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Degradation of Lignin with Aqueous Ammonium-Based Ionic Liquid Solutions under Milder Condition

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Abstract

This study investigates the performance of two aqueous ionic liquids (ILs), dimethylbutylammonium acetate ([DMBA][Ac]) and dimethylbutylammoniumbutanoate ([DMBA][B]), solutions for depolymerizing alkali lignin into valuable phenolic compounds. The favorable operation conditions, including reaction temperature and reaction time, are explored. The extent of depolymerization of the lignin is evaluated by analysis with gel permeation chromatography (GPC). The results show that the average molecular weights of the depolymerized lignin samples can be reduced by as high as 93.8 % and 86.8 % after treating with the aqueous [DMBA][Ac] and [DMBA][B], respectively. Moreover, the aromatic chemical species in the depolymerized solutions are identified by using Gas Chromatography-Mass Spectrophotometer (GC-MS). The confirmation of the chemical species is further made by using series of spectroscopic techniques, such as FT-IR, ^{1}H NMR, and ^{13}C NMR. Promising results have been achieved for the depolymerization of the lignin into valuable chemicals by using the proposed green media, aqueous solutions of ionic liquids [DMBA][Ac] and [DMBA][B], under milder condition.

Keywords: lignin; aqueous ionic liquid; depolymerization; aromatic chemicals

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Introduction

Lignin has been recognized as a potential resource for producing valuable aromatic chemicals in the recent years. Additionally, various applications of the lignin such as an additive in plastic, biofuel, and bioactive compounds have also been reported in literature.[1-7] It is one of the major components in the biomass, found from woody materials, agricultural waste, and also produced as a byproduct in paper or pulp industries.[8,9] Its readily availability in enormous amount makes it as a potential candidate to fulfill our future demand of valuable chemicals as well as energy. Although the importance of the lignin material is well noticed worldwide in the general practice, it is mainly burned in the atmosphere to get energy and only a few amount of it is used for the other purposes.[2] Therefore, developing an efficient method to utilize those lignin raw-materials as a feedstock for producing the specific chemicals could be highly advantageous. However, the inherent complexity and the heterogeneity in the structure make its solvation and controlled depolymerization to be a challenging task and also prevent us to have a deep understanding on the mechanism of lignin depolymerization.

The main challenge in selective depolymerization of lignin arises from its polymeric network, which is formed by the strong C-C and C-O-C linkages. The presence of those strong linkages limits the depolymerization process. However, apart from the challenges associated with the depolymerization of the lignin, considerable amount of researches have been conducted to convert lignin into low molecular weight chemicals.[10-15] Among several others, pyrolysis,[16,17], hydrolysis,[18,19] treatments with super- or sub-critical solvents,[20-24] hydrogenolysis,[25] and catalysis[26-29] have been proposed to solvate and depolymerize the lignin. However, most of the reported methods used conventional volatile organic solvents with homogeneous or

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heterogeneous catalyst. In addition, the proposed methods, such as pyrolysis, require high energy input and lead to the non-selective depolymerization of the lignin and produce high amount of char in the final product. The use of subcritical water shows promising results in dissolution of lignin, but overall process is very complex and also energy consumption is still high.

As an ideal solvation and depolymerization medium for the lignin, it should be non-volatile, biodegradable, easy to recycle and thermally stable. Ionic liquid, a new user tailor medium, emanates as an alternative solvent and appears to fulfill all those expectations of an ideal medium for lignin research. In the last decade, using ionic liquids in the lignin researches is gaining great attention.[30,31] The main advantage associated with the use of ionic liquid is that its structure and thus properties can be tuned to increase the interactions and the reaction site with lignin.

The suitability of the ILs to solvate the range of lignocellulosic material at comparatively milder condition is well documented in the literature.[32] Recently, Singh et al.[33] reported that the use of ionic liquid ([C_3SO_3HMIM][HSO_4]), formed by combination of the imidazolium as a cation and sulfate as an anion, for the depolymerization of lignin yielded high concentration of low molecular weight compounds at 120 °C. Xue et al.[34] have demonstrated that by using imidazolium-based ILs, such as 1-methyl-3-benzylimidazolium chloride ([Bnmim][Cl]) and 1-methyl-3 benzylimidazoliumtrichloroacetate ([Bnmim][TFA]) with HCl as a catalyst, about 75.5 % (mass basis) of the lignin can be depolymerized at the optimized reaction condition. Moreover, the fractionate solution is found to contain about 60 wt% of low molecular weight phenolic compounds. The fractionation of about 40 % lignin in the aqueous solutions of IL, such as 1-ethyl-3-methylimidazolium acetate [C_2mim][OAc], was also observed from the

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reaction taking place at 150 ºC for 3 hours.[35] Some other studies[6,8] also highlighted the potential of the imidazoilum-based ionic liquids for depolymerization of lignin in cooperating with an external catalyst or promoter. Moreover, to avoid using an external catalyst or promoter, the IL such as 1-H-3-methylimidazolium chloride with bi-functional activity (solvent + degradation agent) for depolymerization of lignin was also reported in literature.[36]

Since imidazolium-based ionic liquids are categorized as non-biodegradable in nature[37,38], the use of the non-immidazolium based ionic liquids for improving the utilization of the lignin is suggested. For example, Prado et al.[39] utilized ionic liquid ([ET_3NH][HSO_4]), derived from ammonium as a cation and sulfate as a anion, as a solvent for the lignin from willow biomass. The lignin in the ionic liquid solutions was depolymerized by using homogeneous H_2O_2 as well as heterogeneous TiO_2 catalysts. The depolymerized solution catalyzed by $TiO_2$was found rich in phenolic derived compounds. Kim et al.[40] have shown that the new class of non-imidazolium IL, choliniumlysinate ([Ch][Lys]), was applicable to extract lignin from the switch grass. In order to fractionate the lignin, they have used isopropyl alcohol (IPA) as a hydrogen transfer catalyst. As the reaction was operated at 300 °C, about 27 wt% of monomers was produced with low char formation in the depolymerized solution. Moreover, they have also found that on prolong heating the solution in the presence of Ru/C catalyst, the depolymerization of lignin was significantly enhanced and yielded low molecular weight value-added chemicals with greater extent of alkylation on the aromatic ring. The reaction is initiated by dehydrogenation of the ether bond via formation of Ru(0) complex which leads to Ru-enolateformation which yields phenolic monomer through reductive elimination. Our literature survey reveals that the ILs may serve as an important role in the utilization of the enormously available

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lignin materials. It is reported that the anion of the ionic liquids stabilizes the hydroxyl group of lignin which speed up the cleavage of C-O bond. In addition to the coordination ability of an IL anion for lignin depolymerization, they act as nucleophiles by attacking the highly electron deficient protonated C–O bonds.[41] Some studies showed the suitability of imidazolium-based ionic liquids in combination with heterogeneous catalyst for the depolymerization of the lignin, the reports on the non-imidazolium-ammonium-based ionic liquids, which could serve as both a solvent and a degradation agent for the lignin depolymerization process, are rather scarce in the literature. Most of the references related to the use of ionic liquids for depolymerization of lignin are summarized in Table 1.

Table 1

Ionic liquid assisted depolymerization of lignin at various reaction conditions.

Types of lignin	Ionic liquid	Reaction condition	Reference
Oak wood lignin	[HMIM][Cl]	110–150 ºC,	[36]
Organosolv lignin	[Emim][ABS]	180 °C, 6 h	[8]
Klason lignin	[Bmim][$MeSO_4$]	180 °C, 6 h	[8]
Organosolv lignin	[Bmim][$MeSO_4$]	180 °C, 6 h	[8]
Klason lignin	[Emim][ABS]	180 °C, 6 h	[8]
Alkali lignin	[C2mim][OAc]	110–170 °C, 1–16 h	[42]
Alkali lignin	[DIPEA][Ac]	100-170 ºC, 0.5-1.5 h	[43]
Alkali lignin	[DIPEA][B]	100-170 ºC, 0.5-1.5 h	[43]
Enzymatic lignin	[C4mim][Cl]	150 °C, 3 h	[44]

In the present study, we investigate the performance of two ammonium-based ILs, dimethylbutylammonium acetate ([DMBA][Ac]) and dimethylbutylammoniumbutanoate ([DMBA][B]), for the degradation of the alkali lignin. The favorable operating conditions, including reaction temperature and time, are explored for the lignin depolymerization in several specific concentrations of the aqueous ILs solutions. The depolymerized solutions are characterized by using series of techniques, including FTIR, GPC, ^{13}C and ^{1}H NMR, and GC-MS. We select these

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two ionic liquids ([DMBA][Ac] and [DMBA][B]) to get more insight into the behavior of non-symmetrical ammonium ion on the depolymerization of the lignin. Also, these two ionic liquids having common ammonium cation and different anions of varying alkyl chain length can enhance the knowledge on the effect of increasing hydrophobicity on the results of lignin depolymerization.

Materials and methods

Materials

Alkali lignin with low sulfonate content (Sigma-Aldrich, USA) was used for depolymerization process. Acetic acid (mass fraction purity > 0.998, Sigma-Aldrich, USA), butyric acid (mass fraction purity > 0.99, Sigma-Aldrich, USA), and dimethylbutylamine (mass fraction purity > 0.99, Sigma-Aldrich, USA) are the raw materials for the synthesis of the ionic liquids. The ionic liquids ([DMBA][Ac] and [DMBA][B]) were synthesized in our laboratory according to the method reported in literature.[45,46,47] While sodium nitrate (mass fraction purity > 0.99, Sigma-Aldrich, USA) was used as a mobile phase for GPC analysis, pullulan (Mw ~10000, Sigma-Aldrich, USA) was served as a standard for calibrating GPC. Methanol (mass fraction purity > 0.999, Sigma-Aldrich, USA) was employed to sample preparation for GC-MS analysis. Dimethyl sulfoxide-d6 (mass fraction purity > 0.999, Sigma-Aldrich, USA) was taken as a solvent for the preparation of samples for NMR analysis. All the chemicals were used as obtained from the supplier without further purification. Double-distilled deionized water was prepared by using NANO Pure-Ultra pure water purifying system at the resistivity of 18.3 M Ω-cm.

Depolymerization of alkali lignin

A modified high pressure and temperature autoclave reactor (Model: series 4576, T316 stainless steel, Parr Instrument Co., USA) was used for the depolymerization of

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the alkali-lignin. This reactor is commonly used for high-pressure and high-temperature studies. The apparatus consists of an equilibrium cell with a 187 cm^3 maximum working capacity. Automatic temperature control was provided by a heater surrounded the cell together with a cooling water system. The cell is connected to a controller series type 4843 (Parr Instrument Co., USA), which consists of a digital pressure display and a high-temperature cutoff (J-type thermocouple) for safety purposes. Stirring was accomplished by a variable speed stirrer with a magnetic drive. Two valves are attached to the cell head: (a) a sample inlet valve which is connected to a burette (made up of IWAKI code 7740 glass, USA) and (b) the gas release valve which is connected to a vacuum pump. Before loading liquid mixtures into the cell, it is necessary to vacuum the system thoroughly to evacuate the air and traces impurities inside the cell.[43] The freshly prepared solution of the alkali lignin in 30, 50 or 80 wt% of the aqueous ILs solution was injected into the autoclave reactor and heated at a given temperature over a preset reaction time. After completion of the reaction, the autoclave reactor was cooled down to the room temperature and then the sample was withdrawn from the reactor for analysis. Before conducting the next experimental run, the reactor was washed many times, dried overnight, and then vacuumed.

Characterization of depolymerized samples

The FT-IR spectrum of each sample was measured by using Nicolet FTIR-iS10 instrument with the attenuated total reflectance (ATR) method in the range of 4000 - 650 cm^{-1} and collected at a resolution of 4 cm^{-1} with 200 scans. At least 5 repeated measurements are made for each sample and the average of those repeated measurements is considered as a final result.

The molecular weight distributions of lignin before and after depolymerization were analyzed by gel permeation chromatography (GPC, Aqueous phase, Waters 1525

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HPLC Pump). An aqueous solution of $NaNO_3$ (0.05 M) was used as a mobile phase with a flow rate of 0.5 $mL.min^{-1}$. Prior to the analysis of the samples, the GPC was calibrated by using pullulan as a standard. Each sample was prepared by dissolving 2 mg of pre-treated and post-treated samples of lignin in per milliliter of degassed distilled water. The mobile phase and samples were filtered by using a 0.2 μm membrane filter. The filtered solution is injected into the GPC with an air tight glass-made micro syringe.

To identify the species obtained after depolymerization of the lignin, the GC-MS spectra of the post-treated samples of lignin were measured by using a chromatograph (HP model 6890 series GC system). This GC-MS was equipped with a 5973 mass selective detector and Agilent, DB-5MS capillary column (size 30 m x 0.25 mm, J&W Scientific). The temperature program was set as 523 K to 573 K with heating rate of 10 $^{\circ}C.min^{-1}$. Helium is used as a carrier gas with flow rate of 1.0 $mL.min^{-1}$. The National Institute of Standards and Technology (NIST) library of mass spectroscopy was used for identification of the compounds.

The ^{1}H NMR and ^{13}CNMR spectra for the depolymerized lignin in 50 *wt*% and 80 *wt*% of [DMBA][Ac] aqueous solutions or 30 *wt*%, 50 *wt*% and 80 *wt*% of [DMBA][B] aqueous solutions, after the treatment at 180 ºC for 60 min, were measured by using a Bruker-Biospin 500 MHz instrument. The samples were prepared in deuterated dimethyl sulfoxide (D_6-DMSO). Each NMR spectrum was recorded by using tetramethylsilane (TMS) as an internal standard and with an average of 120 scans. The operation parameters of the NMR analyses are pulse sequence: zg30; relaxation delay: 2.00000000 sec; acquisition time: 3.0277631 sec.

Results and discussion

The main objective of this study is to investigate the effect of operating

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parameters on the solvation and depolymerization of the alkali lignin by using the aqueous solutions of ammonium-based ILs ([DMBA][Ac] and [DMBA][B]). For this purpose, the aqueous solutions of lignin (0.1g.mL^{-1}) containing 50 and 80 *wt*% of [DMBA][Ac] and 30, 50, 80 wt% of [DMBA][B] are prepared. Each prepared solution is heated under different temperatures (90, 120, 150 and 180 °C) and periods of reaction time (30, 60 and 120 min). After the treatment at pre-specified reaction condition (temperature and time interval), the product sample is withdrawn from the autoclave reactor for characterization. On the basis of the results obtained from a series of analyses, including GPC, FT-IR, GC-MS, ^{1}H NMR and ^{13}C NMR, the performances of the selected ionic liquids for depolymerizing lignin into low molecular weight compounds are studied and the molecular structures of the major species obtained from the depolymerization of lignin are identified.

Molecular weight distribution

To evaluate the performance of the aqueous ionic liquid solutions for the depolymerization of the lignin, we monitor the change in average molecular weight (*Mw*) of the samples of lignin after the treatment under different reaction temperatures and time intervals. The results are compared with the *Mw* of the lignin sample in pristine solution. GPC was used to determine the molecular weight distribution of the samples before and after treatment.[48] The results of GPC analysis for the samples of depolymerized lignin in the aqueous solutions of [DMBA][Ac] and [DMBA][B] are graphically presented in electronic supplementary information (ESI), Fig. S1 and Fig. S2, respectively. In some cases, more than one peak are shown on their GPC graphs. The corresponding molecular weight (*Mw*), poly-dispersity index (PDI), and the retention time (RT) of each peak obtained from each experimental run are reported in Table 2. Prior to any treatment, the *Mw* of the lignin in aqueous solution is found to be

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6436 g.mol^{-1}.

Effect of the temperature on lignin depolymerization

According to the tabulated values in Table 2, the average *Mw* of the major species in the products are about 1369, 1337, 1279, 1130 g.mol^{-1} after the treatment by 50 *wt%* aqueous solution of [DMBA][Ac] at 90, 120, 150, and 180 ˚C for 60 min, respectively. As also illustrated in Fig. 1, increasing reaction temperature obviously enhances the depolymerization of the lignin in the aqueous solutions of [DMBA][Ac]. Similar trend of temperature-effect is also revealed in Fig. 1, Table 2, and Fig. S2 by using the aqueous [DMBA][B] solution. However, the average *Mw* of [DMBA][B] system is generally greater than those of [DMBA][Ac] system under the same reaction condition. For example, after the treatment at 180 ˚C for 60 min, the average *Mw* of depolymerized lignin in 80 *wt%* [DMBA][B] aqueous solution is 912 g.mol^{-1} (reduced by about 86% after treatment), while that in 80 wt% [DMBA][Ac] aqueous solution decreases down to 437 g.mol^{-1} (reduced by about 93%). It appears that the ionic liquids with less hydrophobic ion may provide better performance for the lignin depolymerization.

Singh et al.[49] indicated that processing the lignin at higher reaction temperatures may not only increase the production cost but also lead to formation of unnecessary by products, which may become more difficult in the further separation. Additionally, Opriset al.[50] conducted research on the fragmentation of lignin over magnetically recyclable composite in a temperature range of 100-230 °C. Analyzing the fragmented intermediates by GC-MS, they found the formation of dimers and trimers at lower reaction temperatures. At 180 °C good performance was achieved, but rising the temperature from 180 to 230 °C could decrease the yield of the product. In this study,

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Table 2

GPC results of depolymerized lignin in aqueous solutions of [DMBA][Ac] or [DMBA][B] at various reaction temperatures (*T*) and time intervals (*t*).

T (ºC)	*t* (min)	Lignin in 50 *wt*% [DMBA][Ac]					Lignin in 50 *wt*% [DMBA][B]			
		M_w	average Mw	PDI	*RT* (min)	remark	M_w	average Mw	PDI	*RT* (min)
90	60	1937		1.10	24.90	Peak 1	3632		1.20	25.07
		801	1369	1.02	26.05	Peak 2	934	2283	1.07	26.73
120	60	1909		1.07	24.84	Peak 1	1880		1.11	25.13
		766	137.5	1.02	26.55	Peak 2				
150	60	1820		1.12	25.02	Peak 1	1627		1.19	25.13
		738	1279	1.01	26.28	Peak 2				
180	30	1671		1.05	25.00	Peak 1	1826		1.13	25.02
		745	1208	1.01	26.50	Peak 2	758	1292	1.01	26.05
180	60	1527		1.05	25.13	Peak 1	1202		1.20	26.88
		734	1130.5	1.01	26.65	Peak 2				
180	120	1787		1.13	25.02	Peak 1	851		1.05	26.99
		734	1260.5	1.01	26.30	Peak 2				
Lignin in 80 *wt*% [DMBA][Ac]							Lignin in 80 *wt*% [DMBA][B]			
		M_w	average Mw	PDI	*RT* (min)	remark	M_w	average Mw	PDI	*RT* (min)
180	30	476		1.09	26.50	Peak 1	1055		1.16	26.07
	60	437		1.06	26.53	Peak 1	912		1.05	26.08
	120	399		1.04	26.57	Peak 1	983		1.11	26.31
Lignin in 30 *wt*% [DMBA][B]										
		M_w	average Mw	PDI	*RT* (min)	remark				
180	30	1527		1.26	27.40	Peak 1				
	60	1475		1.23	27.42	Peak 1				
	120	4283		1.07	24.38	Peak 1				
		1245	2764	1.21	27.35	Peak 2				

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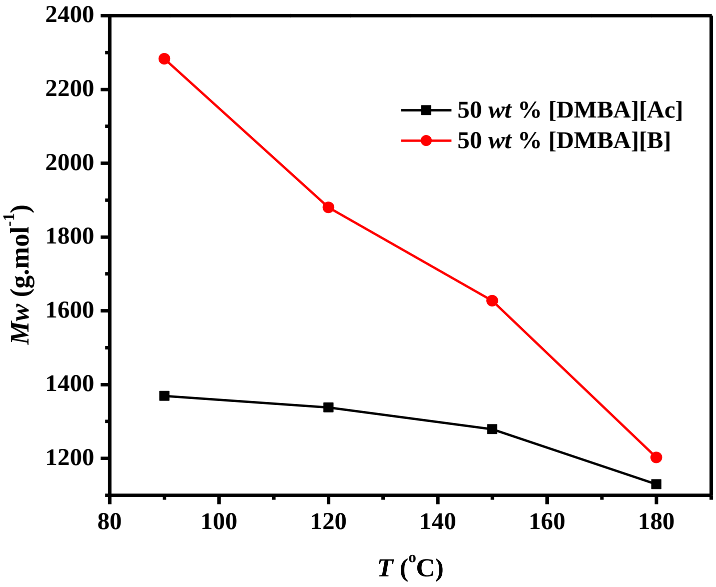

Fig. 1 The effect of reaction temperature on the averaged molecular weight of the products of lignin depolymerization in the aqueous solutions of 50 *wt*% ILs at *t* = 60 min.

lower molecular weight compounds were also produced at 180°C. The analysis with GC-MS later confirms that aromatic valuable chemicals are produced from the lignin depolymerization at 180 °C.

Effect of the reaction time on lignin depolymerization

As shown in Table 2 and Fig. 2, the average *Mw* of the product can be significantly reduced to 476 g.mol^{-1} by heating the lignin in higher concentration (80 *wt%*) of aqueous [DMBA][Ac] solution at 180 ˚C for 30 min. Increasing the reaction time to 60 min and120 min, the values of average *Mw* further decrease down to 437 and 399 g.mol^{-1}, respectively. The reduction in the average *Mw* is as high as by about 94% after the treatment of lignin in 80 *wt%* [DMBA][Ac] aqueous solution at 180 ˚C for 120 min as comparing with the pristine lignin (6436 gmol^{-1}). This indicates that [DMBA][Ac] efficiently enhances the depolymerization of the lignin.

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However, increasing reaction time appears not to always decrease the average *Mw* of the products as presented in Table 2 and Fig. 2. For example, the average *Mw* of the products are about 1208, 1130, and 1260 g.mol^{-1} for the lignin in 50 *wt%* [DMBA][Ac] aqueous solution at 180 ˚C after processing 30, 60, and 120 min, respectively. It reveals that the extent of depolymerization increases as the increase of reaction time from 30 to 60 min, but further increasing reaction time to 120 min, instead of enhancing the depolymerization, the repolymerization of the fractionate species takes place.[51] Similar behavior is also clearly found from the case of using 30 wt% of [DMBA][B] aqueous solution as shown in Fig. 3.

Effect of ionic liquid concentration on lignin depolymerization

As seen from Figs. 2 and 4, the aqueous ionic liquids are able to degrade the lignin to smaller compounds and the average *Mw's* of the depolymerized lignin decrease with increasing the concentration of ionic liquids [DMBA][Ac] and [DMBA][B], respectively, as the reaction time intervals are no greater than 60 min. The average *Mw* of the lignin decreases by 76% when the lignin is heated at 180˚C for 30 min in 30 *wt* % of [DMBA][B] aqueous solution. Increasing the concentration of [DMBA][B] to 50 *wt*% under the same reaction time the average *Mw* decreases by 80%. Further increasing the concentration of the ionic liquid to 80 *wt*% the average *Mw* of lignin reduces by 84%. However, repolymerization is shown in Fig. 4 in case of using 80 wt% of [DMBA][B] aqueous solution for 120 min at 180 ˚C. This phenomenon is not found as the concentrations of the IL are 30 wt% and 50 wt%. Repolymerization was also shown in Fig. 2 for the case of using 50 wt% [DMBA][Ac] aqueous solution at 180°C for 120 min.

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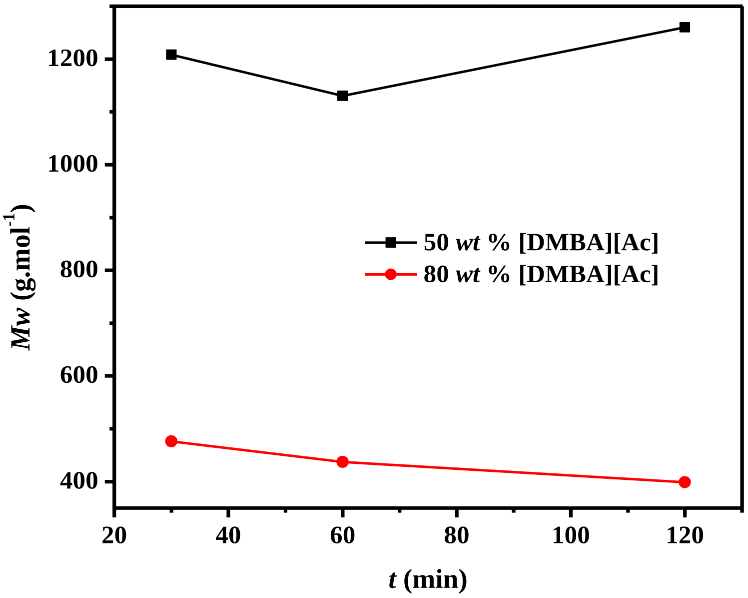

Fig. 2 The effect of reaction time on the averaged molecular weight of the products of depolymerized lignin in the aqueous solutions of [DMBA][Ac] at T = 180 °C.

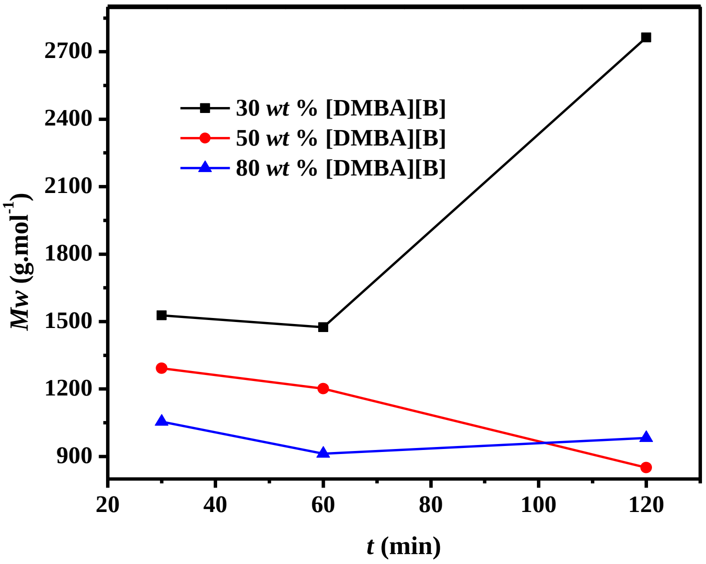

Fig. 3 The effect of reaction time on the averaged molecular weight of the products of depolymerized lignin in the aqueous solutions of [DMBA][B] at T = 180 °C.

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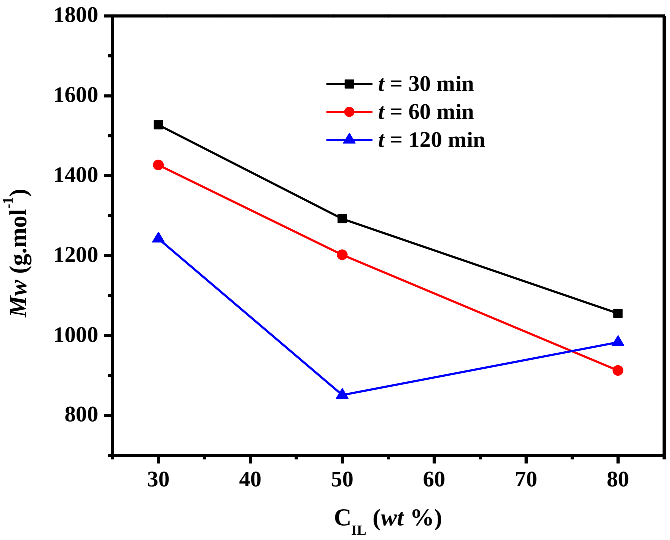

Fig. 4 The effect of concentration of [DMBA][B] on the averaged molecular weight of the products of depolymerized lignin in the aqueous solutions of [DMBA][B] at various reaction time intervals and *T* = 180 ˚C.

Structure identification for the depolymerized lignin

FT-IR

After confirming that these selected ammonium-based ionic liquids ([DMBA][Ac] and [DMBA][B]) are able to assist the depolymerization of lignin, we attempt to identify the major functional groups in the depolymerized species by using FT-IR. The FT-IR spectra for the samples of lignin treated by [DMBA][Ac] and [DMBA][B] are given in Fig. 5(a-c) and Fig. 6(a-d), respectively. Based on those FT-IR spectra, various possible functional groups are identified and compiled in Table S1. It can be seen from Fig. 5 (a-c) that the FT-IR spectra of all the samples of depolymerized lignin treated by [DMBA][Ac] possess the characteristic peak in the region of 3382-3358 cm^{-1}, which indicates the presence of hydroxyl group in the depolymerized species.[8,17] The vibrational spectrum for C-H group is also found from the peak in the region 2909-2908 cm^{-1}.[49] Additionally, the presence of aromatic compounds is noted by their characteristic peaks around 1648-1631 cm^{-1}. A small spectral peak is also

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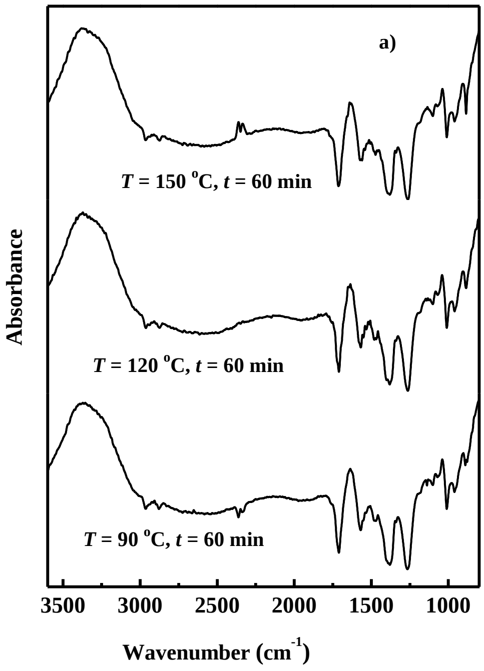
observed in the lower wavenumber region (1170-1028 cm^{-1}), which indicates the existence of species with Ar-O linkages of ether or alcohol.[26]

Similar spectral peaks are noted in the spectra of lignin samples treated by the aqueous [DMBA][B] solutions over the entire experimental conditions as shown in Fig. 6 (a-d). The presence of hydroxyl functional group is noted which corresponds to the peak in the wavenumber region of 3408-3358 cm^{-1}.[52] The intense spectral peak appeared around 1648 – 1631 cm^{-1} is the characteristic peak for benzene ring. The stretch of C-H bond is observed at 2921 cm^{-1} and C-O stretch is also found in the wavenumber region of 1170-1068 cm^{-1}. Comparing the untreated alkali lignin and aqueous ionic liquid treated lignin, the later somewhat shift towards higher wavenumber. Overall, our FT-IR analyses indicate that the lignin treated by the aqueous [DMBA][Ac] and [DMBA][B] solutions produces a wide variety of polyhydroxy and alkoxy aromatic compounds.



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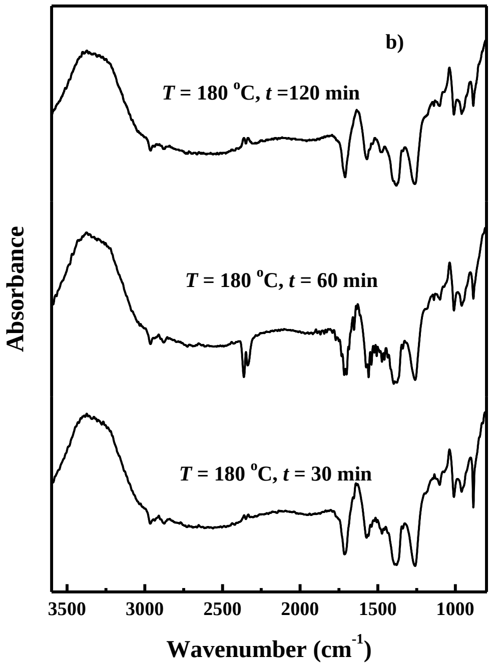

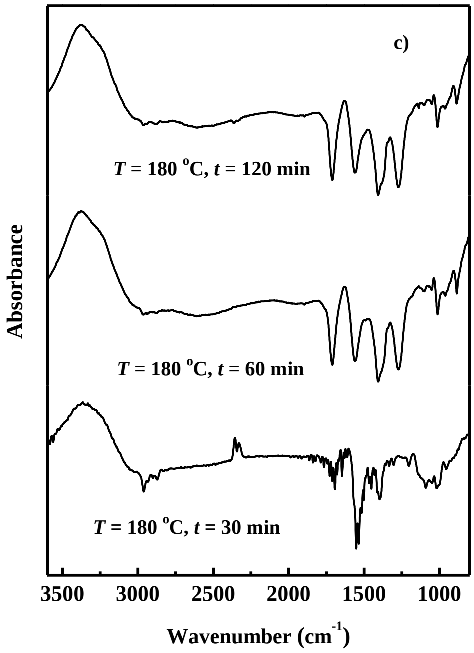

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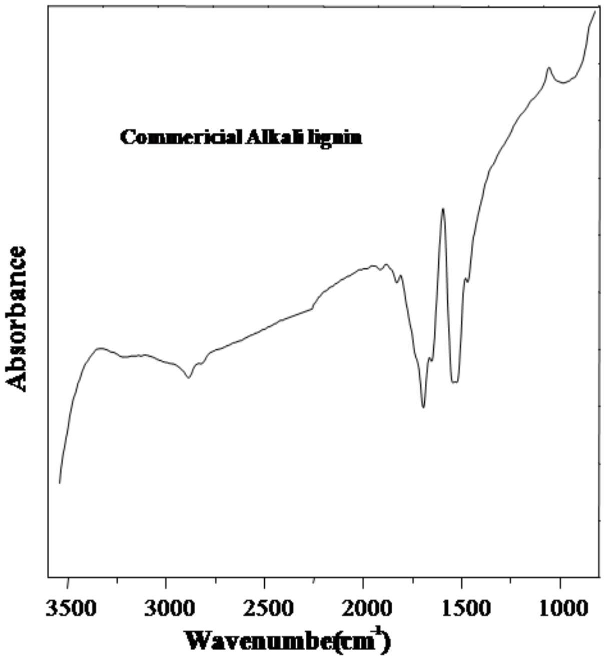
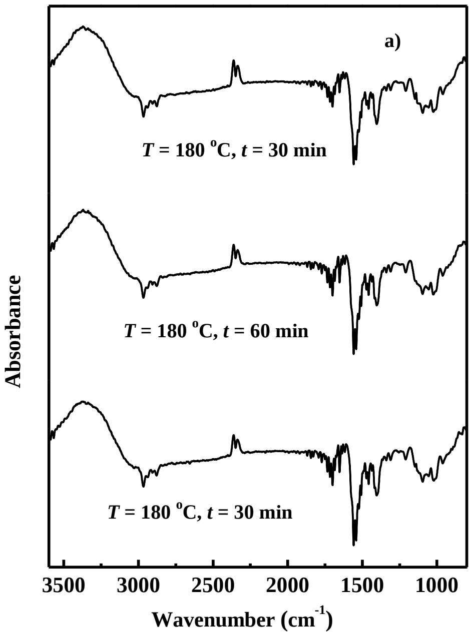


Fig. 5 FT-IR spectra of commercial alkali lignin and the depolymerized lignin treated by the 50 *wt*% (a,b) and 80 *wt*% (c) of [DMBA][Ac] aqueous solutions at different experimental conditions.



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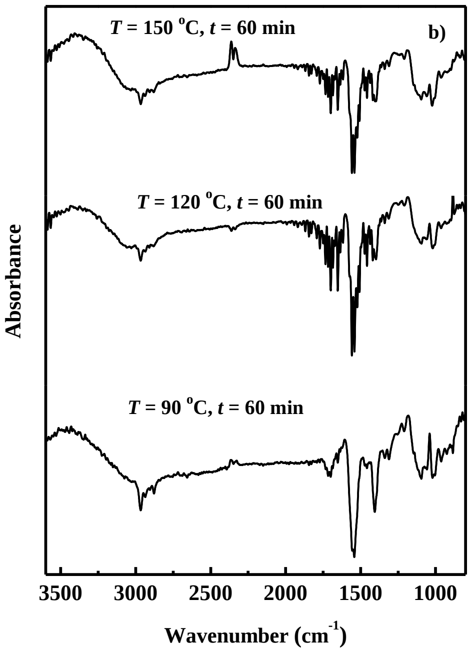

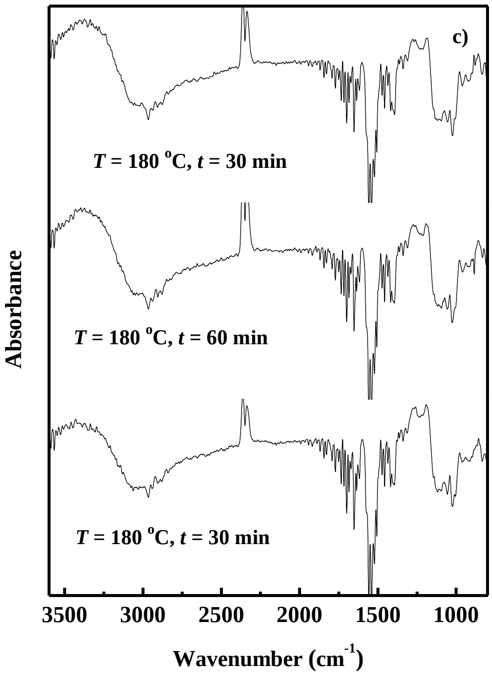

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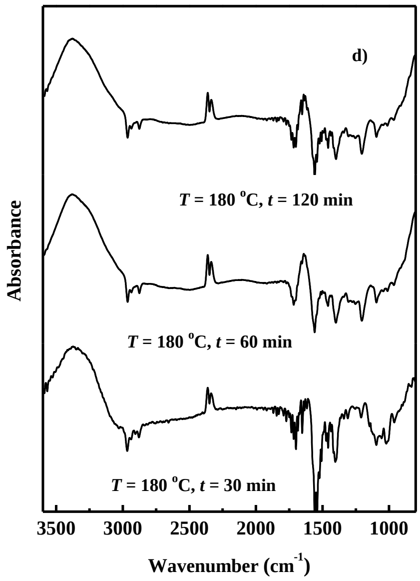

Fig. 6 FT-IR spectra of the depolymerized lignin treated by the 30 *wt*% (a), 50 *wt*% (b, c) and 80 *wt*% (d) of [DMBA][B] aqueous solutions at different experimental conditions.

GC-MS

As mentioned previous, this study used GC-MS to identify the chemical species after the depolymerization of lignin in aqueous [DMBA][Ac] and [DMBA][B] solutions. The samples to be analyzed are the depolymerized solutions of lignin in 50 *wt*% and 80 *wt*% [DMBA][Ac] and in 30 *wt*%, 50 *wt*% and 80 *wt*% [DMBA][B] at 180 °C for 60 min. The results of measurements, including all the identified compounds with corresponding molecular weight as well as retention time, are compiled in Table 3. The mass spectra with the structures of the identified molecules are shown in Fig. S3. From the provided values of the identified compounds in Table 3, we can see that a variety of valuable aromatic compounds are identified from the samples treated by both two ionic liquids and those compounds are almost identical over the entire investigated concentrations of the ionic liquids. The results also confirm that these two selected ionic liquids not only promote the depolymerization process of the lignin but also produce a variety of valuable chemical species.

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Table 3

Lignin-derived monomeric compounds in the depolymerized lignin treated by the aqueous ionic liquid solutions at 180 °C for 60 min

IL Conc. (wt%)	*RT* (min)	Identified compound	Relative area (%)	*Mw*
Lignin in aqueous [DMBA][Ac]solution				
50	4.5	*o*-Guaiacol	16.4	124
	7.4	Isoeugenol	14.3	164
	6.4	*p*-Propylguaiacol	12.8	166
	3.5	1,2,3-Trimethoxy-5-(1-propenyl)benzene	8.6	208
80	6.4	1,2-(Methylendioxy)benzene	3.2	122
	2.1	2-Allylphenol	17.6	134
	6.2	3-Allyl-6-methoxyphenol	13.2	164
	6.4	*p*-Propylguaiacol	13.0	166
	6.42	3-Hydroxy-4-methoxy- benzaldehyde	2.8	152
Lignin in aqueous [DMBA][B]solution				
30	4.5	*o*-Guaiacol	8.5	124
	8.1	2-methoxy-4-(1-propenyl)- Phenol	10.8	164
	6.4	*p*-Propylguaiacol	7.4	166
	8.6	(E)- 4,4'-(3-Ethenyl-1-propene-1,3-diyl)bis-phenol	1.8	252
50	4.5	*o*-Guaiacol	9.4	124
	8.1	2-Methoxy-4-(1-propenyl)- phenol	12	164
	6.4	*p*-Propylguaiacol	9.6	166
	8.0	1,4-Diol-1,4-diphenyl-2-butene	2.4	240
	5.3	(E)-4,4'-(3-Ethenyl-1-propene-1,3-diyl)bis-phenol	2.8	252
80	4.5	*o*-Guaiacol	11.2	124
	3.3	2-Allylphenol	14.3	134
	3.6	p-Propylphenol	8.9	136
	8.1	2-Methoxy-4-(1-propenyl)- phenol	12.5	164
	6.4	*p*-Propylguaiacol	9.8	166
	2.6	1,2-Dimethoxy-4-(1-methoxy-1-propenyl)benzene	2.6	208

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NMR analysis

In the present study we used nuclear magnetic resonance spectroscopy (*^{1}H* NMR and *^{13}C* NMR) to further reconfirm the identified species, which are produced from the lignin treated by 50 *wt*% of [DMBA][Ac] or [DMBA][B] aqueous solution at 180 °C for 60 min. The ^{1}H NMR spectra of the depolymerized lignin by using the aqueous [DMBA][Ac] and [DMBA][B] solutions are depicted in Fig. S4 and Fig. S5, respectively, and the *^{13}C* NMR spectra of the depolymerized lignin in the aqueous [DMBA][Ac] and [DMBA][B] solutions are shown in Fig. S6 and Fig. S7, respectively. From the spectra of NMR of both aqueous ionic liquids solution assisted lignin depolymerization, peaks are observed at δ_{H} (0.8-1.8 ppm, 2.1 – 2.5 ppm and 6.9-7.4 ppm) and δ_{C} (13-19 ppm, 39-40 ppm, 48-50 ppm, 128-134 ppm and 167-168 ppm). From peak assignment on ^{1}H, and ^{13}C-NMR spectra, The results of *^{13}C* NMR of depolymerized lignin in aqueous [DMBA][Ac] solution presents a chemical shift at 167.99 ppm, which is an indication of presence of carbonyl compound. A characteristic peak of aromatic compounds is also observed at chemical shifts of 133.6-128 ppm and 6.9 ppm on the spectra of *^{13}C* NMR and *^{1}H* NMR, respectively. In addition to the aromatic compounds, C-C and protons on methyl group are observed in the range of aliphatic regions, 40-13 ppm on *^{13}C* NMR and 0.8-2.5 ppm on *^{1}H* NMR, respectively. A spectral peak of *^{13}C* NMR is noted at a chemical shift of 50 ppm, which shows the presence of electronegative element adjacent to carbon, especially alkoxy group.

Similar functional groups are also found from the samples of depolymerized lignin by using the aqueous [DMBA][B] solutions. For instance, the presence of carbonyl and alkoxy functional groups is confirmed by the chemical shifts of 168 ppm and 48 to 50 ppm on the spectra of *^{13}C* NMR, respectively. The aromatic group is also identified by the chemical shifts of 133-128 ppm on *^{13}C* NMR spectrum and 7.4 ppm

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on ^{1}H NMR spectrum. Generally, from the spectral analyses of ^{13}C NMR and ^1H NMR the presence of hydroxyl, alkoxy, aromatic and aliphatic groups are confirmed. The results obtained from the analyses of NMR spectra are consistent with those from FT-IR.

Conclusions

The possibility of using aqueous ionic liquid ([DMBA][Ac] or [DMBA][B]) solutions for the production of valuable chemicals from lignin is investigated. The performance of depolymerization of the lignin is found to be substantially influenced by reaction temperature, reaction time, and the concentration of the ionic liquid. The samples of depolymerized lignin by using the aqueous ionic liquid solution are characterized by GPC, GC-MS, FT-IR, and NMR. Promising results have been achieved when the depolymerization of the lignin was conducted at 180 °C for 60 min. The depolymerizing ability of both two aqueous ionic liquid solutions to disconnect C–O–C linkages are found even at low concentration of ionic liquid. According to the GPC analysis, the average *Mw's* of the depolymerized lignin are reduced by about 82.4% and 93% in 50 *wt*% and 80 *wt*% aqueous [DMBA][Ac] ionic liquid solutions, respectively, and reduced by 77%, 81.3% and 86% in 30 *wt%*, 50 *wt*%, and 80 *wt*% aqueous [DMBA][B] ionic liquid, respectively, as the lignin was treated at 180 °C for 60 min. The analyses results from GC-MS, FT-IR, and NMR confirm the presence of aromatic polyhydroxyl compounds in the depolymerized lignin. It is concluded that these two investigated aqueous ionic liquid solutions have great potential to degrade the lignin into phenolic compounds under milder reaction condition.

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Conflicts of interest

There are no conflicts to declare.

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Degradation of Lignin with Aqueous Ammonium-Based Ionic Liquid Solutions under Milder Condition

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Graphical Abstract

Ammonium-based ionic liquids can be served as solvent and promoter for lignin depolymeriazation.