Kraft Lignin Depolymerization in an Ionic Liquid without a Catalyst

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In this paper, the depolymerization of lignin was successfully achieved by the thermal treatment of kraft lignin in butyl-1,8-diazabicyclo[5.4.0]undec-7-enium chloride ($[DBUC_4^+][Cl^-]$) without a catalyst. The thermal treatment experiments were performed in an oven at 150, 200, and 250 °C for 1 h. The changes in kraft lignin structure over the course of depolymerization were characterized by gel permeation chromatography (GPC), Fourier transform infrared (FTIR) spectroscopy, and ^{1}H / ^{31}P NMR analyses. GPC chromatograms indicated that the retention time of the original kraft lignin had shifted toward higher values after the thermal treatment, which indicated lignin depolymerization. The average molecular weight of the lignin obtained after 1 h reaction time decreased by 23, 70, and 58 wt% for the treatment at 150, 200, and 250 °C, respectively. FTIR spectra indicated the cleavage of *β-O*-4 bonds of kraft lignin. The ^{1}H NMR spectra showed demethylation of all treated kraft lignins. Moreover, the ^{31}P NMR analysis demonstrated that the demethylation phenomenon of the treated kraft lignin contributed to the formation of catechol groups.

Keywords: Kraft lignin; Depolymerization; Renewable resources; Ionic liquid; Thermal treatment

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INTRODUCTION

In recent years, efforts have been devoted to the development of new materials derived from renewable bio-based products, which have the potential to replace petroleum-based resources while providing equivalent assets (Ragauskas *et al*. 1997). Lignocellulosic biomass is a potential renewable resource for the production of fuels and commodity chemicals. Over the last few decades, the research community has focused on the development of processes for valorizing cellulose and hemicelluloses (Alonso *et al*. 2010; Tuck *et al*. 2012). However, lignin, an amorphous three-dimensional polymer that represents 15 to 30% of biomass, is still underused and is burned for its heat value to generate power because of its inherent heterogeneity and recalcitrance.

The structure of lignin is based on three phenylpropane monomer units: *p*-hydroxylphenylpropane, guaiacylpropane, and syringylpropane. Lignin basically consists of a variety of linkages irregularly connecting the various phenylpropane monomers to one another (Amen-Chen *et al*. 2001; Zakzeski *et al*. 2010). The most common functionality, which accounts for about one-half of the bonds between the monomers in protolignin, is the *β-O*-4 linkage (Fig. 1) (Kukkola *et al*. 2004). Therefore, a lignin depolymerization strategy may target cleaving the *β-O*-4 ether linkage while preserving the aromatic character of the fragments.

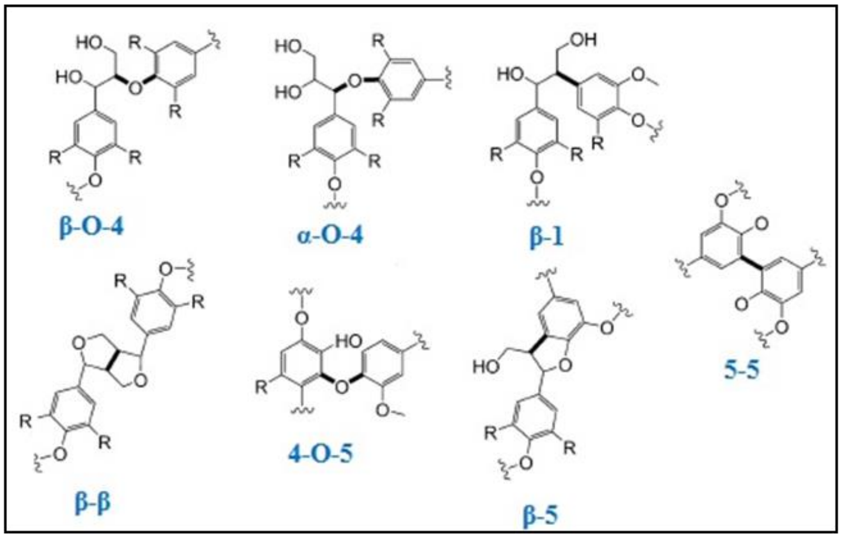

Fig. 1. Major linkages found in lignin

In this context, the major challenge in lignin depolymerization is the cleavage of *β*-*O*-4 bonds. For this reason, several approaches have been developed in order to depolymerize lignin, such as pyrolysis, hydrogenolysis, hydrolysis, and enzymatic reactions (Saisu *et al.* 2003; Zhang *et al.* 2014; Long *et al.* 2014). However, these methods require extreme reaction conditions to achieve depolymerization of the lignin. In the same context, there have been studies carried out using acid- and base-catalyzed routes to lignin depolymerization; as these processes involve the use of strong acids or alkali, these chemicals can have negative effects when discharged to the environment (Adler *et al.* 1957; Venica *et al.* 2008). Investigators have studied various lignin depolymerization methods using hydrogenation in the presence of catalysts, such as nickel oxide, chromium, or molybdenum, at 400 °C (Oasmaa and Alen 1993; Toledano *et al.* 2012). Schultz *et al.* (1982) used the alkaline hydrolysis of lignin at 250 °C to produce phenols. Other studies depolymerized lignin in the presence of Lewis acid, *i.e.*, $ZnCl_2$, $FeCl_3$, and $AlCl_3$ (Kudsy *et al.* 1995).

The mechanism of lignin depolymerization during ionic liquid (ILs) pretreatment was recently examined, and preferential lignin dissolution was often observed due to the chemical nature of lignin according to the inter-unit linkages and the nature of the ionic liquid (Varanasi *et al.* 2012; Long *et al.* 2013; Long *et al.* 2015; Ragauskas *et al.* 2014; Sathitsuksanoh *et al.* 2014; Wen *et al.* 2014). The advantages of working in ionic liquid media are that the volatile aromatic products can be removed by distillation and the by-products of degradation can be precipitated with water or be separated by selective membrane technologies. Ionic liquids (ILs) have been used in many research fields, because they are non-flammable, non-volatile, and recyclable (Zhang 2006). ILs have been shown to dissolve wood, cellulose, and lignin, which opens new opportunities in biomass conversion (Fort *et al.* 2007; Li *et al.* 2010).

In previous research (Diop *et al.* 2013), the authors have developed a new ionic liquid, butyl-1,8-diazabicyclo[5.4.0]undec-7-enium chloride $[DBUC_4^+][Cl^-]$, to be used as an aprotic green solvent to dissolve kraft lignin from black liquor. This IL appeared more efficient than other ILs, especially in the dissolution of kraft lignin at 105 °C in proportions of 20% (w/w).

The present work studied the chemical depolymerization of kraft lignin in ionic liquids by characterizing the compounds formed and by observing the cleavage of *β-O*-4 ether linkages. Indeed, cleavage of the *β-O*-4 linkage is a method for both general delignification of biomass and utilization of lignin as a raw material for fuel and chemical production (Okuda *et al.* 2008; Cox and Ekerdt 2012). However, most investigators have used lignin model compounds to study the delignification phenomenon (Binder *et al.* 2009; Cox *et al.* 2011). One of the simplest treatments of lignin models in ionic liquids is thermal treatment for a desired period of time. Kubo *et al.* (2008) carried out a series of heat treatments at 120 °C with guaiacyl glycerol-*β*-guaiacyl (GG) in a chloride medium 1-butyl-3-methylimidazolium (BMIMCl) chloride and 1-3-ethylmethylimid-azolium chloride. Jia *et al.* (2011) used veratryl glycerol ether-*β*-guaiacyl (VG) as a model for the cleavage of the *β-O*-4 ether linkage of lignin by combining the effect of a catalyst, $FeCl_3$, $CuCl_2$, or $AlCl_3$, with the ionic liquid.

In their research, Nanayakkara *et al.* (2014) showed that the two lignins (organosolv and Klason) can be extensively depolymerized under oxidative conditions using a Cu/EDTA complex in ILs at 180 °C. Furthermore, Stärk *et al.* (2010) developed a method for the oxidative depolymerization of lignin in ionic liquid using $Mn(NO_3)_2$ as the catalyst.

To the best of our knowledge, there have been no published works demonstrating lignin depolymerization in ILs without the aid of a catalyst. Despite many studies on the pretreatment of the lignin in ionic liquid medium, a clear impact of ionic liquid without catalyst on lignin structure has not yet been established. To achieve this goal, we studied the depolymerization process using kraft lignin instead of lignin models. However, it should be possible to more precisely ascertain the effect of the ionic liquid on the structure of lignin at different temperatures.

The main target of this research was to elucidate the mechanisms involved in kraft lignin depolymerization in an IL ($[DBUC_4^+][Cl^-]$) at relatively high temperatures without the aid of a catalyst. After that, the cleavage phenomenon of *β-O*-4 bonds within the three-dimensional lignin structure and the change of average molecular weights of lignin was investigated through different characterization techniques. Finally, lignin fragments obtained from depolymerization could be used as a suitable feedstock for further processing into aromatic commodity chemicals or polymers.

EXPERIMENTAL

Materials

Samples of kraft black liquor were supplied by the Kruger mill in Trois-Rivières, PQ, Canada. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 98%), 1-chlorobutane (99%), ethyl acetate (99%), and tetrahydrofuran (≥ 99.9%) were purchased from Sigma-Aldrich. Chloroform, pyridine and 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP, 95%) were also purchased from Sigma-Aldrich. All solvents and chemicals were commercially available, and unless otherwise stated, were used as received without further purification.

Methods

Isolation of the lignin from the kraft black liquor

The extraction of the lignin from kraft black liquor was accomplished by following a published method (Nagy *et al.* 2010) that was adapted to be conducted at atmospheric pressure. The black liquor, with a pH of 13.4, was poured into a flask. Then, CO_2 was bubbled at atmospheric pressure in order to decrease the pH to 9.8 and to further precipitate the lignin. The precipitated lignin was first washed with a 0.5 M sulfuric acid solution, and then washed with deionized water.

Synthesis of ionic liquid

The authors demonstrated the good efficiency of the IL $[DBUC_4^+][Cl^-]$ for the dissolution of the kraft lignin in earlier published research (Diop *et al*. 2013). The IL butyl-1,8-diazabicyclo[5.4.0]undec-7-enium chloride $[DBUC_4^+][Cl^-]$ was synthesized according to the method described by Diop *et al.* (2013). The excess reagents and impurities were removed with ethyl acetate. The traces of ethyl acetate were removed by a rotary evaporator at 50 °C for about 2 h. At the end, a very hygroscopic orange solid was produced.

Thermal treatment of lignin in ionic liquid

Kraft lignin (1 g) was added in 10 g of $[DBUC_4^+][Cl^-]$, and the resulting mixture was placed in an oven at 150, 200, or 250 °C for 1 h. This temperature range was chosen because the ionic liquid maintains its thermal stability until 300 °C; however, the thermal degradation of this IL appeared to be significant for higher temperatures (> 300 °C) (Diop *et al.* 2013). Afterwards, the obtained lignin solution was then cooled down to room temperature. The lignin was regenerated by the addition of deionized water to the solution under vigorous agitation for 2 h. Finally, the precipitated lignin was collected by centrifugation at 3400 RPM, dried, and stored until it could be characterized by different analytical techniques.

Analytical method

The molecular weight distribution analysis of kraft lignin before and after depolymerization was carried out using gel permeation chromatography (GPC) after the acetylation of the lignin samples. All samples were subjected to acetylation in order to enhance their solubility in tetrahydrofuran (THF), which is used as the mobile phase with the GPC. Then, the dried and acetylated lignin was dissolved in THF (1 wt %), and injected into the GPC apparatus (Agilent HPLC 1200), which included a refractive index (RI) detector. Tetrahydrofuran was used as the mobile phase at a flow rate was 0.6 mL/min. Calibration curves were obtained by using polystyrene (Ye *et al.* 2012). The FTIR spectra were obtained with a Perkin Elmer System 2000 instrument using pellets of lignin mixed with KBr (lignin content of 1 wt %). Spectra were recorded between 400 and 4000 cm^{-1} with a resolution of 4 cm^{-1}.

^1H NMR spectra were recorded on a Bruker 500 MHz spectrometer at a frequency of 250 MHz with an acquisition time of 0.011 s at 25 °C. Prior to analysis, samples were acetylated to improve their solubilities in chloroform, which was used as solvent.

^{31}P NMR spectra of the lignin samples were obtained using published procedures (Granata and Argyropoulos 1995) with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMD) as the phosphitylating reagent and *N*-hydroxynaphthalimide as the internal standard. The ^{31}P NMR spectra of the resulting mixtures were obtained by using a Bruker 500 MHz spectrometer equipped with a broad-band inverse probe dedicated to ^{31}P. An acquisition time of 0.2 s, a delay time of 5.00 s, and a number of scan of 512 were used in each analysis. The content of hydroxyl groups was obtained by the integration of the following spectral regions: aliphatic hydroxyls (149.1-144.6 ppm), syringyl (S) phenolics (143.3-141.9 ppm), condensed phenolic units (by difference of 144.3-141.3 ppm from

143.3-141.9 ppm, as previously reported by Cateto *et al.* (2008)), guaiacyl (G) phenolics (140.6-138.6 ppm), *p*-hydroxyphenyl (H) phenolics (138.4-137.2 ppm), and carboxylic acids (135.3-134.4 ppm).

RESULTS AND DISCUSSION

GPC Analysis

It is known that the reaction temperature is an important parameter in the depolymerization processes (Nowakowski *et al.* 2010; Lavoie *et al.* 2011; Ye *et al.* 2012). Raising the IL treatment temperature should simultaneously promote the fragmentation of lignin and the condensation of the intermediate fragments.

In the present work, the influence of the thermal treatment on the distribution of lignin fragmentation products was investigated at different temperatures (150, 200, and 250 °C) with a 10% (w/w) kraft lignin concentration in the ionic liquid [$DBUC_4^+$][Cl^-]. In order to reduce the contribution of the condensation process, the residence time for delignification was fixed to be approximately 1 h. Thus, GPC analysis was performed to examine the molecular weight distribution of the kraft lignin before and after depolymerization. As shown in Fig. 2, GPC chromatograms (using RI detector) indicated that the retention time for the kraft lignin (~27.4 min) had shifted toward higher values after the thermal treatment, which was evidence of lignin depolymerization.

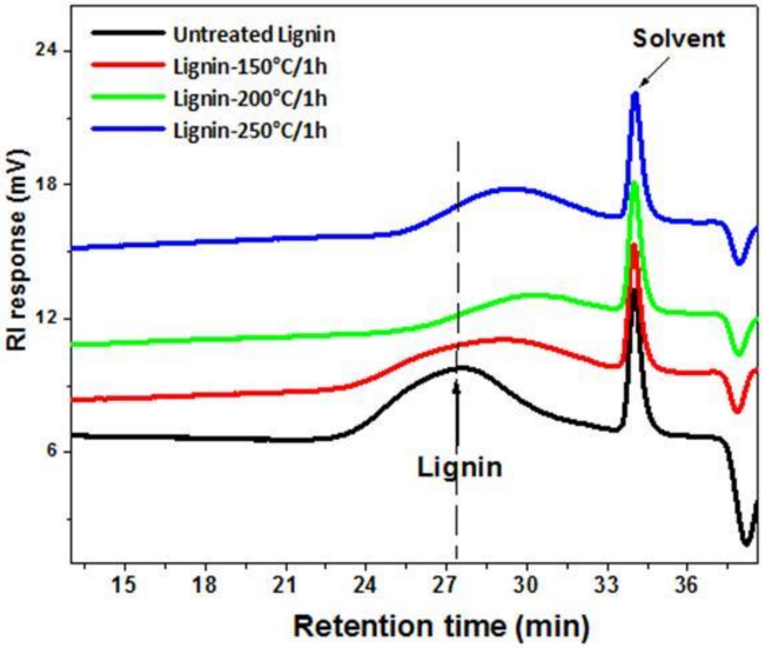

Fig. 2. GPC refractive Index (RI) traces of the depolymerization of kraft lignin in [$DBUC_4^+$][Cl^-] at different temperatures for 1 h

In addition, the retention time values were significantly increased with increasing temperature from 150 to 250 °C, which may be explained by the decomposition of lignin into low molecular weight compounds. However, the retention time of the depolymerized lignin at 250 °C (~29.5 min) seemed to be lower than that of the lignin treated at 200 °C (~30.5 min). Such results could be attributed to the condensation of degraded intermediates at the higher temperature (*i.e.*, 250 °C), which resulted in larger fragments that eluted more quickly during GPC analysis and decreased the retention time.

Average molecular weights (*M*) and polydispersity indices (PDIs) were determined for the samples to confirm the amount of lignin fragmentation that occurred during the IL treatments. Results of these analyses, shown in Table 1, clearly demonstrated that the average molecular weight (*M*) of this fraction decreased significantly as the treatment temperature was increased up to 200 °C; at treatment temperatures above 200 °C, the average *M* started to increase versus the minimum at 200 °C. It had been reported that unsaturated bonds in lignin can undergo condensation reactions when the reaction temperature is higher than 240 °C (Ralph and Landucci 2010). Molecular weight values obtained in our study were similar to those obtained by Nanayakkara *et al*. (2014) for lignin fragmentation in an ionic liquid in the presence of a catalyst.

Table 1. Molecular Weight and Polydispersity Index of Kraft Lignin Before and After Depolymerization in IL at Different Temperatures

Depolymerization temperature (°C)	M_w (g/mol) (1 h)	PDI (M_w/M_n) (1 h)
25	6175	2.8
150	4767	3.4
200	1868	1.9
250	2585	2.2

In the same context, the oligomers formed at 150 °C yielded a broad RI peak of high molecular weight lignin with a higher PDI (3.4) than the untreated lignin (2.8). However, the PDI values decreased from the maximum value (at 150 °C) as the reaction temperature was increased from 150 to 250 °C. Of course, this result could be attributed either to: (i) the condensation phenomena of several phenolic oligomers (re-polymerization); and (ii) the additional decomposition of the lignin coupled to the loss of low molecular weight compounds during the washing and filtration processes. Our results suggest that the fragmentation reactions were more dominant at 200 °C, while the condensation reactions became predominant at relatively higher temperatures (≥ 250 °C). Thus, it was concluded that 200 °C was the optimum treatment temperature for lignin depolymerization in the ionic liquid [$DBUC_4^+$][Cl^-]. These results are in accordance with earlier published research for lignin depolymerization in an ethanol-water medium (Ye *et al.* 2012).

In the present study it appears important to point out the contribution of the ionic liquid [$DBUC_4^+$][Cl^-] on lignin fragmentation without the aid of a catalyst. Contrary to the work published by Nanayakkara *et al.* (2014), the thermal energy supplied to the reaction medium of lignin in an IL was clearly sufficient to start lignin fragmentation at 150 °C without the use of a catalyst; this was not the case in the work of these authors using 1-ethyl-3-methylimidazolium xylenesulfonate ([emim][ABS]) and 1-butyl-3-methyl-imidazolium methylsulfate ([bmim][CH_3SO_4]) as ionic liquids. This contradiction could be attributed to the nature of the ionic liquids used. A likely explanation is the ability of the anion of the IL to interact with the hydroxyl groups on the fragments *via* hydrogen bonding. Cox *et al.* (2011) have demonstrated in their study on the delignification of lignin models that the coordination of the IL's anion with the hydroxyl groups can stabilize the intermediates, which facilitates the cleavage of the ether bond (*β*-*O*-4 or *α*-*O*-4) and the formation of new fragments. Consequently, this coordination decreases the condensation of lignin fragments during fragmentation. The basicity of Cl^-, Br^-, HSO_4^-, and BF_4^- anions has been measured in ionic liquids by Oehlke *et al*. (2006). The cited authors have shown that these ions (Cl^-, Br^-, HSO_4^-, and BF_4^-) have a different ability to interact with the hydrogen of the phenol. They succeeded in classify them according to their ability to develop a hydrogen bond: $Cl^- > Br^- > HSO_4^- > BF_4^-$ (ABS-based ILs were not tested).

The efficient depolymerization of lignin in the [$DBUC_4^+$] [Cl^-] could be explained by the interactions of the ionic liquid with the various fragments of lignin. Cleavage of bonds seems to be assisted by these interactions. Indeed, the structures of ILs and lignin can result in hydrogen bonds and π-π interactions. To further elucidate and explain the physical and chemical phenomena that occurs during IL delignification, ^{1}H NMR, ^{31}P NMR, and FTIR spectroscopic techniques were used to characterize the kraft lignin before and after delignification.

FTIR Analysis

The infrared spectra recorded for untreated and IL-treated lignins are presented in Fig. 3.

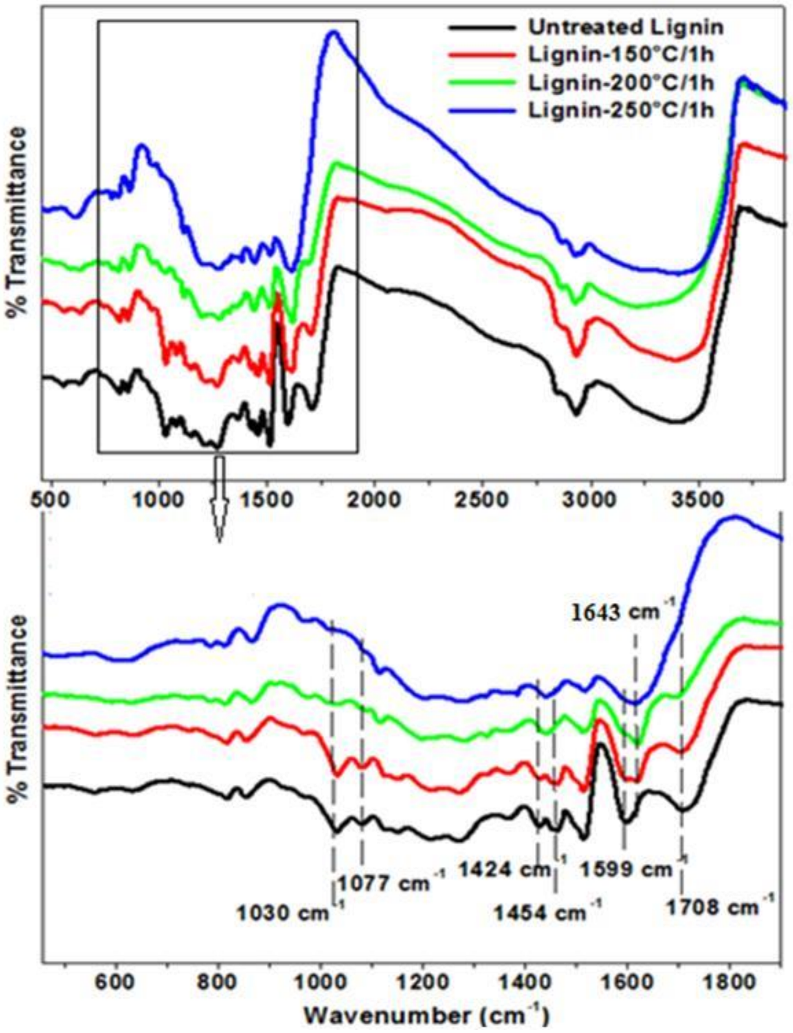

Fig. 3. FTIR spectra of kraft lignin before and after treatment in [$DBUC_4^+$][Cl^-] at 150, 200, and 250 °C for 1 h

The analysis of the FTIR spectra of the untreated kraft lignin revealed characteristics that are in agreement with the literature (Xiao *et al.* 2001; El Mansouri and Salvado 2006; Tejado *et al.* 2007; El Mansouri *et al.* 2011). These spectra showed a large band at 3400 cm^{-1} that was attributed to phenolic and aliphatic OH groups, followed by bands for C-H stretching for methyl and methylene groups (2933 cm^{-1}), C-H stretching for methoxy groups (2863 cm^{-1}), unconjugated C=O stretching at 1708 cm^{-1}, aromatic skeleton C-C stretching at 1599 cm^{-1} and 1509 cm^{-1}, and asymmetric C-H deformation of methyl groups at 1454 cm^{-1}. The peaks at 1424 cm^{-1} and 1454 cm^{-1} are related to C-H asymmetric deformations in the CH_3 portion of methoxy groups; and the peak at 1271 cm^{-1} is attributed to the C-O stretching of guaiacyl groups. The peak at 1077 cm^{-1} is assigned to C-H deformation in secondary alcohols, as well as aliphatic or aromatic ethers. In addition, the C-O(H) and C-O(C) stretching bands of the first order, aliphatic OH and ether groups (1030 cm^{-1}), as well as aromatic C–H out of plane bending at 817 cm^{-1}, were also present.

The increase of the treatment temperature from 150 to 250 °C for 1 h had a significant effect on the basic kraft lignin structure. The absorption band at 1643 cm^{-1} could be attributed to the C=O conjugate. This band was more pronounced in the IL-treated lignin than in the untreated lignin, which suggested that the treated lignin contained more conjugated C=O groups than the untreated lignin. This observation could be explained by the appearance of electronegative substituents during the treatment, which attach to the conjugated lignin units. A reduction in the intensity of the methoxy band at 2933, 2863, 1454 cm^{-1}, and 1424 cm^{-1} was also observed in the IL-treated lignins, which implied that the kraft lignin was demethylated. This observation is in agreement with the analysis of ^1H NMR of the IL-treated lignin (Fig. 4). According to Sun *et al.* (2014), the treatment of the lignin at 170, 210, and 230 °C caused demethylation. In addition, the intensity of bands at 1077 and 1030 cm^{-1} decreased as the IL treatment temperature increased. This result suggested that the ether linkages (*β*-*O*-4 or *α*-*O*-4) in the lignin were cleaved in significant numbers when the IL temperature reached 200 and 250 °C. However, the disappearance of the 1030 cm^{-1} peak at 250 °C, which corresponded to the vibrations of primary alcohols, showed a condensation of primary alcohols. This observation was in good agreement with the GPC chromatogram (Fig. 2), and could explain the higher amounts of high molecular weight lignin at a 250 °C treatment temperature (Table 1).

^1H NMR Analysis

The chemical structure of the kraft lignin treated in an ionic liquid medium at different temperatures was examined by ^1H NMR. Figure 4 shows the ^1H NMR spectra of the kraft lignin before and after treatment at temperatures of 150, 200, and 250 °C for 1 h in $[DBUC_4^+][Cl^-]$.

As shown in the ^1H NMR spectrum of untreated kraft lignin, the signals between 7.0 and 6.0 ppm were assigned to aromatic protons of guaiacyl units (G), whereas those between 0.5 and 1.0 ppm represent the aliphatic protons. Methoxy groups, closely linked to the guaiacyl units, afforded a strong signal centered at 3.35 ppm. Acetyl, aromatic, and aliphatic groups were offset differently (1.82 and 1.56 ppm, respectively), which resulted in separate peaks. This result was in good agreement with the data found in the literature (Hoareau *et al.* 2004; Garcia *et al.* 2009; Ghatak *et al.* 2010). After the treatment of the lignin in ionic liquid (150, 200, 250 °C for 1 h), the disappearance of the methoxy peaks can be clearly observed. This result is attributed to the demethylation of the kraft lignin during the IL thermal treatment. A similar change has been previously reported when heating alkaline solutions of lignin up to 315 °C (Beauchet *et al*. 2012). Acetylated aromatic lignins (1.82 ppm) treated in the ionic liquid had the most intense peaks compared to those of the untreated lignin. This result could be explained by the appearance of new phenolic groups after the cleavage of intramolecular bonds, such as *β*-*O*-4, which suggested that lignin depolymerization had occurred. Moreover, treated lignins had a higher acetyl aromatic-to-acetyl aliphatic ratio than that of the untreated lignin. Such a result could be explained by: (i) the formation of catechol groups; and (ii) the condensation of aliphatic hydroxyl during the IL treatment of the lignin.

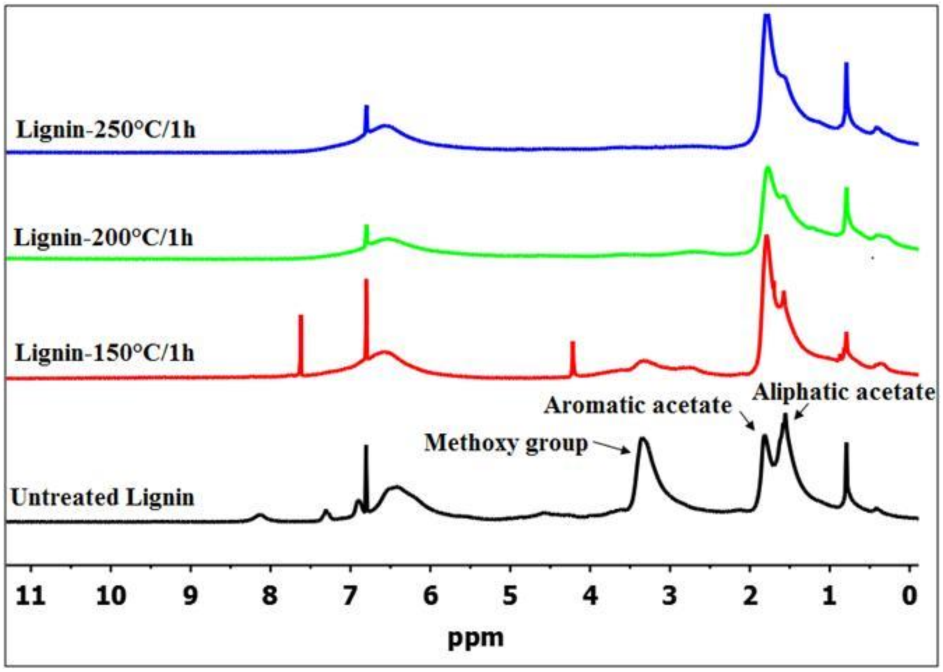

Fig. 4. Signals assignment for ^{1}H NMR spectrometry of acetylated kraft lignin before and after treatment in [DBUC$_4^+$][Cl$^-$] at 150, 200 and 250 °C for 1 h

^{31}P NMR Analysis

To better explain the delignification during IL treatment, ^{31}P NMR analysis was conducted. The ^{31}P NMR spectra of the kraft lignin before and after IL treatment at 200°C/h are presented in Fig. 5.

Table 2. Phenolic, Aliphatic, and Carboxylic Hydroxyl Groups, in mmol·g^{-1}, Present in Untreated Lignin and IL-Treated Lignin at 200 °C/1 h using ^{31}P NMR in Pyridine/CdCl$_3$ after Phosphitylation

Sample	Total	Total	Phenolic OH				Total	Total
	COOH	Aliphatic OH	**G^a**	**C^a**	**S^a**	**H^a**	Non-condensed Phenolic-OH	Condensed Phenolic-OH
Untreated Lignin	0.38	1.80	2.16	0.0	0.0	0.24	2.40	1.87
Lignin-200°C/1 h	0.53	0.70	4.72^b				4.72	1.85

^{a} H: Hydroxyphenyl; C: catecholic; G: Guaiacyl; S: Syringyl phenolic groups.
^{b} G^a + C^a + H^a = 4.72

In all spectra, a sharp signal at 153.7 ppm corresponded to *N*-hydroxynaphthalimide, which was used as an internal standard, and added at a known amount in the NMR tubes of all samples. The hydroxyl content analytical data for the untreated lignin and depolymerised lignin are shown in Table 2.

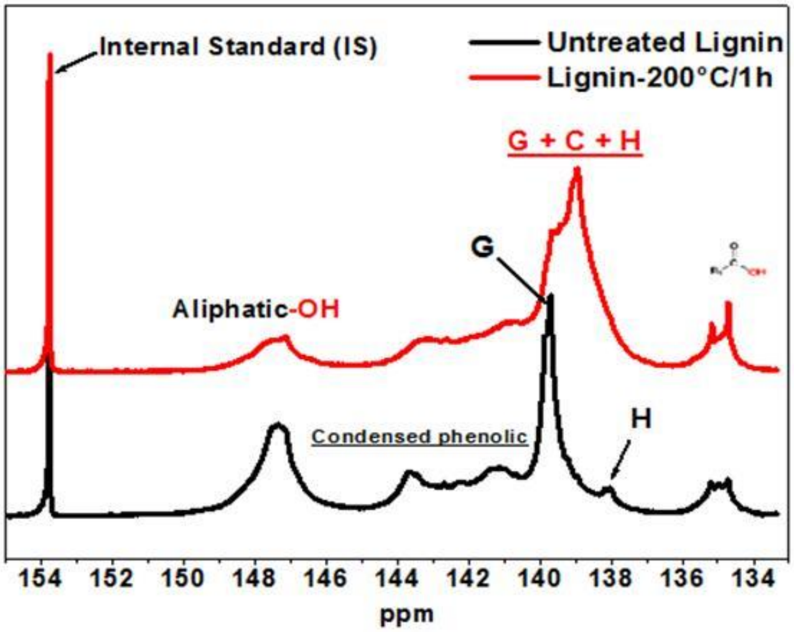

Fig. 5. ^{31}P NMR spectra of kraft lignin before and after treatment at 200 °C for 1 h in IL (analysis occurred in pyridine/$CDCl_3$ after derivatization with TMDP)

The untreated kraft lignin is a softwood lignin, as supported by the high content of guaiacyl (G) phenolic groups (Fig. 5; Table 2). The spectrum of the 200 °C/1 h IL-treated lignin showed a decreased content of aliphatic OH groups, an up-field shift of condensed phenolic groups, and a widening of the G signal towards lower chemical shifts (Fig. 5). This is typical of a modified softwood lignin, where the methoxy (OMe) groups of the G groups have been demethylated to afford catechol (C) groups (signal at 139 ppm). Beauchet *et al*. (2012) observed a similar change.

The depolymerization of lignin begins with the cleavage of inter-unit linkages (such as *β*-*O*-4). The *β*-*O* bond is first cleaved because of its low bond dissociation energy (268 kJ/mol) (Tejado *et al*. 2007). The disappearance of methoxy groups with the ^{1}H NMR spectra (Fig. 3) showed that the demethylation reactions occurred to produce catechol-type compounds.

CONCLUSIONS

1. The molecular weight of lignin was lowered without the use of catalyst. Delignification occurred because of the cleavage of ether bonds and methoxyl bonds. However, it was observed that the cleavage of bonds was not sufficient to form monomeric phenolic entities. The major products obtained were oligomers.

2. The GPC results showed that the molecular weight of kraft lignin decreased by 23% (w/w), 70% (w/w) and 58% (w/w) for the IL treatments at 150 °C/1 h, 200 °C/1 h, and 250 °C/1 h, respectively.
3. The FTIR, ^{1}H NMR, and ^{31}P NMR analyses suggested the cleavage of the ether bonds (such as *β*-*O*-4) and the demethylation of kraft lignin. The results also showed that the optimum processing temperature is 200 °C.
4. ^{31}P NMR analyses showed the presence of catechol groups on the oligomers obtained after depolymerization.

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REFERENCES CITED

Adler, E., Pepper, J. M., and Eriksoo, E. (1957). "Action of mineral acid on lignin and model substances of guaiacylglycerol-*beta*-aryl ether type," *Ind. Eng. Chem*. 49(9), 1391-1392. DOI: 10.1021/ie50573a037

Alonso, D. M., Bond, J. Q., and Dumesic, J. A. (2010). "Catalytic conversion of biomass to biofuels," *Green Chem*. 12(9), 1493-1513. DOI: 10.1039/C004654J

Amen-Chen, C., Pakdel, H., and Roy, C. (2001). "Production of monomeric phenols by thermochemical conversion of biomass: A review," *Bioresour. Technol.* 79 (3), 277-299. DOI: 10.1016/S0960-8524(00)00180-2

Beauchet, R., Monteil-Rivera, F., and Lavoie J.-M. (2012). "Conversion of lignin to aromatic-based chemicals (L-chems) and biofuels (L-fuels)," *Bioresour. Technol.* 121(2012 Oct.), 328-334. DOI: 10.1016/j.biortech.2012.06.061

Binder, J. B., Gray, M. J., White, J. F., Zhang, Z. C., and Holladay, J. E. (2009). "Reactions of lignin model compounds in ionic liquids," *Biomass Bioenerg.* 33(9), 1122-1130. DOI: 10.1016/j.biombioe.2009.03.006

Cateto, C. A., Barreiro, M. F., Rodrigues, A. E., Brochier-Salon, M. C., Thielemans, W., and Belgacem, M. N. J. (2008). "Lignins as macromonomers for polyurethane synthesis: A comparative study on hydroxyl group determination," *J. Appl. Polym. Sci.* 109(5), 3008-3017. DOI: 10.1002/app.28393

Cox, B. J., and Ekerdt, J. G. (2012). "Depolymerization of oak wood lignin under mild conditions using the acidic ionic liquid 1-*H*-3-methylimidazolium chloride as both solvent and catalyst," *Bioresour. Technol.* 118(2012 Aug.), 584-588. DOI: 10.1016/j.biortech.2012.05.012

Cox, B. J., Jia, S., Zhang, Z. C., and Ekerdt, J. G. (2011). "Catalytic degradation of lignin model compounds in acidic imidazolium based ionic liquids. Hammett acidity and anion effects," *Polym. Degrad. Stabil.* 96(4), 426-431. DOI: 10.1016/j.polymdegradstab.2011.01.011

Diop, A., Bouazza, A. H., Daneault, C., and Montplaisir, D. (2013). "New ionic liquid for the dissolution of lignin," *BioResources* 8(3), 4270-4280. DOI: 10.15376/biores.8.3.4270-4282

El Mansouri, N. E., and Salvado, J. (2006). "Structural characterization of technical lignins for the production of adhesives: application to lignosulfonate, kraft, soda anthraquinone, organosolv and ethanol process lignins," *Ind. Crops Prod*. 24(1), 8-16. DOI: 10.1016/j.indcrop.2005.10.002

El Mansouri, N. E., Yuan, Q., and Huang, F. (2011). "Synthesis and characterization of Kraft lignin-based epoxy," *BioResources* 6(3), 2492-2503. DOI: 10.15376/biores.6.3.2492-2503

Fort, D. A., Remsing, R. C., Swatloski, R. P., Moyna, P., Moyna, G., and Rogers, R. D. (2007). "Can ionic liquids dissolve wood? Processing and analysis of lignocellulosic materials with 1-*n*-butyl-3-methylimidazolium chloride," *Green Chem*. 9(1), 63-69. DOI: 10.1039/B607614A

Garcia, A., Toledano, A., Serrano, L., Egues, I., Gonzalez, M., Marin, F., and Labidi, J. (2009). "Characterization of lignins obtained by selective precipitation," *Sep. Purif. Technol.* 68(2), 193-198. DOI: 10.1016/j.seppur.2009.05.001

Ghatak, H. R., Kundu, P. P., and Kumar, S. (2010). "Thermochemical comparison of lignin separated by electrolysis and acid precipitation from soda black liquor of agricultural residues," *Thermochim. Acta* 502(2010), 85-89. DOI: 10.1016/j.tca.2010.02.012

Granata, A., and Argyropoulos, D. S. (1995). "2-Chloro-4,4,5,5-tetramethyl-1,3,2 dioxaphospholane, a reagent for the accurate determination of the uncondensed and condensed phenolic moieties in lignins," *J. Agr. Food Chem.* 43(6), 1538-1544. DOI: 10.1021/jf00054a023

Hoareau, W., Trindade, W. G., Siegmund, B., Castellan, A., and Frollini, E. (2004). "Sugar cane bagasse and curaua lignins oxidized by chlorine dioxide and reacted with furfuryl alcohol: Characterization and stability," *Polym. Degrad. Stabil.* 86(2004), 567-576. DOI: 10.1016/j.polymdegradstab.2004.07.005

Hu, J., Shen, D., Xiao, R., Wu, S., and Zhang, H. (2013). "Free-radical analysis on thermochemical transformation of lignin to phenolic compounds," *Energ. Fuels* 27(1), 285-293. DOI: 10.1021/ef3016602

Jia, S., Cox, B. J., Guo, X., Zhang, Z. C., and Ekerdt, J. G. (2011). "Hydrolytic cleavage of *β-O*-4 ether bonds of lignin model compounds in an ionic liquid with metal chlorides," *Ind. Eng. Chem. Res.* 50(2), 849-855. DOI: 10.1021/ie101884h

Kubo, S., Hashida, K., Yamada, T., Hishiyama, S., Magara, K., Kishino, O. H., and Hosoya, S. (2008). "A characteristic reaction of lignin in ionic liquids; glycelol type enol-ether as the primary decomposition product of *β-O*-4 model compound," *J. Wood Chem. Technol*. 28(2), 84-96. DOI: 10.1080/02773810802124845

Kudsy, M., Kumazawa, H., and Sada, E. (1995). "Pyrolysis of kraft lignin in molten $ZnCl_2$-KCl media with tetralin vapor addition," *Can. J. Chem. Eng.* 73(3), 411-415. DOI: 10.1002/cjce.5450730319

Kukkola, E. M., Koutaniemi, S., Poellaenen, E., Gustafsson, M., Karhunen, P., Lundell, T. K., Saranpaeae, P., Kilpelaeinen, I., Teeri, T. H., and Fagerstedt, K. V. (2004). "The dibenzodioxocin lignin substructure is abundant in the inner part of the secondary wall in Norway spruce and silver birch xylem," *Planta* 218(3), 497-500. DOI: 10.1007/s00425-003-1107-3

Lavoie, J. M., Bare, W., and Bilodeau, M. (2011). "Depolymerization of steam-treated lignin for the production of green chemicals," *Bioresour. Technol.* 102(7), 4917-4920. DOI: 10.1016/j.biortech.2011.01.010

Li, B., Filpponen, I., and Argyropoulos, D. S. (2010). "Acidolysis of wood in ionic liquids," *Ind. Eng. Chem. Res*. 49(7), 3126-3136. DOI: 10.1021/ie1000983

Long, J., Li, X., Guo, B., Wang, L., Zhang, N. (2013). ″Catalytic delignification of sugarcane bagasse in the presence of acidic ionic liquids,” *Catal. Today* 200, 99-105.

Long, J., Lou, W., Wang, L., Yin, B., and Li, X. (2015). ″[$C_4H_8SO_3$Hmim]HSO_4 as an efficient catalyst for direct liquefaction of bagasse lignin: Decomposition properties of the inner structural units,” *Chemical Engineering Science* 122 (2015), 24-33.

Long, J., Xu, Y., Wang,T., Shu,R., Zhang,Q., Zhang,X., Fu, J., and Ma, L., (2014). “Hydrothermal depolymerization of lignin: Understanding the structural evolution,” *BioResources* 9(4), 7162-7175. DOI: 10.15376/biores.9.4.7162-7175

Nagy, M., Kosa, M., Theliander, H., and Ragauskas, A. J. (2010). “Characterization of CO_2 precipitated kraft lignin promote its utilization,” *Green Chem.* 12(1), 31-34. DOI: 10.1039/B913602A

Nanayakkara, S., Patti, A. F., and Saito, K. (2014). “Lignin depolymerization with phenol *via* redistribution mechanism in ionic liquids,” *ACS Sustain. Chem. Eng.* 2(9), 2159-2164. DOI: 10.1021/sc5003424

Nowakowski, D. J., Bridgwater, A. V., Elliott, D. C., Meier, D., and De Wild, P. (2010). “Lignin fast pyrolysis: Results from an international collaboration,” *J. Anal. Appl. Pyrol.* 88(1), 53-72. DOI: 10.1016/j.jaap.2010.02.009

Oasmaa, A., and Alen, R. (1993). “Catalytic hydrotreatment of some technical lignins,” *Bioresour. Technol*. 45(3), 189-94. DOI: 10.1016/0960-8524(93)90111-N

Okuda, K., Ohara, S., Umetsu, M., Takami, S., and Adschiri, T. (2008). “Disassembly of lignin and chemical recovery in supercritical water and *p*-cresol mixture. Studies on lignin model compounds,” *Bioresour. Technol.* 99(6), 1846-1852. DOI: 10.1016/j.biortech.2007.03.062

Oehlke, A., Hofmann, K., and Spange, S. (2006). “New aspects on polarity of 1-alkyl-3 methylimidazolium salts as measured by solvatochromic probes,” *New J. Chem.* 30(4), 533-536. DOI: 10.1039/B516709D

Ragauskas, A. J., Beckham, G. T., Biddy, M. J., Chandra, R., Chen, F., Davis, M. F., Davison, B. H., Dixon, R. A., Gilna, P., Keller, M., Langan, P., Naskar, A. K., Saddler, J. N., Tschaplinski, T. J., Tuskan, G. A., and Wyman, C. E. (2014). ″Lignin valorization: Improving lignin processing in the biorefinery,” *Science* 344, 1246843 (2014). DOI: 10.1126/science.1246843.

Ragauskas, A. J., Williams, C. K., Davison, B. H., Britovsek, G., Cairney, J., Eckert, C. A., Frederick, W. J. Jr., Hallett, J. P., Leak, D. J., Liotta, C. L., Mielenz, J. R., Murphy, R., Templer, R., and Tschaplinski, T. (1997). “The path forward for biofuels and biomaterials,” *Science* 311(5760), 484-489. DOI: 10.1126/science.1114736

Ralph, J., and Landucci, L. L. (2010). “NMR of lignins,” *Lignin and Lignans: Advances in Chemistry,* Heitner, C., Dimmel, D. R., and Schmidt, J. A. (eds.), CRC Press, Boca Raton, FL, pp. 137-234. DOI: 10.1201/EBK1574444865-c5

Saisu, M., Sato, T., Watanabe, M., Adschiri, T., and Arai, K. (2003). “Conversion of lignin with supercritical water-phenol mixtures,” *Energ. Fuels*, 17, 922-928. DOI: 10.1021/ef0202844

Sathitsuksanoh, N., Holtman, K. M., Yelle, D. J., Morgan, T., Stavila, V., Pelton, J., Blanch, H., Simmons, V., and George, A. (2014). “Lignin fate and characterization during ionic liquid biomass pretreatment for renewable chemicals and fuels production” *Green Chem.* 16, 1236-1247. DOI: 10.1039/C3GC42295J.

Schultz, T. P., Chen, C. L., and Goldstein, I. S. (1982). “The attempted depolymerization of HCl lignin by catalytic hydrogenolysis,” *J. Wood Chem. Technol.* 2(1), 33-46. DOI: 10.1080/02773818208085118

Stärk, K., Taccardi, N., Bösmann, A., and Wasserscheid, P. (2010). "Oxidative depolymerization of lignin in ionic liquids," *ChemSusChem*. 3(6), 719-723. DOI: 10.1002/cssc.200900242

Sun, S. L., Wen, J. L., Ma, M. G., and Sun, R. C. (2014). "Structural elucidation of sorghum lignins from an integrated biorefinery process based on hydrothermal and alkaline treatments," *J. Agr. Food Chem*. 62(32), 8120-8128. DOI: 10.1021/jf501669r

Tejado, A., Pena, C., Labidi, J., Echeverria, J. M., and Mondragon, I. (2007). "Physico-chemical characterization of lignins from different sources for use in phenol-formaldehyde resin synthesis," *Bioresour. Technol*. 98(8), 1655-1663. DOI: 10.1016/j.biortech.2006.05.042

Toledano, A., Serrano, L., and Labidi, J. (2012). "Organosolv lignin depolymerization with different base catalysts," *J. Chem. Technol. Biotechnol*. 87(11), 1593-1599. DOI: 10.1002/jctb.3799

Tuck, C. O., Pérez, E., Horváth, I. T., Sheldon, R. A., and Poliakoff, M. (2012). "Valorization of biomass: Deriving more value from waste," *Science* 337(6095), 695-699. DOI: 10.1126/science.1218930

Varanasi, P., Singh, P., Arora, R., Adams, P. D., Auer, M., Simmons, B. A., and Singh, S. (2012). "Understanding changes in lignin of *Panicum virgatum* and *Eucalyptus globulus* as a function of ionic liquid pretreatment," *Bioresour. Technol*. 126, 156-161. DOI: 10.1016/j.biortech.2012.08.070.

Venica, A. D., Chen, C., and Gratzl, J. S. (2008). "Soda-AQ delignification of poplar wood. Part 1: Reaction mechanism and pulp properties," *Holzforschung* 62(6), 627-636. DOI: 10.1515/HF.2008.118

Wen, J. L., Yuan, T. Q., Sun, S. L., Xu, F., and Sun, R. C. (2014). "Understanding the chemical transformations of lignin during ionic liquid pretreatment," *Green Chem*. 2014, (16), 181-190. DOI: 10.1039/C3GC41752B.

Xiao, B., Sun, X. F., and Sun, R. C. (2001). "Chemical, structural and thermal characterization of alkali soluble lignins and hemicelluloses and cellulose from maize stems, rye straw and rice straw," *Polym. Degrad. Stabil.* 74(2), 307-319. DOI: 10.1016/S0141-3910(01)00163-X

Ye, Y., Zhang, Y., Fan, J., and Chang, J. (2012). "Novel method for production of phenolics by combining lignin extraction with lignin depolymerization in aqueous ethanol," *Ind. Eng. Chem. Res*. 51(1), 103-110. DOI: 10.1021/ie202118d

Zakzeski, J., Bruijnincx, P. C. A., Jongerius, A. L., and Weckhuysen, B. M. (2010). "The catalytic valorization of lignin for the production of renewable chemicals," *Chem. Rev*. 110 (6), 3552-3599. DOI: 10.1021/cr900354u

Zhang, X., Zhang, Q., Long, J., Xu, Y., Wang, T., Ma, L., and Li, Y. (2014). "Phenolics production through catalytic depolymerization of alkali lignin with metal chlorides," *BioResources* 9(2), 3347-3360. DOI: 10.15376/biores.9.2.3347-3360

Zhang, Z. C. (2006). "Catalysis in ionic liquids," *Adv. Catal.* 49, 153-237.

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