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The Use of Calcium Hydroxide Pretreatment to Overcome Agglomeration of Technical Lignin during Fast Pyrolysis

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Abstract

Technical lignin extracted from lignocellulosic biomass melts and agglomerates when heated, making its thermal processing problematic and impeding this pathway to low-cost renewable aromatics. We have developed a simple pretreatment of technical lignin with $Ca(OH)_2$ that made possible the continuous pyrolysis of lignin in a fluidized bed reactor to produce a phenolic-rich bio-oil. The yield of bio-oil was approximately 38 wt% for pyrolysis in the temperature range of 450 to 600°C. Average molecular weight of bio-oil was less than 288 Da indicating that the lignin was extensively depolymerized to phenolic monomers and dimers. Char from pyrolysis of pretreated lignin was fine powder in contrast to the large agglomerates of char produced from untreated lignin. The surface area of char from pyrolysis of pretreated lignin was relatively less than for char obtained from pyrolysis of whole biomass. The melting and agglomeration behavior of lignin appears to be due to the presence of phenolic hydroxyl, carboxylic acid and aldehyde groups in lignin. Pretreatment with $Ca(OH)_2$ reduced these functional groups by forming hydroxylcalcium phenoxides, phenolic alcohols, and phenolic carboxylate salts that inhibited agglomeration.

Keywords: Lignin, agglomeration, pretreatment, pyrolysis, fluidized bed

1. Introduction

Lignin is the second most abundant natural polymer in the biosphere followed by cellulose, accounting for up to 30% of lignocellulosic biomass. Over 50 million tons of so-called technical lignin is annually extracted from lignocellulosic biomass as a byproduct of the pulp and paper industry with increasing amounts from the emerging cellulosic ethanol industry [1, 2]. Lignin is a phenylpropane-based polymer biosynthesized from random polymerization of three precursor monomers. Because of its abundance and availability in low cost, lignin has potential as a renewable source of aromatics. At present, most lignin is burned as boiler fuel while only 2% of it is upgraded to biobased products, such as binder, resin, and dispersant [3-6]. Developing effective upgrading methods to convert lignin into value-added products could reduce dependency on petroleum and also improve the economic prospects for companies producing lignin as a co-product of biomass processing.

Depolymerizing lignin by either biological or thermochemical means has been extensively studied over the past several decades [7-10]. Solvent liquefaction using a variety of solvents at elevated temperatures and pressures is the most common method for deconstructing lignin [11-13]. Despite the advantages of solvent liquefaction, the consumption of solvent and the need for separating reaction products from solvent, char and/or catalysts present both economic and technical challenges.

Fast pyrolysis is an alternative thermal depolymerization technique. Fast pyrolysis has been widely explored for the conversion of whole plant biomass into liquid products [14-16]. Fast pyrolysis rapidly heats the feedstock (usually < 2s) in the absence of oxygen and usually at atmospheric pressure. Lignocellulosic biomass is substantially decomposed to form liquid, called bio-oil, char, and non-condensable gases. Bio-oil from fast pyrolysis is similar to the liquid produced by solvent liquefaction. It can be upgraded to hydrocarbon fuels or other chemicals. The char product (also known as biochar) has several applications such as solid fuel, soil amendment and activated carbon [17].

Despite its potential, fast pyrolysis of technical lignin has been infrequently studied, usually limited to batch experiments involving only small quantities of lignin [18-20]. Although these previous studies have provided valuable insight into lignin depolymerization, continuous pyrolysis relevant to commercial applications are lacking [21]. Efforts to continuously pyrolyze lignin have been largely unsuccessful due to the melting and subsequent agglomeration of lignin particles to form "hard shell" solid material, which clogs the reactor and forces shut-down. This problem was highlighted by an international collaboration in 2010 [22]. Two types of lignin, one from soda pulping of non-woody biomass and the other from weak acid hydrolysis of softwood, were distributed to seven laboratories for pyrolysis in small-scale, fluidized bed pyrolyzer. None of the laboratories were able to pyrolyze the soda pulp lignin due to plugging of the feeder or defluidization of the reactor. Pyrolysis of the acid hydrolysis lignin was only marginally better, possibly because of the presence of a large amount of carbohydrate in this particular feedstock.

Several researchers have attempted to pyrolyze lignin by adding cooling jackets or making other design changes to the feeder tubes, installing mechanical stirrers inside the reactors, pelletizing lignin, or performing pyrolysis in the presence of oxygen [23-25]. None of these efforts were completely successful in eliminating agglomeration. In a recent review paper, Ragauskas et al. [1] warned that the inability to continuously feed lignin to large-scale reactors is the primary technical barrier to pyrolyzing lignin for the production of fuels and chemicals.

Pretreating lignin is another approach to improving the pyrolysis of lignin. Mukkamala et al. [26] pretreated an acid hydrolyzed kraft lignin with 50-100% weight equivalence of calcium formate using a two-step process before pyrolysis in an entrained flow reactor. In their study, fluidizing sand was removed from the reactor during pyrolysis in order to avoid agglomeration between sand and lignin particles. A patent filed by Wilberink et al. [27] describes a slurry of lignin and clay (1:1 weight ratio) mixed in water and extruded as pellets and then dried in a two-step heat treatment prior to pyrolysis. Upon pyrolysis in an auger reactor, phenolic-rich bio-oil was produced. The solid residue from pyrolysis of lignin-clay pellets were pellets containing char and the clay binder. Wilberink et al. [21] also pyrolyzed in a fluidized bed the pellets formed from the lignin co-product of organosolv processing of straw. They concluded that a dedicated feeding system and careful control of pyrolysis conditions are required to pyrolyze lignin even when pelletized.

Because of this difficulty of pyrolyzing lignin, the products of lignin pyrolysis have yet to be fully characterized. One previous study reported the composition of pyrolysis vapor but not char [21]. A study conducted by Sharma et al. [20] characterized the agglomerated char produced from slow pyrolysis of lignin in a batch reactor but did not give information about volatile products.

We hypothesize that lignin will have to be chemically modified to prevent its melting and subsequence agglomeration upon heating. We have developed a simple chemical pretreatment of lignin that prevents its agglomeration, allowing its continuous pyrolysis in a fluidized reactor. We report the properties of the resulting pyrolysis products and propose a mechanism by which pretreatment prevents lignin agglomeration.

2. Materials and methods

2.1. Materials

Lignin from acetosolv processing of corn stover was provided by Archer Daniels Midland (ADM). Lignin from supercritical hydrolysis of pine wood was provided by Renmatix. Lignin derived from enzymatic hydrolysis of cornstover was provided by POET. Lignin from alkaline extraction from softwood was purchased from Sigma Aldrich. All experiments were performed with acetosolv lignin from ADM unless otherwise specified. Phenol and vanillin, used as model compounds to represent lignin-derived pyrolysis products, and calcium hydroxidewere purchased from Sigma-Aldrich. Solvents including methanol, acetone, tetrahydrofuran and 1, 4-dioxane, were also purchased from Sigma-Aldrich.

2.2. Characterization of lignin

Ultimate analysis of lignin samples was determined with a Vario Micro Cube CHN elemental analyzer (Elementar, Germany). Proximate analysis was performed by a Mettler Toledo TGA/DSC system. The sample was first heated to 105°C at 10°C/min to determine moisture content. The temperature was increased to 900°C at 10°C/min to determine volatile content. Finally, air was introduced at 900°C for another 30 min to determine fixed carbon and ash content. Inorganics in the lignin were analyzed by Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) (Optima 8000, PerkinElmer). Volatile organic compounds in untreated lignin were measured by dissolving 1g of lignin in 9 ml of methanol and analyzing using GC/MS.

2.3. Lignin pretreatment method

A 950 g of as-received lignin was mixed with 50 g of $Ca(OH)_2$ in water at room temperature (equivalent to 5% concentration). The mixture was dried in an oven at 50°C to remove water until the moisture content of the mixture dropped to below 5%. The pinewood lignin was also prepared using the same concentration of $Ca(OH)_2$.

2.4. Pyrolysis experiments

Fast pyrolysis of untreated and pretreated lignin was conducted in a lab scale, fluidized bed reactor. Detailed information of the reactor system can be found elsewhere [28]. Briefly, the reactor system consists of a biomass feeder, an injection auger, a stainless steel reactor, and a bio-oil recovery system. The pyrolytic vapors exiting the reactor passed through two stages of gas cyclones to remove biochar. This was followed by an electrostatic precipitator (ESP) at 90°C and a condenser cooled to -10°C. The bio-oil recovered by the ESP is referred to as heavy oil, while the bio-oil collected in the condenser is referred to as light oil. Nitrogen was used as sweep gas, 9 standard liters per minute (SLPM) was introduced into reactor and 1 SLPM was purged through the feeding system. The feeding rate was set up at 100 g/h. Pyrolysis temperatures were 450, 500, 550, and 600°C, respectively. The tests were run in triplicate at each temperature and average mass yields were reported.

Pretreated lignin was also pyrolyzed in a Frontier micropyrolyzer (Frontier laboratory, Japan) coupled to an Agilent GC-MS/FID/TCD (7890B GC, 5977A MSD). Detailed description of the system can be found elsewhere [29]. In brief, 500 μg of sample was placed in a deactivated stainless cup and pyrolyzed in a micro furnace preheated to 500°C. Helium gas was used as the carrier gas to sweep pyrolytic vapor into online GC columns with split ratio of 50:1. The GC oven was set at 40°C, then ramped up to 280°C at 6°C/min. The volatiles were identified by MS and quantified by FID. The standard compounds were purchased from Sigma-Aldrich.

Pyrolysis tests of untreated and pretreated enzymatic hydrolysis lignin and alkali lignin were performed by a Mettler Toledo TGA/DSC system. Approximately 10 mg of sample was placed in a

900 μL crucible. The sample was heated from 25 to 500°C at 50°C/min. The char residue remained in crucible was collected to observe its agglomeration problem.

2.5. Characterization of pyrolysis products

The amount of bio-oil was calculated by weighing the reactor parts and condenser bottles before and after runs. Total char amount includes the char recovered in the two cyclones and the char remaining in the bed. Non-condensable gases (NCG) were analyzed with a micro-GC (Varian CP-4900) and gas yields calculated using the ideal gas law based on the measurement from a drum-type gas meter (Ritter, Germany). Standard gas mixtures of CO, CO_2, H_2, CH_4, C_2H_4, C_2H_6, C_3H_6 and C_3H_8 were purchased from Praxair and calibrated for quantification of the gas yield.

The composition of bio-oil was analyzed using the Agilent GC-MS by replacing the micropyrolyzer with a liquid auto sampler. Water content of bio-oil was determined by Karl-Fisher titration (KEM, MKS-500). The acidity of bio-oil was measured by modified acid number (MAN) with titrator (Metrohm, 789 MPT Titrino). The acidity is measured as mg KOH/g bio-oil.

The molecular weight distribution of bio-oils was measured with a gel permeation chromatograph (GPC) (Ultimate 3000, DIONEX) equipped with a Shodex Refrative Index (RI) detector and a UV detector. Tetrahydrofuran was used as eluent at flow rate of 1 ml/min. The signal at 254 nm was used to calculate molecular weight distribution. Elemental composition of bio-oil and char was analyzed using the CHN analysis method described above.

FTIR (SMART iTR NICOLET iS10, Thermo Scientific) was used to analyze char. Each sample was scanned 32 times from 4000 cm^{-1} to 650 cm^{-1} with resolution of 4 cm^{-1}. Inorganics in the bio-oil and char were analyzed using the ICR method described above. Brunauer-Emmet-Teller (BET) surface area of char was measured by nitrogen gas sorption analysis at 77 K using a physisorption analyzer

(Micrometitics ASAP 2020). Approximately 0.2 - 0.3 g char was loaded into the sample tube. The sample was first degassed at 300 °C for 4 hours prior to analysis.

Scanning electron microscope (SEM) of char produced from untreated or pretreated lignin was conducted using a FEI Quanta-250 FE-SEM. For pH test, 1g of char was added to 20 ml of deionized water and equilibrated for 1.5 hours on the shaker at room temperature and its pH value is determined using pH test strip.

2.6. Comparison of untreated and pretreated lignin prior to pyrolysis

Untreated or pretreated lignin was dissolved in acetone, methanol, tetrahydrofuran, and 1,4-dioxane. The solvent soluble fractions were filtered and the solvent was evaporated at 40°C in a rotary evaporator. The insoluble fractions were dried at 50°C in a vacuum oven. Both solvent soluble lignin fraction and insoluble fraction were weighted before heating to 450°C for 1 min to test thermal agglomeration. Untreated and the solvent soluble fractions of untreated lignin were also analyzed in GPC for molecular weight distribution.

Untreated and pretreated lignins were also analyzed by FTIR. Prior to FTIR tests (FTIR method was described above), the lignin samples were placed in a vacuum oven at 50°C for 72 hours to completely remove moisture and other volatiles.

2.7 Model compound study

Phenol and vanillin were used as model compounds to better understand the mechanism by which pretreatment prevented lignin agglomeration. Phenol in the amount of 0.2g was mixed with 0.16g of $Ca(OH)_2$ in 5ml of deionized water. The mixture was stirred for an hour and kept in a vacuum oven at 50 °C till water was removed. The same amount of vanillin was mixed with 0.04 g of $Ca(OH)_2$ in 1ml of deionized water and otherwise prepared in the manner of the phenol. Both untreated and $Ca(OH)_2$ treated phenol and vanillin samples were analyzed by FTIR.

3. Results and discussions

3.1 Performance of untreated and pretreated lignin in fluidized bed reactor

The proximate and ultimate analysis results of lignin are given in Table S1. As-received lignin contained 6.1% of ash and also contained 2.25% of acetic acid as residue from the acetosolv process.

Fig. 1 compares the visual appearance of untreated lignin and pretreated lignin prior to pyrolysis. Untreated lignin had a dark brown color (Fig. 1a) and the pretreated lignin showed a lighter color (Fig. 1b), both were fine powders.

To confirm that the untreated lignin used in this study melted and agglomerated upon heating, it it was pyrolyzed in the fluidized bed reactor at 500°C as a control case. As expected, the pressure at the inlet of the biomass feeder started increasing immediately after the lignin was fed into the reactor. The operation was terminated after 40 min due to defluidization of the sand in the reactor. Upon disassembly of the reactor, large, smooth chunks of carbonaceous material were found in both the feeder tube and the reactor bed with sand-char agglomerates stuck to the bottom of the reactor (Fig. 1c). No char was recovered in the gas cyclones, suggesting that little char left the reactor. Agglomeration of char and absence of fine char in the cyclones were similarly observed in previous studies of (untreated) lignin pyrolysis [22].

In comparison, we successfully pyrolyzed pretreated lignin at all temperatures attempted. Pressure did not increase at any point in the system and char agglomerates were absent from the reactor upon completion of the tests. Char was collected as fine particulate matter in the gas cyclones (Fig. 1d), as occurs for pyrolysis of whole biomass [30]. Pretreated lignin was continuously pyrolyzed for three hours under very stable operation with no indication that experiments could not have been continued longer.

The technical lignins from organsolv processing of cornstover, supercritical hydrolysis of mixed hardwoods, enzymatic hydrolysis of cornstover, and alkali extraction of softwood were pretreated with $Ca(OH)_2$ and pyrolyzed to determine whether our method for overcoming lignin agglomeration was generalizable to other kinds of lignin. The appearance of the resulting pyrolysis chars these other lignins are shown in Fig. 2. The untreated lignins all formed char agglomerates whereas the pretreated lignins produced fine char powders, similar to the behavior observed for organsolv lignin. Furthermore pretreated supercritical hydrolysis lignin was successfully pyrolyzed in the continuous fluidized reactor, producing fine char similar to that observed from organsolv lignin. We conclude that the pretreatment can prevent char agglomeration during pyrolysis of a wide range of technical lignins. The technical lignins from organsolv processing of cornstover, supercritical hydrolysis of mixed hardwoods, enzymatic hydrolysis of cornstover, and alkali extraction of unknown plant material were pretreated with $Ca(OH)_2$ and pyrolyzed to determine whether our method for overcoming lignin agglomeration was generalizable to other kinds of lignin. The appearance of the resulting slow pyrolysis chars produced from these other lignins is shown in Fig. 2. The untreated lignins all formed char agglomerates whereas the pretreated lignins produced fine char powders, similar to the behavior observed for organsolv lignin. Furthermore pretreated supercritical hydrolysis lignin was successfully pyrolyzed in the continuous fluidized reactor, producing fine char similar to that observed from organsolv lignin. We conclude that the pretreatment can prevent char agglomeration during pyrolysis of a wide range of technical lignins.

3.2 Pyrolysis product distribution

The distribution of pyrolysis products from pretreated acetosolv lignin is given in Fig. 3. The yields of bio-oil (the sum of heavy oil and light oil), char, and NCGs are reported on an ash- and $Ca(OH)_2$-free basis for the lignin feedstock. Mass closure was in the range of 87 to 90%. Bio-oil yield was not significantly influenced by temperature. The highest bio-oil yield was 38.4% at 500°C with only slightly lower yields at other temperatures. Char yield decreased from 38.4 to 30.4% and NCG yield increased from 11.9 to 20.8% as temperature increased from 450 to 600°C. Previous researchers reported similar results for pyrolysis of lignin pretreated with clay or formate salt, with bio-oil yields of 23 - 44%, char yields of 35 - 41% and NCG yields of 15 - 39% even though the kinds of lignin were distinct from that of the present study [21, 26].

Pyrolysis of technical lignin produced both higher yield of NCG and char and lower yield of bio-oil compared to pyrolysis of whole lignocellulosic biomass [31]. We hypothesize that technical lignin produces more char than lignin still contained in plant cell walls because it contains more thermally stable bonds between aromatic rings.

3.3 Characterization of bio-oil

As shown in the properties of whole bio-oil listed in Table 1 (properties of the heavy and light oil fractions are provided in Table S3), up to 34.2% of the bio-oil was water. Up to 13.0% of bio-oil was light oxygenates (Table S1 for detailed yields), mostly acetic acid derived from the solvent used in this acetosolv process. Acetol and acetol acetate were also found in bio-oil, derived from decomposition of carbohydrate residue in the lignin. However, the yields were low. The compositional distribution of the whole bio-oil is plotted in Fig. 4. This shows that 55 - 60% of the bio-oil was phenolic compounds. The GC/MS chromatograms in Fig. 5 show that the bio-oil contains phenolic monomers from thermal depolymerization of lignin. Some examples include 4-vinylphenol, 2-methoxy-4-vinylphenol, guaiacol, syringol, phenol, trimethoxyl benzene, and ethyl, methylphenols. Vinylphenols were the major monomers derived from ether cleavage of lignin. The GC/MS-detected phenolic monomers accounted for up to 16% of whole bio-oil (equal to 6% per lignin weight). The yields of these phenolic monomers were lower than that were quantified by analyzing pyrolysis vapor before condensing determined by pyrolyzing the pretreated lignin in the micropyrolyzer (11.8% per lignin weight). The decrease in vinylphenols and other phenolic monomers in bio-oil due to polymerization catalyzed by acetic acid has been previously reported [32, 33].

As shown in Table 1, the average molecular weight (MW) of whole bio-oil ranged from 252 to 288 Da with maximum molecular weight occurring for bio-oil produced at 500°C. Polydispersity (PD) was below 1.66 for bio-oil produced at various temperatures (Table 1). In the GPC chromatograms of bio-oils given in Fig. 6, the major peak appears at 141 Da, which corresponds to phenolic monomers. The smaller peaks at 359 Da and 78 Da represent phenolic dimers [34] and light oxygenates, respectively. These results suggest that phenolic monomers represent the majority of UV detectable compounds in bio-oil (i.e., phenols and light oxygenates). Although GC/MS analysis indicated a lesser amount of phenolic monomers, this is probably because GC/MS is not able to detect many higher boiling point phenolic monomers [29] and [35]. Despite the condensation and repolymerization reactions possibly occurred during storage [33], average MW of bio-oil was very low suggesting the pretreated lignin was intensively depolymerized during fast pyrolysis.

As shown in Table 1 and Table S3, bio-oil acidity is mostly due to the presence of acetic acid. Higher pyrolysis temperatures increased acidity. The oxygen content of the bio-oil was similar to the carbon content, in the range of 40 - 50%, due to the high moisture content of the oil. Bio-oil produced at 500°C had the highest carbon and hydrogen content and lowest oxygen content. Nitrogen was also present in lignin-derived bio-oil, similar to what is found in bio-oil derived from whole biomass [36]. Bio-oil produced at 500°C had higher heating value (HHV) of 19.1 MJ/kg, which is similar to that of bio-oil produced from pyrolysis of whole biomass at comparable temperature [31].

As given in Table 2, lignin bio-oil contained only small amounts of Ca, Fe, S and P despite the presence of a significant amount of these metals in the lignin and introduced during the pretreatment process. The inorganics mostly remain in the char, as further discussed in Section 3.5.

3.4. Gas products

Detailed composition of gaseous products is given in Table 2. CO_2 was the major NCG followed by CO. Overall all NCGs increased with increasing pyrolysis temperature. The yield of CO_2 was much higher than the yield of CO, similar to it was observed when the untreated lignin was pyrolyzed in a micropyrolyzer [32].

3.5. Characterization of pyrolysis char

The SEM images of the char produced from untreated and pretreated lignin are compared in Fig. 7. The char from untreated lignin was smooth structured with imbedded sand particles, indicating that the lignin particles melted together, forming liquid that subsequently dehydrated to form agglomerated char [20]. The microstructure of char from pyrolysis of pretreated lignin was quite different, with no evidence of melting and particle shapes similar to that of the lignin powders prior to pyrolysis.

FTIR spectra of chars are given in Fig. 8. Peaks correspond to OH (3306 cm^{-1}), methyl (2928 cm^{-1}) and methoxyl (2844 cm^{-1}). Aromatic skeleton vibrations are represented by 1589, 1504 and 1423 cm^{-1}. The peak at 1328 cm^{-1} is syringol plus guaiacol ring condensed. The shift in the band at 1423 to 1409 cm^{-1}, along with a newly formed band centered at 873 cm^{-1} confirms the presence of CaO in the chars of pretreated lignin. The undulating peaks below 873cm^{-1} are related to fused aromatic structures such as naphthalene, anthracene etc. Other bands at 1086 and 1035 cm^{-1} correspond to C-O deformation in alcohols and aliphatic ethers and also unconjugated C=O stretch. The bands between 1200-1300 cm^{-1} associated with C-C plus C-O plus C=O stretching. These bonds also continue to decrease at higher pyrolysis temperature due to decomposition of lignin structure at higher extent. Higher degree of demethoxylation and demethylation was also observed at higher pyrolysis temperature. Overall char of pretreated lignin had strong aromatic structure and it retained less C-O associated bonds.

Properties of char produced from fast pyrolysis of corn stover biomass [37] and corn stover lignin are compared in Table 4. Ash content of char from corn stover biomass was significantly higher than char from corn stover lignin. Volatile matter and fixed carbon were higher in char obtained from pyrolysis of corn stover lignin than from cornstover biomass. Increasing pyrolysis temperature decreased the volatile content and increased the fixed carbon content of char from cornstover lignin. The BET surface area of char from corn stover lignin was in the range of 0.71 to 1 m^2/g, which is lower than for char from corn stover biomass. Previously Sharma et al. [20] also reported similarly low BET surface area for agglomerated char from lignin pyrolysis due to the melting of lignin particles. Pyrolysis of pretreated lignin did not produce micropores despite the absence of lignin melting. Carbon content of char from cornstover lignin was much higher than the char from corn stover biomass. Carbon content increased with increasing temperature accompanied by decreasing H and O. The char from corn stover lignin contained significantly higher amounts of nitrogen and sulfur than the char from corn stover biomass. At 500ºC, N and S were 1.14 and 0.2% for char from corn stover lignin compared to 0.6 and 0.02% for char from corn stover biomass. HHV values of ash containing char from corn stover lignin were between 17.64 and 18.70 MJ/kg, much higher than for char from corn stover biomass (10.86 MJ/kg) probably due to its lower ash content. As shown in Table 2, the majority of inorganics in the original lignin and pretreated lignin were recovered in the char. Calcium accounted for 7.59% of lignin char obtained at 500ºC. Potassium (K) was also the major inorganic in the char along with S, P and Fe. The pH of char from cornstover lignin slurried in water was between 8 and 9.

3.6. The role of $Ca(OH)_2$ pretreatment in modifying lignin structure

We were able to continuously pyrolyze the pretreated lignin since it did not melt or agglomerate. After performing fractionation on the lignin using various solvents, we found that the solvent-soluble fractions of lignin had a much stronger tendency to agglomerate during heat treatment than did the insoluble fractions. The average MWs of the solvent-soluble fractions were also lower compared to the solvent-insoluble fractions. We also found that $Ca(OH)_2$ pretreatment of lignin reduced the solvent-soluble fractions of lignin. Mörck et al. [38] reported that lower MW fraction of lignin contains higher amount of phenolic OH and carboxylic acid groups than in the higher MW fraction of lignin. Sundin [39], on the other hand, reported that chemical binding of Ca^{2+} with lignin increases its precipitation from solvent during kraft process. Thus, it is highly probable that the pretreatment process modified the functional groups that are responsible for melting and subsequence agglomeration of lignin.

FTIR spectrums of the dried, pretreated lignin, moisture and acetic acid-free untreated lignin and calcium hydroxide are compared in Fig. 9. The spectrum of $Ca(OH)_2$ has a sharp peak at 3640 cm^{-1} for OH absorption whereas this peak was not apparent in the pretreated lignin samples, indicating $Ca(OH)_2$ reacted with lignin [39] through chemical bonding. In lignin, the peak corresponding to OH (the broad peak centered at 3318cm^{-1}) also decreased upon pretreatment. While this peak could represent both phenolic OH and OH on side chain of benzene rings, it was also noted that the band with the peak at 1367 cm^{-1} which represents phenolic OH group also decreased. Thus, it is likely that phenolic OH decreased upon pretreatment.

Divalent cations like Ca^{2+} could promote crosslinked structure of lignin by reacting phenolic OH group to form $Ca(aryl\text{-}O)_2$, promoting agglomeration and char formation. Since this did not occur in the experiments, more likely $Ca(OH)_2$ reacted with phenolic OH to form aryl-O-CaOH, which would discourage cross-linking. Evidence for this was reported by Schlosberg and Scouten [40] who observed that a slurry of phenol, with $Ca(OH)_2$, and water heated to 85-90 °C formed hydroxyl calcium phenoxide (PhO-Ca-OH), which subsequently decomposed to phenol and CaO when pyrolyzed at 550-650 °C. Phenol was recovered at near theoretical yield, which confirms that it did not cross-link via Ca^{2+} as calcium diphenoxide would have formed irreversibly.

We reacted phenol with $Ca(OH)_2$ at 50 °C, the same temperature at which pretreated lignin was dried and compared the FTIR spectrum of the reaction product with those of hydroxylcalcium phenoxide and calcium diphenoxide [40]. This revealed the pretreated phenol to contain hydroxycalcium phenoxide rather than the crossed linked diphenoxide (See Fig. S1 in Supplemental Material).

Another significant change in the lignin IR spectrum after pretreatment was the complete elimination of the band centered on 1693 cm^{-1}, which corresponds to conjugated aldehydes and carboxylic acids. Carboxylic functionality in lignin could react with $Ca(OH)_2$ to form either cross-linked $Ca(aryl\text{-}COO)_2$ or non-crosslinked aryl-COO-CaOH, although we suspect it is more likely the latter based on the observations on reaction of phenol and $Ca(OH)_2$. Aldehydes could react with $Ca(OH)_2$ through the

Cannizzaro reaction [41] to form phenolic alcohols and phenolic calcium carboxylates. After pretreatment, the band centered on 1656 cm^{-1}, representing C=O stretch in conjugated p-substitute aryl ketones, combines with the peak for aromatic ring vibration (1602 cm^{-1}) and becomes a broader peak shifted to the right due to C=O stretch (1592 cm^{-1}) C=O by calcium ion attachment. Hydroxylcalcium bonded phenolic structure would have lower solubility in organic solvents [40] and may explain the decreased solubility of pretreated lignin in solvents.

The proposed reaction mechanism was further explored by treating vanillin, a phenolic aldehyde that is also produced from lignin, with $Ca(OH)_2$ and analyzing with FTIR (See Fig. S2 in Supplemental Material). In the spectrum of $Ca(OH)_2$-treated vanillin there was a dramatic decrease in phenolic OH, disappearance of aldehyde groups, and an increase in the alcohol group peak (1035m^{-1}) compared to untreated vanillin. A shift in the peak for C=O stretch due to Ca attachment was also found. The solubility of $Ca(OH)_2$-treated vanillin in solvent decreased and the color of treated vanillin also changed from white to yellow due to the loss of phenolic hydroxyl group.

The reactivity of phenolic hydroxyl or aldehyde groups for polymerization and crosslinking is well known [42]. Decreasing the content of these reactive functionalities in lignin by forming aryl-O-CaOH and aryl-COO-CaOH by $Ca(OH)_2$ pretreatment likely prevented polymerization of the phenols during pyrolysis to form resin-like polymers.

Pyrolysis of pretreated lignin is suspected of decomposing aryl-O-CaOH and aryl-COO-CaOH to phenolic compounds, CaO, CO_2, CO and H_2O. The proposed reaction mechanism of $Ca(OH)_2$ and lignin during pretreatment and pyrolysis process are illustrated in Fig. 10.

The above findings suggest that phenolic hydroxyl, carboxylic acids and aldehydes groups are likely responsible for agglomeration behavior of untreated lignin. Polymerization reactions among these functional groups are suspected of forming resin-like products at relatively low temperatures during pyrolysis. Dehydration of the liquid forms a large solid mass, thus impeding heat and mass transfer to and from the lignin particles. The fact that agglomerated char of untreated lignin still retains some of phenolic structure is evident in the FTIR spectrum of Fig. 6. The peaks at 777 cm^{-1} and 694 cm^{-1} (related to phenolic rings) only appeared in the agglomerated char of untreated lignin. Also, the bands associated with oxygen bonding and phenolic structure increased dramatically whereas the bands for aromatic ring vibration reduced significantly for (agglomerated) char from untreated lignin compared to (fine) char from pretreated lignin.

4. Conclusions

We successfully continuously pyrolyzed technical lignin in a fluidized bed reactor without reactor modification. Pretreatment of the lignin by adding 5% $Ca(OH)_2$ prevented melting and agglomeration of lignin particles. Pyrolysis products included phenolic-rich bio-oil, light gases and fine char powder. Phenolic compounds in the bio-oil were mainly phenolic monomers and dimers with average MW less than 288 Da. Char from lignin was less porous compared to char from whole biomass and contained lower amounts of ash but significantly more N, S, K, and P. FTIR analysis of untreated and pretreated lignin suggests that phenolic hydroxyl, aldehydes and carboxylic acid groups are responsible for melting and agglomeration of lignin. $Ca(OH)_2$ pretreatment likely reduced or eliminated these functionalities by forming calcium hydroxyl phenoxides, phenolic calcium carboxylates and phenolic alcohols. Upon pyrolysis, Ca was converted to CaO and recovered in char.

Calcium hydroxide represents a low cost and low hazard pretreatment that is readily available. The amounts of $Ca(OH)_2$ required for pretreatment are very small, and easily recovered by burning the char and leaching the ash with water. The heat of combustion from this regeneration process can be used to heat the pyrolyzer. Alternatively, the char has potential as biobased fertilizer, and/or converted to activated carbon if the ash content of the lignin is relatively low.

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Table 1. Properties of total bio-oil

Temperature (°C)	450	500	550	600
Water (% in bio-oil)	31.78	33.11	34.18	29.23
Molecular weight distribution				
Mw (Da)	274	288	268	252
Mn (Da)	167	174	170	157
PD	1.66	1.66	1.56	1.58
MAN (mg KOH/g)	119.52	104.78	118.13	145.50
Elemental composition (%)				
C	43.90	46.18	42.69	41.87
H	6.92	7.55	6.84	6.55
O*	47.66	44.51	48.57	49.54
N	1.50	1.73	1.86	2.02
S	0.03	0.03	0.02	0.02
Heating value (MJ/kg)**				
As-is bio-oil	18.35	19.11	16.29	15.41
Dry bio-oil	23.92	27.52	23.64	20.91

*by difference; ** calculated based on the formula provided in reference [43].

Table 2. ICP-OES analysis of untreated lignin and bio-oil and char from the pyrolysis of pretreated lignin at 500ºC

Inorganic (%)	Al	Ca	Cu	Fe	Mg	Mn	P	S	Zn	Na	K
Lignin*	0.36	0.60	-	0.39	0.09	0.02	0.26	0.20	-	0.03	0.64
Bio-oil	-	0.04	-	-	-	-	-	0.03	-	-	0.01
Char**	0.74	7.59	-	0.81	0.21	0.03	0.55	0.20	-	0.07	1.36

- Non-detectable * untreated **pyrolysis char of pretreated lignin

Table 3. Yields of non-condensable gases

Temp (°C)	H_2 (%)	CH_4 (%)	C_2H_4 (%)	C_2H_6 (%)	CO (%)	CO_2 (%)
450	0	0.64	0.19	0.2	1.88	10.12
500	0.1	1.41	0.19	0.29	2.53	10.76
550	0.23	1.89	0.37	0.25	3.85	12.88
600	0.24	1.88	0.44	0.3	4.46	12.1

Table 4. Properties of chars produced from pretreated corn stover lignin and corn stover biomass[a]

		Char from corn stover lignin				Char from corn stover biomass [a]
Temperature (°C)		450	500	550	600	500[a]
Proximate analysis (%)						
	Moisture	2.85	3.08	3.42	3.46	1.7[a]
	Volatile	39.27	33.82	30.16	29.25	13.8[a]
	Fixed C	37.46	43.32	42.56	44.72	25.2[a]
	Fixed C/volatiles	0.95	1.28	1.41	1.53	1.83[a]
	Ash	17.81	20.70	20.61	20.14	59.3 [a]
BET surface (m^2/g)		1.00	0.78	0.71	0.89	8.5 [a]
Elemental composition (%)[b]						
	C	51.83	52.92	53.16	55.80	29.5 [a]
	H	3.26	2.68	2.43	2.32	1.6 [a]
	N	1.31	1.14	1.10	1.09	0.6 [a]
	S	0.20	0.20	0.20	0.25	0.02 [a]
	O (by difference)	25.60	22.36	22.5	20.40	7.9 [a]
HHV(MJ/kg)[c]		17.86	17.94	17.64	18.70	10.85

[a] Fast pyrolysis biochar of corn stover, data are from reference;[37] [b] based on as-is pyrolysis char that containing ash and pretreatment agent; [c] as-is char, calculated based on the formula provided in reference [43].

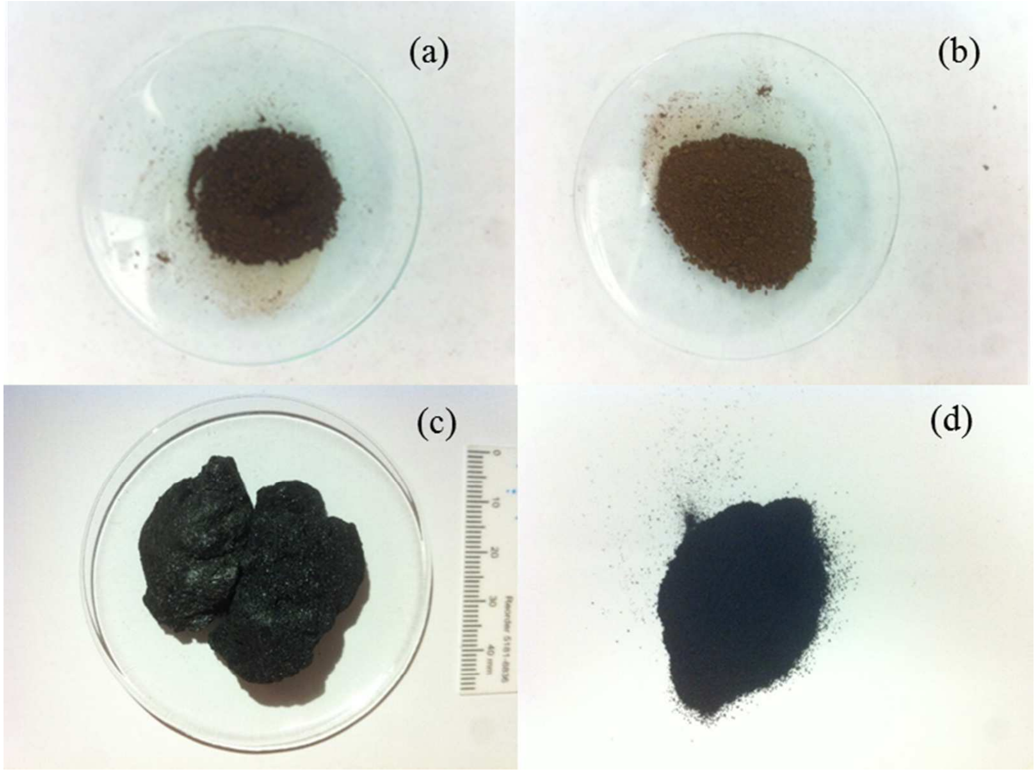


Fig. 1. Organosolv lignin feedstocks and solid products recovered from the fluidized bed after pyrolysis; (a). untreated lignin; (b). pretreated lignin; (c). char/sand agglomerates from the pyrolysis of untreated lignin; (d). char from pyrolysis of pretreated lignin.

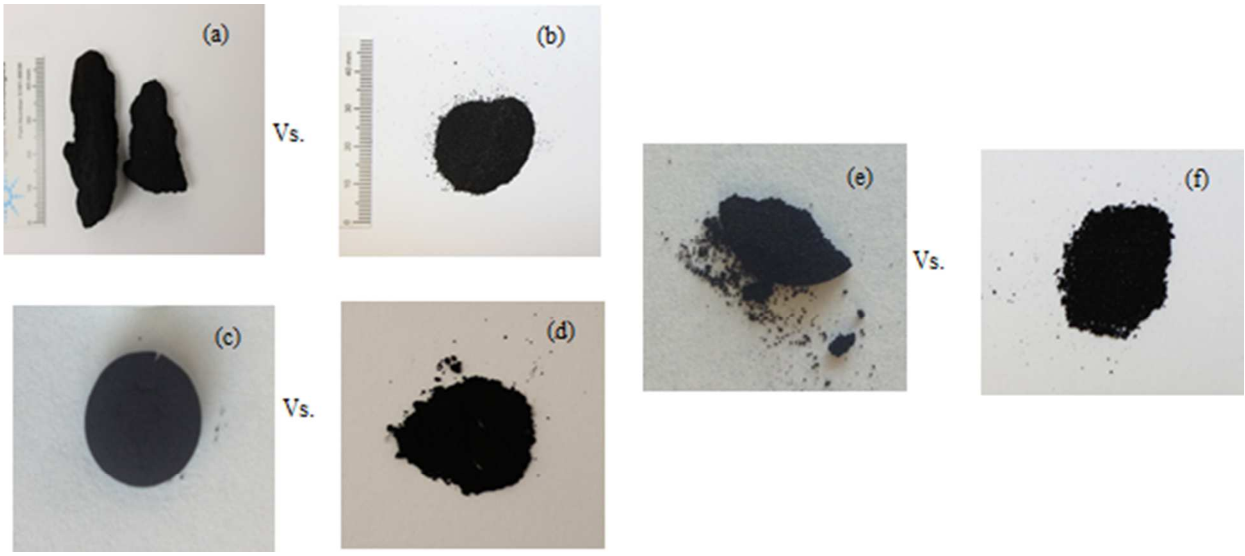


Fig. 2. Comparison of pyrolysis chars produced from untreated and pretreated lignins; Pyrolysis char from (a). untreated supercritical hydrolysis lignin; (b) pretreated supercritical hydrolysis lignin; (c). untreated enzymatic hydrolysis lignin; (d) pretreated enzymatic hydrolysis lignin; (e). untreated alkali lignin; (f). pretreated alkali lignin. The chars shown in (a) and (b) are recovered from the fluidized reactor, and the rest chars are recovered from sample cups in a TGA oven. The circular shaped agglomerated char in (c) is due to the cylindrical sample cup.

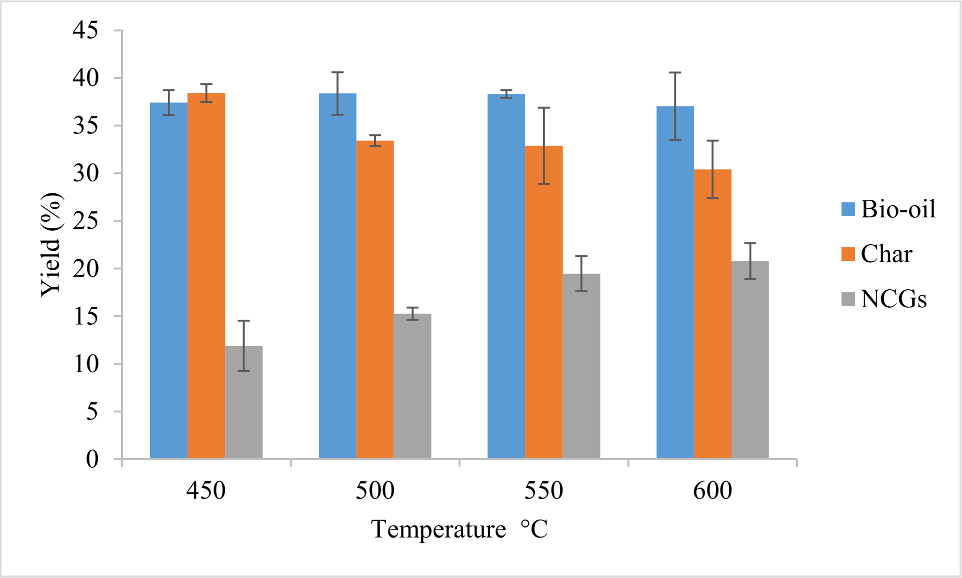


Fig. 3. Distribution of products from the pyrolysis of pretreated lignin at different pyrolysis temperatures (calculated on an ash-free and $Ca(OH)_2$-free basis for the feedstock lignin)

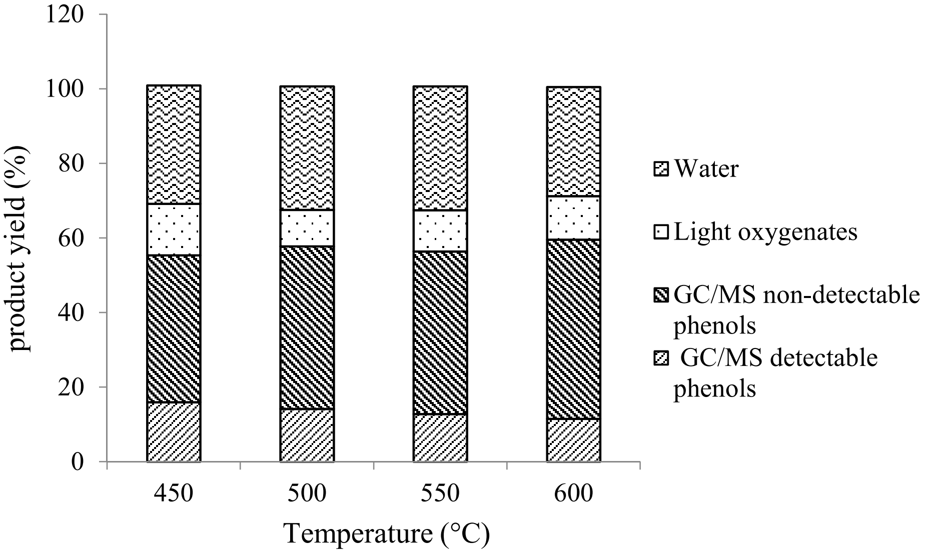


Fig. 4. Product distribution of bio-oil as a function of pyrolysis temperature.

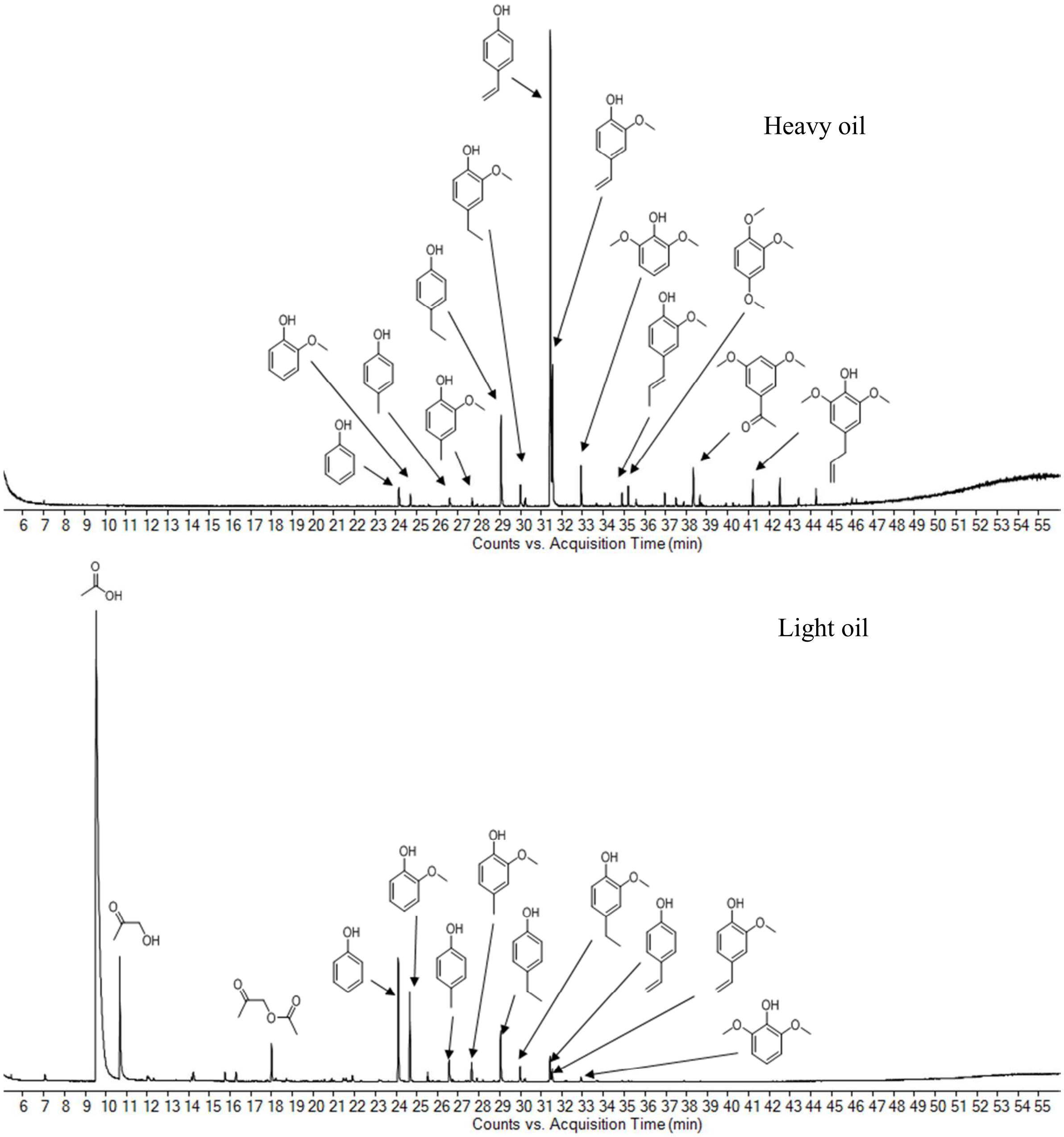


Fig. 5. GC/MS chromatograms of heavy oil and light oil produced from the pyrolysis of pretreated lignin at 500°C .

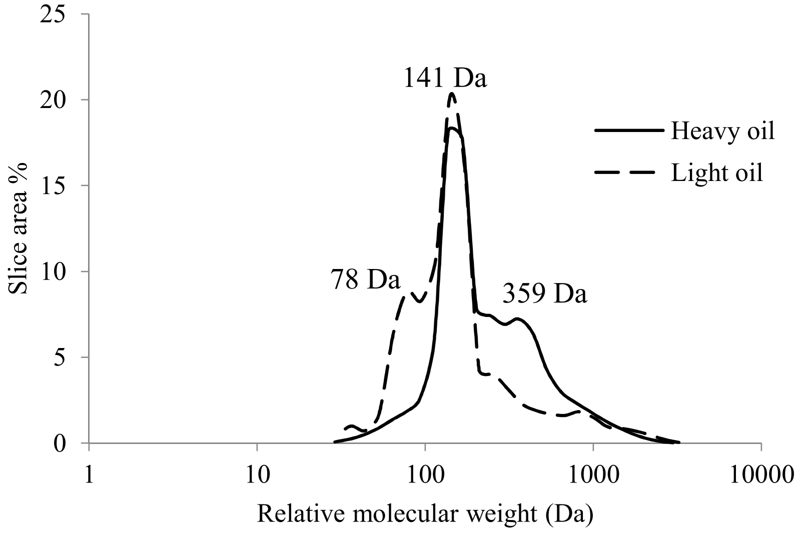
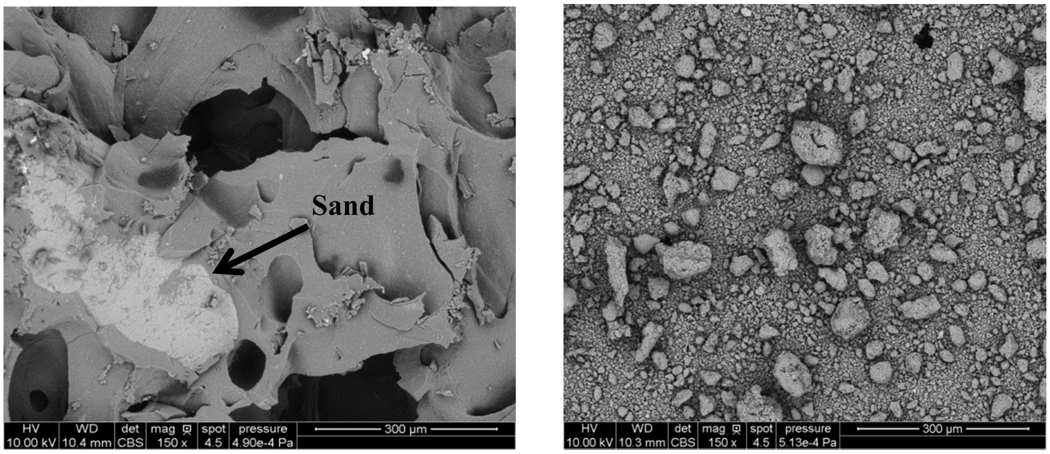


Fig. 6. Molecular weight distribution of heavy oil and light oil produced at 500°C (obtained from gel permeation chromatography).



a. b.

Fig. 7. SEM images of chars obtained from the pyrolysis of untreated (a) and pretreated lignin (b) at 500ºC.

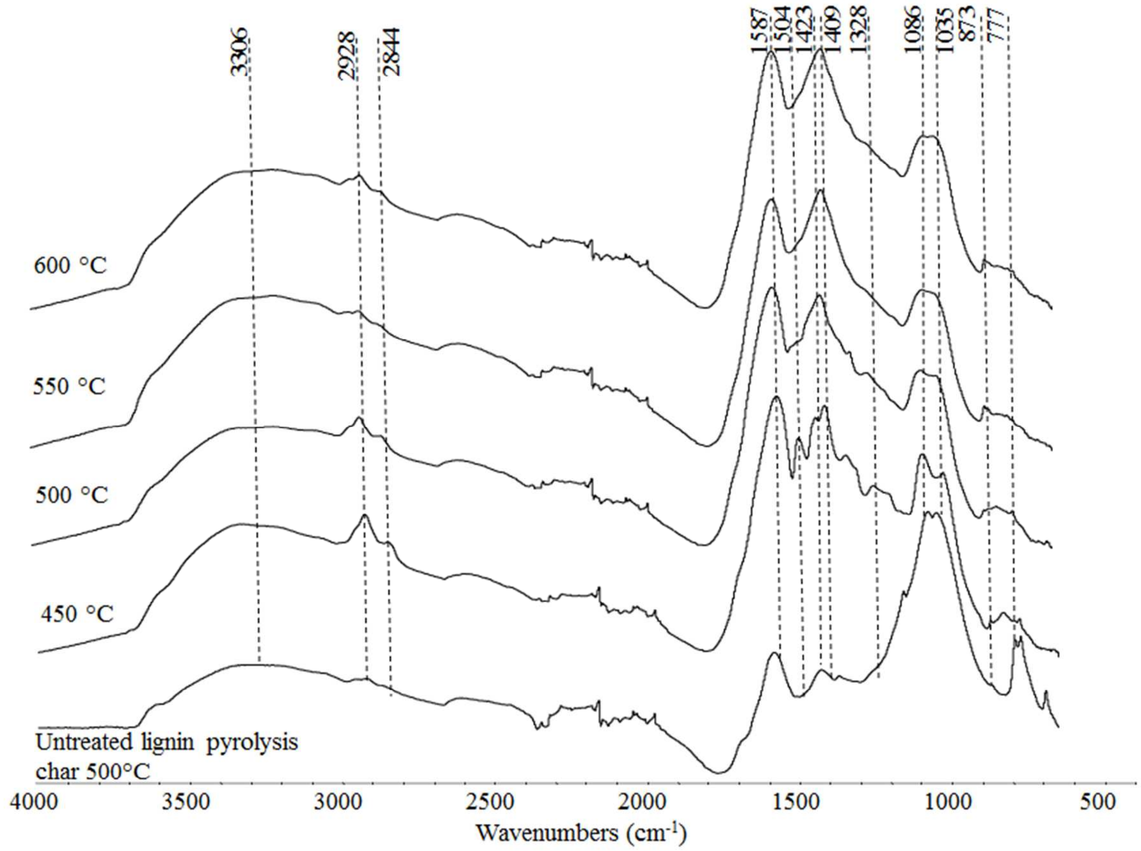


Fig. 8. FTIR spectra of char from the pyrolysis of untreated lignin at 500°C and the pyrolysis of pretreated lignin at several temperatures

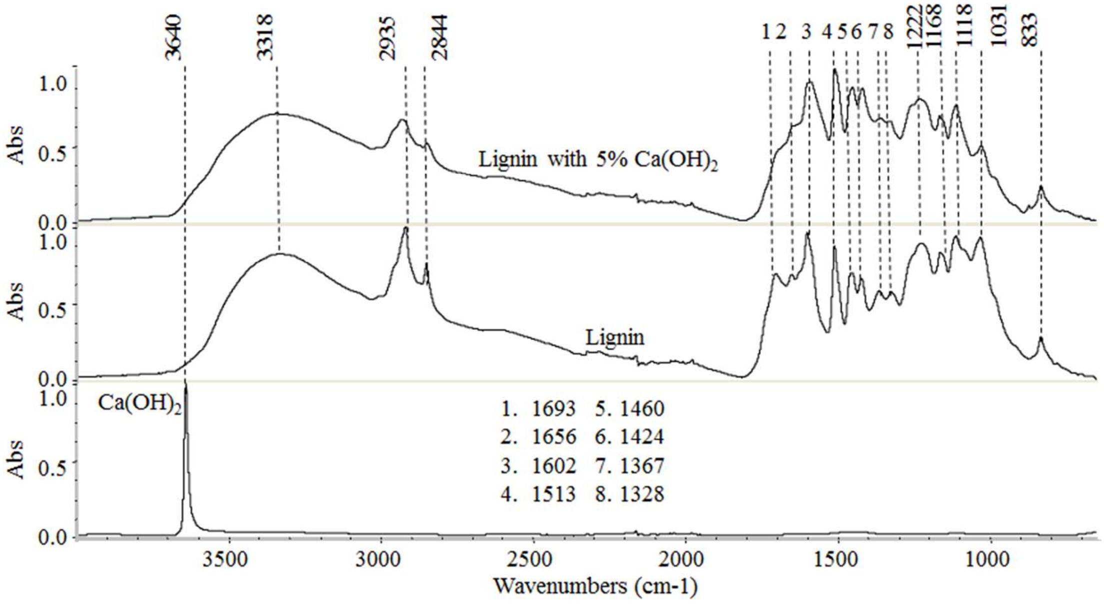


Fig. 89. Comparison of FTIR spectra of untreated lignin, pretreated lignin and $Ca(OH)_2$.

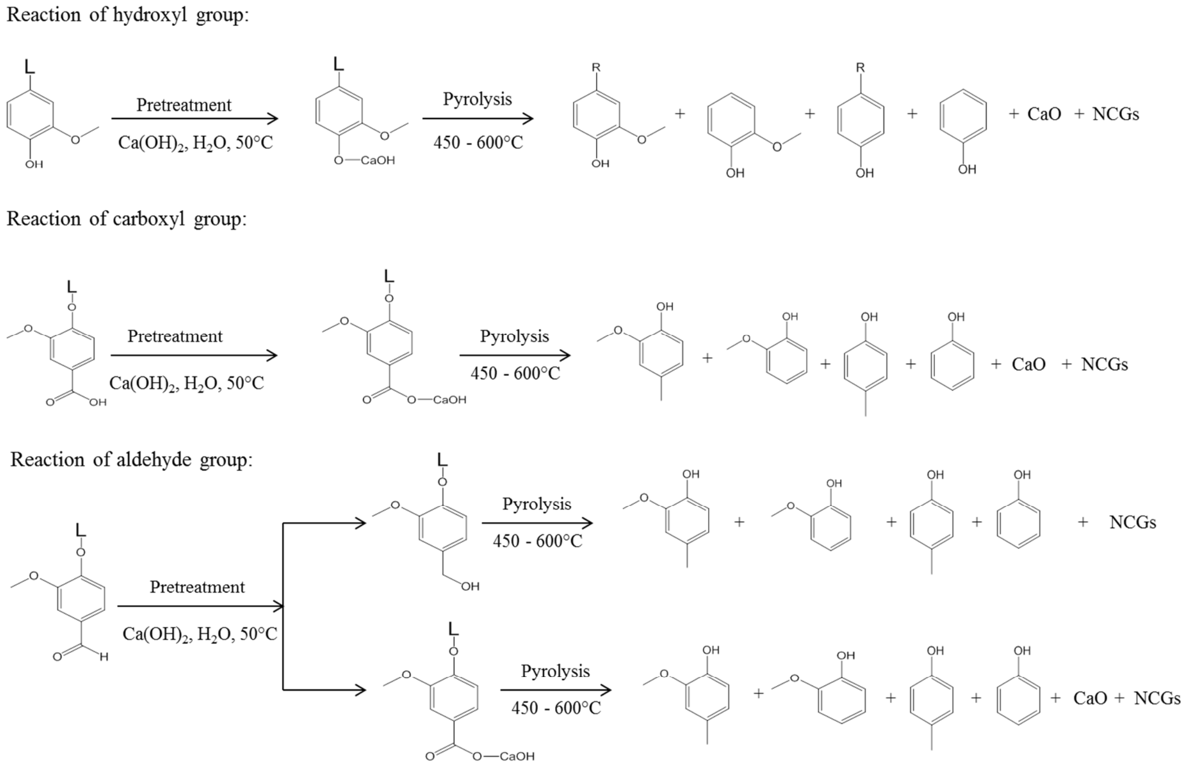


Fig. 10. Proposed reaction mechanism of lignin and calcium hydroxide during pretreatment and pyrolysis.