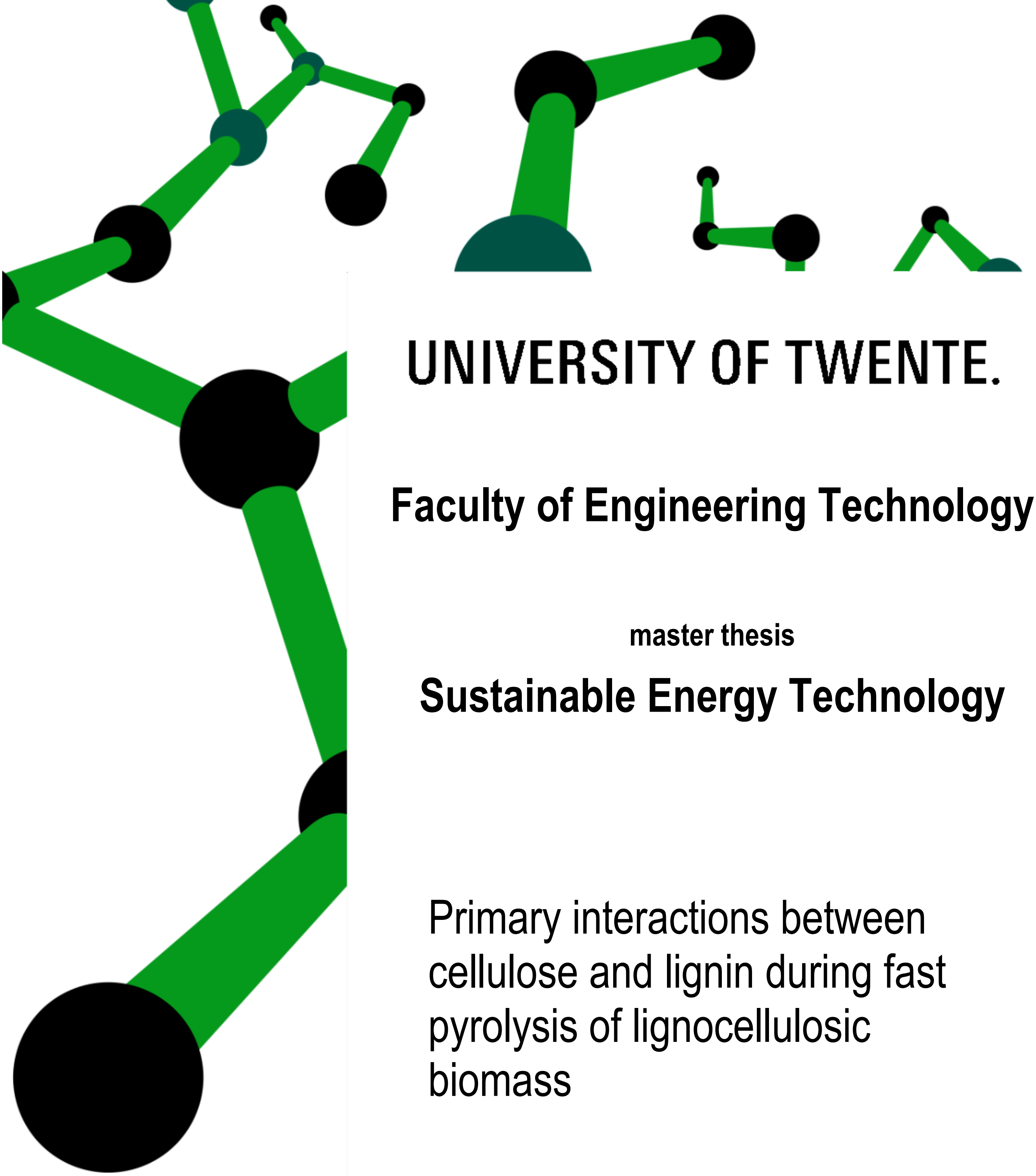

UNIVERSITY OF TWENTE.

Faculty of Engineering Technology

master thesis

Sustainable Energy Technology

Primary interactions between cellulose and lignin during fast pyrolysis of lignocellulosic biomass

Pedro O. Villavicencio Arzola

Sustainable Process Technology

30/01/2020

Graduation Committee
Prof. dr. Sascha R. A. Kersten
Dr. Ir. M. Pilar Ruiz Ramiro
Prof. dr. Marteen Arentsen

Master Graduation Assignment for the master's programme Sustainable Energy Technology

University of Twente
Enschede, January 2020

Abstract

In order to overcome the current necessity for the replacement of fossil resources, fast pyrolysis has emerged as a promising technology for the efficiently use of biomass as a valuable and sustainable resource. It is a thermochemical process in which lignocellulosic biomass is converted, in absence of oxygen at 450-600° C for very short residence times, to obtain mainly bio-oil, gas, and char. Although, many studies have been developed to understand the behaviour of biomass components during fast pyrolysis, the interaction between them in the process reactions are known to a lesser extent. The purpose of this study is to advance on the understanding of the fast pyrolysis of lignocellulose, specifically in whether there is an interaction between two of the main lignocellulose components, cellulose and lignin.

To do so, a fully operational screen-heater reactor developed in the SPT group has been used to process samples prepared with blends of cellulose with extracted lignin and cellulose impregnated with potassium (1, 100, 1000, 10000 ppm) with lignin. Liquid chromatography analytical techniques are used to analyze the composition of the produced bio-oil. The results indicated that the presence of lignin could have enhanced the levoglucosan yield in the produced oil, but no effect was observed on the glucose recovery from the oil samples. In addition, native samples of lignocellulose with different lignin content are tested, in order to analyze the influence of this component in the pyrolysis product composition. An interesting trend was found, indicating that both yields of levoglucosan and glucose recovery increased as the lignin content in the samples also did. These could be attributed to, thermal ejection of cellulose-derived products from the reaction zone, and also a possible thermal stabilization of anhydrosugars on the presence of lignin-derived aromatics compounds.

Finally, a state-of-the-art of fast pyrolysis of biomass towards bio-oil applications for heat and power generation, and as a potential source for platform chemicals are explained; as well as the possible contributions of this study for its further development are addressed.

Table of Contents

1. Introduction

One of the most important challenges for our society is the replacement of fossil resources as the main provider for the energetic and chemical industries. This challenge should be addressed simultaneously through the development of sustainable technologies that would enable the efficient utilization of renewable resources. The new European energy legislative framework has recently set new targets for 2030, aiming to increase at least 32% share for renewable energy and to reduce at least in 40% the greenhouse gases emissions from the 1990 levels [1]. In addition, it has been reported that bioenergy is the largest renewable source in EU and is expected to remain as key component of the energy mix for the mentioned 2030 targets. Over the past period between 2010-2015, the use of biomass for the production of energy increased 32%. In the other hand, the use of biomass for the production of raw materials, as valuable chemicals, also increased by 5.6% under the same period [2].

In order to take advantage of this valuable and sustainable resource, lignocellulosic biomass is nowadays processed in mainly two ways to efficiently produce energetic appliances. First, the most common and the earliest way to produce energy for the human being is the direct combustion to produce heat; however, the low efficiency, ash buildup, and the huge amount of CO_2 produced as a by-product represent enormous disadvantages for this process according to current standards of sustainability [3]. In the other hand, the conversion of biomass into biofuels and valuable hydrocarbons using thermochemical or biochemical processes, represent a promising strategy to efficiently use this renewable source.

In thermochemical process of biomass, heat and catalysts are used to transform lignocellulose; in contrast, biochemical processes utilize enzymes and microorganisms. In comparison with bio-processes, thermochemical processes occur faster (from seconds to hours). Another advantage of thermochemical methods, is that they are not feedstock specific and can even process the combinations of feedstocks [4]. Among these methods, gasification and pyrolysis represent two of the most developed processes; where gasification provides fuel gas, that can be combusted for heat generation, and pyrolysis yields a liquid fuel that can be used for heating or electricity generation.

Pyrolysis is a thermal decomposition of a substance into smaller components by heating it in the absence of oxygen. The main benefit of pyrolysis process over gasification is that the reaction conditions favor the production of vapors that are condensed to obtain an organic liquid, commonly known as bio-oil, which after post-treatment can be easily stored and transported for a later use as fuel [5]. Among pyrolysis processes, fast pyrolysis has been highlighted over the last years because the increased efficiency for the continuous production of bio-oil. The purpose of fast pyrolysis is to prevent further cracking of the pyrolysis products into non-condensable compounds, therefore primary reactions are dominant [6].

However, it is still very difficult to predict the product composition because it does not only depend on the feedstock composition, but also on the reaction parameters and reactor configuration (chemical and mass transfer conditions. Therefore, fast pyrolysis of biomass has not been stablished at industrial scale [7]. In addition, interactions between the lignocellulose constituents, such cellulose and lignin, during fast pyrolysis have been studied previously, still without a consensus in the conclusion; making prediction of biomass pyrolytic behavior even more difficult.

1.1 Scope

The purpose of this study is to advance on the understanding of fast pyrolysis process of lignocellulose, specifically in whether there is or not interaction between two of the main lignocellulose components, cellulose and lignin. To do so, an experimental set-up developed in the Sustainable Process Technology (SPT) group in the University of Twente has been used, known as the screen-heater; because it combines very fast heating rates of the sample with also very fast removal of the product from the reaction zone, and high quenching rate of the condensable product. All these characteristics allow to study the primary reactions during fast pyrolysis of different samples.

Analyzed samples are prepared with blends of crystalline cellulose with extracted lignin and cellulose impregnated with potassium salts with lignin. From these experiments, liquid chromatography analytical techniques are used to analyze the composition of the produced bio-oil. The results are compared with those obtained for the pyrolysis of pure components, previously developed in this research group using the same screen-heater set-up under similar conditions.

In addition, native samples of lignocellulose with different lignin content are tested, in order to analyze the influence of this component in the pyrolysis product composition, using the above mentioned techniques. Finally, the possible impact of the contribution of this work towards a better understanding of pyrolytic reactions is addressed.

1.2 Research questions

- Are there any interactions between cellulose and lignin during the primary reactions of fast pyrolysis of lignocellulose?
- How these interactions between cellulose and lignin possibly occur?
- What is the influence of minerals content in lignocellulosic biomass on the production of sugars and the molecular weight of the oil produced during fast pyrolysis?

2. Literature review

2.1 Lignocellulosic biomass

Lignocellulose, also called lignocellulosic biomass, refers to dry plant matter and can be considered the most abundant and renewable resource of organic carbon on earth. It has attracted considerable attention in recent years and has been projected to serve as ideal, abundant and carbon-neutral source that will help mitigate CO_2 emissions and therefore the climate change [8]. Nevertheless, in contrast to fossil resources, lignocellulose is a highly oxygenated, solid, and heterogeneous substance, mainly composed of three highly functional bio-polymers: cellulose, hemicellulose, and lignin, forming a composite material which is resistant to bio-chemical conversion, a characteristic commonly known as biomass recalcitrance [9].

2.1.1 Cellulose

Cellulose is the most abundant biomass component, accounting for approximately 50% by weight of lignocellulose. It is present in every cell wall of the plants and almost in pure form in the cotton fibers. It is composed of repeating D-glucose units, a six-carbon ring, also known as pyranose [4]. The three hydroxyl groups in each ring interact with another one to form intra- and intermolecular hydrogen bonds which give a crystalline structure to cellulose, and its unique properties of mechanical strength and chemical stability. It has a linear uniform chemical structure as a linear homopolymer connected by glycosidic linkages, as shown in Figure 1, in spite of its feedstock origins, but is different in the chain-ends and degree of polymerization. The degree of polymerization of the native cellulose depends on the source and can reach more than 5000; depending on the degree of organization of its structure, cellulose is composed of crystalline (highly ordered) and amorphous (randomly distributed) phases [10].

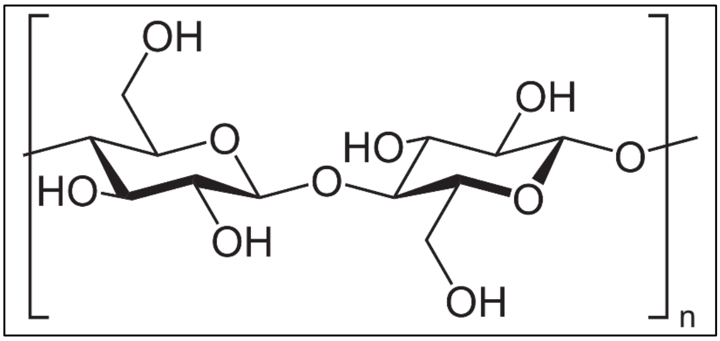

Figure 1. Building units of cellulose, D-glucose units connected by glycosidic bonds [10].

2.1.2 Hemicellulose

In addition to cellulose, a number of other polysaccharides called hemicellulose are present in lignocellulosic biomass, accounting for about 15–35% by weight. Hemicellulose surrounds the cellulose fibers and stands as a connecting link between cellulose and lignin, as shown in Figure 2. Hemicellulose is mainly composed of pentose and hexose sugar building blocks, such as xylose, arabinose, mannose, and galactose, which have been used as the structural elements of hemicellulose. While cellulose has a hydrolysis-resistant crystalline structure, hemicellulose is completely amorphous, with little physical strength. It is readily hydrolyzed by dilute acids or bases, as well as hemicellulose enzymes [11].

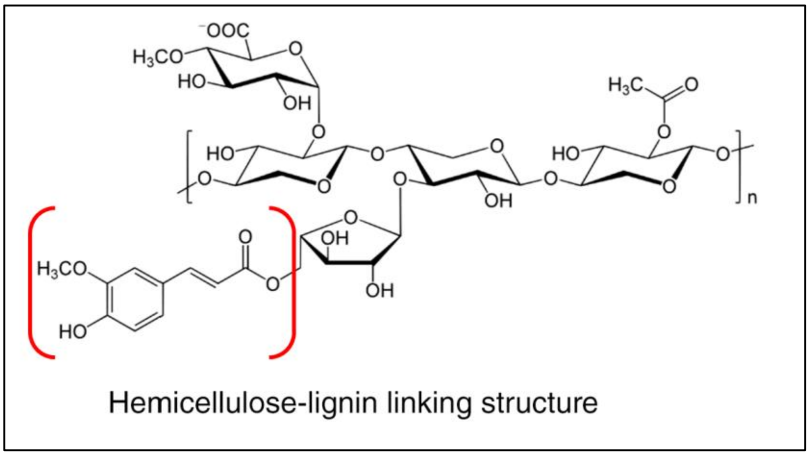

Figure 2. Representation of hemicellulose structure with a lignin linkage [11].

2.1.3 Lignin

Lignin is a very complex aromatic, three-dimensional and cross-linked polymer that consists of a random assortment of differently bonded phenylpropane units, as can be seen in Figure 3; these monomers are categorized as guaiacyl, syringyl and p-hydroxylphenyl units. Lignin is mainly present in the outer layer of the fibers and is responsible for the structural rigidity, and holding the fibers of polysaccharides together. Lignin percentage may vary from 23% to 33% in softwoods, 16% to 25% in hardwoods, and for the lignocellulosic biomass a percentage up to 40% has been reported [12]. Physically, cellulose is coated with hemicellulose, whose empty spaces are filled up with lignin. Therefore, lignin plays a binding role between hemicellulose and cellulose within the cell wall.

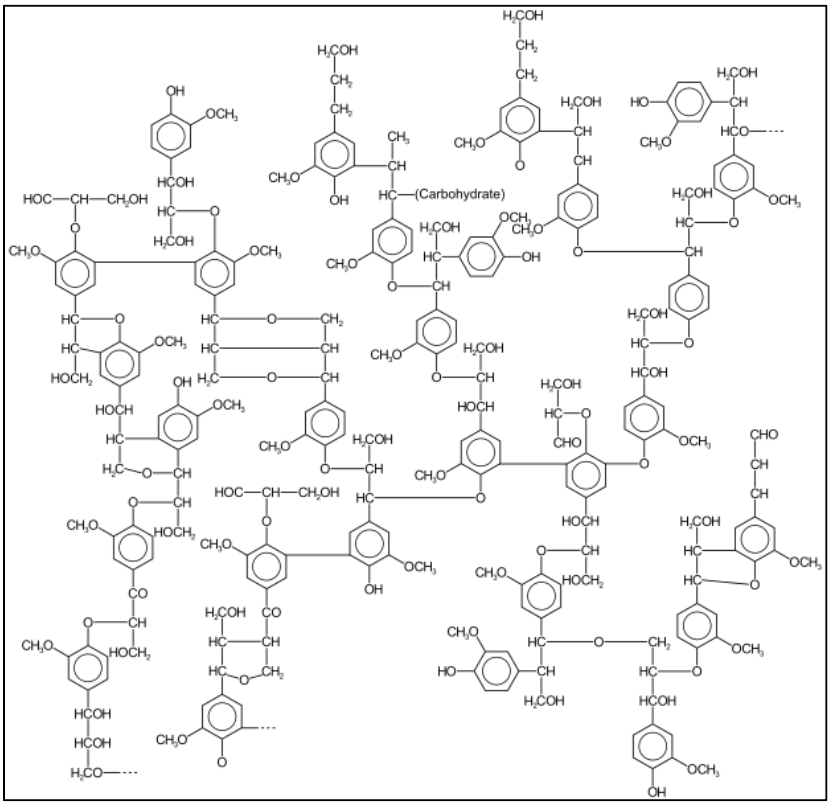

Figure 3. Complex structure of lignin [13].

The specific structure of lignin varies depending with feedstock origins and may also have differences based on the extraction method when isolated from the other components. Monolignol structural units, *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, undergo enzymatic radical coupling polymerization to produce lignin. It has been identified that peroxidase-mediated dehydrogenation of monolignol units results in a heterogeneous structure of lignin by the formation of C–C bonds and aryl ether linkages [13]. These alcohols are referred to as *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units within the lignin structure, as shown in Figure 4. Softwood and hardwood lignin have different structures, guaiacyl dominant lignin is predominantly found in softwoods, as a polymer of higher fraction of coniferyl phenylpropane units; on the other hand, guaiacyl-syringyl lignin is typically found in hardwoods as a co-polymer of both coniferyl and sinapyl phenylpropane units [14].

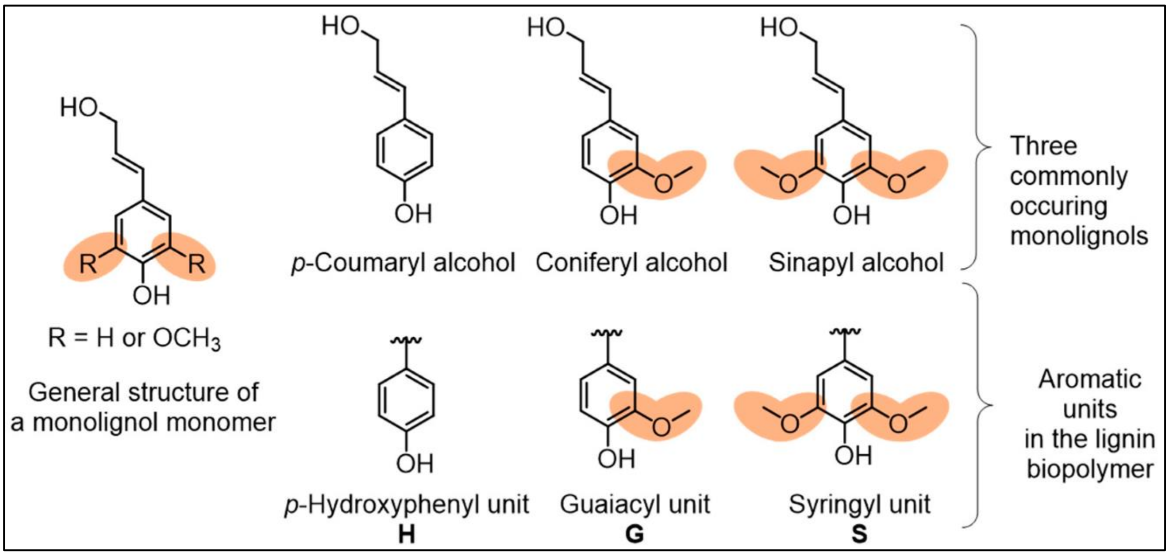

Figure 4. Monolignol structural blocks and the resulting aromatics present in lignin [13].

2.2 Fast pyrolysis of lignocellulosic biomass

Fast pyrolysis is an advanced technology focused on the production of liquid fuel from biomass, that has been gaining attention over conventional pyrolysis (slow) because it can have several applications, as is further discussed in Chapter 5.1. The purpose of fast pyrolysis is to prevent further cracking of the pyrolysis products into non-condensable compounds, as CO_2, CO, etc. The process parameters should be carefully controlled to give high bio-oil yields, where the most important requirement is a high heat transfer rate, which can be achieved by finely grounding the feed biomass. The feed is typically heated at high temperatures (450-600° C) for short residence times (less than 2 s) [8]. Since the reaction takes place for a very short duration, not only kinetics are involved, but also heat and mass transfer plays a crucial role in the product outcome. Therefore, the desirable products can be produced by setting process parameters at optimum conditions.

The fast pyrolysis process typically results in bio-oil, gas, and char yields of 60–70%,13–25%, and 12–15%, based on dry biomass feed weight [7]. Bio-oil is also referred to as pyrolysis oil, pyrolysis liquid, pyrolysis tar, bio-crude, wood liquid, wood oil or wood distillate. It is a dark brown organic liquid mixture, which generally comprises of a great amount of water (15–35 wt%) and hundreds of organic compounds, such as acids, alcohols, ketones, aldehydes, phenols, ethers, esters, sugars, furans, alkenes, nitrogen compounds and miscellaneous oxygenates, as well as solid particles [15]. The water content of the bio-oils depends on the initial moisture content of the feedstock and the water formation. Nevertheless, it is still hard to achieve chemically accuracy on identification of some individual components in the bio-oils due its intrinsic complexity.

The higher heating value (HHV) of the bio-oils typically ranges between 15 and 20 MJ/kg, which is only 40–50% of the conventional oil fuels HHV (42–45 MJ/kg). This is due to the considerable oxygen content present in bio-oils, which is in the extent of 35-40 % on dry basis weight [7].

2.3 Fast pyrolysis of cellulose

Due to its predominant content in biomass, fast pyrolysis of cellulose has been widely studied regarding the yield of gas, liquid and solid product and the distribution of specific compounds and their formation pathways. Most of the studies have focused on the influence of reaction parameters, as well as reactors configurations (temperature, residence time, heating rate, pressure, and particle size). It has been demonstrated that bio-oil yield can be increased at pressures close to vacuum, compared to atmospheric processes [16].

Levoglucosan (1,6-anhydro-β-D-glucopyranose) is considered the most prevalent compound produced from fast pyrolysis of cellulose. The primary reaction pathways for cellulose pyrolysis proposed involve the formation of oxygenated compounds; from this it has been established that the cleavage of the glucosidic bonds initiates the formation of levoglucosan (LG) through the intramolecular rearrangement of the monomer units [17]. Regarding yields of LG, several numbers have been reported under fast pyrolysis conditions (from 20 to 60%), depending on different parameters, as the reaction temperature. To have an idea of this variation, the LG yields (DP_1, in Figure 5) obtained at different temperatures from fast pyrolysis of cellulose are shown, as well as the yields of the sum of others anhydrosugars detected ($DP_{>2}$, Figure 5) [18].

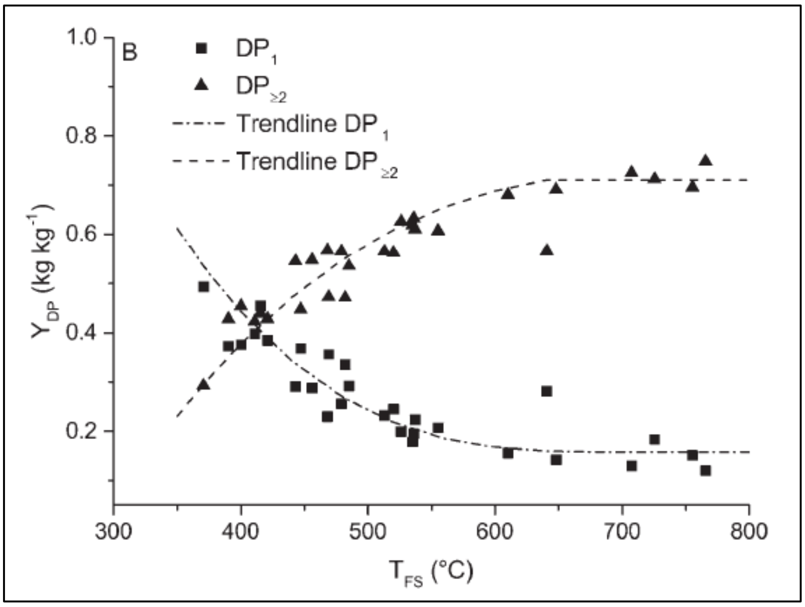

Figure 5. Yields obtained from fast pyrolysis of cellulose, DP_1 refers to LG and $DP_{>2}$ is refers to the sum of higher anhydrosugars detected [18].

In addition, the degree of polymerization (DP) of the cellulose also has an important impact on its pyrolysis behavior. The chemical formula of cellulose is often denoted as $(C_6H_{10}O_5)_n$, where n refers to the DP. The average DP for cellulose from woody biomass is at least 9000 and possibly as high as 15,000 [15]. It has been confirmed that the formation of LG and other pyrans was directly correlated with the DP of a sample, and a higher DP favored the formation of pyrans [19].

Apart from LG, the presence of hydroxyacetaldehyde and acetol have also been detected in the oxygenated compounds from cellulose pyrolysis, with reported yields from 3% to 19% and from 0.8% to 6% respectively, presenting the same trend with the increased temperature (450 to 930° C) as with LG [16].

2.4 Fast pyrolysis of lignin

Lignin is the most thermally stable component in lignocellulose, therefore is degraded in a broad range of temperature, from 200° to 500° C or even higher. The fast pyrolysis of isolated lignin, under already stablished systems, has produced high yields of char (from 30–50%) and low yields of bio-oil (around 30%) mostly composed by a great number of aromatic compounds (phenolics and hydrocarbons). As well as with cellulose, processing at vacuum close pressures relatively increases the bio-oil yield [16].

Due to the high volatility of the mentioned compounds, it has been very difficult to accurately detect all, as well as their composition. Nevertheless, an analytical technique, pyrolysis-gas chromatography-mass spectrometry (Py-GC–MS) has been applied to examine the oil product composition from fast pyrolysis of pine (softwood) lignin, where more than 50 phenolic compounds were found in the bio-oil, including guaiacol, 4-methylguaiacol, 4-vinylguaiacol and vanillin. On the other hand, more syringol-type compounds were detected from the pyrolysis of oak (hardwood) lignin. Therefore, the composition of bio-oil produced from lignin completely depends on its nature, due to the different chemical structures as explained in Chapter 2.1.3.

Another important characteristic that has been considered for the characterization of lignin pyrolysis is the molecular weight. It has been demonstrated that the temperature has no influence in the number average molecular weight (M_n) of the produced bio-oil. In contrast, pressure at which pyrolysis is carried out, does have an effect in the M_n of the bio-oil. At vacuum pressure, higher M_n has been obtained compared to the one obtained at atmospheric conditions [20]. Moreover, the molecular weight distribution has been considered as one of the most important characteristic of the lignin due to it has a direct influence in the product distribution of the obtained bio-oil, this could have been explained because heavier molecules polymerize faster than lighter ones.

2.5 Effect of inorganic salts during fast pyrolysis

Biomass itself contains inorganic minerals, such as K, Ca, Na, and Mg. Depending on the type of biomass and harvesting method, the total content of these species ranges from 0.5% to 15% of the biomass composition. Alkali and alkaline earth metals (AAEMs), such as K, Na, Mg and Ca, are the most abundant inorganic ions in biomass and, despite of their very low concentration, have been demonstrated to catalyze several pyrolysis reactions, completely changing the pyrolysis product distribution, from yields of solids, condensable and non-condensable products, to the chemical composition of the resulting bio-oil [21]. Inorganic salt concentrations as low as 50 ppm have been found sufficient to dramatically change the resulting pyrolysis product selectivity [8].

These salts, or ashes, catalyze the primary reactions during pyrolysis process leading to the formation of lower molecular weight species (especially formic acid, glycolaldehyde and acetol) from cellulose; therefore, lower LG yields are obtained. It has been reported a trend of activity according to LG yields, for the following cations this trend has been observed: $Na^+ > K^+ > Ca^{2+} > Mg^{2+}$, where for Na^+ produces the highest LG yield and for Mg^{2+} is the lowest [22]. In contrast, for several anions the following trend on LG was observed: $Cl^- > NO^- > OH^- > CO_3^{2-} > PO_4^{3-}$ [23].

A similar investigation has recently been developed in our work group (SPT), where the effects of potassium concentrations of 1, 100, 1000 and 10,000 ppm, during the primary products of cellulose fast pyrolysis in vacuum and at atmospheric pressures has been analyzed [24]. It has been highlighted that potassium salts are catalytically active during the primary reactions of pure cellulose fast pyrolysis. This catalytic activity leads to a significantly lower yield of condensed product, as well as lower yields of anhydrosugars in the bio-oil. In contrast, the production of non-condensable gas increased, even at low potassium content. Another interesting finding is that the anions that have been used, follow a particular order of activity; regarding the yield of LG: $Cl^- > OH^- > CO_3^{2-}$ [24].

In addition, another important effect of inorganic salts that has been noticed during the fast pyrolysis of cellulose is the ability to catalyze dehydration and ring fragmentation reactions of the anhydrosugar components. Levoglucosenone, which is formed from LG when it loses two molecules of water, has been used to identify dehydration reactions. On the other hand, acetol, which is the simplest hydroxy ketone structure, has been used to identify fragmentation reactions during fast pyrolysis [24]. In Figure 6, the levoglucosenone production as a function of potassium concentration during fast pyrolysis of cellulose is presented, where can be observed that with increase potassium concentration up to 1000 ppm leads to an increase in the yield of levoglucosenone increases from 0.25 wt% to 1 wt%.

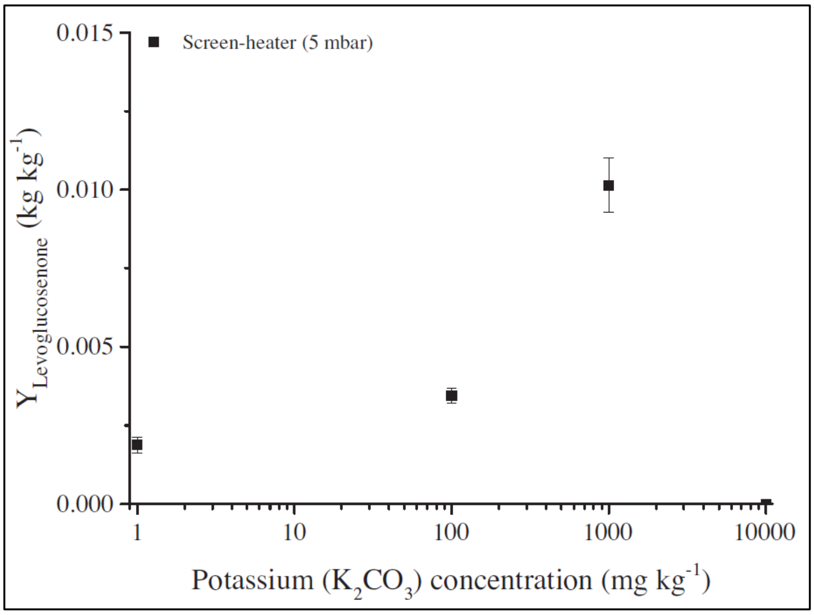

Figure 6. Levoglucosenone production as a function of potassium concentration during fast pyrolysis of cellulose [24].

2.6 Interactions between biomass components during fast pyrolysis

During the past decade, the fast pyrolysis of cellulose and lignin as separate components has been widely studied. Unfortunately, less information is available regarding possible interactions between the different biomass building blocks. It is interesting to note that, even investigations about interactions between three main components have been developed, there is no definite conclusion on whether there is interaction and how it actually works. An example of this is shown in Table 1 and 2, where several studies that have been done are listed according to its conclusion of whether there is or not interaction among the biomass components.

Table 1. Different studies developed with a conclusion of no interaction among biomass components during fast pyrolysis.

Authors	Reactor / Conditions	Conclusion
Yoon et al. **[25]**	TG-GC / Air/steam atmosphere, 10° C/min, 140°-900° C.	No interaction on product yields and carbon conversions.
Skreiberg et al. **[26]**	TG and macro-TG / Air atmosphere, 5°, 20°, and 100° C/min, 60°-900° C.	No interactions on product composition.
Qu et al. **[27]**	Tube furnace / 350°-600° C	No interactions on product yields.
Wang et al. **[28]**	TG / Hydrogen/syngas, 10°, 15°, 20° C/min, 300° - 600° C	No interactions on gas yields and gas composition.
Yang et al. **[29]**	TG / Nitrogen atmosphere, 10° C/min, 105°-900° C	Negligible interaction, on product yields (oil, gas, solid).

Table 2. Different studies developed with a conclusion of interaction among biomass components during fast pyrolysis.

Authors	Reactor / Conditions	Conclusion
Wang et al. **[30]**	TG-FTIR / Nitrogen atmosphere, 20° C/min, 300°-800° C	Interaction between cellulose and hemicellulose inhibits the formation of LG.
Hosoya et al. **[31]**	Ampoule reactor / Nitrogen atmosphere, 600° C, 40-80 s residence time	Cellulose – lignin interactions, the cellulose-derived volatiles act as H-donors while the lignin-derived volatiles act as H-acceptors.
J.Hilbers et al. **[32]**	TGA / N_2 atmosphere, 10° and 50° C/min Py-GC-MS / 350° C and 500° C	Cellulose – lignin interactions, lignin enhanced LG yields, but decreased dehydration products.
Zhang et al. **[33]**	Py-GC-MS / Helium atmosphere, 500° C	Cellulose – lignin interactions, increased yields of low MW and furans, but decreased yield of LG.
Wu et al. **[34]**	Py-GC-MS / 500°, 600°, and 700° C), mixing mass ratios 1:1, and 2.1:1	Cellulose – lignin interactions, promote low MW products, while inhibited LG formation.
Yu et al. **[35]**	Wire mesh reactor / N_2 atmosphere 50° C to 900° C, heating rate of 30° C/min	Interactions were observed between cellulose and the other two components, while comparing yields of gas, char and oil.

From the lists above, it is remarkable how different conclusions have been reported, even when similar reactors and conditions are used. One of the reasons for this discrepancy could be that biomass pyrolysis models are based on the behavior of the three main components, where the effects of interaction on thermogravimetric (TG) reactors cannot be easily noticed, so people tend to neglect the interactions between the three main components [34]. Another reason is that usually, the yields of non-condensable gas, bio-oil and char are always similar to those when pure components are reacted, because there are no change of H:C:O ratios in biomass, therefore it is really difficult to come to the conclusion with interaction [33]. However, in order to produce liquid fuels and valuable platform chemicals, detailed information about the compounds obtained in bio-oil and a complete biomass decomposition mechanism are needed.

As mentioned in Table 2, fast pyrolysis has also been studied using Pyrolysis-Gas Chromatography/Mass Spectroscopy (Py–GC/MS), where crystalline cellulose (Avicel), amorphous cellulose, organosolv lignin, and their blends containing 20, 50, and 80 wt.% of lignin were used; it was found that the presence of lignin enhanced the yield of LG, but decreased the yield of some of their dehydration products (levoglucosenone) [32]. In contrast, cellulose-lignin interactions were also investigated in a Py-GC-MS with different temperatures (500°, 600°, and 700° C), mixing ratios (mass ratio 1:1, and 2:1), and mixing methods (physical mixture and native mixture); and it has been found that cellulose-lignin copyrolysis could promote low weight molecular products (esters, aldehydes, ketones, and cyclic ketones) from cellulose and lignin-derived products (phenols, guaiacols, and syringols), while inhibiting formation of anhydrosugars, especially the formation of LG [34]. Therefore, it is necessary to gain more information about biomass components during fast pyrolysis process in order to better support the models that have been developed until today.

3. Experimental

3.1 Materials

3.1.1 Feedstocks

Cellulose Avicel PH101 from Sigma-Aldrich (particle size ~50 µm, 60.5% crystallinity, ash content 0.005 wt%, AAEM content 1 ppm, degree of polymerization specified < 350, average 220) was used as a representative of cellulose for the blends prepared. Spruce organosolv lignin provided by the Energy Research Centre of the Netherlands (ECN), of whose isolation process has already been described elsewhere [36], was also used as lignin representative to prepare the blends.

In addition, cellulose samples impregnated with potassium (100 ppm, 1000 ppm, and 10000 ppm), previously developed for a study on this research group (SPT) were also used, where potassium carbonate (K_2CO_3, Sigma Aldrich, purity > 99%) was used as source of K for 100 ppm and 10000 ppm samples, and potassium chloride (KCl, Sigma Aldrich, purity > 99%) for 1000 ppm sample. The impregnation procedure was done dissolving the respective amount of K_2CO_3 and KCl in Milli-Q water to then mixing it with pure avicel. The mixture was thoroughly mixed (T = 20° C) in a round bottom flask for 1 h. After mixing, the Milli-Q water was removed using a rotary evaporator (Büchi Rotavapour R-200, T = 65° C, P = 100 mbar, for 1 h). Finally, impregnated cellulose samples were dried for 24 h using a vacuum oven (Heraeus FVT420, T = 20° C, P = 1 mbar) [24].

From these materials, four blends were created using a physical mixture only. Mixture method was not important on these experiments due to the characteristics of the screen-heater, that will be deeper explained. The composition of the blends was kept 70 wt% of cellulose and 30 wt% of lignin under ash-free basis, as described in Table 3.

Table 3. Composition of the blends used as feedstock, ash-free basis.

Blend	Cellulose (% wt, ash free)	Lignin (% wt, ash free)	Potassium (ppm)
A / L	70	30	1
A / L 100	70	30	100
A / L 1000	70	30	1000
A / L 10000	70	30	10000

Apart from these blends, four more samples were used as feedstock for the experiments, which were kindly provided by the PhD candidate Thimo te Molder, also from STP group. These samples, obtained from poplar wood, contain different lignin content, as can be seen in Table 4.

Table 4. Poplar samples content.

Sample	Lignin content (% wt)	Ash content
Poplar	25	High
Poplar AL	25	Low
PT19	11.5	Low
PT17	3.6	Low

3.1.2 Analysis materials

The condensed product was recovered from the reactor by rinsing it with tetrahydrofuran (THF, Merck LC LiChrosolv, Purity≥99.8%) or with Milli-Q water, depending whether the GPC or HPLC, respectively, was used for analysis. A dissolution of sulfuric acid at 72% v/v, was prepared in the SPT group with sulfuric acid (Sigma Aldrich, purity 99.99%) and was used for the hydrolysis of the condensed product to analyze its sugar content; and barium carbonate (Sigma Aldrich, purity >99%) was used to neutralize the hydrolyzed samples before HPLC analysis. Levoglucosan (1,6-Anhydro-b-D-glucopyranose, Carbosynth purity >98%) and glucose (Sigma-Aldrich purity 99.5%) were used as standards for calibration of the HPLC.

3.2 Screen-heater

The screens used for the reactor were cut 2.5 cm x 5 cm, from a large stainless steel wiremesh (Dinxperlo, Wire Weaving Co. Ltd, mesh 200 wire thickness 0.06 mm * 0.06 mm, twilled weave, AISI 316). The screens were cleaned with Milli-Q water followed by acetone (Sigma Aldrich, purity >99.5%) before use for each experiment.

Approximately, 40 to 60 mg of feedstock for each experiment was evenly distributed over one screen, by using a sieve in order to facilitate the process. A little space of 0.5 cm of the screen was kept free of feedstock in order to be able to clamp the screen between the electrodes. A second screen was pressed on top of it with a hydraulic press (Rodac RQPPS30 30t) at 250 kg/cm^2. The exact amount of feedstock between the screens was determined by weighing the pressed screens, including the feedstock, on an analytical balance (Mettler Toledo, max 220 g, readability 0.01 mg) and subtracting the weight of the initial screens. In Figure 7 is shown the front view of the screens with the feedstock sample between.

Figure 7. Screens coupled together with sample in between after press.

3.3 Screen-heater set-up

Before each experiment the screens & feedstocks (Figure 8.2), copper clamps (Figure 8.5), vessel (Figure 8.1) and Teflon tape (two pieces of 70 cm long) (Figure 8.6) were weighed. The screen-heater reactor consists of a glass vessel (Duran 250 mL, round bottom, D=5 cm). In this glass vessel, the pressed screens with between the feedstock in between (Figure 8.2) were clamped between two electrodes (Figure 8.5). Teflon tape was wrapped around the electrodes to be able to quantify the condensed products on this part. After installing, a vacuum was created of 0.05 mbar using a vane vacuum pump (10, Edwards E2M-1.5). The reactor was filled with nitrogen gas at least three times to remove as much as possible any remaining oxygen inside. After this procedure again a vacuum was created of 0.05 mbar. A liquid nitrogen bath (Figure 8.4) was placed around the vessel to cool the vessel wall to approximately -100 °C.

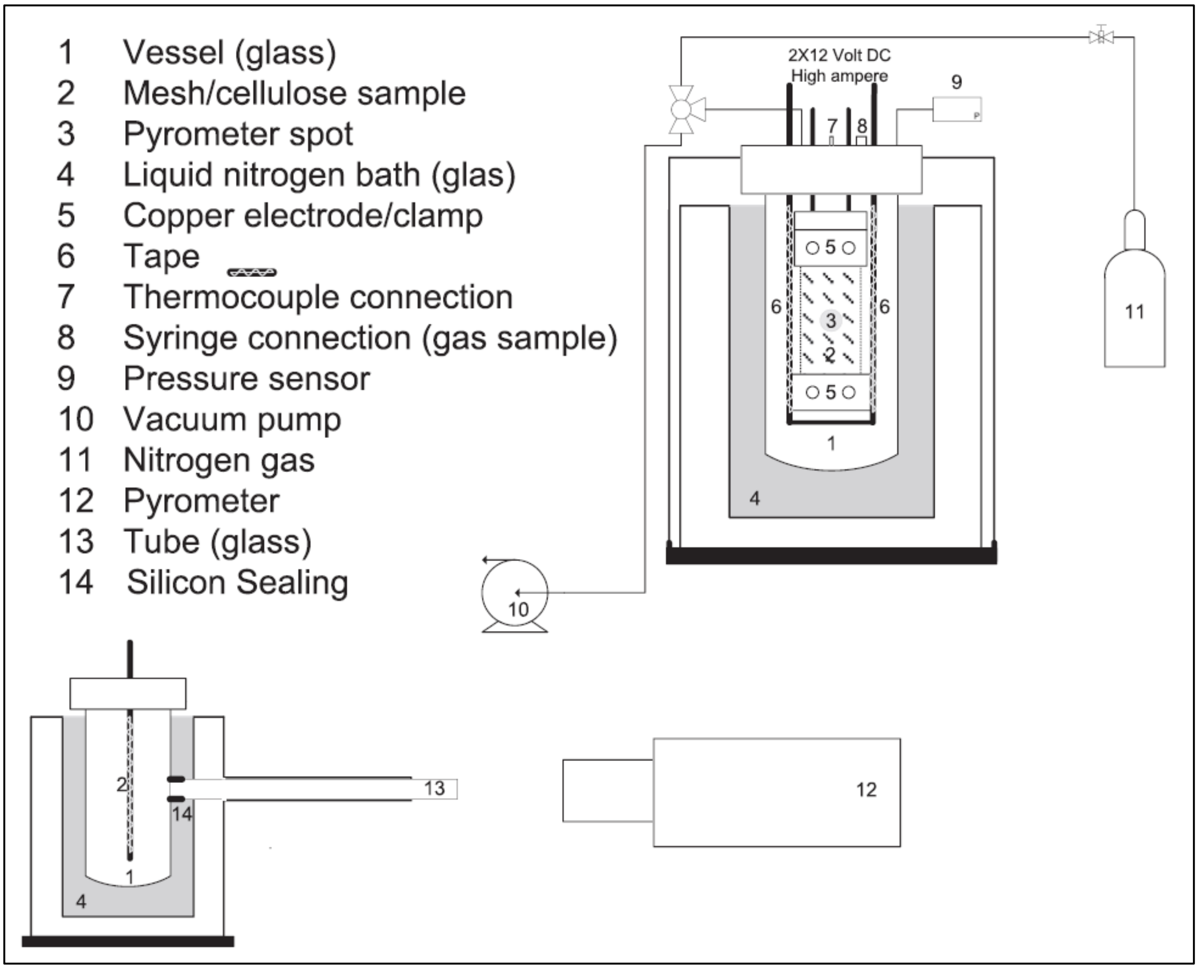

Figure 8. Schematic representation of the screen-heater reactor.

All the experiments made in this study were performed at 0.05 mbar. After the experiment the valve was opened and the reactor was warmed to ambient temperature. In addition, a 10 mL syringe was installed in all experiments. This syringe was used to collect a gas sample (Figure 8.8) after each experiment.

The pressure was precisely monitored during the experiment using an accurate pressure gauge (Heise DXD3765, Figure 8.8). A pyrometer (Figure 8.12) was used to monitor the temperature. To prevent disturbance in measuring the thermal radiation emitted by the screens while the liquid nitrogen is added during the experiment, a glass tube (Figure 8.13) with a silicone sealing (Figure 8.14) was placed in the liquid nitrogen bath. During the experiment an electrical current was passed through the wires, which served as an electrical resistance heater. This method supplies the heat required for heating the sample and maintaining it at the set temperature, the final screen temperature (T_{FS}), for a specified time called the holding time of 5 seconds.

It has been found in previous works with the screen heater [18], [24], [20], for the pyrolysis of cellulose,that upward of 530 °C the condensable product yield became constant, and optimal yield of condensed product can be achieved with less than 1 wt% of solid residue, and gas yield; therefore, all experiments in this work were performed at a T_{FS} of 530 °C.

The required power was supplied by two sets of two batteries connected in series. For the heating period these were two Varta Silver Dynamic batteries (12 V/100 Ah, 830 A) and for the supply of heat during the reaction two Varta Pro Motive batteries (12 V/225 Ah/1150 A) were used. The temperatures and pressures were recorded using a DAQ card (NI PCI-6281). The data was processed in a Labview program, which regulated the screen temperature via a PID control system.

After everything was in position, the pyrolysis run was started following a pre-programmed procedure using the Labview program (with the set temperature, holding time and PID value). After the run, the setup was removed from the liquid nitrogen bath and consequently warmed till ambient temperature.

3.4 Sample recovery and mass balance

In order to recover the pyrolysis products after each experiment and to obtain the yields of each product (non-condensable, condensable and solid) and the mass balance closure, to know the reproducibility of the experiments; the following procedure was applied. After the experiment was performed and the reactor reached ambient temperature, it was filled with dry nitrogen gas until the pressure in the reactor reached approximately 950 mbar. A gas sample was taken from the reactor using a 10 ml syringe. Gas samples were analyzed using gas chromatography (GC). The gas yield was calculated as shown in Equation 1:

$$Y_{gas} = \sum_{i=1}^{n} \frac{\frac{P_{sample}\, Vol_{\%i}\, V_{vessel}}{RT_{ambient}} MW_i}{M_{feedstock}} \qquad \text{(Eq. 1)}$$

where, $M_{feedstock}$ is the mass of dry cellulose feedstock. Where, $_i$ is the number of components detected in the gas sample, produced by pyrolysis reactions (CO, CO_2, etc.); P_{sample} is the pressure at which sample is taken; $Vol_{\%i}$ is the volume percentage of each component $_i$ in the gas sample, determined by GC; V_{vessel} is the volume of vessel; MW_i is the molecular weight of component $_i$; $T_{ambient}$ was the temperature at which sample was taken; R is the universal gas constant.

As mentioned before, to obtain the yield of the solid residues produced, the weight of the screens was measured with and without feedstock before the start of the experiment. After the experiment the screens are weighed again. However, the solid residue was not corrected for salts. The yield of solid residue can be calculated as shown in Equation 2:

$$Y_{solid\ residue} = \frac{M_{screens+residue} - M_{screens}}{M_{feedstock}} \qquad \text{(Eq. 2)}$$

where, $M_{screens\ +\ residue}$, $M_{screens}$ are the mass of the screens with and without the solid residue, respectively. After every experiment, the glass vessel (Figure 8, 1) was removed and immediately weighed. After that, the glass vessel was sealed with parafilm to prevent evaporation of volatile compounds. The tape (Figure 8, 6) was removed from the electrodes, clamps and screws (Figure 8, 5) and weighed together. The yield of condensed product was calculated by the following Equation 3:

$$Y_{condensed\ product} = \frac{(M_{vessel+CP} - M_{vessel}) + (M_{TCS+CP} - M_{TCS})}{M_{feedstock}} \qquad \text{(Eq. 3)}$$

where, $M_{vessel + CP}$, M_{vessel} are the mass of the vessel with and without the condensed product, respectively. Similarly, $M_{TCS + CP}$, M_{TCS} are the mass of the tape, clamps, and screws with and without condensed product, respectively. The mass balance closure is calculated as shown in Equation 4:

$$Balance\ closure\ (\%) = \left(Y_{gas} + Y_{solid\ residue} + Y_{condensed\ product}\right) * 100 \quad \textit{(Eq. 4)}$$

3.5 Analytical techniques

3.5.1 Gas Chromatography (GC)

In order to know the composition of the non-condensable product of the pyrolysis reaction, and to be able to compute the gas yield produced; a micro-GC (Varian MicroGC CP4900, 2 analytical columns, 10 m Molsieve 5A, 10 m PPQ, Carrier gas: Helium) calibrated for N_2, O_2, CO, CO_2, CH_4, C_2H_6, C_2H_4, C_3H_6, C_3H_8, was used. The gas samples taken after the screen-heater pyrolysis experiments were analyzed twice to ensure reproducibility. It is important to mention that, for all the experiments done in this work, only in a few CH_4 was detected, while heavier gases were not detected.

3.5.2 Gel Permeation Chromatography (GPC)

The molecular weight distribution (MWD) of the condensable product obtained was determined by using GPC (Agilent Technologies 1200) equipped with three columns (7.5mm×300 mm, particle size 3 μm) placed in series packed with highly cross-linked polystyrene-divinylbenzene copolymer gel (Varian PLgelMIXED E). The column temperature was maintained at 40° C during analysis. Samples were dissolved in tetrahydrofuran (THF) in a 1:100 mass ratio and were filtered through a 0.45 μm Whatman RC Agilent filter. THF was used a mobile phase at a flowrate of 1 mL min. A variable wavelength detector (VWD, 254 nm), already available in the equipment, was used for the computation. The calibration line was made with ten polystyrene standards with molecular weights ranging from 162 Da to 29510 Da.

3.5.3 High Performance Liquid Chromatography (HPLC)

Levoglucosan and glucose in the condensed product were analyzed using HPLC (Agilent 1200 series, column: Hi-Plex-Pb maintained at 70° C, mobile phase: Milli-Q water, 0.6 mL/min). All samples were measured its pH and neutralized with barium carbonate if needed, then, were filtered (Whatman RC Agilent 0.2 mm filter) prior to analysis. The quantification of LG and glucose in the condensed product was done by using a four-point calibration.

3.5.4 Acid Hydrolysis for quantification of sugars

The total amount of hydrolysable anhydro-sugars (including oligomers) were determined, after hydrolysis, as glucose. The NREL LAP method ‘‘Determination of sugars, byproducts, and degradation products in liquid fraction process samples” was used [37]. To do this, 20 mg–50 mg of condensed product was dissolved in Milli-Q water, while rinsing the vessel after the experiment was carried out. The diluted sample was then added 350 μL of concentrated H_2SO_4 (at 72% v/v) to obtain a final concentration of 3.5 vol.%. Finally, the sample was heated in an autoclave at 120° C for 1 h. After hydrolysis the condensed product was neutralized by adding $BaCO_3$. The condensed product was then filtered to remove the formed precipitates. The glucose concentration was determined using HPLC. Glucose is a representative of all hydrolysable sugars including levoglucosan, cellobiosan, cellotetrasan, etc. The yield of hydrolysable anhydrosugars is therefore expressed as the ratio of carbon in glucose to carbon in cellulose. This method (NREL LAP) needs a correction for the recovery products, because even when using pure glucose, it is not possible to recover it 100%; therefore, the data obtained in previous work in STP [18], was used to correct the glucose recovery from levoglucosan at different known concentrations, as described elsewhere [18].

4. Results and discussion

4.1 Pure components and model mixtures.

4.1.1 Cellulose-lignin interaction effects on gas, solid and condensed product yields.

Firstly, is was analyzed whether exist cellulose-lignin interactions have an effect on the products yields of primary reactions during fast pyrolysis of blends listed on Table 3, where concentration of potassium (K^+) in cellulose was varied between 1 and 10,000 ppm; as well as the fast pyrolysis of pure components in order to compare the obtained results. The cellulose impregnated samples were predetermined in a previous work done in SPT group [24].

The non-condensable gas yields, at 0.05 mbar, and 530° C, is shown in Figure 9. It can be seen that the highest non-condensable gas yield is produced at the blend with highest potassium concentration (0.033 g/g sample). This behavior is similar at which has been reported from previous work, in the screen-heater with slightly different conditions (5 mbar, 530° C) [24]. Therefore, even if the vapor phase reactions are suppressed in the screen-heater, the primary reactions catalyzed by potassium salts are the main responsible for the non-condensable gas production.

In addition, it is important to mention that gasses like CH_4 or higher, typically found in gas composition of pyrolysis processes [7], were not detected in any of the experiments. However, few experiments shew a small concentration of H_2 (less than 0.01% respect to the total gas production). It was seen that the individual yield of CO_2 is dominant for all blends experiments; being the highest for the blend with highest K^+ concentration. Once again, this behavior was similar to that already reported for only cellulose impregnated experiments [24].

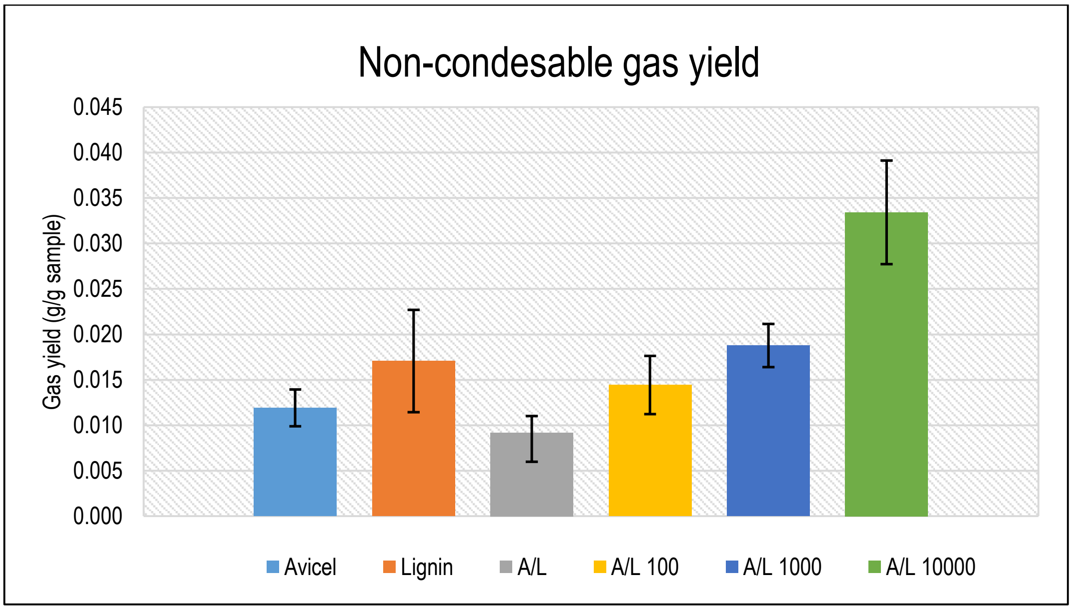

Figure 9. Gas yield obtained of avicel, lignin and their blends.

On the other hand, the solid residue yields are presented in Figure 10. It can be seen that, for pure avicel experiments, the lowest yield of solid is obtained (0.029 g/g sample); in contrast, for pure lignin experiments the highest yield was produced (0.166 g/g sample). For the blends, a general trend can be observed: when the K^+ concentration increases the solid residue yield also increases; trend which was also observed in previous work [24] for cellulose pyrolysis. The solid residue yield to 0.059 (g/g sample) when avicel and lignin are mixed, compared to 0.029 (g/g sample) when pure avicel is used. From these, it can be said that the presence of lignin increased the yield of solid residue, when the concentration of the salts is low.

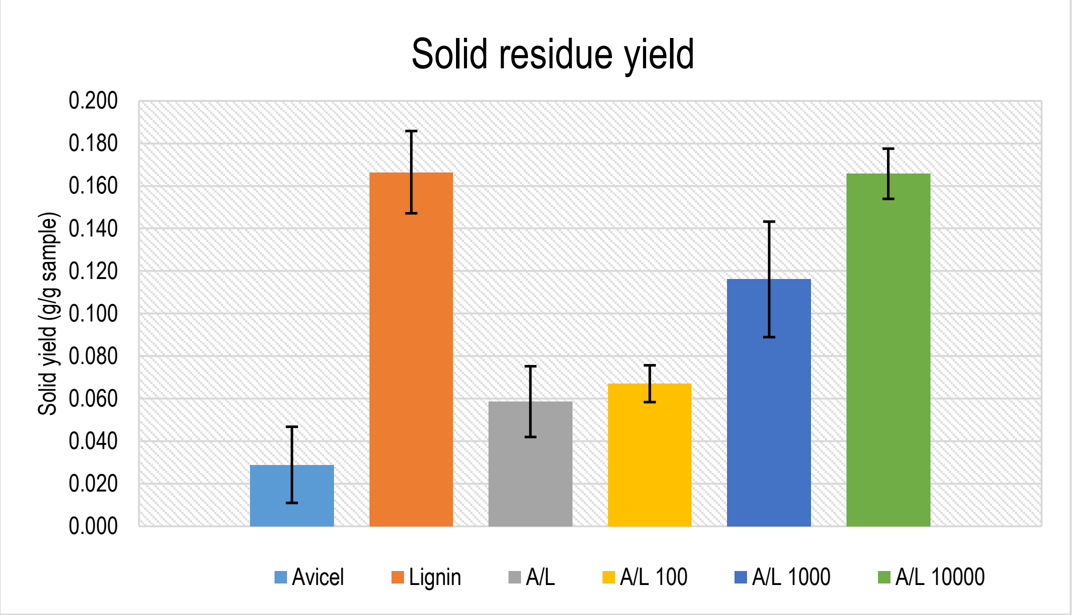

Figure 10. Solid residue obtained from avicel, lignin and blends experiments.

To analyze the most important product for a pyrolysis process, Figure 11 shows the condensed product yield obtained in the experiments with pure components and blends. It can be seen that, as an effect of the presence of lignin, the condensed product yield decreases from 0.91 to 0.85 (g/g sample) when avicel and avicel/lignin are used as feedstock respectively.

In addition, a clear trend can be observed when the concentration of salts increased, decreasing the production of condensable yield, till 0.58 g/g sample when the concentration of K^+ was 10000 ppm. The pyrolysis at vacuum pressure (0.05 mbar) implies high product escape rates of reacting particle from the reaction zone; however, even in this short time, potassium causes the oil yield to decrease as the concentration of salts increases. This trend was also presented in previous work [24]; therefore, it can be said that the presence of lignin does not have a significant influence in the production of pyrolysis oil, for the conditions hereby used.

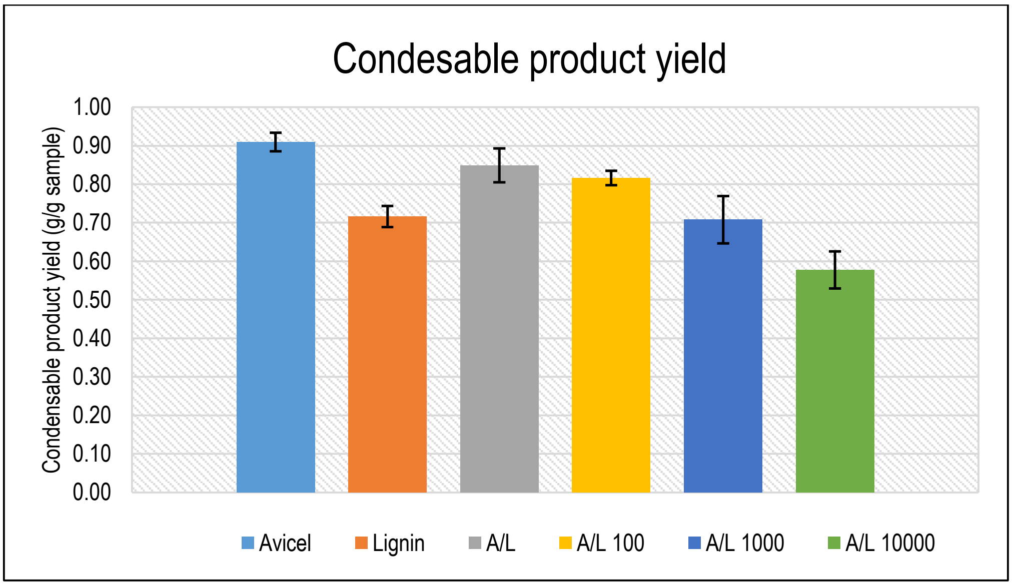

Figure 11. Condensable product yield obtained from avicel, lignin and blends experiments.

The obtained mass balance closure of all experiments was between 78% and 95%, being for avicel the highest, and for the blend with the highest salt content, the lowest; as was expected. It has been already explained that the reason for a not complete mass balance closure is that water and some of the light oxygenates lost during dismantling of the set-up [18]. The number of experiments in the screen-heater performed, for each feedstock used, was at least 6, except for the A/L 10000 blend (only 4). As shown in Figure 12, the reproducibility of the experiments was satisfactory.

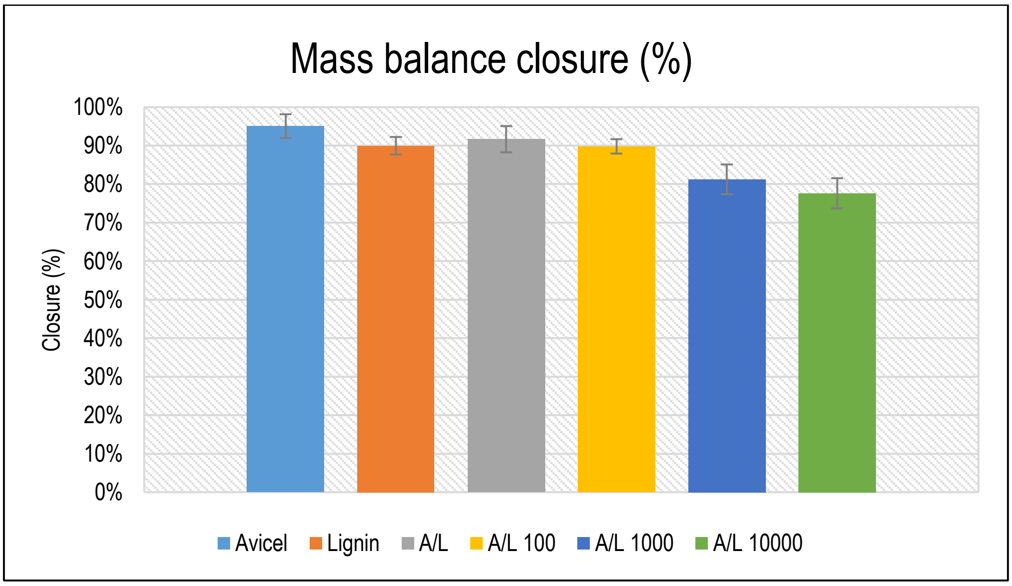

Figure 12. Mass balance closure obtained from avicel, lignin, and blends experiments.

4.1.2 Cellulose-lignin interaction effects on molecular weight of condensed product.

The molecular weight distribution (MWD) of bio-oils represents an important characteristic towards its possible upgrading for use as fuel or as raw chemical source [13]. Therefore, the MWD, as well as the molecular numbers, mass average molecular weight (M_W) and number average molecular weight (M_n) were also analyzed in this work, in order to see any potential effect of cellulose-lignin interactions during fast pyrolysis reactions.

Figure 13 shows the MWD of the condensed product from avicel/lignin blends used in this study, as well as the MWD of the condensed oil produced from the pyrolysis of lignin only. If we take the last one as basis to compare the behavior of the MWD presented, we cannot observe a possible effect of the cellulose-lignin interactions, for the conditions used. In contrast, the effect of the K^+ concentration in the blends can be noticed for molar mass less than 200 g/mol; and also for molar mass above 300 g/mol, it is here where a trend can be observed: for lignin only and A/L samples the behavior of MWD is similar, it decreases when the concentration of potassium increases.

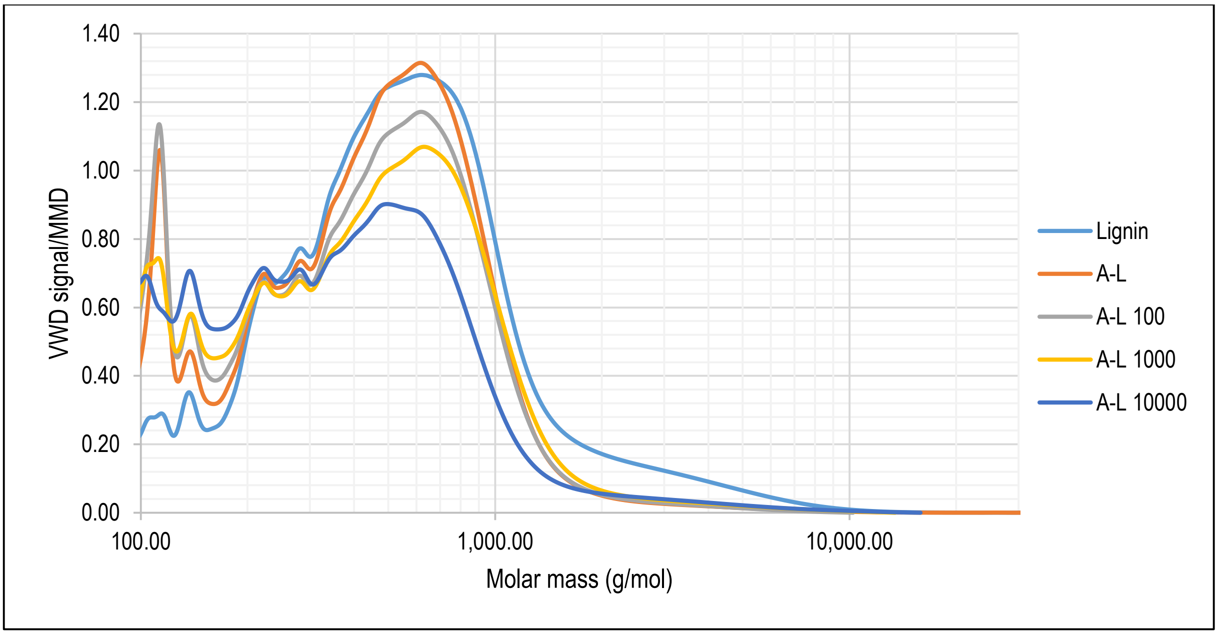

Figure 13. Molecular weight distribution (MWD) of condensed product from blends experiments.

This trend can also be observed when the molecular numbers (Mn and Mw) and the polydispersities (Mw/Mn) are compared in Figure 14. Firstly, it can be seen that the molecular numbers of the condensed product decrease as the concentration of potassium increases, being for the lignin only the highest (Mw = 837 g/mol) and for the blend A/L 10000 the lowest (Mw = 517 g/mol). This could mean that oligomers generated from pyrolysis decreased as the concentration of potassium potentially increased . In contrast, polydispersity value (Mw/Mn), which is also a parameter for a material to be considered with potential for use as fuel [14], was observed to increase as the potassium concentration also increased. These values were 2.82 for the condensed product of lignin only, and 3.68 for the bio-oil obtained with the A/L 10000 sample.

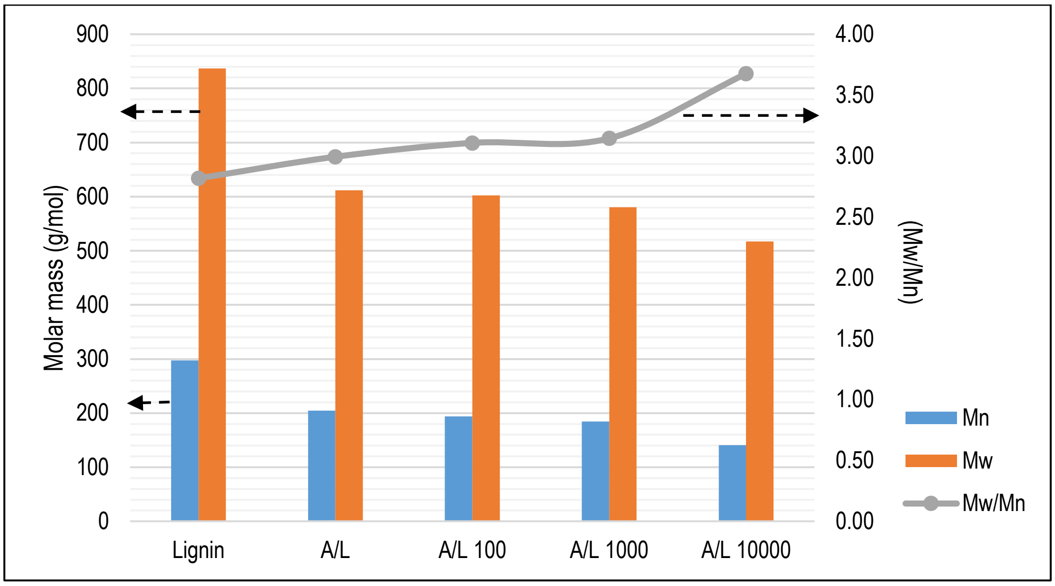

Figure 14. Molecular weight numbers and polydispersity of condensed product from blends experiments.

In order to be able to observe a clearer trend of the MWD behaviour, these values were discretized into 50 segments of 200 g/mol, between 1 and 10000 g/mol and divided by the total to obtain the MWD in terms of mass fractions, as proposed in previous work [20]. The results are shown in Figure 15, where it cannot be seen relevant effect on the behaviour of the MWD of the produced bio-oils due to interactions between cellulose and lignin. However, it can be observed that as the concentration of K^+ increases, more light weight components are obtained in the condensed products.

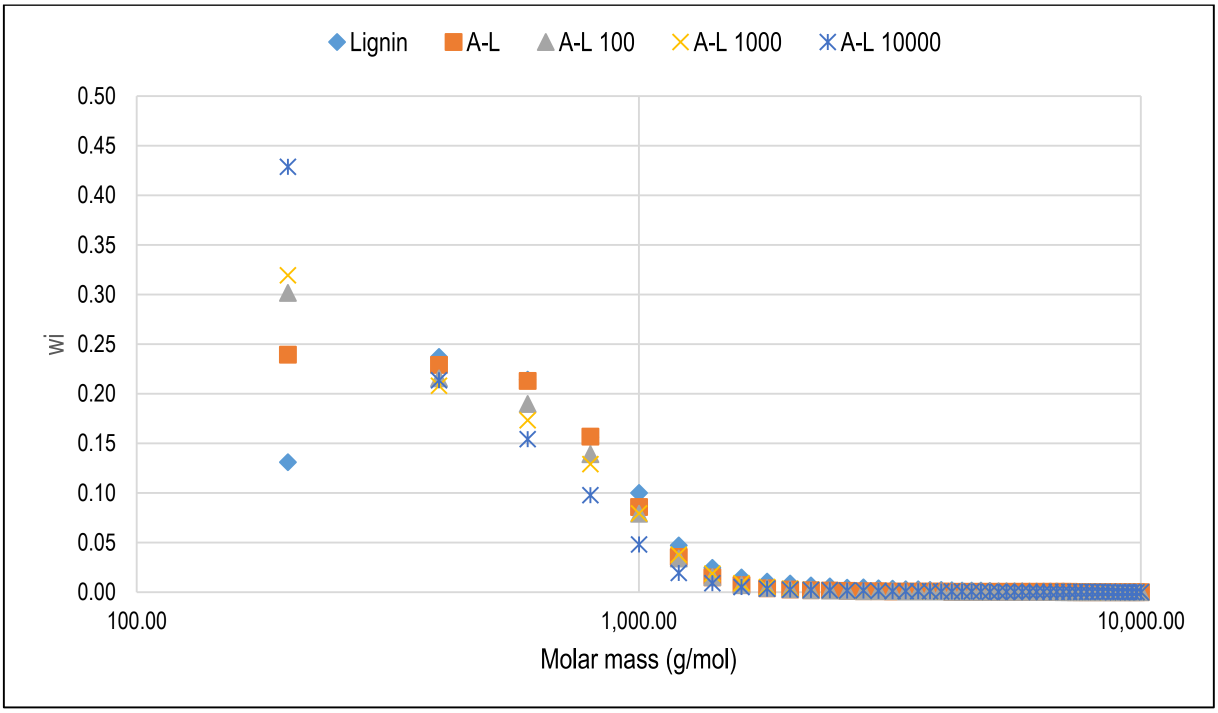

Figure 15. Discretized MWD of condensed product from blends experiments.

4.1.3 Cellulose-lignin interaction effects on condensed product composition.

One of the most remarkable findings done in this work is shown in Figure 16, where the levoglucosan yield with respect of the cellulose content in the sample is presented as function of the potassium content of the samples. Moreover, the results obtained in this work are compared to those obtained in a previous work in the screen-heater with a slightly different condition (5 mbar), for only cellulose impregnated experiments [24].

It is observed that the production of LG increased with the presence of lignin, if compared to that when only cellulose was used; this is only valid when the concentration of K^+ is low (1 and 100 ppm). When pure components were used, for the avicel/lignin blend, a LG yield of 0.26 g/g of converted cellulose in the sample was obtained; compared to that obtained when only cellulose was pyrolyzed (0.2 g/g) [24]. Similarly, when the concentration of potassium was 100 ppm, a LG yield of 0.17 g/g cellulose was produced; compared to the value obtained for cellulose only (0.1 g/g) [24]. Nevertheless, when the composition of the salts increased to 1000 and 10000 ppm (0.08 and 0.02 g/g cellulose respectively), the LG yields remained similar to those previously obtained for cellulose only samples.

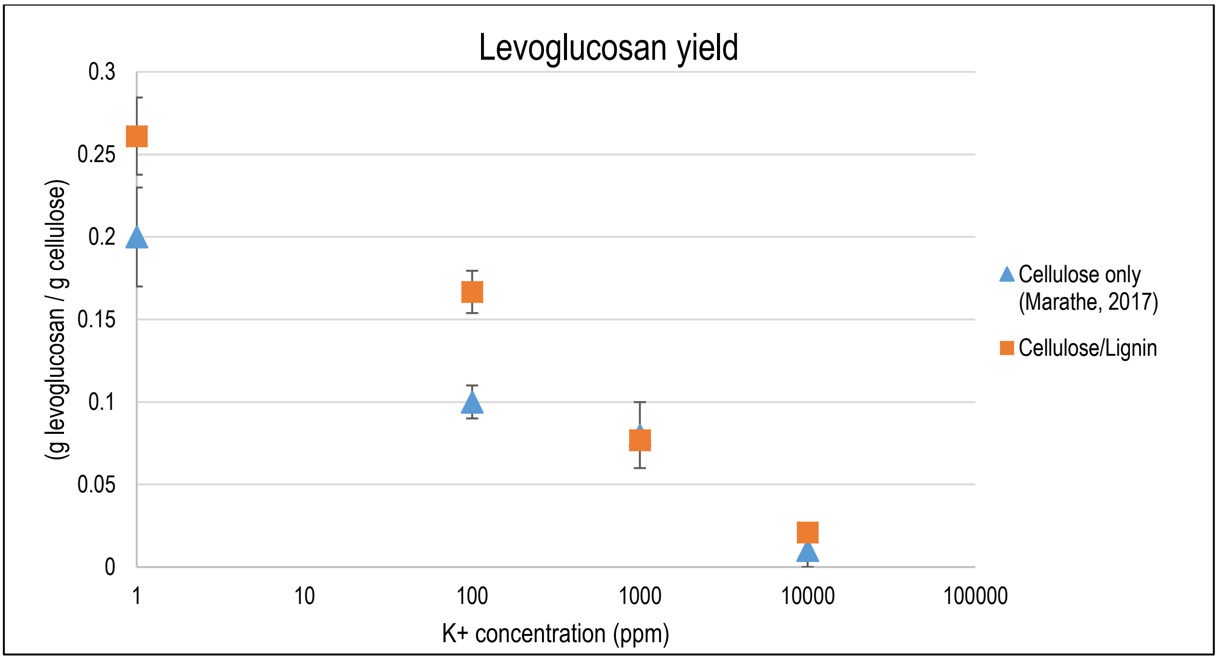

Figure 16. LG yield obtained from condensed product as a function of potassium concentration in cellulose, compared to data obtained from a previous study with only cellulose [24].

These results could indicate that there are interactions between cellulose and lignin which have an effect, enhancing the LG yields at low potassium concentrations. It should be noted that the pressure used in the previous work was slightly different than the used in this study (5 to 0.05 mbar, respectively), and this factor could also have influenced the obtained results [24]. Similar results have been reported in previous studies, as explained in Chapter 2 of this report; especially where a pyrolyzer coupled to a GC-MS was used [32], where was also detected that the presence of lignin limited the yields of some dehydration products from anhydrosugars, like levoglucosenone, 5-HMF, and furfural. It seems that the presence of a liquid lignin intermediate produces a thermal ejection of LG from the reaction zone, limiting in this way its further degradation [38]. In addition, it has also been reported that thermal degradation of LG is suppressed in the presence of aromatic compounds [39]. This is only valid at low concentrations of AAEMs; therefore, as has been concluded in many previous works, a pre-treatment of lignocellulose biomass in order to remove AAEMs content as much as possible is needed.

Moreover, Figure 17 shows the glucose recovery as a function of the potassium concentration in the blends. Glucose was obtained after hydrolysis of levoglucosan and oligomeric anhydrosugars present in the condensed product. The glucose recovery is expressed as the ratio between the carbon in glucose and carbon in cellulose, where also the results from a previous work are shown in order to compare the values obtained [24]. In this case, an effect on the glucose recovery due to cellulose-lignin interactions could not be observed while comparing to previous work results.

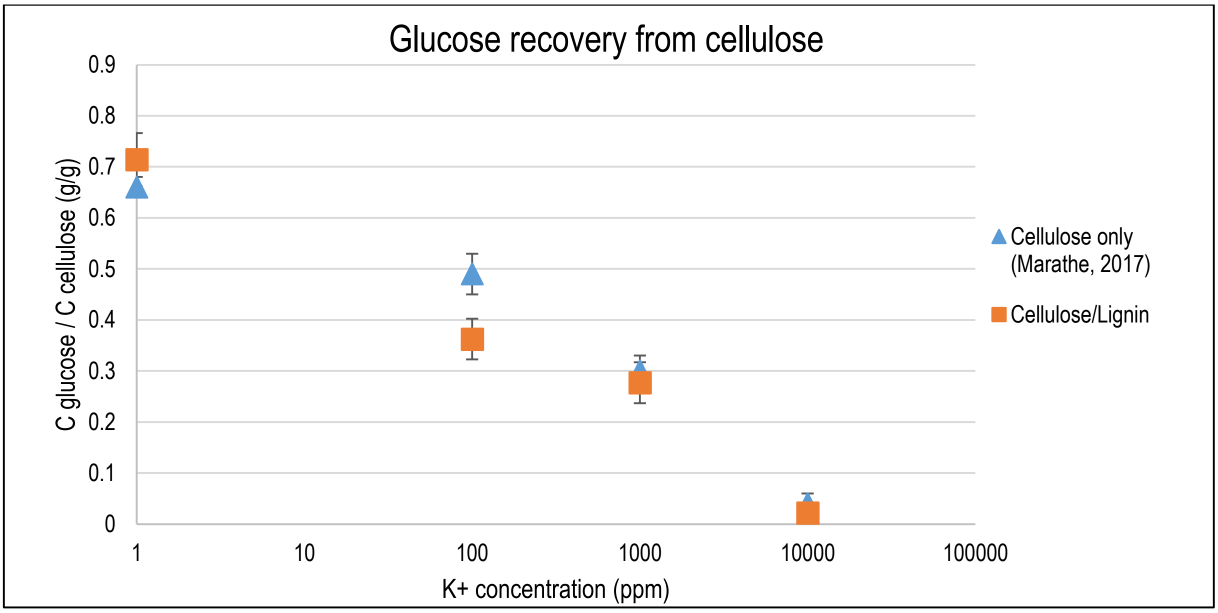

Figure 17. Glucose recovery after hydrolysis of the condensed product as function of potassium concentration in cellulose, compared to data obtained from a previous study with only cellulose [24].

4.2 Lignocellulose samples from poplar.

4.2.1 Cellulose-lignin interaction effects on gas, solid and condensed product yields.

Furthermore, the possible cellulose-lignin interactions different lignin content were analyzed in this part of the study, where samples of native and treated poplar were used as feedstock. The lignin content of these samples as presented on Table 4, which is 25%, 11.5% and 3.6% wt; as well as one untreated sample with approximately > 10000 ppm content of salts.

The effect of the lignin content on non-condensable gas yield, for the poplar treated and untreated samples is shown in Figure 18. It can be seen that the highest non-condensable gas yield is produced at the untreated poplar sample, 0.03 g/g sample, which comparable with the yield obtained for the blend A/L with 10000 ppm of potassium. This result was expected due to the high content of salt which quickly catalyze the primary pyrolysis reactions. Unfortunately, there was not found a trend for the treated samples with different lignin content Therefore, can be said that the content of lignin has no influence in the gas yield for the samples used, but the AAEM content does.

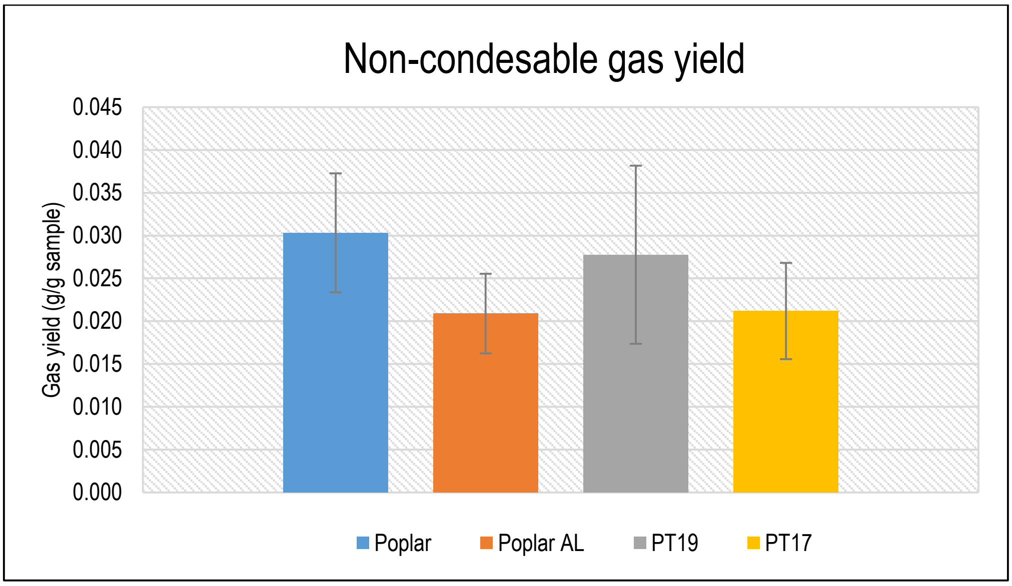

Figure 18. Gas yield obtained from poplar samples experiments.

Moreover, the solid residue yields are presented in Figure 19. It can be seen that, the highest yield of solid was obtained for the native sample (0.07 g/g sample), as expected, due to its high AAEM content; in contrast, the lowest yield was produced from the acid leached (25% wt lignin) and the PT17 pulp samples (3.6% wt of lignin) with 0.025 g/g sample for both. As well as the gas yield, no trend was found due to the lignin content. Because of this, it can be said that the content of lignin, for the samples and conditions used in this study, has no effect on the solid residue production.

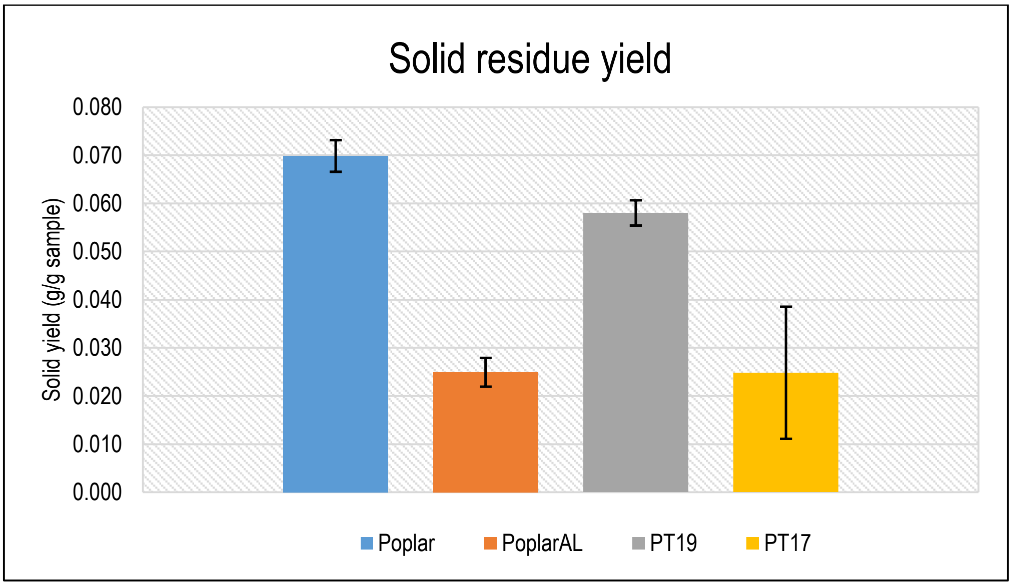

Figure 19. Solid residue yield obtained from poplar samples experiments.

Figure 20 shows the condensed product yield obtained in the experiments with poplar samples. It can be observed that, as expected, the untreated sample produced the lowest condensed product (0.68 g/g sample); opposite to the acid leached sample (0.85 g/g sample) which generated the highest yield of condensed product. This results reinforced fact that, it is mandatory to pre-treat the lignocellulose, reducing the AAEM content, in order to increase the bio-oil yield.

No trend was found related to the lignin content of the samples, as mentioned for gas and solid yields, therefore, an effect of the lignin content over the condensed product yield cannot be established, for the conditions used.

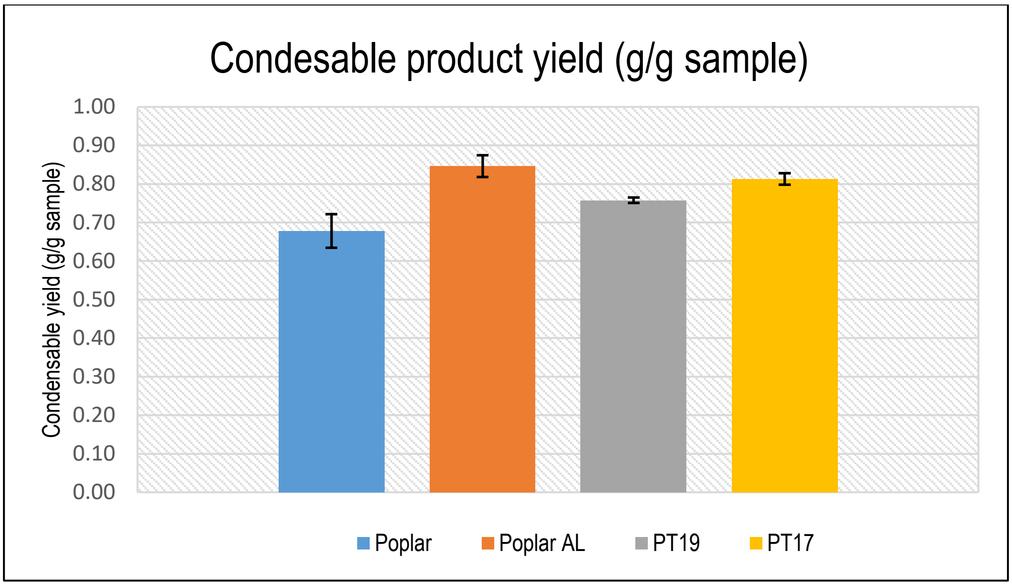

Figure 20. Condensable product yield obtained from poplar samples experiments.

The mass balances of all experiments was between 78% and 89%, being for the untreated poplar the lowest, as expected, and for the treated sample with 25% content of lignin the highest. Unfortunately, due to the limited availability of the samples, the number of experiments performed, were three for the poplar and AL poplar samples; and only two for PT19 and PT17. Nevertheless, as shown in Figure 21, the reproducibility of the experiments was good.

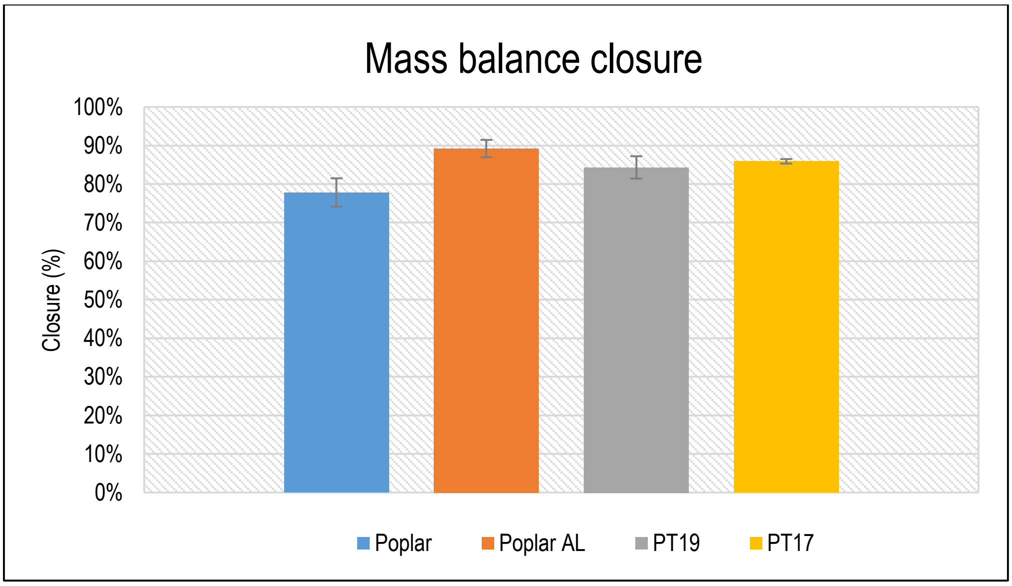

Figure 21. Mass balance closures obtained from poplar samples experiments.

4.2.2 Cellulose-lignin interaction effects on molecular weight of condensed product.

The molecular numbers and the polydispersity values obtained from the condensed product of the poplar samples are shown in Figure 22. For the treated samples (Poplar AL, PT 19, and PT17), a trend can be highlighted, because the molecular weight numbers (Mw and Mn) decreased as the lignin content in the sample decreased, which could indicate that the amount of oligomers decreased as the lignin content also did. In contrast, polydispersity values increased when the lignin content was lower.

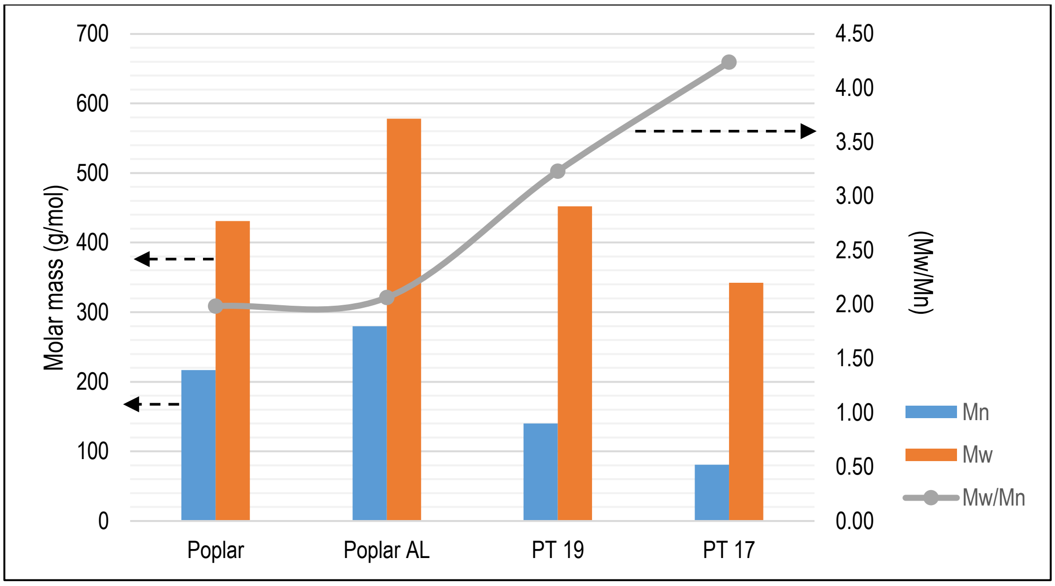

Figure 22. Molecular weight numbers and polydispersity of condensed product from poplar experiments.

4.2.3 Cellulose-lignin interaction effects on condensed product composition.

LG yields and glucose recovery were also computed for the condensed product from the poplar samples experiments and are shown in Figure 23 and Figure 24, respectively. Interestingly, for both results, a perfectly visible trend can be observed, LG yield and glucose recovery increased as the concentration of lignin in the samples also did. These trends have also been reported in previous work [32], where the concentration of LG was also higher at a 20% wt lignin content. This could also be related to the possible thermal stabilization of anhydrosugars in the presence of aromatics previously mentioned [39].

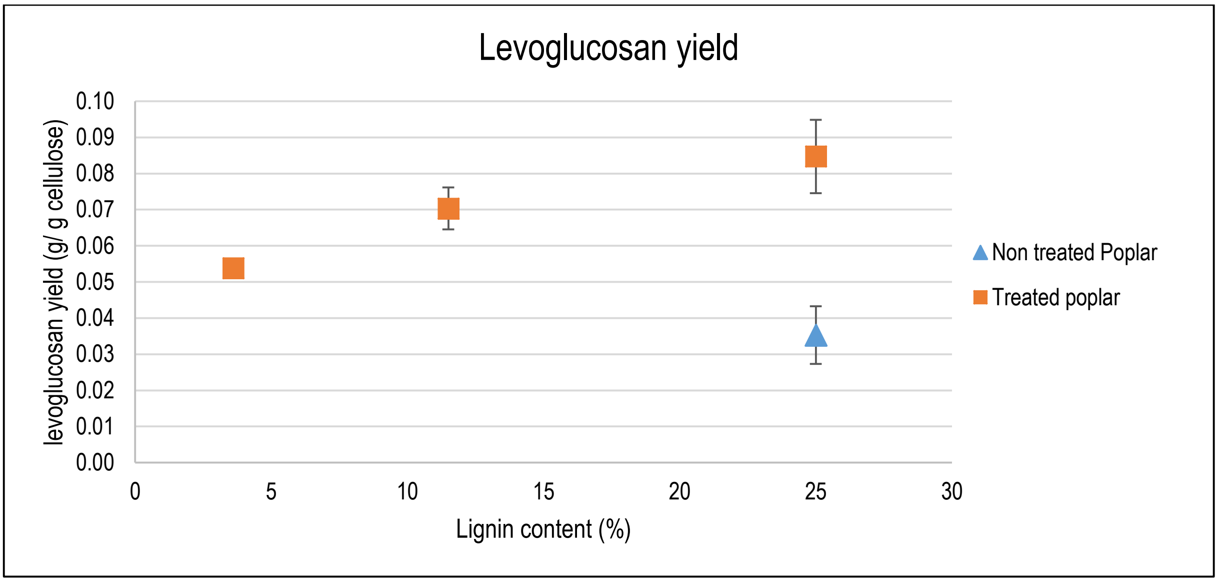

Figure 23. LG yield obtained in condensed product of poplar experiments as a function of lignin content in the feedstock.

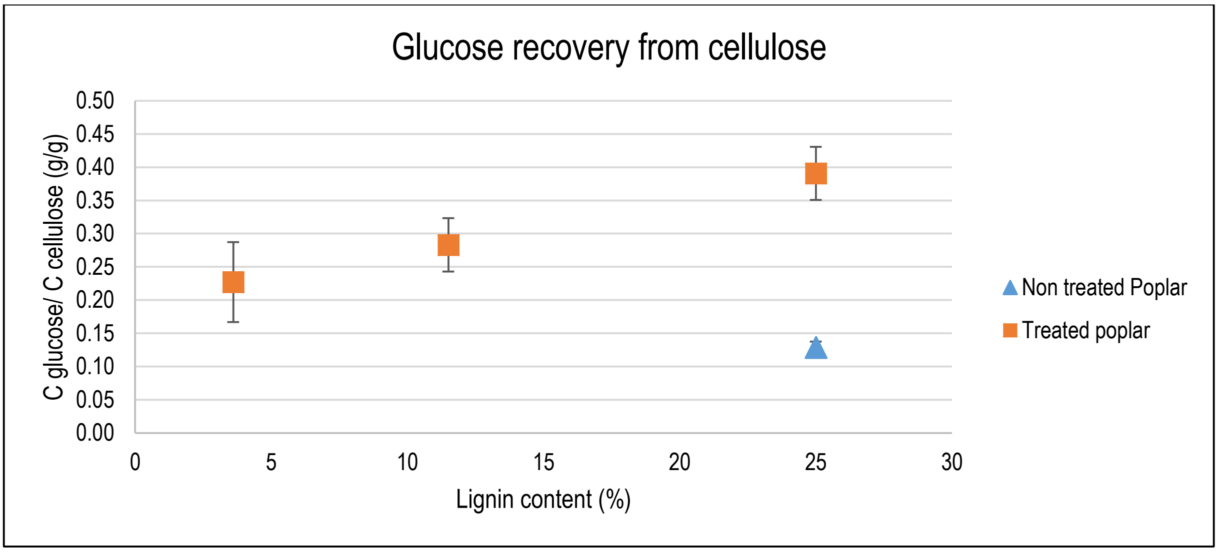

Figure 24. Glucose recovery after hydrolysis of the condensed product as a function of lignin content in the feedstock.

5. Possible contributions of present study towards fast pyrolysis applications improvements

5.1 Applications of fast pyrolysis of biomass

Fast pyrolysis of lignocellulosic biomass is focused on the production of bio-oil, which can be converted into several forms of energy carriers and into platform chemicals; representing an advantage over other renewable technology options by providing a potential substitute of fossil feedstocks in the petrochemical sector. The use of biomass for chemical and energy applications is part of the current EU's bioeconomy strategy [40]. For applications of lignocellulosic biomass for energy, there are already many incentives on the way, like electricity subsidies, tax reliefs, and bioenergy schemes [41]. For biobased chemicals, a potential market is expected to grow quickly; however, further research and development is still needed as well as raising awareness of policies, which are now without clear incentives for deployment [42]. In Figure 25, an overview of the potential applications of fast pyrolysis of biomass products is presented.

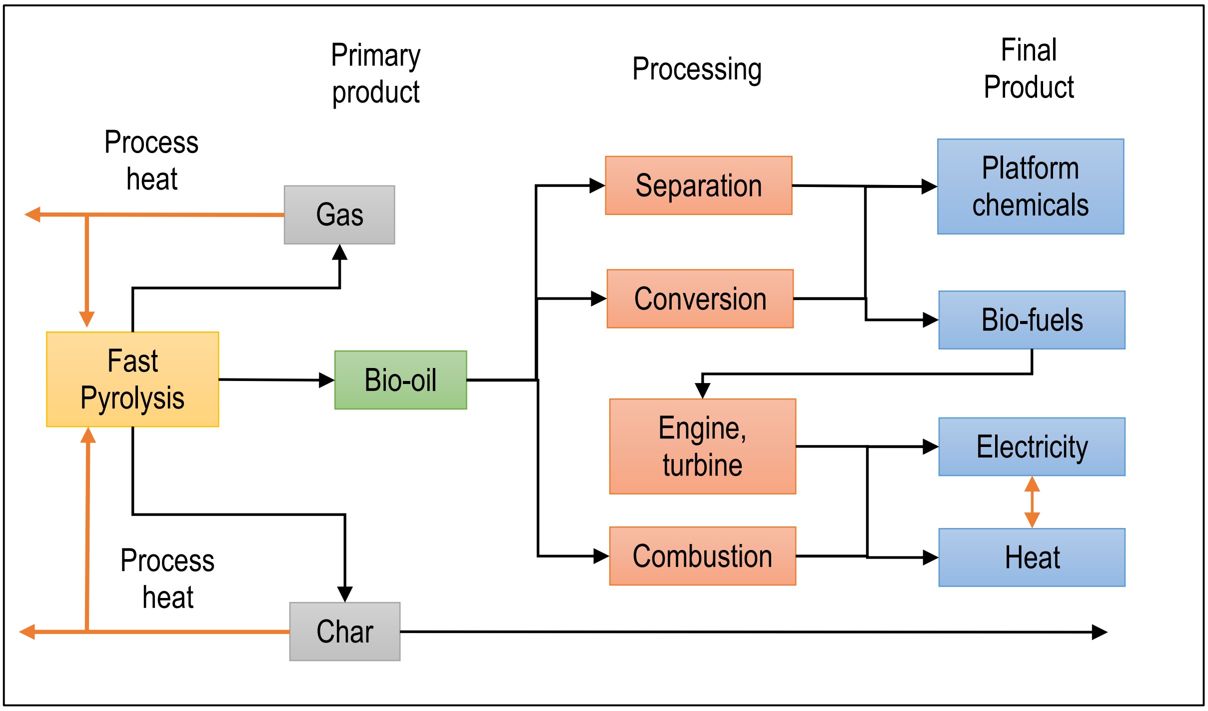

Figure 25. Applications for fast pyrolysis products [43].

Fast pyrolysis of biomass has an enormous potential as a pre-treatment method to produce an effective energy carrier, the bio-oil. One of main disadvantages of biomass, is a widely dispersed resource that has to be harvested and transported to a conversion facility. The low bulk density of biomass, which can be as low as 50 kg/m^3, means that transport costs are high and the number of vehicle movements for transportation to a large scale processing facility are also very high, with consequent substantial environmental impacts [44]. Assuming that, processing is carried out in a close-by to source facility, this conversion of biomass to a liquid by fast pyrolysis would reduce transport costs and reduce environmental concerns as the liquid has a density of 1200 kg/m^3, which represents more than ten times higher than harvested biomass [41]. This could also reduce costs of handling by taking into account a liquid that can be pumped. This is currently developing a concept of small decentralised fast pyrolysis plants of 50,000 to 250,000 tonnes per year for the production of bio-oil to be transported to a central processing plant [44].

In addition, the direct production of high yields of liquids by fast pyrolysis have always caused attention to focus on their use as biofuels to supplement and further replace fossil derived transport fuels. However, the high oxygen content of bio-oil and its non-miscibility or incompatibility with hydrocarbon fuels has made this possible transition a very difficult process [45]. Because the qualities above mentioned, bio-oil needs to be post-treated, commonly known as upgrading, in order to be able for using it as fuel. Among the several methods that have been proposed for the upgrading of bio-oil, hydrodeoxygenation can be highlighted. Practically, it is a process of liquid bio-oil that rejects oxygen as water by catalytic reaction with hydrogen. This process gives a naphtha-like product that requires orthodox refining to derive conventional transport fuels. Therefore, it could to take place in a conventional refinery to take advantage of know-how, existing processes and economies of scale. It has been projected that a typical yield of naphtha equivalent from biomass could be about 20% by weight or 55% in energy terms, excluding provision of hydrogen [46].

On the other hand, some platform chemicals could also be obtained from pyrolysis bio-oil after some separation or conversion methods. Although bio-oil contains in excess of 1000 individual chemicals, few are present in sufficient concentrations to be feasible its recovery. Among these compounds, levoglucosan has a great potential of being recovered in high purity and high yield, nevertheless until recently has been perceived as having an upcoming market value; because of more attention has been paid to its potential of producing sugars by hydrolysis or fermentation [47].

Moreover, under the biorefinery concept development, fast pyrolysis has the potential of both producing bio-oil as a precursor for second generation biofuels for transport, and generating platform chemicals. A key feature of the biorefinery concept is the co-production of fuels, chemicals and energy. There is a clear economic advantage in building a similar flexibility into the biofuels market by devoting part of the biomass production to the manufacture of chemicals [43]. In fact, under this concept, a pilot plant has been recently developed by BTG company, in The Netherlands. It is an innovative two-step conversion process were a fast pyrolysis of biomass is followed by a fast pyrolysis of the previously produced bio-oil. Three main products are then obtained: pyrolytic lignin, which is suitable for the production of renewable bitumen or various resins, as a replacement for fossil phenol; pyrolytic sugars, suitable for the production of furan-based resins and can be obtained with various water contents; and extractives, a raw material for specialty chemicals [48].

5.2 Reinforcement of fast pyrolysis current behaviour models

As mentioned on Chapter 2.1 in this study, biomass feedstock comes in many varieties, but have common main constituents as cellulose, hemicellulose, and lignin. As the relative proportions of these constituents vary depending on many factors, customization of the pyrolysis process conditions is required to produce a desired product profile, i.e. pyrolytic sugars. Therefore, recognizing these sources of variation, mathematical models could be built to further applications on simulators, allowing to set reactor settings in order to achieve an optimal operation. These considerations might include biomass classification, feed rate, moisture content, particle size, and thermal and mass transport gradients of the desired reactor [49].

The recent advances in the understanding of the fundamental reaction pathways have been widely described, including the description of pyrolysis as a two-step process, primary and secondary pyrolysis reactions, the effect of the operational pressure, the effect of the presence of an intermediate liquid compound, and the influence of inorganic salts. Among the several approaches that have been used to model, the description of biomass pyrolysis as the sum of the contributions of its individual components has been highlighted. This method has been widely employed to examine the reactions pathways, confirming that pyrolysis of biomass appeared to behave as the sum of its constituents [50].

Nevertheless, evidence of the interactions among the components under pyrolytic conditions would give a conceptual guide to modify the understanding of pyrolytic mechanism of biomass from this point of component view, and help to design a new-concept of co-pyrolysis process for promoting the production of value-added compounds. The interactions between chemical components in biomass under pyrolytic conditions have been evidenced and discussed within recent years, as mentioned in Chapter 2.6. However, the understanding has been greatly limited and two main issues were needed to be addressed for specifying the possible interaction mechanisms: sample preparation representing the natural information between components in biomass, chemical pathways for the interaction and quantitative assessment for the interactive extent [16].

In this regard, the present study intended to solve the two above mentioned issues, by using the already described experimental configuration and a quantitative estimation of the product composition. Therefore, the results obtained could provide valuable experimental information which can be used to create a better and more complete model for the prediction of the product selectivity. However, experimental studies still have to be done to enhance the modelling of pyrolysis process towards building of a robust simulation technology tool, and finally help this promising technology to an industrial application.

6. Conclusions

In this study, the possible interactions between cellulose and lignin during the primary reactions of fast pyrolysis of different feedstocks were analyzed. The experiments were carried out in a reactor developed in SPT group, a screen-heater which enables a very fast heating rate (5000° C/s), short vapor residence time (< 79 ms), and fast quenching of the products; in order to recover the primary products of the reaction. The obtained results from the model mixtures were compared to those previously reported using also the screen-heater, with similar reaction conditions. It was not found a considerable effect, for the non-condensable gas, solid residue, condensed product yields, due to interactions between cellulose-lignin. In addition, the glucose recovery from cellulose was also computed in order to estimate the total sugar content from anhydrosugars; discarding also relevant effects due to cellulose-lignin interaction.

However, it should be highlighted from this work, that interactions between cellulose and lignin were found when comparing the obtained levoglucosan yields from the condensed product of the blends with the results previously reported for only cellulose experiments. The presence of lignin enhances the production of LG, when the potassium concentrations remain low (till 100 ppm). This could be attributed mainly to two processes: 1) lignin promotes the thermal ejection of the cellulose derivatives from the reaction zone, and 2) thermal degradation of levoglucosan is partially suppressed by the presence of aromatic compounds. Moreover, results obtained from poplar samples also did not show a consistent to relate the lignin content by analyzing the non-condensable gas, solid residue and condensed product yields. Nevertheless, a trend was obtained when comparing the LG yields and glucose recovery from the condensed product composition. It seems that both yields increase as the lignin content present in the sample increases, which could be attributed as an effect of cellulose-lignin interactions in the pyrolysis process.

6.1 Recommendations

In order to reinforce the results obtained in this work, using similar conditions and feedstock for the screen-heater, two recommendations can be done for analyzing the composition of the condensed product: 1) to analyze the composition of anhydrosugars with a higher degree of polymerization (cellobiosan, cellotriosan, cellotetrasan); 2) to analyze the composition of dehydration products from anhydrosugars (levoglucosenone). These could help for the previously developed models to be more robust, in order to be able to predict more accurately lignocellulosic biomass behaviour during fast pyrolysis.

In addition, the screen-heater could also be used to study the effects of possible catalysts under the primary reactions of fast pyrolysis, using firstly model mixtures as the ones used in this work, to further analyze its effect on native biomass samples. This experimental set-up could be used to help building the basis for the development of biomass fast pyrolysis towards its many applications as a possible replacement of fossil resources.

References

[1] European Comission, “2030 climate & energy framework,” European Comission, 2019.

[2] E. Comission, “Food, feed, fibres, fuels. Enough biomass for a sustainable bioeconomy?,” European Comission, 2019.

[3] A. Bridgwater, D. Meier and D. Radlein, “An overview of fast pyrolysis of biomass,” *Organic Geochemistry,* vol. 30, pp. 1479-1493, 1999.

[4] P. Harmsen, W. Huijgen, L. Bermudez and R. Bakker, “Literature Review of Physical and Chemical Preatreatment Processes for Lignocellulosic Biomass,” Wageningen UR, Wageningen, 2010.

[5] A. Bridgwater and G. Peacocke, “Fast pyrolysis processes for biomass.,” *Renewable and Sustainable Energy Reviews,* vol. 4, pp. 1-73, 2000.

[6] E. Butler, G. Devlin, D. Meier and K. McDonnell, “A review of recent laboratory research and commercial developments in fast pyrolysis and upgrading.,” *Renewable and Sustainable Energy Reviews,* vol. 15, p. 4171–4186, 2011.

[7] T. Kan, V. Strezov and T. Evans, “Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters,” *Renewable and Sustainable Energy Reviews,* vol. 57, p. 1126–1140, 2016.

[8] B. Dhyani and T. Bhaskar, “A comprehensive review on the pyrolysis of lignocellulosic biomass,” *Renewable Energy,* vol. 129, pp. 695-716, 2018.

[9] R. C. Brown, Thermochemical Processing of Biomass: Conversion into Fuels, Chemicals and Power, Iowa: John Wiley & Sons, Ltd, 2011.

[10] D. Shen and S. Gu, “The mechanism for thermal decompsition of cellulose and its main products,” *Bioresources Technology,* pp. 496-504, 2009.

[11] X. Zhou, W. Li, R. Mabon and L. D. Broadbelt, “A Critical Review on Hemicellulose Pyrolysis,” *Energy Technology,* vol. 5, pp. 52-67, 2017.

[12] M. Carrier, A. Loppinet and C. Aymonier, “Thermogravimetric analysis as a new method to determine the lignocellulosic composition of biomass,” *Biomass energy,* vol. 35, pp. 298-307, 2011.

[13] M. Ganewatta, H. Lokupitiya and C. Tang, “Lignin Biopolymers in the Age of Controlled Polymerization,” *Polymers,* vol. 11, p. 1176, 2019.

[14] A. Grossman and V. Wilfred, “Lignin-based polymers and nanomaterials.,” *Curr. Opin. Biotechnol.,* vol. 56, p. 112–120, 2019.

[15] S. Wang, G. Dai, H. Yang and Z. Luo, “Lignocellulosic biomass pyrolysis mechanism: A state-of-the-art review,” *Progress in Energy and Combustion Science,* vol. 62, pp. 33-86, 2017.

[16] D. Shen, W. Jin, J. Hu, R. Xiao and K. Luo, “An overview on fast pyrolysis of the main constituents in lignocellulosic biomass to valued-added chemicals: Structures, pathways and interactions,” *Renewable and Sustainable Energy Reviews,* vol. 51, p. 761–774, 2015.

[17] X. Zhang, W. Yang and W. Blasiak, “Kinetics of levoglucosan and formaldehyde formation during cellulose pyrolysis process,” *Fuel,* vol. 96, p. 383–391, 2012.

[18] R. J. A. Westerhof, S. Oudenhoven, P. S. Marathe, M. Engelen, M. Garcia-Perez, Z. Wang and S. R. A. Kersten, “The interplay between chemistry and heat/mass transfer during the fast pyrolysis of cellulose,” *React. Chem. Eng.,* vol. 1, pp. 555-566, 2016.

[19] L. Chen, W. Liao, Z. Guo, Y. Cao and X. Maa, “Products distribution and generation pathway of cellulose pyrolysis,” *Cleaner Production,* vol. 232, pp. 1309-1320, 2019.

[20] P. S. Marathe, R. J. A. Westerhof and S. R. A. Kersten, “Fast pyrolysis of lignins with different molecular weight: Experiments and modelling,” *Applied Energy,* vol. 236, p. 1125–1137, 2019.

[21] E. Leng, M. Costa, X. Gong, A. Zhen, S. Liu and M. Xua, “Effects of KCl and CaCl2 on the evolution of anhydro sugars in reaction intermediates during cellulose fast pyrolysis,” *Fuel,* vol. 251, pp. 307-315, 2019.

[22] R. Mahadevan, S. Adhikari, R. Shakya, R. Wang, D. Dayton, L. L. and S. E. Taylor, “Effect of Alkali and Alkaline Earth Metals on in-Situ Catalytic Fast Pyrolysis of Lignocellulosic Biomass: A Microreactor Study,” *Energy & Fuels,* vol. 30, pp. 3045-3056, 2016.

[23] P. Patwardhan, J. Satrio, R. Brown and B. Shanks, “Influence of inorganic salts on the primary pyrolysis products of cellulose,” *Bioresource Technology,* vol. 101, p. 4646–4655, 2010.

[24] P. S. Marathe, S. Oudenhoven, P. Heerspink, S. R. A. Kersten and R. J. A. Westerhof, “Fast pyrolysis of cellulose in vacuum: The effect of potassium salts on the primary reactons,” *Chemical Engineering Journal,* vol. 329, pp. 187-197, 2017.

[25] H. C. Yoon, P. Pozivil and A. Steinfeld, “Thermogravimetric Pyrolysis and Gasification of Lignocellulosic Biomass and Kinetic Summative Law for Parallel Reactions with Cellulose, Xylan, and Lignin,” *Energy & Fuels,* vol. 26, pp. 357-364, 2012.

[26] A. Skreiberg, Ø. Skreiberg, J. Sandquist and L. Sørum, “TGA and macro-TGA characterisation of biomass fuels and fuel mixtures,” *Fuel,* vol. 90, pp. 2182-2197, 2011.

[27] T. Qu, W. Guo, S. Shen, J. Xiao and J. Zhao, “Experimental Study of Biomass Pyrolysis Based on Three Major Components: Hemicellulose, Cellulose, and Lignin,” *Industrial & Engineering Chemical Research,* vol. 50, pp. 10424-10433, 2011.

[28] G. Wang, W. Lia, B. Lia and H. Chena, “TG study on pyrolysis of biomass and its three components under syngas,” *Fuel,* vol. 87, pp. 552-558, 2008.

[29] H. Yang, R. Yan, H. Chen, C. Zheng, D. H. Lee and D. T. Liang, “In-Depth Investigation of Biomass Pyrolysis Based on Three Major Components: Hemicellulose, Cellulose and Lignin,” *Energy & Fuels,* vol. 20, pp. 388-393, 2005.

[30] S. Wang, X. Guo, K. Wang and Z. Luo, “Influence of the interaction of components on the pyrolysis behavior of biomass,” *Analytical and Applied Pyrolysis,* vol. 91, pp. 183-189, 2011.

[31] T. Hosoya, H. Kawamoto and S. Saka, “Solid/liquid- and vapor-phase interactions between cellulose- and lignin-derived pyrolysis products,” *Analytical and Applied Pyrolysis,* vol. 85, pp. 237-246, 2009.

[32] T. Hilbers, Z. Wang, B. Peccha, R. Westerhof, S. Kersten, M. Pelaez-Samaniego and M. Garcia-Perez, “Cellulose-Lignin interactions during slow and fast pyrolysis,” *Journal of Analytical and Applied Pyrolysis,* vol. 114, pp. 197-207, 2015.

[33] J. Zhang, Y. Choi, C. Yoo, T. Kim, R. Brown and B. Shanks, “Cellulose−Hemicellulose and Cellulose−Lignin Interactions during Fast Pyrolysis,” *ACS Sustainable Chemistry & Engineering,* vol. 3, pp. 293-301, 2014.

[34] S. Wu, D. Shen, J. Hu, H. Zhang and R. Xiao, “Cellulose-lignin interactions during fast pyrolysis with different temperatures and mixing methods,” *Biomass and Bioenergy,* vol. 90, pp. 209-217, 2016.

[35] Y. Yu, N. Paterson, J. Blamey and M. Millan, “Cellulose, xylan and lignin interactions during pyrolysis of lignocellulosic biomass,” *Fuel,* Vols. 140-149, p. 191, 2017.

[36] J. Wildschut, S. A., R. J. and W. Huijgen, “Ethanol-based organosolv fractionation of wheat straw for the production of lignin and enzymatically digestible cellulose,” *Bioresource Technology,* pp. 58-66, 2013.

[37] A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter and D. Templeton, “Determination of Sugars, Byproducts, and Degradation Products in Liquid Fraction Process Samples,” NREL, LAP, Golden, 2008.

[38] M. J., B. Pecha, F. Janna and M. Garcia-Perez, “Micro-explosion of liquid intermediates during the fast pyrolysis of sucrose and organosolv lignin,” *Journal of Analytical and Applied Pyrolysis,* vol. 122, p. 106–121, 2016.

[39] T. Hoyosa, H. Kawamoto and S. Saka, “Thermal stabilization of levoglucosan in aromatic substances,” *Carbohydrate Resaerch,* vol. 341, pp. 2293-2297, 2006.

[40] European Commission, “A sustainable bioeconomy for Europe: strengthening the connection between economy, society and the environment,” Publications Office of the European Union, Brussels, 2018.

[41] M. Banjaa, R. Sikkemab, M. Jégarda, V. Motolac and J. F. Dallemanda, “Biomass for energy in the EU. The support framework,” *Energy Policy,* vol. 131, pp. 215-228, 2019.

[42] J. Spekreijse, T. Lammens, C. Parisi, T. Ronzon and M. Vis, “Insights into the European market for bio-based chemicals.,” Publications Office of the European Union, Luxembourg, 2019.

[43] A. V. Bridgwater, “Upgrading options and promising applications in energy, biofuels and chemicals,” *Johnson Matthey Technol. Rev.,* vol. 62, pp. 150-160, 2018.

[44] A. V. Bridgwater, “Technical and Economic Assesment of Thermal Processes for Biofuels,” Assessment of the Northeast Biomass to Liquids Project, Solihull, 2009.

[45] A. A. Safana, I. I. Idowu, I. Saadu, B. I. Adamu, I. Murtala Musa and S. Habibu, “Potential Application of Pyrolysis Bio-Oil as a Substitute for Diesel and Petroleum Fuel,” *Petroleum Engineering & Technology,* vol. 7, pp. 19-29, 2017.

[46] Q. Zhang, J. Gong, M. Skwarczek, D. Yue and F. You, “Sustainable process design and synthesis of hydrocarbon biorefinery through fast pyrolysis and hydroprocessing,” *Process Systems Engineering,* vol. 60, pp. 980-994, 2014.

[47] L. Jiang, Z. Fang, Z. Zhao, A. Zheng, X. Wang and H. Li, “Levoglucosan and its hydrolysates via fast pyrolysis of lignocellulose for microbial biofuels: A state-of-the-art review,” *Renewable and Sustainable Energy Reviews,* vol. 105, pp. 215-229, 2019.

[48] S. Hunkin, “BTG commissions world-first fast pyrolysis biorefinery pilot plant,” Greenovate! Europe , Brussels, 2019.

[49] U. B. Ragula, S. Devanathan and S. Subramanian, “Modeling and Optimization of Product Profiles in Biomass Pyrolysis,” *InTechOpen. Recent Advances in Pyrolysis,* 2019.

[50] G. SriBala, H. H. Carstensen, K. M. Van Geem and G. B. Marin, “Measuring biomass fast pyrolysis kinetics: State of the art,” *Energy & Environment,* vol. 8, p. 236, 2018.

[51] M. N. Uddin, K. Techato, J. Taweekun, M. M. Rahman, M. G. Rasul, T. M. I. Mahlia and S. M. Ashrafur, “An Overview of Recent Developments in Biomass Pyrolysis Technologies,” *Energies,* vol. 11, p. 3115, 2018.

[52] Q. Liua, Z. Zhonga, S. Wang and Z. Luo, “Interactions of biomass components during pyrolysis: A TG-FTIR study,” *Analytical and Applied Pyrolysis,* vol. 90, pp. 213-218, 2011.

Acknowledgement

Firstly, I would like to thank Pilar for helping me to choose a master thesis assignment and for the opportunity to do this research at the SPT group, also for her supervision during the past few months and for always being available and willing to help me. Secondly, I would like to thank Sascha also for giving me the opportunity to be part of this amazing research group, and for his valuable feedback. I also would like to thank Marteen for always being available to help me develop the socio-economical part of this work.

Special thanks should be given to all the technical staff of the SPT group, Erna and Benno for all the help in the process. I would also like to thank Thimo for all the help on the laboratory and also for providing me with the poplar samples. Pushkar, thanks for all your advises, really help me a lot during my work.