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# Fast Pyrolysis of Lignin Using a Pyrolysis Centrifuge Reactor

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**ABSTRACT:** Fast pyrolysis of lignin from an ethanol plant was investigated on a lab scale pyrolysis centrifuge reactor (PCR) with respect to pyrolysis temperature, reactor gas residence time, and feed rate. A maximal organic oil yield of 34 wt % dry basis (db) (bio-oil yield of 43 wt % db) is obtained at temperatures of 500–550 °C, reactor gas residence time of 0.8 s, and feed rate of 5.6 g/min. Gas chromatography mass spectrometry and size-exclusion chromatography were used to characterize the chemical properties of the lignin oils. Acetic acid, levoglucosan, guaiacol, syringols, and p-vinylguaiacol are found to be major chemical components in the lignin oil. The maximal yields of 0.62, 0.67, and 0.38 wt % db were obtained for syringol, p-vinylguaiacol, and guaiacol, respectively. The reactor temperature effect was investigated in a range of 450–600 °C and has a considerable effect on the observed chemical components and molecular mass distribution of the lignin oils. The obtained lignin oil has a very different components composition when compared to a beech wood oil.

## 1. INTRODUCTION

Lignin, with a typical biomass weight fraction of 15–33 wt %, is the second most abundant component in biomass<sup>1</sup> and may account for up to 40% of the biomass energy content. Lignin has a complex, amorphous cross-linked and highly branched structure,<sup>2</sup> and it is biosynthesized by nonspecific radical reactions using only a few aromatic building blocks such as p-coumaryl, coniferyl, and sinapyl alcohols derivatives.<sup>1,2</sup> Today lignin is mainly produced by the pulp and paper industry. In the near future it is expected also to appear as a byproduct in the second generation bioethanol industry based on lignocelluloses. The potential of lignin produced as a residue in the paper industry is more than 50 million tons/year, but only about 2% of the lignin residue is used as commercial products for producing lignosulfonates (1,000,000 tons/year) and kraft lignins (less than 100,000 tons/year).<sup>3</sup> Most of the lignin is used as a low-value fuel for pulping boilers. Thus lignin may be a potential source for bio-oil production by fast pyrolysis.

The research on fast pyrolysis of lignin shows some initial promising results for lignin utilization.<sup>4–6</sup> However plugging/agglomeration in the fuel feeder system of a fluidized bed reactor and condenser have been observed and is probably due to low melting point of lignin and high molecular mass of lignin oil.<sup>5,6</sup> Also a low bio-oil yield of lignin fast pyrolysis (20–58 wt % db)<sup>5–7</sup> has been obtained compared to that of wood fast pyrolysis.<sup>8–10</sup> New strategies of fast pyrolysis of lignin that could enhance the lignin value have been suggested: 1) Catalyst fast pyrolysis using some kind of catalysts such as a zeolite<sup>7,11</sup> could produce a higher fraction of high value aromatics. 2) Formate-assisted fast pyrolysis<sup>12</sup> using calcium formate/formic acid as a hydrogen production source for the chemical transformation in situ could produce a bio-oil almost free of oxygen (O/C of 0.067 on dry basis).<sup>12</sup> However catalyst deactivation, decrease of bio-oil yield, and cost of formic acid are some possible barriers of these strategies. Thus efforts on reactor modifications or new reactors designs for conventional fast pyrolysis (without catalyst) are

conducted to overcome these barriers and enhance the bio-oil yield.

Bubbling fluidized bed reactors, circulating fluidized bed reactors, rotary cone reactors, auger reactors, and ablative reactors are close to commercialization for the use for fast biomass pyrolysis.<sup>13</sup> The main difference among these reactors is the applied heat transfer method, and heating rates of 700–1500 K/s<sup>14,15</sup> are often obtained. The ablative pyrolysis reactor was developed by Diebold et al.<sup>16</sup> In their approach, the centrifugal forces are used to press the biomass on to a hot surface, and a high biomass heating rate can be obtained by this technology. The pyrolysis centrifuge reactor (PCR), a type of ablative reactor, has been developed at the CHEC center at DTU Chemical engineering.<sup>15</sup> By a high centrifugal force, biomass particles can gain a heating rate of 200–2000 K/s.<sup>15</sup> The main advantage of this concept compared to fluid bed reactors is a compact design that uses a low flow rate of carrier gas, and the biomass pyrolysis is obtained without a heat carrier. Also, the PCR can treat relatively large biomass particles.

Lignin fast pyrolysis is found to be a promising method to produce monomeric phenols.<sup>6,17</sup> Guaiacols, syringols, alkyl phenols, and catechols<sup>5,6,17</sup> are known as major phenols to be present in lignin oil. These phenols are known to have economic potential in the use for petrochemical products and transportation fuels. Yields of 1.5–3, 0.8–2.6, 0.3–1.2, and 0.4–1.2 wt % (on dry basis) from lignin pyrolysis have been obtained for guaiacols, syringols, alkylphenols, and catechols, respectively,<sup>5,11,17</sup> and a total monomeric phenols yield of 5–7 wt % db<sup>5,17</sup> is also reported when pyrolyzing lignin in bubbling fluidized bed reactors.

The PCR uses centrifugal forces for obtaining a high heat transfer rate. Also the PCR reactor rotor continuously moves the lignin that is fed into the reactor by the feeder. Thus the PCR may

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provide less problems with plugging/agglomeration in the feeder compared to fluidized bed reactors. Only little information of the effects of lignin fast pyrolysis conditions with respect to temperature, gas residence time, and feed rate on product yields, monomeric phenols yields, and molecular weight distribution of bio-oil is provided by the available literature.<sup>5,6</sup> Thus the objectives of this work were to provide detailed knowledge on the lignin fast pyrolysis process and the properties of the obtained lignin bio-oil. Also, a comparison between the lignin pyrolysis and beech wood fast pyrolysis is conducted. Wood is an appropriate benchmark fuel, because there is often obtained high bio-oil yields with wood.

## 2. EXPERIMENTAL SECTION

**2.1. Experimental Apparatus.** The pyrolysis centrifuge reactor was developed at the CHEC center (Technical University of Denmark) and is described in detail elsewhere.<sup>15</sup> A sketch of the PCR is presented in Figure 1, and pictures of the reactor are shown in Figure 2. The

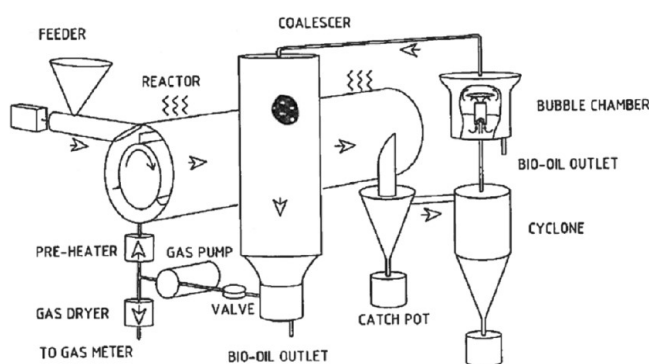


Figure 1. Sketch of the pyrolysis centrifuge reactor (PCR).

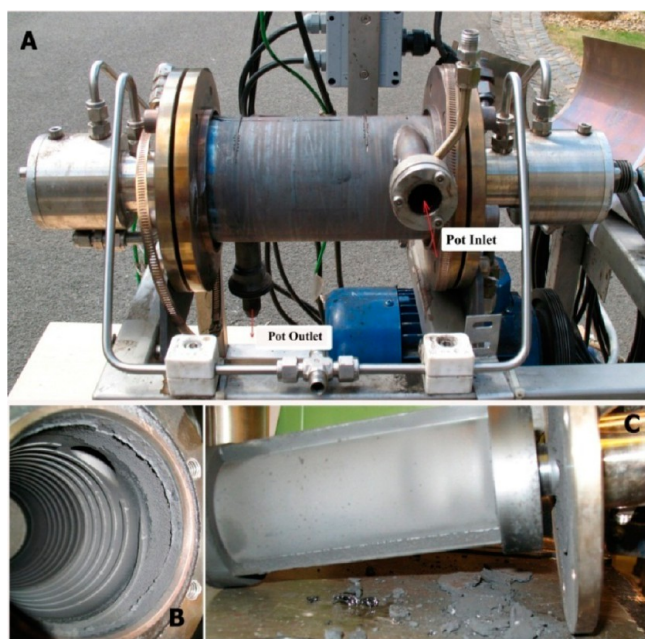


Figure 2. The reactor (A) is shown with insulation and electrical heating elements removed, reactor wall (B) and rotor (C) after few hours run with lignin pyrolysis.

centrifuge reactor is made of stainless steel and has an inner diameter of 85 mm. It is electrically heated by four independent heating zones along the reactor length. The lignin is introduced into the reactor by a screw

feeder. Pyrolysis of lignin takes place inside the reactor, whereby char, bio-oil, and gas are produced. The char particles are collected by cyclones heated to 500 °C. The bio-oil is condensed in a bubble chamber filled with isopropyl alcohol as a condensing solvent. The temperature in the bubble chamber is controlled to be 30–50 °C by means of a water cooling system. Possible ester formation reactions between isopropyl alcohol and carboxylic acids are believed to be negligible at the low temperature and in the absence of strong acid or base catalysts. The isopropyl alcohol was also used as a condensing solvent in fast pyrolysis experiments by Fonts et al.<sup>18</sup> and Trinh et al.<sup>19,20</sup> The light oil fraction and aerosols are further condensed by a coalescer filled with Rockwool. A recycled gas product is pumped back to maintain a desired reactor gas residence time (0.5–5 s). Before entering the reactor, the gas is heated to 500–550 °C. The gas products are dried by a water condenser and a gas filter to totally remove liquid before entering a gas meter.

The lignin PCR pyrolysis experiments were performed with the following operation conditions: a rotor speed of 18000 rpm, a reactor gas residence time of 0.8 s (and 4.2 s for investigation of the influence of reactor gas residence time), a total fuel feeding time of 50–62 min, a feed consumption of 204–481 g lignin for each run, and feeder rates of 4.1–10.4 g/min. The obtained mass balance closures were in the range of 93–96%.

The liquid fraction collected from the bubble chamber, coalescer, and water condenser is filtered through a Whatman filter paper (pore size of 5 μm). The char left on the filter is washed thoroughly by ethanol and then dried in an oven at 100 °C. The bio-oil yield is determined from the liquid that passed through the filter paper. The organic oil yield (db) is the bio-oil yield (db) subtracted the reaction water yield. The char yield is determined from the chars collected in the cyclones and the char left on the filter paper. The gas yield is calculated based on a gas volume determined from a gas meter and gas components compositions obtained from Gas Chromatography (GC) analyze.

**2.2. Characterization of Lignin, Bio-Oil, and Gas Products.** The applied lignin sample provided by Inbicon A/S, DONG Energy, Denmark was a dried sample of distillation residual remaining from hydrolyzed, fermented wheat straw. The wheat straw was pretreated to a severity of  $\log(R_0) = 3.70$ . The severity factor is typically expressed as a log value such that  $\log(R_0) = t \times \exp(T - T_{ref})/14.75$ , where  $R_0$  is the severity factor,  $t$  is the residence time in minutes,  $T$  is the temperature, and  $T_{ref}$  is the reference temperature, typically 100 °C.<sup>21</sup> The lignin has particle sizes of less than 840 μm. The properties of the lignin were measured by the following methods: the moisture content by ASTM D2216, the ash content by ASTM D1102-84, and higher heating value by a bomb calorimeter (IKA C-200). The element contents of the lignin sample were analyzed by flash combustion (Thermo Finnigan, Flash EA1112) for CHN, by ICP-OES axial for Cl and S, and by ICP-OES radial for Al, Fe, P, Si, Ca, Mg, K, and Na. The oxygen content was calculated by difference.

The biomass components of the lignin sample were analyzed following the NREL/TP-510-42618 protocol.<sup>22</sup> The biomasses were diluted in a strong acid for determination of the structural carbohydrates. The soluble aliquot was used to analyze sugars that are formed from decomposition of cellulose (glucan) and hemicelluloses (xylose, galactose, mannaose, arabinanose, and rhamnose) by a HPLC (Shimadzu Prominence - HPLC, Shimadzu Corporation, Kyoto, Japan, the refractive index detector (RID-10A)) with an Aminex HPX-87H Ion Exclusion column (Bio-Rad Laboratories, USA) (eluent 12 mM H<sub>2</sub>SO<sub>4</sub>, flow 0.6 mL/min, column temperature of 63 °C). The Klason lignin content was determined as the residue left after acid digestion.

Thermogravimetric analysis (TGA) of the lignin was carried out in the temperature range of 25–1000 °C at a constant heating rate of 10 °C/min in a N<sub>2</sub> flow using a TGA instrument (Netzsch STA 449 F1).

Noncondensable gas components (H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>, C<sub>3</sub>) were analyzed by a GC (Agilent Technologies, 6890N, USA, 10 ft Porapak N and 14 ft 13 × Molsieve columns) using FID and TCD detection systems and He carrier gas. The gas product collected from the PCR was sent to gas chromatography to analyze within 15 min in order to minimize the hydrogen loss.

Higher heating value (HHV) of bio-oil and char were measured by a bomb calorimeter (IKA C-200), while the HHV of the gas product is calculated based on HHV of individual gas components.

The chemical components of the bio-oils were analyzed by Gas Chromatography Mass Spectrometry (GC-MS) using a Hewlett-Packard HP 6890 Gas Chromatograph interfaced to a HP5973 Mass Selective Detector (Agilent, Denmark). Samples (1  $\mu\text{L}$ ) were injected in split mode (1:20) using an HP 7683 autosampler (Agilent, Denmark). The source and rod temperatures were 230 and 150  $^{\circ}\text{C}$ , respectively. The products were separated using a 0.32 mm i.d.  $\times$  30 m WCOT fused silica column coated with VF-23 ms at a thickness of 0.25  $\mu\text{m}$  (Analytical, Denmark). The carrier gas was He at a flow rate of 1.2 mL/min. Separation of a wide range of products was achieved using a temperature program from 70 to 250  $^{\circ}\text{C}$  at 10  $^{\circ}\text{C}/\text{min}$ . The applied ionization energy was 70 eV. Full mass spectra were recorded every 0.3 s (mass range  $m/z$  40– $m/z$  450). Products were identified using NIST search engine version 2.0 f. (Agilent, Denmark). In order to identify components in the bio-oil samples, 100  $\mu\text{L}$  of bio-oil added to the 600  $\mu\text{L}$  of deuterated phenol solution then was analyzed on GC-MS. In order to quantify some of the identified components in the bio-oils, standard solutions were added to each sample, with known amounts of the compounds of interest. Standard solutions of glacial acetic acid, o-guaiacol, syringol, and p-vinylguaiacol were prepared in isopropyl alcohol. 100  $\mu\text{L}$  of bio-oils was taken, and 600  $\mu\text{L}$  of the standard solutions was mixed in. Blank samples were prepared using bio-oil and deuterated phenol solutions. Besides the compound identification, calculations were carried out to estimate the amount of organic compounds in the bio-oils, separated by GC-MS. The total peak area for all eluted compounds was calculated for each lignin sample, and the area of the added deuterated standard was subtracted (sum of peak areas). The known amount of deuterated phenol solution was responsible for the relevant deuterated phenol area, and it was compared with the sum of peaks areas. Hence an estimate could be made for the weight of the eluted organic compounds.

The molecular weight distribution of the bio-oils was analyzed by size-exclusion chromatography (SEC) using the following instrument: Viscotek GPCmax VE-2001 equipped with Viscotek TriSEC Model 302 triple detector using two PLgel mixed-D columns from Polymer Laboratories. The samples were run in THF at 30  $^{\circ}\text{C}$  (1 mL/min). The molar-mass characteristics were calculated using polystyrene standards. In order to take a representative sample for the analysis the bio-oils were diluted with ethanol to make it homogeneous and then passed through a 0.2  $\mu\text{m}$  filter.

### 3. RESULTS AND DISCUSSION

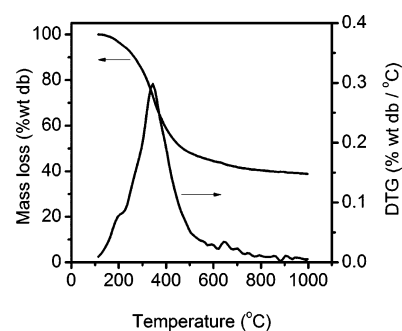
The properties of lignin were measured and can be seen in Table 1. The lignin has a volatile content of 61.2 wt % on dry basis (db) (determined at 950  $^{\circ}\text{C}$ ) and an ash content of 12.1 wt % db and a relatively low potassium content of 0.13 wt % db. The potassium content is important as it is found to influence the pyrolysis process through catalysis that increases the char formation and decreases the production of bio-oil.<sup>7,23,24</sup> The lignin was collected from a wheat straw ethanol plant, and it was thus treated and washed several times; consequently although the lignin has a high ash content, it contains a relatively low potassium content when compared to virgin wheat straw.<sup>24</sup> The lignin sample has a Klason lignin content of 78.8 wt % dry ash free basis (daf) and a higher heating value (HHV) of 22.4 MJ/kg db.

Figure 3 shows the TGA and DTG profiles of the lignin sample. The thermal decomposition appears in a temperature range of 150–550  $^{\circ}\text{C}$ . A main temperature peak at 350  $^{\circ}\text{C}$  and a shoulder at 220  $^{\circ}\text{C}$  were observed in the DTG curve. The peak and the shoulder are believed to correspond to decompositions of lignin having a content of 79 wt % daf<sup>5,6</sup> and hemicellulosic components,<sup>25</sup> respectively. The TGA and DTG of lignin results are consistent with data in the literature.<sup>5,6</sup> The TGA char yield at 550  $^{\circ}\text{C}$  is 46 wt % db.

**Table 1. Lignin Properties**

parameter	value
moisture (wt %)	4.7
volatile (wt % db)	61.2
fixed carbon (wt % db)	26.7
ash (wt % db)	12.1
HHV (MJ/kg on db)	22.4
elemental content (wt % db)	
C	57.8
H	5.7
O <sup>a</sup>	23.6
N	1.2
Cl	0.02
S	0.14
Al	0.07
Fe	0.30
P	0.06
Si	4.18
Mg	0.02
Ca	0.43
K	0.13
Na	0.28
biomass components (wt % daf)	
Klason lignin <sup>b</sup>	78.8 $\pm$ 0.23
cellulose	8.3
glucan	8.3
hemicellulose	3.6
xylose	2.7
galactose	0.7
mannose	trace
arabinose	0.2
rhamnose	trace

<sup>a</sup>By difference. <sup>b</sup>The Klason lignin content was determined as the residue left after acid digestion.



**Figure 3.** TGA and DTG profiles of lignin.

Compare with wood, lignin is generally found to be more difficult to use in a fast pyrolysis reactor.<sup>6</sup> Pluggings/agglomerations in the feeder of fluidized bed reactors are reported when pyrolyzing a pure lignin material.<sup>5,6</sup> The PCR lignin fast pyrolysis experiments were also observed to be more difficult than that of wood, straw, or algae<sup>19</sup> because of plug formation in the tubes between the reactor outlet and the condenser. A plug at the pot outlet (char pot) was observed within 10 min of the PCR operation at a pyrolysis temperature of 400  $^{\circ}\text{C}$  and a feed rate of 10.4 g/min (see the char block in Figure 4). Melting of the





Figure 4. The block at outlet pot.

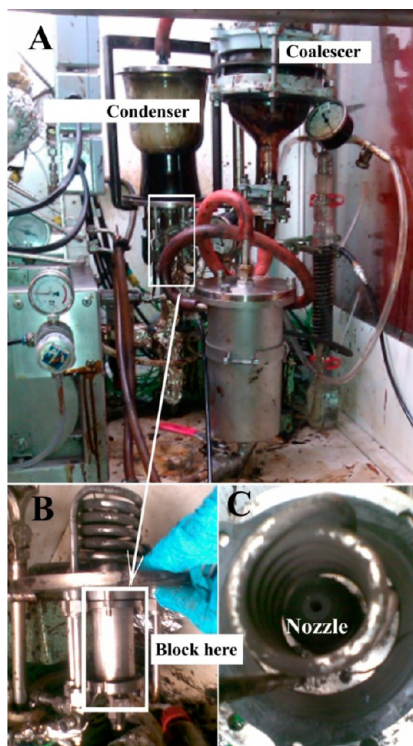


Figure 5. The block at nozzle (A: bio-oil condensing system, B: nozzle in front view, C: nozzle in top view).

unconverted lignin at low temperature and consequently its agglomeration at the pot outlet probably cause the plugging. The phenomenon disappears when the reactor temperature is higher than 450 °C.

However a plugging of the nozzle connecting the cyclone and the condenser on the laboratory PCR (see Figure 5) appeared after 60–70 min operation at the runs conducted at temperatures higher than 450 °C. The deposits probably contain heavy tar and fine lignin char particles (particles with a size smaller than 10  $\mu\text{m}$  that cannot be separated efficiently in the cyclones). The nozzle has a low temperature, and this may cause the plugging. Furthermore, the nozzle diameter of 4.8 mm may be too small to avoid the plug for a long PCR test. The limitations can probably be solved for longer tests of lignin pyrolysis with modifications of the nozzle and adding a hot gas filter that may remove the fine char particles.

The results of the effect of changed pyrolysis conditions with respect to temperature, reactor gas residence time, and feed rate on product yields distribution are presented in Figures 6–8. The effect of temperature on lignin pyrolysis product yields is

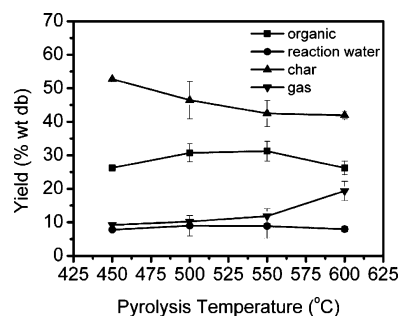


Figure 6. The effect of pyrolysis temperature at a reactor gas residence time of  $0.8 \pm 0.07$  s and a feed rate of 10.4 g/min.

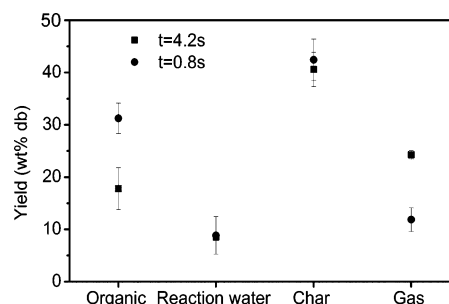


Figure 7. The effect of reactor gas residence time at temperature of 550 °C and feed rate of 10.4 g/min.

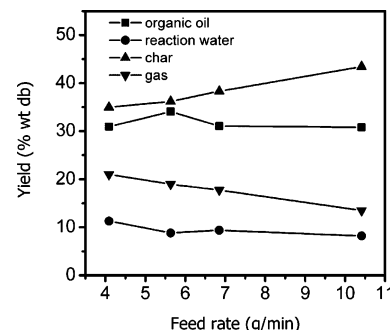


Figure 8. The effect of feed rate at reactor gas residence time of 0.8 s and temperature of 550 °C.

observed to be similar to that of wood pyrolysis.<sup>26</sup> A maximal organic oil yield of 30–31 wt % db is obtained at temperatures of 500–550 °C (see Figure 6). A decrease of the organic oil yield from 31 to 25 wt % db is observed when the temperature is increased from 550 to 600 °C. The decrease of the organic oil yield together with a large increase of the gas yield indicate that secondary reactions are important at temperatures higher than 550 °C, and the phenomena is consistent with other biomass fast pyrolysis studies.<sup>27,28</sup> A decrease of the char yield from 53 to 43 wt % db and an increase of the gas yield from 9 to 20 wt % db were obtained when increasing the temperature from 450 to 600 °C. In contrast the water reaction yield of 8 wt % db seems not to be significantly influenced by the pyrolysis temperature.

The reactor gas residence time has a large influence on the organic oil yield and gas yield (see Figure 7). The organic oil yield decreases from 31.2 to 17.8 wt % db, and the gas yield increases from 11.8 to 24.3 wt % db when the reactor gas residence time increases from 0.8 to 4.2 s. Cracking of organic vapors (secondary reactions) to generate noncondensable gases increase with a longer gas residence time,<sup>27,28</sup> and this explains the results.

**Table 2. Proximate Analysis of the Char Sample Produced at Temperature of 550 °C, Reactor Gas Residence Time of 0.8 s, and Feed Rate of 10.4 g/min**

parameter	value
volatile (wt % db) <sup>a</sup>	26.2
fixed carbon (wt % db)	46.4
ash (wt % db)	27.4

<sup>a</sup>Determined at 950 °C.

The char obtained at the temperature of 550 °C, with a reactor gas residence time of 0.8 s and a feed rate of 10.4 g/min, has a volatile content of 26.2 wt % and an ash content of 27.4 wt % (see Table 2). Because of the high char volatile content it may be possible to enhance the organic oil yield if the PCR pyrolysis conditions are optimized.

Bio-oil yield depends on feed rate, gas residence time and pyrolysis temperature.<sup>29</sup> The feed rate is often investigated to determine a maximal capacity of a reactor for bio-oil production obtaining a high yield. An increase of the feed rate at a constant temperature is known to slightly increase bio-oil yield<sup>29–31</sup> in fluidized bed reactors. An initial increase of the feed rate possibly increases the amount of gas produced at temperatures of 450–550 °C, and probably minimizes secondary reactions. However, a further increase of the feed rate will reduce the heating rate of the biomass particles, leading to a decreased bio-oil yield. In this study the feed rate is investigated in a range of 4.1–10.4 g/min. The organic oil yield obtains a maximum of 34 wt % db at a feed rate of 5.6 g/min (see Figure 8) and slightly decreases from 34 to 31 wt % db with an increasing feed rate from 5.6 to 10.4 g/min, while the gas yield decreases from 21 to 13 wt % db and the char yield increases from 35 to 43 wt % db with an increasing feed rate from 4.1 to 10.4 g/min.

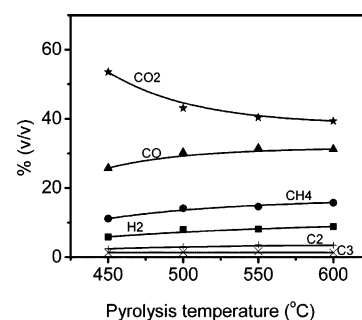
At the maximal organic oil yield of 34 wt % db, a PCR char yield of 36 wt % db was obtained at a temperature of 550 °C, a reactor gas residence time of 0.8 s, and a feed rate of 5.6 g/min. The char yield is 10 wt % lower than the TGA char yield at 550 °C (46 wt % db) and 3 wt % lower than the TGA char yield at 950 °C (39 wt % db) (see Figure 3). This indicates that the lignin PCR fast pyrolysis probably obtained optimal conditions for a maximal organic oil yield.

The feedstock ash influences the pyrolysis products distribution of biomasses.<sup>8,23,32</sup> However the roles of the individual ash

components on the pyrolysis process are not well understood. Potassium has been found to considerably catalyze the pyrolysis<sup>8,23,24</sup> by decreasing the bio-oil yield and increasing the gas and char yield,<sup>8,32</sup> whereas silicate seems to be inactive to pyrolysis of biomass. The feedstock lignin content has a major influence on the product distribution.<sup>8,32</sup> The lignin component produces a low bio-oil yield and a high char yield compared to cellulose.<sup>5,6</sup> Table 3 summarizes data on feedstock ash, potassium and lignin contents, with pyrolysis product yields of wood and lignin. With a low potassium content (less than 0.12 wt % db) and a lignin content of 16–29 wt % daf, wood fast pyrolysis often provides a high bio-oil yield of 67–76 wt % daf.<sup>8–10</sup> Thus wood is considered as the best material for producing bio-oil. Lignin samples from ethanol plants and pulp and paper mills have a negligible potassium content (less than 0.13 wt % db)<sup>5,6</sup>

**Table 4. Higher Heating Value (HHV) of the Lignin Pyrolytic Products and Energetic Distribution at the Reactor Pyrolysis Temperature of 550 °C, Reactor Gas Residence Time of 0.8 s, and Feed Rate of 10.4 g/min**

pyrolysis products	HHV (MJ/kg) on dry feedstock basis	product yields (wt % dry feedstock basis)	energetic yield (%)
gas	10.6	13.1	6.3
bio-oil <sup>a</sup>	24.8	40.3	44.6
char	20.6	42.7	39.2
total	-	96.1	90.1

<sup>a</sup>A water content of 20 wt % that is reaction water.**Figure 9.** The effect of pyrolysis temperature on gas components at reactor gas residence time of 0.8 s and feed rate of 10.4 g/min.**Table 3. Relation of the Lignin, Ash Content, and Potassium Content of Biomasses and the Pyrolytic Product Yields**

sample	lignin content (wt % daf)	ash content (wt % db)	K content (wt % db)	yield (wt % daf) <sup>a</sup>			tech <sup>b</sup> -temp	ref
				bio-oil	char	gas		
Wood								
beech	24	2.7	0.14	68	12	19	PCR, 550 °C	this study
beech	22	0.7	0.12	67	10	23	FBR, 470 °C	10
spruce	29	0.4	0.04	67	10	23	FBR, 470 °C	10
poplar aspen	16	0.4	-	76	14	11	FBR, 500 °C	9
willow	20	1.3	0.20	70	21	9	FBR, 507 °C	8
Lignin								
straw lignin	79	12	0.13	47	27	19	PCR, 550 °C	this study
alcell lignin	96	0	-	39	43	21	FBR, 500 °C	5
granit lignin	90	<2	-	48	39	15	FBR, 500 °C	5
organosolv lignin	96	0.0	-	55	36	15	FBR, 500 °C	5
organosolv lignin	95	0.1	-	52	31	17	FBR, 500 °C	5
ALM lignin <sup>c</sup>	94	1.1–1.3	0.04	31	48	6	FBR, 530 °C	6

<sup>a</sup>The bio-oil yield on daf was calculated from available data. <sup>b</sup>FBR: fluidized bed reactor, PCR: pyrolysis centrifuge reactor. <sup>c</sup>The ALM lignin manufactured by Asian Lignin Manufacturing India Pvt. Ltd. was a coproduct in the manufacture of pulp for printing and writing papers.

Table 5. GC-MS Results on % Peak Area of Bio-Oils

component <sup>a</sup>	% peak area					
	lignin oil <sup>b</sup>					wood oil
	450 °C, 0.8 s <sup>c</sup>	500 °C, 0.8 s	550 °C, 0.8 s	600 °C, 0.8 s	550 °C, 4.2 s	550 °C, 0.8 s
acids	6.76	6.02	6.15	8.33	8.55	25.88
acetic acid	6.76	6.02	6.15	8.33	8.55	25.88
nonaromatic ketones	3.01	2.66	2.55	3.42	3.74	13.3
hydroxyacetone	3.01	2.66	2.55	3.42	3.04	7.16
1,2-ethanediol, monoacetate	- <sup>d</sup>	-	-	-	-	3.93
1-(acetyloxy)-2-propanone	-	-	-	-	-	0.73
2,3-butanedione	-	-	-	-	0.70	-
2-hydroxy-3-methyl-2-cyclopenten-1-one	-	-	-	-	-	0.69
2-methyl-cyclopentanone	-	-	-	-	-	0.79
furans	4.13	5.09	1.01	0.6	1.3	8.61
furfural	1.02	1.20	0.51	-	0.74	5.16
5-methyl-furfural	2.56	2.79	-	-	-	-
furfuryl alcohol	0.55	0.50	0.50	0.60	0.56	1.35
5-hydroxymethylfurfural	-	0.60	-	-	-	0.84
γ-crotonolactone	-	-	-	-	-	1.26
glycerol	2.48	2.12	2.91	3.36	2.38	-
levoglucosan	5.60	8.04	2.55	2.49	3.76	7.10
lignin-derived phenols	1.89	1.94	2.89	7.85	3.23	0.48
phenol	1.11	0.92	1.52	2.79	1.59	0.48
2,4-dimethylphenol	-	-	-	0.70	-	-
4-methylphenol	-	-	-	3.09	-	-
p-ethylphenol	-	-	0.73	1.27	0.78	-
2,4,6-trihydroxyphenyl-2-pentanone	0.78	1.02	0.64	-	0.86	-
guaiacols	24.35	20.94	27.4	18.26	23.56	11.4
o-guaiacol	5.50	4.65	6.18	5.40	5.78	1.85
p-methylguaiacol	2.73	2.27	3.21	2.29	2.69	1.27
p-ethylguaiacol	2.07	1.77	2.95	-	2.41	0.75
p-vinylguaiacol	8.31	7.37	9.35	7.32	7.14	2.12
isoeugenol	2.08	2.05	2.29	1.47	1.85	2.48
acetoguaiacon	0.65	0.77	0.80	-	0.83	-
coniferyl alcohol	3.01	2.06	2.62	1.78	2.86	2.93
syringols	17.16	17.03	18.3	13.12	18.34	10.3
syringol	7.39	6.88	9.03	8.77	7.79	3.08
methoxyeugenol	3.77	3.83	3.57	1.19	2.89	2.50
3',5'-dimethoxyacetophenone	3.41	2.94	3.37	2.10	3.01	2.09
syringaldehyde	0.97	0.91	0.72	-	0.73	0.74
acetosyringone	1.62	2.47	1.61	1.06	3.92	1.89
methoxy benzenes	3.99	3.81	4.43	2.08	4.53	3.05
trimethoxybenzene	1.93	1.75	1.95	1.13	1.70	1.29
1,2,3-trimethoxy-5-methyl-benzene	0.56	0.78	0.80	-	0.67	-
benzenemethanol, 2,5-dimethoxy-, acetate	1.50	1.28	1.68	0.95	2.16	1.76
sterols <sup>e</sup>	6.02	5.04	6.46	4.22	5.49	0.59
stigmasterol	2.06	1.47	2.84	1.78	2.53	-
sitosterol	2.79	2.01	3.62	2.44	2.96	0.59
isofucosterol	1.17	1.56	-	-	-	-
stigmastan-3,5-diene	-	0.59	0.69	-	0.91	-

<sup>a</sup>Identified components having peak area less than 0.5% are not listed in this table. <sup>b</sup>The max molecular weight observed in this study is 400–450 g/mol (in the case of sterols). <sup>c</sup>Temperature and reactor gas residence time. <sup>d</sup>Peak <0.5%. <sup>e</sup>Sterols replied on the computer's suggestion for identification.

and high lignin contents of 79–96 wt % daf, resulting in relatively low bio-oil yields of 31–55 wt % daf for fast pyrolysis. It is seen that the lignin content has a considerable effect on the bio-oil yield.

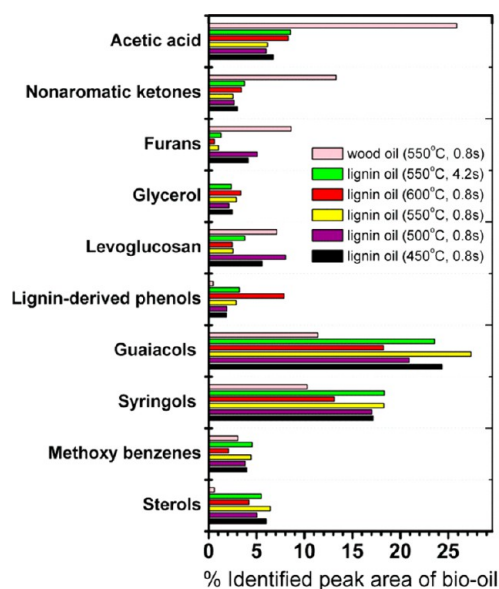
The HHV of the pyrolysis products and the energetic distribution at the reactor pyrolysis temperature of 550 °C, reactor gas residence time of 0.8 s, and feed rate of 10.4 g/min are presented in Table 4. The HHV of the lignin oil is 24.8 MJ/kg on

wet basis (a water content of 20 wt %) or 30.7 MJ/kg db. The HHV of the lignin oil seems to be higher than that of wood oil (typical value of 22–23 MJ/kg db).<sup>8,26,32</sup> This is probably related to the low oxygen content in the lignin feedstock (24 wt % db oxygen in the lignin) when compared to wood (43–47 wt % db).<sup>8,31,32</sup> By pyrolysis of lignin, 45% of the energy content is recovered in the organic oil, 6% in the gas, and 39% in the char. A poor energy recovery of the pyrolysis products (90%) is believed

to be caused of inaccuracies in analyses (e.g., water content, heating value) and a loss of pyrolysis products (4 wt %) that is probably mainly bio-oil. About 5–10% of the feedstock energy in the form of char is often combusted to provide energy for fast pyrolysis process. Alternatively the gases can be used to supply the energy need for the process.

The effect of pyrolysis reactor temperature on gas composition is presented in Figure 9. A decrease of the CO<sub>2</sub> concentration from 54 to 39 v/v % and increase of CO from 25 to 31 v/v % is observed in the temperature range of 450–600 °C. An increasing trend of CO and a decreasing trend of CO<sub>2</sub> with increasing pyrolysis temperature are found.<sup>33</sup> H<sub>2</sub> and hydrocarbon gases are produced by cracking and dehydrogenation reactions on which the temperature has a considerable influence whereby the concentrations of H<sub>2</sub> and hydrocarbon gases increase at higher temperature. The evolution trends of gas components are consistent to other literature data.<sup>27,33</sup> The concentrations of H<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub><sup>+</sup> of 8, 14, and 5 v/v%, respectively, at a temperature of 500–550 °C are similar to gas concentrations obtained by wood, coconut shell, and straw pyrolysis.<sup>27</sup>

The components of lignin oils produced at different pyrolysis temperatures and reactor gas residence times were analyzed by GC-MS. PCR wood oil produced at 550 °C and a reactor gas residence time of 0.8 s was also analyzed. The wood oil is considered as a reference source to compare with the lignin oils. An overall comparison of bio-oil properties from lignin, wood, straw, and macroalgae PCR pyrolysis with respect to HHV, molecular mass distribution, viscosity, pH, density, thermal behaviors, elemental concentrations, phase separation, and aging was published in another work.<sup>18</sup> The identified components of the lignin oils and wood oil are listed in Table 5. The main chemical groups of the lignin oils and wood oil are acids, nonaromatic ketones, furans, glycerol, levoglucosan, lignin-derived phenols, guaiacols, syringols, methoxy benzenes, and sterols (see Figure 10). Major peaks of acetic acid, levoglucosan,

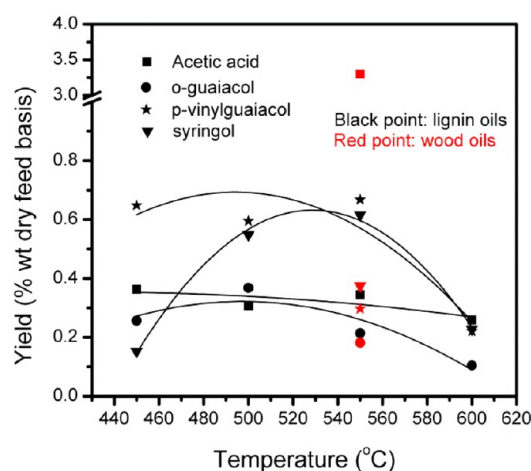


**Figure 10.** A comparison of chemical groups in the lignin oils and wood oil.

o-guaiacol, syringol and p-vinylguaiacol which have proportions of 32–40% (identified peak area) are observed in the bio-oils (see Table 5). The identified GC-MS components are estimated to account for approximately 29–38 wt % db of the bio-oil.

Levoglucosan is product of cellulose degradation,<sup>34</sup> while furans and acetic acid are found to be formed by further degradation of levoglucosan.<sup>34</sup> Phenols (guaiacols, syringols, lignin-derived phenols) are mainly believed to be formed by lignin degradations due to a difference of the lignin and cellulose contents between the wood sample (cellulose content of 40 wt % daf and lignin content of 25 wt % daf) and the lignin sample (cellulose content of 8 wt % daf and lignin content of 79 wt % daf). This may cause the large difference in the relative amount of chemical groups of the wood and lignin oils. The levoglucosan, furans, and acetic acid peak proportions obtained in the lignin oil produced at a temperature of 550 °C and a reactor gas residence time of 0.8 s are 2.6, 1.0, and 6.2%, respectively, and that are 3–10 times lower than that of the wood oil at the same pyrolysis conditions. In contrast the total amount of phenols (sum of lignin-derived phenols, guaiacols, and syringols) of the lignin oil is 48.6%, and this is 2.2 times higher than that of the wood oil. This shows that lignin fast pyrolysis is a promising method to produce phenols. The pyrolysis temperature is found to influence the produced amount of the different chemical groups (see Figure 10). The further degradation of levoglucosan probably leads to a decrease of the levoglucosan proportion and an increase of the acetic acid concentration when the temperature increases from 500 to 600 °C. Cyclization reactions and polymer polycyclic aromatic hydrocarbon formation to form larger molecular masses were found at a pyrolysis temperature range of 600–700 °C by Elliot.<sup>35</sup> These cyclization reactions probably cause a decreased proportion of methoxy benzenes, syringols, guaiacols, and furans for the 600 °C lignin oil samples when compared with the others. The effect of a reactor gas residence time change from 0.8 to 4.2 s is found to be negligible with respect to the chemical groups concentrations (except for the guaiacols group).

Four key chemical components (acetic acid, syringol, p-vinylguaiacol, and o-guaiacol) having a total peak area of 25–32% were quantified to evaluate the effect of pyrolysis temperature on the PCR lignin pyrolysis. The quantified mass yields are presented in Figure 11. The syringol, p-vinylguaiacol, and



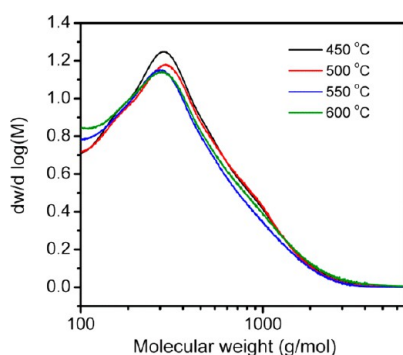
**Figure 11.** The effect of temperature on the yields of selected compounds.

o-guaiacol obtain maximal yields of 0.64, 0.76, and 0.37 wt % db, respectively, at temperatures of 500–550 °C. The acetic acid yield shows a gradual decrease from 0.42 to 0.26 wt % db when the temperature increases from 450 to 600 °C. Figure 11 also presents the acetic acid, syringol, p-vinylguaiacol, and o-guaiacol



yields of the PCR beech wood pyrolysis. As mentioned the lignin and cellulose contents have a considerable influence on phenols and acetic acid yields. Therefore, the PCR lignin pyrolysis obtains 1.7–2.5 times higher yields of the syringol, p-vinylguaicol, and o-guaicol and 10 times lower yield of acetic acid than those of the PCR wood pyrolysis.

The molecular weight distribution of the lignin oil samples is presented in Figure 12. The four oil samples obtained at the



**Figure 12.** The effect of temperature on molecular weight distribution.

different pyrolysis temperatures have nearly similar molar weight profiles. The species of the lignin oils have molecular masses in the range of 100–3000 g/mol. The amount of species with low molecular weight (100–250 g/mol) increases, and the amount of the species with high molecular weight (250–3000 g/mol) decreases with an increase in the temperature from 450 to 550 °C. This indicates that derivatives of lignin which could be oligomers with molecular mass of 250–3000 g/mol appear at higher concentration at a lower pyrolysis temperature. However when the temperature raises from 550 to 600 °C the amount of high molecular weight (250–3000 g/mol) increases again. This result is consistent with the observed decrease of phenols concentration at 600 °C due to cyclization reactions and polymer polycyclic aromatic hydrocarbon reactions (600–700 °C) by Elliot.<sup>35</sup> This probably causes an increase of the high molecular fraction. As can see in Table 6, the mean molecule mass values

**Table 6.** Mean Molecular Mass of Bio-Oils at the Reactor Gas Residence Time of  $0.8 \pm 0.07$  s and Feed Rate of 10.4 g/min

parameter	variable			
temperature (°C)	450	500	550	600
mean molecular mass (g/mol)	428	420	370	429

(420–429 g/mol) of the 450, 500, and 600 °C oil samples are higher than that of the 550 °C sample (370 g/mol). These results indicate that a higher content of the lignin derivatives is observed at the lower temperatures (450–500 °C), and a higher amount of polymers/oligomers is formed at 600 °C.

#### 4. CONCLUSIONS

A residual lignin sample from an ethanol plant with a lignin content of 79 wt % daf was successfully pyrolyzed on a pyrolysis centrifuge reactor (PCR) without plugging of feeder. However, after an hour of operation plugging at the cooling nozzle was observed. The effects of pyrolysis conditions as temperature (450–600 °C), reactor gas residence time (0.9 and 4.2 s), and feed rate (4.1–10.4 g/min) on trends of product yields were similar to those of wood fast pyrolysis. The optimal pyrolysis

conditions of the lignin PCR to obtain a maximal organic oil yield is a temperature of 550 °C, a short reactor gas residence time (0.8 s), and a feed rate of 5.6 g/min. The maximal organic oil yield of 34 wt % db (bio-oil yield of 43 wt % db) is, however, much lower than that of wood fast pyrolysis.

GC-MS analysis of the lignin oil was conducted. Yields of syringol, p-vinylguaicol, and o-guaicol obtained maximal values of 0.62, 0.67, and 0.38 wt % db, at a pyrolysis temperature of 500–550 °C. Molecular mass distributions indicate that a higher content of the lignin derivatives is formed in the lower temperature range (450–500 °C) and formation of oligomer/polymer species takes place above 600 °C.

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##### Notes

The authors declare no competing financial interest.

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#### REFERENCES

- (1) Mohan, D.; Pittman, J.; Mohan, D.; Steele, P. H. *Energy Fuels* **2006**, *20*, 848–889.
- (2) McCarthy, J.; Islam, A. Lignin chemistry, technology, and utilization: a brief history. In *Lignin: Historical, Biological and Materials Perspectives*; Glasser, W. G., Northey, R. A., Schultz, T. P., Eds.; ACS Symposium Series 742; American Chemical Society: Washington, DC, 2000; pp 2–100.
- (3) Gosselink, R. J. A.; de Jong, E.; Guran, B.; Abacherli, A. *Ind. Crops Prod.* **2004**, *20*, 121–129.
- (4) Baumlín, S.; Broust, F.; Bazer-Bachi, F.; Bourdeaux, T.; Herbinet, O.; Toutie Ndiaye, F.; Ferrer, M.; Lédé, J. *Int. J. Hydrogen Energy* **2006**, *31*, 2179–2192.
- (5) de Wild, P. J.; Huijgen, W. J. J.; Heeres, H. J. J. *Anal. Appl. Pyrolysis* **2012**, *93*, 95–103.
- (6) Nowakowski, D. J.; Bridgwater, A. V.; Elliott, D. C.; Meier, D.; de Wild, P. J. *Anal. Appl. Pyrolysis* **2010**, *88*, 53–72.
- (7) Li, X.; Su, L.; Wang, Y.; Yu, Y.; Wang, C.; Li, X.; Wang, Z. *Front. Environ. Sci. Eng.* **2012**, *6*, 295–303.
- (8) Fahmi, R.; Bridgwater, A. V.; Donnison, I.; Yates, N.; Jones, J. M. *Fuel* **2008**, *87*, 1230–1240.
- (9) Scott, D. S.; Plskorz, J.; Radleln, D. *Ind. Eng. Chem. Process Des. Dev.* **1985**, *24*, 581–588.
- (10) Azeez, A. M.; Meier, D.; Odermatt, J.; Willner, T. *Energy Fuels* **2010**, *24*, 2078–2085.
- (11) Hicks, C. J. *J. Phys. Chem. Lett.* **2011**, *2*, 2280–2287.
- (12) Mukkamala, S.; Wheeler, M. C.; van Heiningen, A. R. P.; DeSisto, W. J. *Energy Fuels* **2012**, *26*, 1380–1384.
- (13) Butler, E.; Devlin, G.; Meier, D.; McDonnell, K. *Renewable Sustainable Energy Rev.* **2011**, *15*, 4171–4186.
- (14) Janse, A. M. C.; Westerhout, R. W. J.; Prins, W. *Chem. Eng. Process.* **2000**, *39*, 239–252.
- (15) Bech, N.; Larsen, M. B.; Jensen, P. A.; Dam-Johansen, K. *Biomass Bioenergy* **2009**, *33*, 999–1011.
- (16) Diebold, J. P.; Scahill, J. W. Improvements in the Vortex Reactor Design. In *Developments in Thermochemical Biomass Conversion*; Bridgwater, A. V., Boocock, D. G. B., Ed.; Blackie Academic & Professional: London, 1997; p 242.

- (17) de Wild, P.; Van der Laan, R.; Kloekhorst, A.; Heeres, E. *Environ. Prog. Sustainable Energy* **2009**, *28*, 461–469.
- (18) Fonts, I.; Azuara, M.; Gea, G.; Murillo, M. B. *J. Anal. Appl. Pyrolysis* **2009**, *85*, 184–191.
- (19) Trinh, N. T.; Jensen, A. P.; Dam-Johansen, K.; Knudsen, N. O.; Sørensen, H. R.; Hvilsted, S. A. *Energy Fuels* **2013**, *27*, 1399–1409.
- (20) Trinh, N. T.; Jensen, A. P.; Dam-Johansen, K.; Knudsen, N. O.; Sørensen, H. R. *Energy Fuels* **2013**, *27*, 1419–1427.
- (21) Overend, R. P.; Chornet, E. *Philos. Trans. R. Soc., A* **1987**, *321*, 523–536.
- (22) Sluiter, A.; Hames, B.; Ruiz, R.; Scarlata, C.; Sluiter, J.; Templeton, D.; Crocker, D. *Carbohydrates and Lignin in Biomass Laboratory Analytical Procedure (LAP)*; Technical Report NREL/TP-510-42618; Issue Date: April 2008.
- (23) Abdullah, N.; Gerhauser, H. *Fuel* **2008**, *87*, 2606–2613.
- (24) Jensen, A.; Dam-Johansen, K.; Wojtowicz, M. A.; Serio, M. A. *Energy Fuels* **1998**, *12*, 929–938.
- (25) Sanchez-Silva, L.; Lopez-Gonzalez, D.; Villasenor, J.; Sanchez, P.; Valverde, J. L. *Bioresour. Technol.* **2012**, *109*, 163–172.
- (26) Bridgwater, A. V. *Biomass Bioenergy* **2012**, *38*, 68–94.
- (27) Fagbemi, L.; Khezami, L.; Capart, R. *Appl. Energy* **2001**, *69*, 293–306.
- (28) Boroson, L. M.; Howard, B. J.; Longwell, P. J.; Peters, A. W. *AIChE J.* **1989**, *35*, 120–128.
- (29) Mante, O. D.; Agblevor, F. A. *Biomass Bioenergy* **2011**, *35*, 4417–4425.
- (30) Choi, H. S.; Choi, Y. S.; Park, H. C. *Renewable Energy* **2012**, *42*, 131–135.
- (31) Park, H. J.; Park, Y. K.; Dong, J. I.; Kim, J. S.; Jeon, J. K.; Kim, S. S.; Kim, J.; Song, B.; Park, J.; Lee, K. J. *Fuel Process. Technol.* **2009**, *90*, 186–195.
- (32) Oasmaa, A.; Solantausta, Y.; Arpiainen, V.; Kuoppala, E.; Sipila, K. *Energy Fuels* **2009**, *24*, 1380–1388.
- (33) Jung, S. H.; Kang, B. S.; Kim, J. S. *J. Anal. Appl. Pyrolysis* **2008**, *82*, 240–247.
- (34) Aho, A.; Kumar, N.; Eranen, K.; Holmbom, B.; Hupa, M.; Salmi, T.; Murzin, D. Y. *Int. J. Mol. Sci.* **2008**, *9*, 1665–1675.
- (35) Elliot, D. C. *Analysis and comparison of biomass pyrolysis/gasification condensates – final report*; No. PNL-5943; Pacific Northwest Laboratory: Richland, WA, 1986.