyrolysis, and flash pyrolysis [22]. Table 1 summarizes the differences in operating conditions for these processes.

<table>
<thead>
<tr>
<th>Table 1: Range of main operating parameters for pyrolysis processes [24]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating temperature (°C)</td>
</tr>
<tr>
<td>----------------------------</td>
</tr>
<tr>
<td>300-700</td>
</tr>
<tr>
<td>Heating rate (°C/s)</td>
</tr>
<tr>
<td>Solid residence time (s)</td>
</tr>
<tr>
<td>Particle size (mm)</td>
</tr>
</tbody>
</table>

*a Up to 2000 °C with solar furnaces*
Fast and flash pyrolysis maximize the production of liquids while conventional pyrolysis maximizes the production of char [24]. For the purpose of kinetic studies, conventional pyrolysis with low heating rate and low mass samples is used, allowing the reaction to be kinetically controlled. Thermogravimetric analysers are widely used for this purpose.
3 MATERIALS AND METHODS

3.1 Materials and Preparation Methods
Wood and extracted wood components were used in the present study. The extraction and the chemical analysis of the extracted materials were done in a separate project within the Department of Fibre and Polymer Technology at KTH and were not part of this work. The data and methodology described in this section present a summary of the extraction process. A summary of the cooking conditions and the carbohydrate analysis is given in Table 4 and Table 5. The different entries in Table 4 are described in the following subsections. Figure 1 gives an overview of the sample preparation.
3.1.1 Wood

The wood sample used in the study is Norway spruce (*Picea Abies*). Spruce wood without any chemical pre-treatment, was ground into a powder and screened through mesh 40 sieve (see Figure 2).

![Figure 2: Spruce wood sample](image)

3.1.2 Pulps

The pulps were produced by the kraft cooking method. The white liquor was prepared by mixing distilled water with sodium hydroxide and sodium sulphide such that the final solution had the concentration of 1.5 mol/dm$^3$ Na$^+$, 0.26 mol/dm$^3$ HS$^-$ and 1.2 mol/dm$^3$ OH$^-$. The wood chips were placed in a rotating steel autoclave and the air within the autoclave was sucked out by means of a vacuum pump, creating vacuum for 30 minutes. Afterwards, the white liquor at room temperature was added in 4:1 ratio (liquor : wood) while keeping the vacuum. The autoclave was rotated in a polyethylene glycol hot bath while slightly inclined, to increase the contact between the wood chips and the cooking liquor. The cooking proceeded for a determined period of time for each sample at a cooking temperature of 157°C (see Table 4), with a 10 minutes allowance to reach the cooking temperature. After the cooking, the autoclave was immediately cooled in a water bath, after which the weak black liquor (spent liquor) and pulp were collected and separated.

The collected pulps (shown in Figure 3) were treated by displacement washing using deionized water, in a washing cylinder immersed in a washing bath. After the washing the pulps were oven dried at 40°C. The two pulps differ in lignin content (kappa number); pulp I has low lignin content compared to pulp II (see Table 5). The protocol to produce the two pulps differed only in the cooking time (300 minutes and 100 minutes for pulp I and pulp II respectively).
3.1.3 Xylan-Lignin

The xylan-lignin samples were prepared by precipitation of the black liquors produced at different cooking times (see Table 4). The precipitation was done according to the procedure presented by Axelsson et al. [25], with the exception that in this case the final washing step was performed with acetone instead of ethyl ether.

Acetic acid was slowly added to the black liquor until the volume added equalled the volume of black liquor sample, changing the pH of the solution to pH 3. The black liquor-acetic acid mixture was poured into a volume of ethanol 3 times the volume of black liquor-acetic acid mixture. The solution was then placed in a refrigerator at a temperature of 4°C for 16-24 hours while xylan formed a precipitate. The supernatant was separated by decantation and the precipitate was washed twice with an ethanol-water mixture (1:2), three times in pure ethanol and finally three times with acetone. The precipitate was centrifuged after each washing step with a ROTOFIX 32A centrifuge for 20 minutes at speed of 4 000 rpm.

After the washing process, the precipitate was dried in a desiccator under vacuum to remove acetone. The dry solid content was measured with an infra-red balance, Mettler Toledo PM460.

The resulting compounds (shown in Figure 4, 5 and 6) are designated xylan-lignin I/II/III as a means to facilitate distinction amongst the three. These compounds differ in the lignin content, molecular weight and uronic acid content (see Table 5 and Table 6).
Figure 4: Precipitated Xylan Lignin I from kraft black liquor

Figure 5: Precipitated Xylan Lignin II from kraft black liquor

Figure 6: Precipitated Xylan Lignin III from kraft black liquor
3.1.4 Lignin

Lignin was precipitated from weak kraft black liquor at pH 9 and 70 °C. The pH of the solution was reduced from 12 to the precipitation pH by adding 20% H₂SO₄ solution while stirring. The beaker with the precipitated lignin was cooled in an ice bath and then put in a refrigerator overnight at 5 °C, allowing for the precipitated lignin to settle at the bottom of the beaker. The acidified black liquor supernatant was decanted through a high pH filter and the remaining lignin was dissolved in distilled water. The lignin was washed with acid water of pH 2 while stirring, to remove sodium ions and organic contaminants as much as possible. The solution was then filtered through a low pH filter and the lignin collected. The lignin filtrate had a gel-like texture; it was put on glass dish and then dried in a ventilated oven at 65 °C for 12 hours.

![Precipitated lignin from kraft black liquor](image)

**Figure 7: Precipitated lignin from kraft black liquor**

3.1.5 Sample Analysis

The kappa number was determined according to ISO 302:2004, the residual hydroxide ion concentration according to SCAN N 33:94 and the hydrogen sulphide ion concentration according to SCAN N 31:94.

Klason lignin was determined gravimetrically after hydrolysis with sulphuric acid (125°C, 60 min), for both pulps and xylan-lignins, according to SCAN-CM 71:09. The sample mass was 200 mg for pulps, and about 100 mg for xylan-lignin samples.

The carbohydrate content was determined after acid hydrolysis; it was analysed according to SCAN-CM 71:09, using a high-performance anion exchange chromatograph equipped with pulsed amperometric detection (HPAEC-PAD) and a CarboPac PA1 column (Dionex, Sunnyvale, Ca, USA).
3.2 Thermogravimetric Analysis

3.2.1 Proximate Analysis

The proximate analysis was conducted with a Netzsch STA 449 F3 thermal analyser. The apparatus is equipped with a microbalance, a silicon carbide high temperature furnace (1650 °C maximum) and three mass flow controllers (MFC) for gas flow control. The apparatus is connected to circulating water bath system controlled at 23°C to ensure constant temperature in the balance chamber.

Before carrying out the experiments the apparatus was calibrated both for temperature and sensitivity. The temperature and sensitivity calibration was done using standard metals (Sn, Bi, Zn, Al and Au) provided by the apparatus vendor. The characteristic melting temperatures were recorded and fitted to a polynomial provided in the apparatus software. The metals were selected so as to cover the range of temperatures used in the experiments. Alumina crucibles of 85μL were used for the calibration and experiments.

The temperature program used was devised based on the works of Garcia [21] and Cantrell [26]; nitrogen gas (98.75% purity) was used as inert atmosphere. Two temperature programmes referred as Protocol 1 and Protocol 2 were used for the proximate analysis. The second protocol was devised to compare how the yields of the proximate analysis are affected when the drying, pyrolysis and combustion times are increased.

The proximate analysis of wood was conducted with both protocols whereas the proximate analysis of the extracted components was performed with Protocol 2. A comparison between the results obtained for wood using both protocols showed negligible differences (see section 4.1.1); therefore any of the two protocols could be used to perform the proximate analysis of the remaining samples.

Before subjecting the samples to proximate analysis, the thermobalance was fluxed with nitrogen gas for 1 day before the first experiment, for 10 min after opening and inserting a new sample, to ensure inert atmosphere during the pyrolysis.

Prior to introducing the samples into the sample holder, care was taken to ensure that the samples were evenly distributed in the crucible. This is important to optimize the heat flow between the heat source and the sample, and therefore, reduce thermal lag [27]. The sample size was kept at ~10 mg and the gas flow at 80 mL/min.

The STA is equipped with three mass flow controllers which allows for automatic switch of the gases in order to change from inert to oxidative atmosphere. The mass loss, temperature and flow measurements were recorded by the software provided with the apparatus.
**Protocol 1 temperature program**

The sample is heated in an inert atmosphere, from room temperature to 110 °C at 20K/min and, held at 110 °C during 5 minutes for drying. After drying, the temperature is increased to 950 °C at 50K/min, held isothermally at 950 °C for 7 minutes after which, it is cooled to 110 °C. Immediately after cooling, the nitrogen MFC is shut off and the air MFC opens to start the combustion step. In the oxidative atmosphere the sample is reheated to 950 °C at 50 K/min and, held isothermally for 10 minutes. The sample is then cooled down to 110 °C in the final step (see Figure 8).

The mass loss during drying, pyrolysis and combustion account for the moisture content, volatile matter and fixed carbon respectively; the residual mass gives the ash content.

The TGA used to perform proximate analysis does not have an active cooling system, as result, the furnace did not reach the targeted cooling temperature (110°C) as specified in the temperature program; instead within the time window it cooled down to 460°C with the temperature undergoing an exponential decay.

**Protocol 2 temperature program**

Protocol 2 has a similar temperature program as Protocol 1; it differs from Protocol 1 in the isothermal holding times. In Protocol 2, the drying time was increased to 10 minutes; the pyrolysis and combustion times were both increased to 20 minutes (see Figure 8).

![Temperature program Proximate Analysis](image)

*Figure 8: Proximate analysis temperature program*
3.2.2 Pyrolysis of wood and its extracted components

The pyrolysis study was conducted with a TGA/DSC 1 STAR System from Mettler Toledo. The apparatus is equipped with the following: a microbalance, a high temperature furnace (1600 °C maximum) with an automatic sampler and water cooling system. The calibration of the instrument was done by a third party as part of routine maintenance.

The pyrolysis was performed under nitrogen atmosphere (99.999% purity) with the volumetric flow rate set at 70 mL/min. The samples were heated from 30 °C to 900 °C at 7K/min. The mass of the samples was kept at ~4 mg to minimize temperature gradients in the sample. Additionally, care was taken to ensure that the samples were distributed evenly in the crucible to ensure uniform heat distribution in the sample.
4 RESULTS AND DISCUSSION

4.1 Proximate Analysis Results

4.1.1 Protocol 1 vs Protocol 2

The proximate analysis of spruce wood was carried out with both protocols 1 and 2. The results are presented in Table 2; from the results it can be seen that similar results are obtained for both protocols, also the standard deviations are small. The volatile matter (VM) content and fixed carbon (FC) are on average 81% and 15% respectively, for both protocols. These results are in agreement with results found in literature [28, 29]. The moisture for the first run is relatively low compared to the subsequent runs as result of moisture absorption by the wood as the sample container was opened. The negative values for ash are result of the noisy signal in the scale.

Table 2: Comparison of protocol 1 and protocol 2 results

<table>
<thead>
<tr>
<th></th>
<th>Protocol 1</th>
<th></th>
<th></th>
<th></th>
<th>Protocol 2</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Runs</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>M (wt.%)</td>
<td>1.78</td>
<td>3.48</td>
<td>3.62</td>
<td>4.16</td>
<td>3.26</td>
<td>0.891</td>
<td>4.50</td>
<td>3.62</td>
</tr>
<tr>
<td>VM (wt.%)</td>
<td>82.60</td>
<td>81.65</td>
<td>81.41</td>
<td>80.80</td>
<td>81.62</td>
<td>0.648</td>
<td>80.86</td>
<td>78.28</td>
</tr>
<tr>
<td>FC (wt.%)</td>
<td>15.34</td>
<td>14.95</td>
<td>14.86</td>
<td>14.86</td>
<td>15.00</td>
<td>0.198</td>
<td>14.55</td>
<td>13.98</td>
</tr>
<tr>
<td>Ash (wt.%)</td>
<td>0.28</td>
<td>-0.08</td>
<td>0.12</td>
<td>0.18</td>
<td>0.13</td>
<td>0.131</td>
<td>0.09</td>
<td>4.10</td>
</tr>
</tbody>
</table>

The results show that proximate analysis with TGA is able to give results that are comparable to the results found in literature; additionally it has the advantage of being a fully automated process and requires small sample quantities. Moreover, the time required to perform proximate analysis in a TGA can be optimized as shown by Garcia et al. [21]. The required time can be reduced by using higher heating rates, however in our case, the machine is limited by the maximum heating rate of 50K/min. In work done by others [21, 26], higher heating ramps of 100K/min were used.

As the two protocols did not lead to significant differences, for the analysis of the other samples we used only protocol 2.

4.1.2 Proximate analysis of wood and its extracted components

In Figure 9 is possible to observe and compare the distribution of products obtained when wood and its extracted components are subjected to thermal treatment at specified conditions.
(Protocol 2). The comparison is made on dry basis to exclude the impact of the moisture content in the distribution, since it varies according to the way the sample is handled.

![Figure 9: Comparison of proximate analysis of wood and its extracted components (dry basis)](image)

**Volatile Matter**

From Figure 9 it can be seen that the samples with high cellulose content (pulp I, wood and pulp II) released the largest amount of volatiles (VM) compared to the samples with low cellulose content (xylan-lignin samples and lignin). Pulp I, the sample with the highest cellulose content, released the highest amount of volatiles followed by wood and Pulp II. Although having higher cellulose content, Pulp II has a slightly lower volatile content compared to wood.

Lignin and the xylan-lignin samples released almost the same amount of volatiles (63 wt.% on average). The amount of volatiles released by these samples is about 20-25 wt.% lower than the volatiles from wood and pulps. These samples have low cellulose content and degraded carbohydrates making up to 40 wt.% of the sample (see Table 5).

By comparing the high cellulose content samples to the low cellulose content samples, it can be seen that the presence of cellulose contributes substantially to the amount of released volatiles. Nonetheless, the fact that wood (50 wt.% cellulose content) released about the same amount of volatiles as the pulps (with 85 wt.% cellulose content on average) shows that
the contribution of the remaining components in wood, namely xylan and lignin are also significant.

**Fixed Carbon**

When it comes to fixed carbon (FC), Figure 9 shows an inverse trend of what was observed in the case of volatiles. The lignin rich samples have the highest fixed carbon content compared to the cellulose rich samples.

A plot of produced char (FC with ash included) as function of lignin content is presented in Figure 10. The plot shows an increasing trend with increasing lignin content. Wood however, is an exception to this trend; with twice as much lignin compared to pulp II, it has lower fixed carbon than pulp II.

![Figure 10: Char as function of lignin content for proximate analysis and pyrolysis](image)

The correlation between fixed carbon and lignin content has been previously discussed in literature. Studies by [30, 31] have compared the yield of char for biomasses with different lignin content and found that, the higher the lignin content, the higher the char yield. Apart from the discrepancy between wood and pulp II, lignin and xylan-lignins, these findings are in agreement with our observations since the amount of ash in the samples is negligible compared to fixed carbon.
Accepting that, lignin is the main contributor for the formation of fixed carbon, it would be expected that wood would produce more fixed carbon than pulp II as previously stated. Additionally, the lignin sample should produce less fixed carbon than the xylan-lignin samples.

All samples examined were derived from the kraft cooking of spruce wood except for the wood sample which was not treated chemically. This discrepancy could be a result of component interactions in the case of wood. Another reason for this discrepancy could be the changes introduced in the lignin structure during the treatment and isolation. According to Bozell [32], all lignins are not created equal, and the functional group profile present in a given starting material can vary significantly as a function of biomass source, pre-treatment or fractionation methodology, and isolation technique. Furthermore, the fact that the lignin sample with 12 wt.% less lignin than xylan-lignin II and III, produces about the same amount of char compared to these compounds further supports the role of lignin structure in thermal decomposition.

Ash
The amount of ash found in the biomass samples is very low; it varies between 0.6–4 wt.%. The plot of produced ash as function of lignin content in Figure 11 reveals higher ash content for the lignin rich samples.

The lignin rich samples are obtained by crystallization from black liquor where the lignin/xylan-lignin samples are in contact with the cooking chemicals. During this process the salts from the cooking liquor can bind to the molecules of lignin and therefore increase the resultant ash content [20].
An observation worth mentioning, from the proximate analysis experiments, is the colour of ash produced by the xylan-lignin I sample. The ash exhibited a turquoise colour similar to the colour of copper sulphate (see Figure 12).
The xylan-lignin III sample also had colour in the ash (see Figure 13). Xylan-lignin II only presented traces of the colour. The ash from the other samples, namely wood, pulps and lignin did not present the turquoise colour.

Figure 13: Ash obtained from the proximate analysis of xylan-lignin III
4.2 Pyrolysis Results
The mass loss curves from the pyrolysis of the biomass samples are presented in Figure 14, and the respective time derivatives (DTG) are presented in Figure 15.

![Figure 14: Mass loss curves for the pyrolysis of wood and extracted components](image)

From Figure 14 it is noticeable that the compounds rich in cellulose (wood and pulps) have a similar thermal decomposition profile; the decomposition of these samples is delayed in relation to the xylan-lignin and lignin samples; also the mass loss profile is steeper indicating rapid decomposition.

The lignin thermal decomposition starts earlier than the cellulose rich samples, it is slower and spans through a broad range of temperatures.

The xylan-lignin samples present a mixture of behaviours of the lignin and cellulose rich samples. The thermal decomposition of xylan-lignin samples starts earlier than the cellulose rich samples and, the mass loss profile is similar to the cellulose rich compounds at temperatures lower than 315 °C; at higher temperatures the thermal behaviour is similar to the lignin sample.

The differences in the amount of produced char at the final temperature (residual mass in Table 3) can also be observed from Figure 14. The lignin rich compounds produced more char compared to the cellulose rich compounds. In Figure 10, the amount of char is plotted as function of lignin content and the trend is similar to what was observed for the proximate analysis. The influence of lignin in the char production has been explained in section 4.1.2.

The DTG curves, shown in Figure 15, provide an additional insight to the pyrolysis behaviours previously discussed. From the DTG curves it is possible to observe the range of
decomposition, the maximum weight loss rate and the temperature at which it occurs (peak temperature). These decomposition characteristics are summarized in Table 3.

The low temperature decomposition of xylan-lignin samples and lignin can also be observed from the DTG curves. For the xylan-lignin I sample the maximum weight loss rate occurs at 282°C (see Table 3), which is the lowest peak temperature of all biomass samples; additionally, it has a tail with a small peak at approximately 465°C. The tailing is attributed to the presence of lignin in the sample. Since lignin contains fractions that have high thermal stability, it continues to decompose at higher temperatures [33, 34].

Xylan-lignin II and III show a similar behaviour as xylan-lignin I with a few exceptions; the shift in the peak temperature is the most evident difference. Also, the maximum degradation rate is slightly lower for xylan-lignin II compared to the other xylan-lignin samples (see Table 3).

Table 3: Thermal degradation characteristics of the biomass samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{\text{peak}}$ (°C)</th>
<th>Max. degradation rate $10^{-3}$[1/s]</th>
<th>Residual mass at $T_{\text{final}}$ (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood</td>
<td>361</td>
<td>1.3</td>
<td>14.7</td>
</tr>
<tr>
<td>Pulp I</td>
<td>355</td>
<td>2.1</td>
<td>10.65</td>
</tr>
<tr>
<td>Pulp II</td>
<td>335</td>
<td>1.5</td>
<td>16.25</td>
</tr>
<tr>
<td>Xylan-Lignin I</td>
<td>282</td>
<td>0.64</td>
<td>31.35</td>
</tr>
<tr>
<td>Xylan-Lignin II</td>
<td>291</td>
<td>0.59</td>
<td>33.81</td>
</tr>
<tr>
<td>Xylan-Lignin III</td>
<td>300</td>
<td>0.64</td>
<td>31.88</td>
</tr>
<tr>
<td>Lignin</td>
<td>364</td>
<td>0.36</td>
<td>37.79</td>
</tr>
</tbody>
</table>

Figure 15: Time derivatives from the pyrolysis of wood and extracted components
Nevertheless, all three xylans exhibit tailing and have a small peak around 460 °C (Figure 18). Both the tailing and the small peak are attributed to the decomposition of the stable fractions of the lignin which occurs at high temperatures.

The shift in the peak temperature to higher temperatures implies an increase in the thermal stability of the sample. This increase in thermal stability results from the changes in the cooking conditions. All xylans were produced with the same cooking conditions, except the cooking time (see Table 4). When plotted against the cooking time, it can be seen that the peak temperature increases with the cooking time (see Figure 16).

One of the reasons for the increased thermal stability with cooking time has to do with the fact that, increasing cooking time results in increased delignification [19], which in turn increases the amount of lignin in the sample and therefore its thermal stability. However, the increase in lignin content is not the only factor responsible for the increased thermal stability. From Figure 17, it can be observed that the delignification proceeds from 50 min to 150 min with a 10% increase in the lignin content. However, beyond 150 min up to 250 min there is only 1% increase in the lignin content. This shows that the increasing cooking time does not solely affect the lignin content; it also causes changes in the molecular structure of xylan-lignin complex which ultimately results in higher thermal stability.
The individual features presented by the DTGs of the xylan-lignin samples such as, the shoulders in the xylan-lignin I (after the peak) and in xylan-lignin III (before the peak), could be an indication of the changes in the molecular structure of these compounds (see Figure 18).

In Figure 18 it can also be seen that the region of maximum decomposition rate of the xylan-lignin compounds coincides with the initial region of decomposition of wood which is attributed to the decomposition of xylan [29].
Despite of its early decomposition the lignin sample has its maximum mass loss rate around 364 °C and a small peak around 770 °C; also, the shape of the DTG curve is the broadest among all the samples. Lignin is known to decompose slowly over a wide range of temperatures. This behaviour is attributed to its structure which is full of aromatic rings with various branches, which have chemical bonds with activities that cover wide range of temperatures [35]. These features are reflected on the broadness of the lignin DTG curve and in the fact that it had the lowest maximum mass loss rate compared to all samples (see Table 3); additionally, the tailing in for this sample is more pronounced than any other sample.

As mentioned previously, the wood and pulp samples have similar decomposition behaviours; however, some differences can be pointed out. The DTG curve of the wood sample presents a “shoulder” preceding the main peak, instead of single well defined peak as the pulps. The maximum rate of mass loss (see Table 3) occurs around 361°C, about the same temperature as lignin. The shoulder on the wood DTG curve is attributed to the overlap of the decomposition temperatures of hemicellulose and cellulose [29]. The tailing, resultant from the late decomposition of lignin fractions, is also present, though less pronounced compared to both lignin and xylan-lignin I.

With respect to the wood sample, both pulps have a single peak for the DTG curve, however with individual characteristics. The decomposition of Pulp II starts approximately at the same time as wood; however, it reaches its maximum around 335 °C, earlier than wood and Pulp I. The pulp II peak coincides with the shoulder of the wood DTG (see Figure 19).

The beginning of the decomposition of Pulp I is slightly delayed with respect to wood and Pulp II, and the maximum weight loss rate occurs at 355 °C which is fairly close to the wood peak temperature. The maximum weight loss rate is the highest for pulp I followed by pulp II (see Table 3). A less pronounced tailing is also present in the DTG curves of these two samples.

Figure 19: Differences in the pyrolysis DTGs of pulp samples
From the observations mentioned above, it is clear that, despite originating from the same wood, the two pulps exhibit different thermal behaviours. In terms of composition, Pulp I differs from pulp II in the kappa number which reflects the remaining lignin content in the pulp. This was achieved by using different cooking times as previously mentioned in the methodology section. The increase in cooking time caused an increase in the thermal stability of the pulp, which is reflected in the shift to higher peak temperature (see Figure 20).

Contrary to the samples produced from black liquor, longer cooking times reduces the amount of lignin for the pulps. Besides that, it also affects the structure of the resulting pulp (mainly composed of cellulose).

Wood contains both amorphous and crystalline cellulose [36]. It has been shown by Hult et al. that, during pulping the structures that contribute to inaccessible surfaces in the wood cellulose are converted to the most stable crystal form (Iβ allomorph); also that this increase is accompanied by the conversion of cellulose Iα (meta-stable) to the most stable Iβ. Therefore, increasing the cooking times leads to an increase of stable crystal form of the cellulose [37].

Additionally, it has been shown previously that amorphous cellulose breaks down at lower temperatures compared to crystalline cellulose [38, 39]. For that reason, pulp I with longer cooking time and consequently more crystalline than pulp II, has higher thermal stability than pulp II.

Finally, comparing the rate of pyrolysis of all samples (Table 3), it can be seen that the compounds rich in cellulose have higher rates of pyrolysis compared to the lignin rich compounds. Lv et al. [31] also made the similar observation on their study.
5 CONCLUSIONS

The thermochemical conversion of spruce wood and its extracted components was investigated. The components exhibited thermal behaviour according to two main categories: cellulose rich and lignin rich compounds. The following conclusions can be drawn from this study:

- Components reach in cellulose produce high quantities of volatiles while the components rich in lignin produce more char.
- The deviations observed for the wood sample, regarding the trends seen for volatile and char production are an indication of the role played by the component interactions.
- Both the lignin content and the changes in the structure of the compounds during cooking affect the char production.
- Increasing the cooking time increases the thermal stability of both cellulose and lignin rich compounds. For the cellulose rich compounds this is explained by an increase in crystallinity, while for lignin rich compounds it is explained by increasing the lignin content and/or changing the structure of the compound.
- The rate of pyrolysis is higher for cellulose rich compounds and lower for the lignin rich compounds.
- The wood extracted components are changed in the cooking process; however they retain important properties of the source biomass.
6 RECOMMENDATIONS

The following recommendations are presented for additional research:

1. Run experiments with a lignin sample of higher purity to find out what will be the effect in the char production and thermal stability.
2. The changes in molecular structure and/or increase in the lignin content have shown to improve the thermal stability of the lignin rich compounds. This information could be of interest for the material science field and fire science, for the production of flame retardant materials. Therefore a deeper study on how these changes occur should be performed.
3. Do the evaluation of the kinetic parameters of the extracted samples and compare with original wood.
4. Do a chemical analysis on the xylan-lignin ash to understand the origin of the turquoise colour.
REFERENCES


APPENDIX A: Sample Details

Table 4: Cooking conditions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp. (°C)</th>
<th>Time (min)</th>
<th>[Na⁺] (mol/dm³)</th>
<th>[OH⁻] (mol/dm³)</th>
<th>[HS⁻] (mol/dm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xylan/Lignin I</td>
<td>157</td>
<td>50</td>
<td>1.5</td>
<td>1.2</td>
<td>0.26</td>
</tr>
<tr>
<td>Xylan/Lignin II</td>
<td>157</td>
<td>150</td>
<td>1.5</td>
<td>1.2</td>
<td>0.26</td>
</tr>
<tr>
<td>Xylan/Lignin II</td>
<td>157</td>
<td>250</td>
<td>1.5</td>
<td>1.2</td>
<td>0.26</td>
</tr>
<tr>
<td>Pulp I</td>
<td>157</td>
<td>300</td>
<td>1.5</td>
<td>1.2</td>
<td>0.26</td>
</tr>
<tr>
<td>Pulp II</td>
<td>157</td>
<td>100</td>
<td>1.5</td>
<td>1.2</td>
<td>0.26</td>
</tr>
<tr>
<td>Lignin</td>
<td>157</td>
<td>300</td>
<td>1.5</td>
<td>1.2</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Table 5: Lignin and Carbohydrate Analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lignin* (wt.%)</th>
<th>Ara (wt.%)</th>
<th>Gala (wt.%)</th>
<th>Gluc (wt.%)</th>
<th>Xyl (wt.%)</th>
<th>Man (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xylan/Lignin I</td>
<td>53.68</td>
<td>4.52</td>
<td>8.34</td>
<td>6.27</td>
<td>23.87</td>
<td>3.33</td>
</tr>
<tr>
<td>Xylan/Lignin II</td>
<td>63</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xylan/Lignin III</td>
<td>64</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pulp I (low kappa)</td>
<td>7.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pulp II (low kappa)</td>
<td>16.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spruce wood</td>
<td>33.5</td>
<td>0.5</td>
<td>1.9</td>
<td>49.1</td>
<td>12.6</td>
<td>2.3</td>
</tr>
<tr>
<td>Lignin</td>
<td>51</td>
<td>1.2</td>
<td>20.2</td>
<td>11.0</td>
<td>7.6</td>
<td>1.9</td>
</tr>
</tbody>
</table>

*ash included

Table 6: Properties of extracted xylan-lignin compounds

<table>
<thead>
<tr>
<th>ID</th>
<th>Sample</th>
<th>[Na⁺] (mol/dm³)</th>
<th>Mw (g/mol)</th>
<th>Uronic acid (μmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>05X</td>
<td>Xylan/Lignin I</td>
<td>1.5</td>
<td>8620</td>
<td>517</td>
</tr>
<tr>
<td>09</td>
<td>Xylan/Lignin II</td>
<td>1.5</td>
<td>10130</td>
<td>105</td>
</tr>
<tr>
<td>21</td>
<td>Xylan/Lignin III</td>
<td>1.5</td>
<td>8520</td>
<td>44</td>
</tr>
</tbody>
</table>
## APPENDIX B: Proximate Analysis Results

### Table 7: Proximate Analysis of Spruce wood (Protocol 1)

<table>
<thead>
<tr>
<th>Runs</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>Average</th>
<th>std. dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass (mg)</td>
<td>10.453</td>
<td>10.436</td>
<td>10.38</td>
<td>10.462</td>
<td>10.43</td>
<td>0.032</td>
</tr>
<tr>
<td>M (wt.%)</td>
<td>1.78</td>
<td>3.48</td>
<td>3.62</td>
<td>4.16</td>
<td>3.26</td>
<td>0.891</td>
</tr>
<tr>
<td>VM (wt.%)</td>
<td>82.60</td>
<td>81.65</td>
<td>81.41</td>
<td>80.80</td>
<td>81.62</td>
<td>0.648</td>
</tr>
<tr>
<td>FC (wt.%)</td>
<td>15.34</td>
<td>14.95</td>
<td>14.86</td>
<td>14.86</td>
<td>15.00</td>
<td>0.198</td>
</tr>
<tr>
<td>Ash (wt%)</td>
<td>0.28</td>
<td>-0.08</td>
<td>0.12</td>
<td>0.18</td>
<td>0.13</td>
<td>0.131</td>
</tr>
</tbody>
</table>

### Table 8: Proximate Analysis of Spruce wood (Protocol 2)

<table>
<thead>
<tr>
<th>Runs</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>Average</th>
<th>std. dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass (mg)</td>
<td>10.085</td>
<td>10.085</td>
<td>10.674</td>
<td>10.28</td>
<td>0.278</td>
</tr>
<tr>
<td>M (wt.%)</td>
<td>4.50</td>
<td>3.62</td>
<td>3.50</td>
<td>3.87</td>
<td>0.446</td>
</tr>
<tr>
<td>VM (wt.%)</td>
<td>80.86</td>
<td>78.28</td>
<td>81.93</td>
<td>80.36</td>
<td>1.532</td>
</tr>
<tr>
<td>FC (wt.%)</td>
<td>14.55</td>
<td>13.98</td>
<td>14.83</td>
<td>14.45</td>
<td>0.354</td>
</tr>
<tr>
<td>Ash (wt%)</td>
<td>0.09</td>
<td>4.10</td>
<td>-0.29</td>
<td>1.30</td>
<td>1.986</td>
</tr>
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### Table 9: Protocol Comparison for spruce wood

<table>
<thead>
<tr>
<th></th>
<th>Protocol 1</th>
<th>Protocol 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 2 3 4</td>
<td>1 2 3</td>
</tr>
<tr>
<td>M+VM (wt.%)</td>
<td>85.38 85.13 85.03 84.96</td>
<td>85.36 81.90 85.43 84.23</td>
</tr>
<tr>
<td>VM/FC</td>
<td>5.38 5.46 5.48 5.44</td>
<td>5.56 5.60 5.52 5.56</td>
</tr>
<tr>
<td>(M+VM)/FC</td>
<td>5.50 5.69 5.72 5.72</td>
<td>5.87 5.86 5.76 5.83</td>
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</tbody>
</table>
Table 10: Proximate Analysis of Pulp I (Protocol 2)

<table>
<thead>
<tr>
<th>Runs</th>
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<th>2</th>
<th>3</th>
<th>Average</th>
<th>std. dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass (mg)</td>
<td>9.584</td>
<td>10.068</td>
<td>10.677</td>
<td>10.11</td>
<td>0.447</td>
</tr>
<tr>
<td>M (wt.%)</td>
<td>2.35</td>
<td>3.65</td>
<td>3.17</td>
<td>3.06</td>
<td>0.537</td>
</tr>
<tr>
<td>VM (wt.%)</td>
<td>87.28</td>
<td>85.55</td>
<td>85.38</td>
<td>86.07</td>
<td>0.858</td>
</tr>
<tr>
<td>FC (wt.%)</td>
<td>10.39</td>
<td>10.15</td>
<td>10.26</td>
<td>10.27</td>
<td>0.098</td>
</tr>
<tr>
<td>Ash (wt.%)</td>
<td>-0.02</td>
<td>0.66</td>
<td>1.19</td>
<td>0.61</td>
<td>0.495</td>
</tr>
</tbody>
</table>

Table 11: Proximate Analysis Pulp II (Protocol 2)

<table>
<thead>
<tr>
<th>Runs</th>
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<th>Average</th>
<th>std. dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass (mg)</td>
<td>10.589</td>
<td>10.307</td>
<td>10.45</td>
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</tr>
<tr>
<td>M (wt.%)</td>
<td>3.52</td>
<td>4.06</td>
<td>3.79</td>
<td>0.270</td>
</tr>
<tr>
<td>VM (wt.%)</td>
<td>78.77</td>
<td>78.49</td>
<td>78.63</td>
<td>0.140</td>
</tr>
<tr>
<td>FC (wt.%)</td>
<td>16.14</td>
<td>16.06</td>
<td>16.10</td>
<td>0.040</td>
</tr>
<tr>
<td>Ash (wt.%)</td>
<td>1.55</td>
<td>1.37</td>
<td>1.46</td>
<td>0.090</td>
</tr>
</tbody>
</table>

Table 12: Proximate Analysis Xylan-Lignin I (Protocol 2)

<table>
<thead>
<tr>
<th>Runs</th>
<th>1</th>
<th>2</th>
<th>Average</th>
<th>std. dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass (mg)</td>
<td>10.608</td>
<td>10.523</td>
<td>10.57</td>
<td>0.043</td>
</tr>
<tr>
<td>M (wt.%)</td>
<td>5.24</td>
<td>5.16</td>
<td>5.20</td>
<td>0.040</td>
</tr>
<tr>
<td>VM (wt.%)</td>
<td>60.76</td>
<td>60.28</td>
<td>60.52</td>
<td>0.240</td>
</tr>
<tr>
<td>FC (wt.%)</td>
<td>30.25</td>
<td>30.51</td>
<td>30.38</td>
<td>0.130</td>
</tr>
<tr>
<td>Ash (wt.%)</td>
<td>3.75</td>
<td>4.05</td>
<td>3.90</td>
<td>0.150</td>
</tr>
</tbody>
</table>
### Table 13: Proximate Analysis Xylan-Lignin II (Protocol 2)

<table>
<thead>
<tr>
<th>Runs</th>
<th>1</th>
<th>2</th>
<th>Average</th>
<th>std. dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass (mg)</td>
<td>10.59</td>
<td>10.31</td>
<td>10.45</td>
<td>0.141</td>
</tr>
<tr>
<td>M (wt.%)</td>
<td>2.78</td>
<td>3.02</td>
<td>2.90</td>
<td>0.120</td>
</tr>
<tr>
<td>VM (wt.%)</td>
<td>60.98</td>
<td>60.67</td>
<td>60.83</td>
<td>0.155</td>
</tr>
<tr>
<td>FC (wt.%)</td>
<td>33.64</td>
<td>33.79</td>
<td>33.72</td>
<td>0.075</td>
</tr>
<tr>
<td>Ash (wt.%)</td>
<td>2.51</td>
<td>2.52</td>
<td>2.52</td>
<td>0.005</td>
</tr>
</tbody>
</table>

### Table 14: Proximate Analysis Xylan-Lignin III (Protocol 2)

<table>
<thead>
<tr>
<th>Runs</th>
<th>1</th>
<th>2</th>
<th>Average</th>
<th>std. dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass (mg)</td>
<td>10.26</td>
<td>10.18</td>
<td>10.22</td>
<td>0.040</td>
</tr>
<tr>
<td>M (wt.%)</td>
<td>2.01</td>
<td>2.57</td>
<td>2.29</td>
<td>0.280</td>
</tr>
<tr>
<td>VM (wt.%)</td>
<td>62.77</td>
<td>62.38</td>
<td>62.58</td>
<td>0.195</td>
</tr>
<tr>
<td>FC (wt.%)</td>
<td>32.80</td>
<td>32.49</td>
<td>32.65</td>
<td>0.155</td>
</tr>
<tr>
<td>Ash (wt.%)</td>
<td>2.43</td>
<td>2.55</td>
<td>2.49</td>
<td>0.060</td>
</tr>
</tbody>
</table>

### Table 15: Proximate Analysis of Lignin (Protocol 2)

<table>
<thead>
<tr>
<th>Runs</th>
<th>1</th>
<th>2</th>
<th>Average</th>
<th>std. dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass (mg)</td>
<td>10.63</td>
<td>10.48</td>
<td>10.55</td>
<td>0.071</td>
</tr>
<tr>
<td>M (wt.%)</td>
<td>1.49</td>
<td>1.60</td>
<td>1.55</td>
<td>0.055</td>
</tr>
<tr>
<td>VM (wt.%)</td>
<td>61.36</td>
<td>61.44</td>
<td>61.40</td>
<td>0.040</td>
</tr>
<tr>
<td>FC (wt.%)</td>
<td>32.98</td>
<td>33.16</td>
<td>33.07</td>
<td>0.090</td>
</tr>
<tr>
<td>Ash (wt.%)</td>
<td>4.15</td>
<td>3.81</td>
<td>3.98</td>
<td>0.170</td>
</tr>
</tbody>
</table>
Table 16: Proximate Analysis average results on dry basis (Protocol 2)

<table>
<thead>
<tr>
<th></th>
<th>Wood</th>
<th>Pulp I</th>
<th>Pulp II</th>
<th>Xylan-Lignin I</th>
<th>Xylan-Lignin II</th>
<th>Xylan-Lignin III</th>
<th>Lignin</th>
</tr>
</thead>
<tbody>
<tr>
<td>VM (wt.%)</td>
<td>83.61</td>
<td>88.78</td>
<td>81.74</td>
<td>63.84</td>
<td>62.67</td>
<td>64.04</td>
<td>62.37</td>
</tr>
<tr>
<td>FC (wt.%)</td>
<td>15.04</td>
<td>10.59</td>
<td>16.74</td>
<td>32.05</td>
<td>34.74</td>
<td>33.41</td>
<td>33.59</td>
</tr>
<tr>
<td>Ash (wt.%)</td>
<td>1.35</td>
<td>0.63</td>
<td>1.51</td>
<td>4.11</td>
<td>2.59</td>
<td>2.55</td>
<td>4.04</td>
</tr>
</tbody>
</table>

Figure 21: Proximate analysis comparison on dry and ash free basis

Wood  
Pulp I  
Pulp II  
Xylan-Lignin I  
Xylan-Lignin II  
Xylan-Lignin III  
Lignin
## APPENDIX C: Composition of Nitrogen stream used for proximate analysis

### Table 17: Proximate analysis nitrogen stream composition

<table>
<thead>
<tr>
<th>Gas</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>98.75%</td>
</tr>
<tr>
<td>O₂</td>
<td>10 ppm</td>
</tr>
<tr>
<td>Ar</td>
<td>1.20 %</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.05%</td>
</tr>
<tr>
<td>Ne</td>
<td>23 ppm</td>
</tr>
<tr>
<td>He</td>
<td>7 ppm</td>
</tr>
<tr>
<td>CH₄</td>
<td>2.2 ppm</td>
</tr>
<tr>
<td>Kr</td>
<td>1.5 ppm</td>
</tr>
<tr>
<td>H₂</td>
<td>0.7 ppm</td>
</tr>
</tbody>
</table>