A Critical Comparison of Pyrolysis of Cellulose, Lignin, and Pine Sawdust Using an Induction Heating Reactor

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Abstract

Fast pyrolysis of pinewood sawdust and two of its major components, namely lignin and cellulose was carried out using a laboratory scale induction-heating reactor. The effect of five different temperatures (500°, 550°, 600°, 650° and 700 °C) was tested on the product yield and quality. The products were characterized to evaluate the water content, elemental composition, chemical composition and energy content. The char yield decreased with temperature for all of the biomasses. The maximum liquid yield of 55.28% was achieved at 600 °C for pine sawdust, and the highest liquid yields for cellulose and lignin were obtained at 500 °C. Water content in the liquid fraction decreased as reaction temperature increased. The GC-MS revealed that the bio-oil from cellulose was rich in anhydrosugars while majority of the liquid from lignin had high phenolic contents. Analysis of the gas fraction shows that as the temperature increases the gas yield increases, which, when paired with the declining char masses, showed an increase in the biomass breakdown at higher temperatures. Liquid fraction from pine sawdust has the highest HHV with a peak at 550 °C.

Keywords: Pyrolysis, lignin, cellulose, induction heating, biofuel, bio-oil

1. Introduction

Thermochemical conversion of biomass has an advantage of being capable of readily producing liquid fuel from any organic matter, most importantly lignocellulosic biomass.[15, 41] Pyrolysis is an effective thermochemical process for biomass conversion, which uses an oxygen free environment, and operated at reactor temperatures between 300 °C and 700 °C to produce bio-oil.[15]

There are several different reactor designs that have been tested for the production of bio-oil through pyrolysis including: fluidized bed reactors, ablative pyrolysis reactors, and vacuum pyrolysis reactors, fixed bed reactor.[31, 33] Some of the recent designs for effective pyrolysis include fixed bed drop-type reactor[31], solar pyrolyzer.[55] These systems are all designed to optimize liquid yields from the pyrolysis of lignocellulosic biomass. Despite the distinct differences in design and execution of these different methods, they each share several key features that allow for the maximum liquid yields. These features are important in the design of any pyrolysis reactor where high liquid yields are the primary goal and include rapid heating rates, high heat transfer rates to the biomass, precise control of the reactor temperature, the rapid removal of the pyrolysis vapors from the reactor, and rapid cooling of these vapors.

Many of these traits can be achieved using an induction heating mechanism, which uses an AC power supply to create an oscillating magnetic field which then heats any ferromagnetic material within the confinement of induction coils. Induction heating offers a contactless heating method that meets the required pyrolysis reactor features needed for high liquid yields, which are: rapid heating rates, precise temperature control, and high energy efficiency.[22, 29, 34] Some of the associated drawbacks of this system are high initial cost and energy, low design flexibility and probable scale-up issues. Although there is limited research available in the literature on application of induction heating reactor for pyrolysis, a few detailed studies investigating the effect of a batch scale induction heating reactor shows that induction heating mechanism can be effectively used for pyrolysis of biomass as well as further bio-oil upgrading. [22, 28, 34, 49, 50]

Pyrolysis has multiple drawbacks associated with the quality of bio-oil achieved.[34] The bio-oil is rich in oxygenated compounds and has low energy content. Many studies have investigated different methods for upgrading pyrolytic bio-oil.[8, 17-19, 34] However, the composition of biomass also affects the product yield and quality.[26] This study was concerned with understanding the pyrolysis of pine sawdust, a common waste material from many forestry and industrial sectors, which demonstrates potential to be used as a biofuel feed stock [24]. Pine sawdust, like all woody biomass consists mostly of three compounds that account for the majority of its mass: cellulose, hemicellulose, and lignin, with approximately 40 % cellulose, 10 % hemicellulose, and 30 % lignin with the remainder of the biomass accounting for as extractives such as resins, oil and ash.[3]

The chemistry of pyrolysis has been vastly studied by pyrolyzing wood components separately in order to understand the reaction kinetics and pathways. [5, 39, 42, 43, 48, 53, 54] Yang et al., performed a thermogravimetric (TGA) analysis of cellulose, hemicellulose and lignin pyrolysis and investigated the temperature range at which each component breaks down. They concluded that there is no interaction among the three components on the wood.[54] Similar results were reported by Zhang et al., while studying the pyrolysis of cellulose lignin and hemicellulose and its various mixtures.[56] Beis et al., studied the pyrolysis of different types of lignin [5] and showed that the liquid yield from lignin ranges from 16-20% whereas the kinetic parameters and chemical composition varies considerably for each lignin sample.[5] While Wang et al., studied the effect of catalytic pyrolysis on individual biomass components and showed that cellulose contributed to maximum aromatic yield.[52] Hilbers et al., studied the lignin-cellulose interaction and found that lignin enhances yields of levoglucosan but deceases the yield of dehydration products.[23] Studies have shown that the cellulose fraction is the primary contributor to the production of bio-oils, and that lignin is the primary fraction of biomass to contribute to the char yields.[10, 42, 48] Qu et al., studied the pyrolysis of three major components of wood namely, cellulose, hemicellulose and lignin and showed that the additivity law can reasonably predict the bio-oil yield and quality as long as the biomass composition is known.[42] The study on effect and relationship between the three components on product yield and composition at laboratory scale is limited.[42] Although pyrolysis of wood components has been investigated previously, most of the studied were limited to micro scale pyrolysis studying the kinetics and reaction mechanism. More recently, Stefanidis et al., studied the pyrolysis of biomass components on batch scale (1.5 g sample) as well as TGA analysis along with catalytic upgrading at 500 °C in a traditional reactor and showed that there is a heat transfer lag during pyrolysis for component mixtures.[48]

In this paper we report, for the first time to our knowledge, the effect of pyrolysis of pinewood sawdust and its major components namely; cellulose and lignin using a bench scale induction heating reactor with high biomass loading (30 g). The effect of different temperatures on product yields and quality was investigated for each component (i.e. lignin and cellulose), which were never been reported before. Optimum parameters were reported. The contribution of individual component on the yield and bio-oil composition was studied and the results were compared to the ones reported in the literature. This study can have a significant and profound impact on forestry and pulp and paper industries that generate large quantities of lignin as byproducts, as well as on the nascent cellulosic bioethanol industry that produces large amounts of lignin as well.

2. Materials and Methods

2.1. Materials

The detailed procedure for preparing the pine chips is given elsewhere [21]. Briefly, the pine chips were ground to a particles size in the range of 0.5-1.0 mm in diameter length and then dried overnight at 105 °C. The moisture content of the biomass was determined to be 1.93 % by weight using an LJ16 Moisture Analyzer (Mettler Toledo, Switzerland). The dried biomass was then stored in sealed plastic bags in the freezer to minimize moisture absorption during storage until the experiments were carried out.

The cellulose and lignin were obtained from Pure Lignin Environmental Technology Ltd. (Kelowna, BC, Canada). The cellulose was rinsed thoroughly with hot water over a fine mesh to remove any remaining lignin particulates and water soluble hemicellulose. It was then placed overnight in a 100 °C oven to dry. The moisture content was determined to be 7.027 % by weight using the LJ16 Moisture Analyzer (Mettler Toledo, Switzerland). The material was then sealed in plastic bags and stored in a – 20 °C freezer to prevent water absorption. The lignin supplied was in a suspended solution that needed to be separated to acquire the pure lignin for pyrolysis. This was accomplished by evaporating off the solution leaving behind only the solid lignin fraction as per the procedure provided by Pure Lignin Environmental Technology Ltd. (Kelowna, BC, Canada). The moisture content of the lignin was 6.97 % by weight.

2.2 Equipment

An induction heating system (Low Frequency, RDO Induction L.L.C., Washington, NJ) was used to test a range of experimental temperatures from 500 to 700 °C in 50ºC increments. The details of the equipment are discussed elsewhere.[22] An infrared Omega IR2C PID controller

(Omega Engineering, Inc., Stamford, CT) was used to control the temperature of the reactor. The feedback controller used a 4 – 20 mA signal to control the power output of the induction heater.

The liquid collection system consisted of a round bottomed flask suspended in an ice bath at 0 °C and an electrostatic precipitator to prevent the bio-oil from volatilizing and also lowered their temperature to reduce the occurrence of secondary reactions. The detailed description of the collection system is given elsewhere.[22]

2.3. Experimental procedure

The biomasses (pine sawdust, cellulose, and lignin) were pyrolyzed in a batch induction pyrolysis system at five different operating temperatures: 500, 550, 600, 650, and 700 °C. These experiments were performed in triplicates in order to ensure reproducibility. Preliminary studies at 400 and 450 °C for cellulose and lignin indicated small yields of bio-oil, hence only temperatures above 500 °C were used in this study (ISE document). The biomass was weighed out in 25 g sample sizes, which were then packed into the center of the pyrolysis reaction tube. The empty collection flask was also weighed before the experiments in order close the mass balance and get accurate pyrolysis yield values. The reaction tube was placed between the induction heating coils and connected to the gas inlet and outlet. Nitrogen gas flowing at 1.0 $Lmin^{-1}$ was used to purge the system of oxygen for 20 minutes. The induction heater was then operated based on the reaction temperature. The reaction time for each temperature was previously determined.[34] The pyrolysis reaction produced bio-oil vapors along with non-condensable gases; these were carried out of the reaction chamber using the carrier gas. The vapors then flowed into the collection system that was immersed in an ice bath, where the ESP prevented the vast majority of condensable bio-oil droplets from escaping the collection system [4]. After the predetermined operation time, the induction heater was powered off and the reaction chamber was allowed to cool. The collection flask was then weighed and the oil samples were stored in a scintillation vial at – 20 °C to minimize secondary reactions. The char residue was weighed to obtain the yields. The unaccounted weight after quantifying the char and liquid yields was assumed to be non-condensable gas yield.

2.4. Characterization and analysis

The proximate analysis of the biomass samples were carried out using ASTM standards (moisture analysis: ASTM E871-82, ash content: ASTM E1755-4582, volatile matter using ASTM E872-82, while the fixed carbon was calculated from the difference. The ultimate analysis was carried out using an elemental analyzer 2400 Series 2 CHNS/O (Perkin Elmer, Inc., Waltham, MA).

The products were qualitatively analyzed to better understand the chemical make-up of the different product fractions (char, bio-oil, and non-condensable gases) of the pyrolysis reaction. Char and bio-oil samples were analyzed in a 2400 Series 2 CHNS/O (Perkin Elmer, Inc., Waltham, MA) to determine the carbon, hydrogen, and nitrogen (CHN) content of the samples. The details of the procedure are given elsewhere.[22] The water content of the liquid samples was determined using a Karl-Fischer moisture titration device (Metrohm Model 831 KF Coulometer, Riverview, FL). A GC-MS and GC-FID (Varian Saturn 2200 by Agilent Technologies, Santa Clara, CA) was used to analyze the bio-oil components and to quantify the peak areas.

2.5 Carbon and energy balances

The carbon balance (a primary contributor to the heating value) was performed to determine the carbon distribution in the pyrolysis products, which allows estimations of temperature effects on individual components yields. The energy content of the liquid products was determined by the equation presented by Scholze and Meier (2001) which compute the higher heating value (HHV) of the liquid product using the CHN analysis and Dulong's formula:[45]

$$\text{HHV(MJ/kg)} = \left[338.2 * C\,\% + 1442.8 * \left(H\,\% - \frac{O\,\%}{8}\right)\right] * 0.001$$

The energy content of the biomass and char was obtained using the equation provided by Demirbas (2004):[12]

$$\text{HHV (MJ/kg)} = 0.3856\ (\text{C}\ \% + \text{H}\ \%) - 1.6938.$$

The energy content of the gases was calculated by assuming the yields of CO and CH_4 were the only energy yielding gases produced.

3. Results and Discussion

3.1. Product yields

The proximate analysis of the raw biomass is shown in Table 1. Lignin samples displayed higher percentage of ash content compared to sawdust and cellulose as well as higher fixed carbon content. Cellulose biomass had the highest amount of volatile matter (Table 1). The product yields from pine sawdust, cellulose, and lignin pyrolysis (Figure 1) were studied to better understand the effects of reaction temperature on yields. All biomasses show a decrease in char yield as the temperature increased from 500 °C to 700 °C. However, the decrease in the cellulose char yields with respect to temperature was significantly low compared to the other two biomasses, with the absolute percentage decrease in char yield from 500 °C to 700 °C being 3.78%, 14.65 %, and 9.17% for cellulose, pinewood and lignin respectively. This indicates that cellulose is more thoroughly broken down at lower reaction temperatures than lignin and sawdust.

Table 1. Proximate and Ultimate Analysis of Biomass (in %)

Biomass		**Pinewood Sawdust**	**Cellulose**	**Lignin**
Proximate analysis	% volatile matter	81.59	87.45	58.38
	% fixed carbon	15.96	4.67	31.94
	% ash content	0.52	0.85	2.71
	% Moisture	1.93	7.03	6.97
Ultimate Analysis	% C	46.632	41.53	36.71
	% H	6.434	6.68	4.04
	% N	0.197	0.75	4.97
	% O	46.737	51.04	54.28

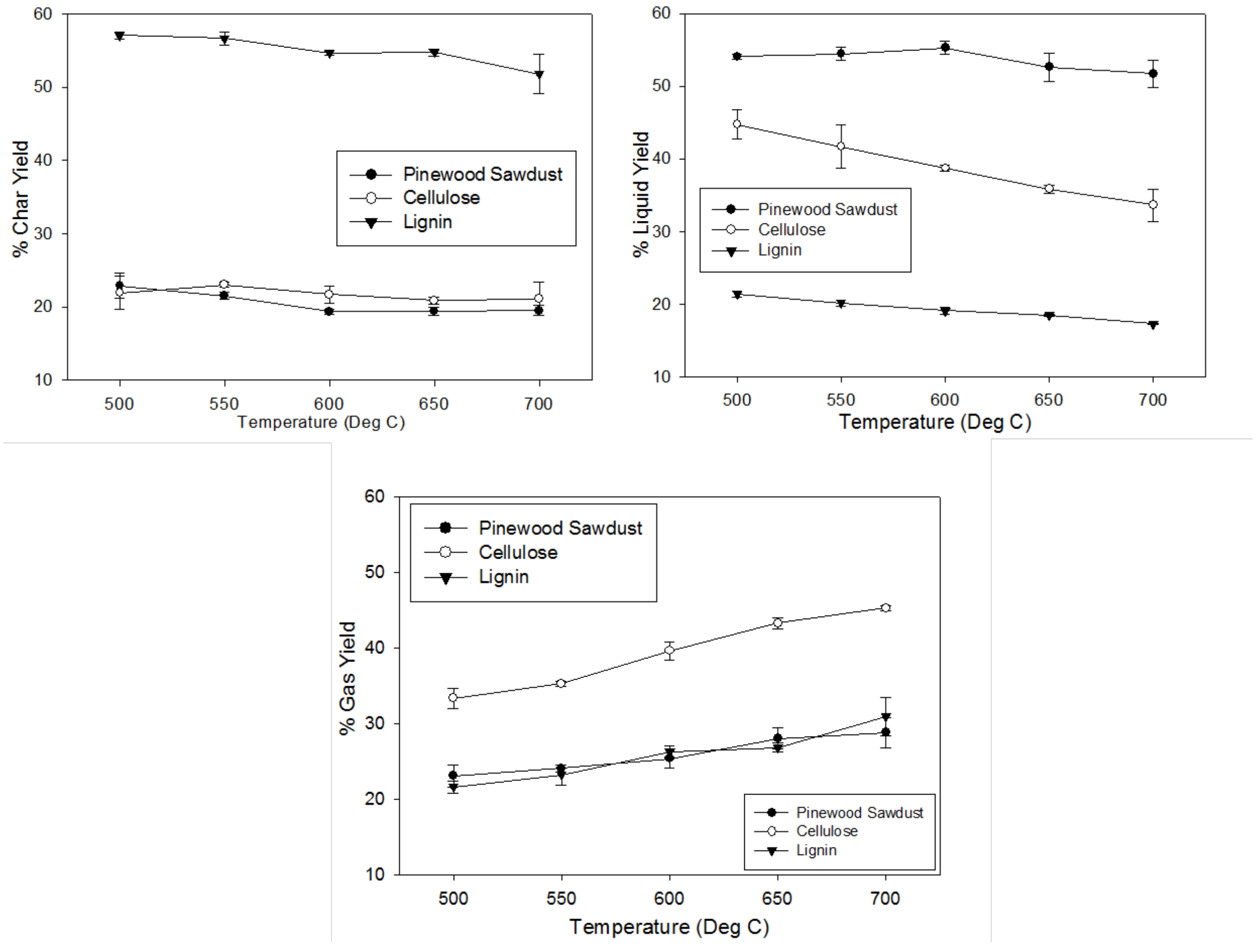

Figure 1. The yields of char, liquids, and gases indicating the effects of changing temperature on the yields from the induction pyrolysis of pine sawdust, cellulose and lignin.

These results are consistent with those reported in literature,[48, 52, 53] and can be ascribed to the physical structure of each biomass. Lignin, a complex organic polymer, is a major component of plant cell wall.[7] It is a cross linked macro molecule consisting of phenylpropane units and three aromatic alcohols (monolignols).[7] These monolignols produce an amorphous lignin polymer.[7] The complex molecular structure of lignin provides good thermal stability during pyrolysis, leading to high char yields.[46] Moreover, lignin displays a higher fixed carbon content of about 30% which also adds to the high char yield.[42] Cellulose, on the other hand, is a crystalline long chain polysaccharide compound consisting of β-linked D-glucose units.[36] Cellulose has low fixed carbon content and lower thermal stability compared to lignin; owing to its simpler molecular structure, it can be more easily broken down during pyrolysis at lower temperatures, yielding lower char yields. From the compositional analysis, sawdust comprises of 40% cellulose and 30% lignin with the rest being hemicellulose and resins. These results demonstrate the impact cellulose and lignin have on the pyrolysis yields of lignocellulosic biomass. However, simple mass balance (additivity) could not be applied in our case to estimate the exact contribution of cellulose and lignin on the product yield from pyrolysis of sawdust based on the compositional analysis of biomass. We did not find any evidence on the interaction between the components, which could be due to high initial biomass loading (30 g), higher the loading, higher is the intra-component interaction in both solid and gas phase. These results are consistent with the literature data that exclusively study the evidence of interaction between biomass components[11]. These results are consistent with literature which state that lignin is the primary contributor to the char yield of pyrolysis of woody biomass.[48] The remaining char yields for the pine sawdust can be attributed to partial degradation of hemicellulose and resins, which are otherwise removed during the cellulose/lignin purification process used in this study.

The liquid yield decreased as the temperature increased[20, 47] reaching a minimum of 33.63 % and 18% achieved at 700 °C for cellulose and lignin respectively. The highest liquid yield of 55.28 % was obtained from pine sawdust at 600 °C (Figure 1). The maximum liquid yield for cellulose and lignin was 44.68 % and 22% respectively, obtained at 500 °C. This indicates that a large portion of the bio-oil is derived from cellulose. These result are consistent with those reported in the literature.[48] [51] However, for a conventional batch scale reactor, the liquid yield from cellulose at 500 ºC was reported to be 68% [48] which is substantially higher than our results. This could be because of higher initial biomass loading (25 g vs 1.5 g for conventional reactor). Product yields tend to decrease with process scale up. The remaining liquid yield of pine sawdust can be attributed to the hemicelluloses and resins, which were not investigated here separately. The reason for higher contribution to bio-oil from cellulose could be due to the fact that while lignin primarily consists of polyaromatic hydrocarbons and complex organic compounds, cellulose is mainly made of carbohydrates such as levoglucosans. The thermal stability of carbohydrates is much lower compared to that of phenols, furfurals and ketones present in lignin and thus decomposes more easily, resulting in higher liquid yields.[42] Pyrolysis temperature has a profound effect on the yield of bio-oil as it defines how the volatile matter is broken down. At lower temperatures 300-450 ºC, carbonization reaction is dominant and yields are lower as the volatile matter evaporates. When the temperature rises to 500-600 ºC, the volatile matter is released at higher rate, increasing the liquid yield however as the temperature increases beyond this point, the volatile matter is further broken down to form incondensable gases. The intermediate instable compounds are also cracked to smaller molecules which may escape at room temperature, decreasing the bio-oil yield.[34, 42]

As expected, all biomasses exhibited an increase in the gas yields as the pyrolysis temperature increased from 500 °C to 700 °C. Lignin displayed the largest percentage increase in gas yields of 43.01% followed by cellulose (35.6%) and pine sawdust (24.6%). The trend of increased gas yields as reaction temperature increased has been shown in previous studies;[34] it is due to the more complete breakdown of the biomasses at the higher reaction temperatures.[1, 9, 32, 34] The optimum operating conditions for highest overall energy efficiency are explored in the energy balance discussion section. No significant effect of induction heating was observed on the product yields.

3.2. Water content of the liquid fraction

Figure 2 shows the results of Karl Fischer titrations performed on the liquid fractions to determine the water yield of the bio-oil. The initial moisture content of the biomass is reported elsewhere. The water yield was found to be significantly high at all temperatures for all biomass types; this has previously been reported to be a side effect of induction pyrolysis.[28, 50] The maximum liquid yield of pine sawdust was shown to occur at 600 °C; the water yield at this temperature was 45.82 % of the liquid fraction. The water yield from cellulose pyrolysis was a maximum of 60.21 % of the liquid yield at 600 °C. The water yield followed a slight negative trend as the reaction temperature increased; this paralleled the negative trend seen in the total liquid yield in the pyrolysis of cellulose. The water yields from lignin pyrolysis was significantly higher than that of the pine sawdust and cellulose, ranging from 69.48 – 76.90 %. This observation is consistent with the reaction mechanisms proposed in the literature,[6] with water formation due to prevalent dehydration of lignin when pyrolyzed.[6] High water content is also a result of the presence of hydrogen bonding between hydroxyl groups and other oxygen bonds in the lignin. [27, 38] Splitting of OH functional group on the aliphatic side chains result in water formation. [38]Additionally, water formation can be considered an indication of deoxygenation reaction from bio-oil as oxygen is removed in the form of water and CO_2. Pinewood sawdust had the highest liquid yield and lowest water content compared to cellulose and lignin pyrolysis.

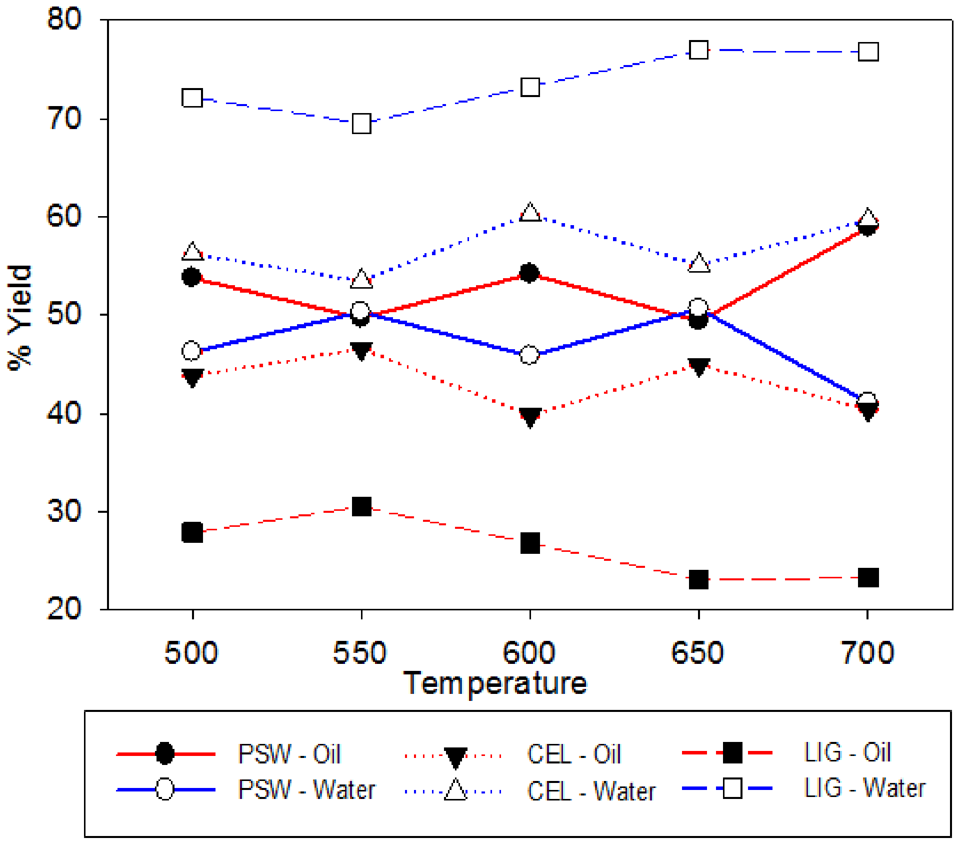

Figure 2. The KF titrations of the three biomasses pine sawdust, cellulose, and lignin. Showing the change in water content of the bio-oil and the bio-oil as a fraction of the total mass compared to reaction temperature.

3.3. Characterization of char

An elemental analysis of the char products was compared to the unpyrolyzed biomass, (Table 2). The unburned pine sawdust sample has a carbon content of 46.63 % almost half to that of the char when processed at 500 °C (81.19 %). This significant change indicates that the oxygen content of biomass, which accounts for the majority of the remaining mass in the unburned biomass CHN, has been significantly reduced during the pyrolysis process. The CHN analysis of char obtained from cellulose pyrolysis show a decrease in carbon content with carbon content of 79.45 % when processed at 500 °C except at 650 °C. The carbon content of unburned cellulose and lignin was 41.53% and 48.34% respectively and follows the same trend as pinewood sawdust. The increase in carbon content is a result of the overall reduced char mass, and the remaining char becomes an increasingly condense carbon matrix [44]. The more reactive oxygen and hydrogen are removed leaving behind a higher concentration of carbon in the char. However, this phenomenon is less pronounced for lignin char fraction of increasing carbon content compared to cellulose and sawdust. The carbon content increases from 500 ºC to 550 °C , but then begins to decline at the higher reaction temperatures, eventually leaving less carbon in the char than was present in the unburned biomass at 700 ºC. This could be a result of the complex and tightly bound structure of lignin, which reduces the heat and mass transfer rate, or from the presence of molecules that were untested for such as sulfur which disrupt the carbon matrix and change the chemical reactions that take place on the surface of the biomass during pyrolysis.[44] Table 2 indicated that a high amount of oxygen is present in the lignin chars even after processing at higher temperatures. These results are consistent with the literature data which also shows that most of the oxygen present in the char is phenolic in nature.[46] High nitrogen content in lignin chars could be a result of presence of nitrogen in original lignin samples, some of which is evolved as volatile nitrogen compounds such as HCN or NH_3 and the remainder is trapped in the char.[25]

Table 2. The CHN analysis results of the char yields from the induction pyrolysis of pine sawdust, cellulose, and lignin compared to the CHNO analysis of their respective biomasses.

Biomass	Temperature (°C)	% Carbon	% Hydrogen	% Nitrogen	% Oxygen
Pine sawdust	Unburned	46.632	6.434	0.197	46.737
	500	81.188	3.498	0.338	14.975
	550	85.997	3.088	0.374	10.541
	600	88.499	2.435	0.527	8.538
	650	89.703	2.009	0.753	7.534
	700	88.516	1.891	1.460	8.133
Cellulose	Unburned	41.531	6.679	0.749	51.041
	500	79.187	3.190	0.998	16.626
	550	76.742	3.291	0.668	19.299
	600	76.274	3.439	0.550	19.737

	650	82.622	1.940	0.535	14.903
	700	78.574	2.470	1.073	17.883
Lignin	Unburned	36.707	4.036	4.974	54.283
	500	46.458	1.754	3.817	47.972
	550	38.251	1.027	2.770	57.953
	600	38.251	0.761	2.243	58.747
	650	36.894	0.874	2.501	59.732
	700	30.680	0.761	2.243	66.318

3.4. Characterization of the liquid fraction

The bio-oil liquid fraction (without water) was characterized using two methods CHN analysis and GC-MS analysis. Table 3 shows the percentage of Carbon, Hydrogen, and Nitrogen in the liquid samples on a weight basis. The oxygen content of the liquid fraction was calculated from the difference. Bio-oil liquid fraction obtained from the pyrolysis of pine sawdust yielded higher carbon content and lower nitrogen content than its subcomponents cellulose and lignin. Higher carbon content could be contributed by bio-oil from hemicellulose, as bio-oil from hemicellulose has been reported to have high content of acids, aromatics, esters and ketones.[42] The oxygen content of the liquids obtained from the pyrolysis of cellulose were much higher than lignin and sawdust, this can be shown by the higher initial oxygen content of the cellulose based upon its chemical formula $(C_6H_{10}O_5)_n$ as compared to $(C_{31}H_{34}O_{11})_n$ of lignin. The maximum oxygen content of the bio-oil from cellulose was 47.76 % at 650 °C, as compared with 25.61 % for pine sawdust at 500 °C and 44.56% for lignin at 550 °C. Lower oxygen content for pinewood bio-oil could be due to high carbon content contributed by hemicellulose. The liquid fraction obtained from the lignin biomass had high hydrogen and nitrogen contents as nitrogen content of the bio-oil excessively depends on the biomass feedstock composition.[14, 35] In this case, unburned lignin had high nitrogen and hydrogen content.

Table 3. The CHN analysis of the liquid fraction showing the change in composition of the bio-oil fraction between the three biomasses due to the change in the pyrolysis reaction temperature

Biomass	Temperature (°C)	% Carbon	% Hydrogen	% Nitrogen	% Oxygen
Pine sawdust	500	59.95	13.74	0.69	25.60
	550	71.12	13.45	0.14	15.27
	600	69.80	10.60	0.13	19.45
	650	65.53	14.06	0.16	20.23
	700	63.87	13.18	0.15	22.77
Cellulose	500	50.45	15.26	0.47	33.80
	550	47.36	12.60	0.41	39.62
	600	57.47	16.55	0.53	25.44
	650	35.28	16.63	0.31	47.76
	700	40.85	19.39	0.39	39.35
Lignin	500	29.59	28.24	13.02	29.15
	550	20.65	23.41	11.35	44.56
	600	22.42	25.93	11.78	39.86
	650	25.72	31.99	17.38	24.89
	700	22.44	31.26	17.31	28.97

The GC-MS spectra of the liquid products were also analyzed (using the method reported by Olazar et al.)[2] to quantify the peak areas of certain compound groups including: ketones, aldehydes, alcohols, acids, phenols, levoglucosans, and fatty alcohols.[37] The quantification of the GC-MS is shown in Table 4. The bio-oils obtained from pyrolysis of cellulose yielded high amount of anhydro-sugars, mainly levoglucosan (40-50%) which is consistent with the previously reported studies.[40, 42, 47] Since cellulose is mainly a glucose polymer, at high temperatures, thermal decomposition disrupts the polymer chain at the glucosidic bond forming anhydrosugars.[40] The formation of levoglucosan is due to the intramolecular rearrangement of the monomer units as per a detailed mechanism given by Piskorz et al. [40, 47] The formation of other anhydrosugars demand high energy compared to formation of levoglucosan and hence are obtained in smaller amounts. Although cellulose bio-oil has highest contribution to the bio-oil from pinewood sawdust, the amount of anhydrosugars in pine wood bio-oil was low, ranging from 6-8%. This is due to secondary reaction involving decomposition of levoglucosan to produce acetaldehyde and other stable products.[47, 57] The lignin GC-MS data revealed that all temperatures yielded high concentration of phenolic compounds; similar results have been reported in literature.[42] Other compounds were not detected in our system for lignin bio-oil, however small amounts of esters and acids have been reported in literature.[42] The phenol yield is much higher in the liquids derived from sawdust; this can be accounted for by the contribution of lignin to the liquid yields [51]. The GC-MS quantification shows that the pyrolysis of the pine sawdust and its constituents yielded a complex mixture of oxygenated compounds, this supports what was found in the CHN analysis of the liquids. The high oxygen content of the liquid product indicates a low heating value of the liquid [37] and requires to be upgraded to higher quality.[34]

Table 4. The quantification (in %) of the GC-MS of the liquid fraction from pine sawdust, cellulose, and lignin

Pine sawdust	Temperature(°C)				
Compound Type	500	550	600	650	700
Furans	9.31	5.80	0.00	7.01	2.80
Ketones	4.23	5.20	10.92	9.27	16.42
Aldehydes	0.00	1.18	15.19	0.00	0.00
Alcohols	1.51	0.50	3.38	0.00	1.63
Acids	0.00	0.39	1.54	10.27	1.60
Phenols	74.46	78.18	51.91	75.42	64.75
Unidentified	1.37	1.87	9.32	0.00	5.11
Anhydro-Sugars	6.23	5.86	7.74	8.30	7.68

Cellulose	Temperature(°C)				
Compound Type	500	550	600	650	700
Furans	6.71	7.85	6.22	7.29	9.18
Ketones	10.53	9.47	11.92	5.64	6.32
Aldehydes	0.00	1.73	0.00	0.00	0.00
Alcohols	8.21	4.04	7.47	6.38	4.02
Acids	10.01	4.40	0.00	8.25	6.31
Phenols	15.94	19.69	20.74	20.68	17.50

Unidentified	4.92	5.49	2.66	3.11	5.47
Anhydro-Sugars	43.68	47.32	50.98	48.65	51.20

Lignin	Temperature(°C)				
Compound Type	500	550	600	650	700
Phenols	100	100	100	100	100

3.5 Carbon and energy balances

A carbon balance was performed on the product of the pyrolysis system, in order to determine the end point of the original carbon found in the biomass as it was pyrolyzed and collected. Table 5 shows the carbon balance for all experiments. It is observed that the carbon yield decreased in all three biomasses as the reaction temperature was increased. Gas fractions from cellulose and lignin saw an increase in carbon as the temperature was increased, with the change being more pronounced for lignin. The carbon values for gas fraction from pine sawdust did not follow a specific trend. The liquid fractions of the cellulose and the lignin both showed a decline in the carbon content as the temperature was increased. However, the liquid yields showed an increase until 600 °C and then a decrease. This data indicated that the carbon from the biomass shifted from the solid state at the lowest temperatures, to the liquid state at the more moderate temperatures, and then to the gas fraction at the highest temperatures. The shifting carbon indicates that at the higher temperatures the biomass is broken into smaller molecular structures (such as CO, CH_4 and CO_2) and that at moderate temperatures the majority of the biomass carbon can be converted into liquids.

Table 5. The Carbon balance performed on the three biomasses at the different operating conditions

Biomass	Temperature (ºC)	Input (g)	Output (g)		
		Biomass	Char	Liquid	Gases
	500	13.99	5.57	5.22	3.20
	550	13.99	5.55	5.77	2.67

PSW	600	13.99	5.14	6.27	2.58
	650	13.99	5.21	5.10	3.67
	700	13.99	5.18	5.41	3.40
CEL	500	12.46	5.21	2.96	4.28
	550	12.46	5.31	2.75	4.40
	600	12.46	4.96	2.65	4.84
	650	12.46	5.17	1.71	5.58
	700	12.46	4.98	1.66	5.82
LIG	500	11.01	7.95	0.53	2.53
	550	11.01	6.50	0.38	4.13
	600	11.01	6.27	0.34	4.40
	650	11.01	6.06	0.33	4.63
	700	11.01	4.77	0.27	5.97

An energy balance over the system for all three biomasses was conducted. The energy balance would help to determine the optimum operating temperatures. Previous studies show that induction heating has an energy efficiency for about 85%, and for a well-insulated reaction chamber, the heat losses can be reduced by 70%.[34] The energy balance for pine sawdust shows that the optimum temperature was 550 °C with the total energy ratio for biomass being 5.03. This reaction temperature also produces high liquid yield and low water yield. However this included the char which is often used for soil amelioration and not combusted for energy; if the char value is not counted to the products energy value, the optimum temperature shifts to 600 °C [13, 16, 30]. This would indicate that at this temperature the maximum liquid yields are obtained and contribute to the most efficient operating parameters. Cellulose biomass has a higher energy content compared to lignin, however since lignin bio-oil displayed a high hydrogen content, the HHV value of lignin bio-oil was higher than cellulose (32-50 MJ/kg vs 27-38 MJ/kg). Sawdust bio-oil had an average high heating value of 38 MJ/kg as expected, since lignin makes up only 25-30% of the sawdust composition (Table 6). The total energy output for sawdust was higher that both cellulose and lignin ranging from 78-82 MJ/kg (Table 6); this added energy could be attributed to compounds formed by pyrolysis of hemicellulose and resins. An overall net positive output was achieved for both biomass and system energy balance. However, induction heating should be further studied to optimize the reaction time and in turn the global energy efficiency of the process.

Table 6. The energy balance comparing the three biomasses and the energy of the products as compared with the energy of their inputs

Biomass	Temperature (°C)	Energy Inputs (MJ/kg)			Energy of the outputs (MJ/kg)				Energy Ratios Outputs/Inputs	
		Biomass energy content	Induction heater power	Estimated power after insulation	Bio-oil	Gas	Char	Total	Biomass	System - estimated
PSW	500	16.61	90.8	27.24	35.49	13.13	29.80	78.42	4.72	2.87
	550	16.61	117.2	35.16	40.71	11.21	31.64	83.56	5.03	2.37
	600	16.61	141.2	42.36	35.40	13.17	31.91	80.48	4.84	1.89
	650	16.61	174.8	52.44	38.80	12.02	31.87	82.69	4.97	1.57
	700	16.61	208.56	62.56	36.52	12.04	31.19	79.75	4.80	1.27
CEL	500	14.48	90.8	27.24	32.98	12.45	28.65	74.08	5.11	2.71
	550	14.48	117.2	35.16	27.06	11.75	27.22	66.03	4.56	1.87
	600	14.48	141.2	42.36	38.73	13.93	27.12	79.78	5.50	1.88
	650	14.48	174.8	52.44	27.31	11.80	28.05	67.16	4.63	1.28
	700	14.48	208.56	62.56	34.70	11.84	25.83	72.37	4.99	1.15
LIG	500	8.45	90.8	27.24	45.50	10.39	10.57	66.46	7.86	2.43
	550	8.45	117.2	35.16	32.73	10.53	4.58	47.84	5.66	1.36
	600	8.45	141.2	42.36	37.80	10.58	3.76	52.14	6.17	1.23
	650	8.45	174.8	52.44	50.37	10.89	12.17	73.43	8.68	1.40
	700	8.45	208.56	62.56	47.47	11.13	3.27	55.33	6.54	0.88

4. Conclusion

In this study, the batch inductive-heating pyrolysis of pine sawdust, cellulose, and lignin were conducted in a fix-bed heating system with high initial biomass loading. The char yields decreased with temperature for all of the biomasses, and the carbon content in the char yields increased in the pine sawdust and cellulose pyrolysis. The maximum liquid yield was achieved at 600 °C for pine sawdust, and the highest liquid yields for cellulose and lignin were obtained at

500 °C. The fact that the cellulose and lignin liquid yields are significantly lower than that of the pine sawdust indicate that the higher liquid yields seen in the pine sawdust are a result of the pyrolysis of other structures, i.e. hemicelluloses and resins. Water content of the liquid fraction tended to decrease as reaction temperature increased. The high amount of water indicates that water is produced during the pyrolysis reactions as the initial moisture content of biomass was maintained under 8%. CHN analysis of the bio-oil product shows high levels of oxygen in the liquid products, and a significant difference between the carbon contents of the liquids showing that bio-oil obtained from pine sawdust has much higher carbon content and therefore a higher heating value. The GC-MS revealed that the majority of the liquid consisted of phenolic and oxygenated hydrocarbons, with lignin displaying a higher content of phenolic compounds as the GC-MS revealed no other groups in the resulting bio-oil.

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Electronic supplementary information

Pyrolysis of lignin and cellulose was studied at 400 ºC and 450 ºC. The product yield data is given below.

Table S.1. Products yield from pyrolysis of pine sawdust, lignin and cellulose at different temperatures.

Biomass	Temperature °C	Char Yield %	Liquid Yield %	Gas Yield %
PSW	500	22.86%	54.03%	23.11%
PSW	550	21.50%	54.42%	24.08%
PSW	600	19.36%	55.28%	25.37%
PSW	650	19.38%	52.59%	28.03%
PSW	700	19.51%	51.68%	28.81%
CEL	**400**	**32.41%**	**34.73%**	**32.86%**
CEL	**450**	**29.06%**	**39.22%**	**31.72%**
CEL	500	21.94%	44.68%	33.38%
CEL	550	23.04%	41.64%	35.31%
CEL	600	21.68%	38.69%	39.63%
CEL	650	20.88%	35.84%	43.28%
CEL	700	21.11%	33.63%	45.26%
LIG	**400**	**63.02%**	**17.33%**	**19.65%**
LIG	**450**	**59.92%**	**19.28%**	**20.80%**
LIG	500	57.03%	21.34%	21.62%
LIG	550	56.64%	20.13%	23.22%
LIG	600	54.66%	19.06%	26.29%
LIG	650	54.73%	18.43%	26.83%
LIG	700	51.80%	17.28%	30.92%

Highlights

- Pine sawdust, lignin, and cellulose were pyrolyzed using induction heating reactor
- Increasing temperature (500 to 700°C) increased gas yield and decreased liquid yield
- Cellulose had higher bio-oil yields than lignin; lignin had highest char yields
- Cellulose bio-oil was rich in anhydrosugars; bio-oil from lignin was rich in phenols
- Overall net positive energy output was achieved for all biomass types and the induction heating reactor