Lignocellulose Fractionation and Lignin Depolymerization Using Glycerol and Acidic Ionic Liquids: Identification of the Main Products by GC-MS

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Difficulties in fractionation and subsequent conversion of lignocellulosic biomass have restricted the development of sustainable biorefineries of lignocellulosic materials. Herein, an aqueous glycerol/acidic ionic liquid (AGAIL) process of coir was carried out under atmospheric and autogenerated pressure to investigate the lignocellulose fractionation and understand the main conversion products generated during the process. Additionally, the depolymerization capacity of the AGAIL system on lignin was also estimated by analyzing the main degradation products. The results indicated that the process under autogenerated pressure presented much higher delignification efficiency and more effective lignocellulose conversion capability than those under atmospheric pressure. Ribitol and monomeric aromatic compounds were identified by gas chromatography-mass spectrometry (GC-MS) as the main conversion products of carbohydrates and lignin, respectively. The glycerol/AIL system was shown to be able to depolymerize coir lignin with a resulting lignin depolymerization extent of 28.1%. The main lignin depolymerization products were monomeric aromatic compounds.

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INTRODUCTION

Lignocellulosic materials are abundant renewable resources and continue to play important roles in the world as energy feedstocks and fundamental materials (Arevalo-Gallegos *et al.* 2017; Kou *et al.* 2017). Lignocellulosic materials are mainly composed of cellulose, hemicellulose, and lignin contained in a cellular structure (Brandt *et al.* 2013). The naturally complex macromolecule structures among them hinder the effective utilization of the lignocelluloses. Thus, an emerging concept of biorefinery aimed to utilize these components encourages the pretreatment or fractionation of the lignocellulosic components followed by further treatment or conversion (Jiang *et al.* 2017). In this context, lignocellulose fractionation is considered to be crucial for the economical and sustainable biorefinery of lignocellulosic materials (Fang and Sixta 2015; Nitzsche *et al.* 2016).

Organosolv pretreatment is a fractionation process of lignocellulosic biomass using organic solvents with or without catalysts, and it can increase cellulose accessibility by fractionating lignocellulose components (Zhang *et al.* 2016). The organosolv process is considered to be a promising way to provide cellulose, hemicellulose, or lignin feedstock for biorefineries producing fuels, chemicals, and materials (Nitzsche *et al.* 2016).

Glycerol, an emerging renewable bio-derived feedstock, can be used to produce value-added chemicals and energy (*e.g.* hydrogen) through various catalytic reactions (Bagheri *et al*. 2015; Anitha *et al*. 2016; Bagnato *et al*. 2017). Additionally, it is a promising high-boiling-point organic solvent for the organosolv process due to its environmentally friendly properties, high accessibility, and good performance (Zhao *et al.* 2009). Numerous studies have investigated the glycerol-based organosolv process of various lignocellulosic materials with or without an alkaline or acid catalyst (Demirba 1998; Sun and Chen 2007; Novo *et al.* 2011; Sun *et al.* 2015). Enhanced enzymatic digestibility of cellulose can be achieved by fractionating the biomass components after the glycerol process. Novo *et al.* (2011) have optimized the aqueous glycerol delignification process of sugarcane bagasse without a catalyst, and the best result, obtained with a glycerol content of 80%, a reaction time of 150 min and a temperature of 198.3 °C, produced pulps with 54.4% pulp yield, 7.75% residual lignin, 81.4% delignification, and 13.7% polyose content.

Recently, the organosolv process has been combined with the catalysis of acidic ionic liquids (AIL) to fractionate lignocellulosic biomass (Cheng *et al.* 2018). The combined system can fractionate lignocellulosic biomass into cellulosic materials with a lignin content as low as 0.95% and shows a delignification rate of up to 98.0%. Interestingly, the solvent system based on aqueous glycol solution and acidic ionic liquid (AGAIL) presented an effective conversion capability on lignocelluloses, although the conversion process and potential products are still unclear. Meanwhile, the literature has focused on the biomass fractionation efficiency of glycerol system and the enhancement of enzymatic hydrolysis of glycerol-treated cellulose materials (Sun *et al.* 2015).

Aimed at comprehensive utilization of biomass, it is important to understand the component degradation and conversion during the glycerol processing of lignocellulosic biomass. Consequently, the present study investigated the effect of reaction conditions on the fractionation efficiency of lignocellulosic biomass in an AGAIL fractionation process and examined the main conversion products generated during the process. The capacity of the glycerol/AIL system on lignin depolymerization was also estimated by analyzing the main lignin depolymerization products.

EXPERIMENTAL

Materials

Glycerol and the other chemical reagents were procured from Tianjin Fuyu Fine Chemical Co., Ltd., Tianjin, China and used as received. The AIL (1-butyl-3-methylimidazolium hydrosulfate, [Bmim][HSO$_4$]) was purchased from the Lanzhou Institute of Chemical Physics of the Chinese Academy of Sciences. Coir was obtained from Weifang Juxin Fiber Co., Ltd. in Shandong, China. It was ground using a mini mill (Model FZ102, Tianjin, China). Coir powder between 60 and 100 mesh was collected and then extracted with acetone in a Soxhlet extractor for 6 h. The extracted coir powder was oven-dried at 70 °C overnight.

Biomass Fractionation Process
Atmospheric process

In a typical run of the atmospheric process, 1 g of ground coir was added to 30 mL of aqueous glycerol solution (24 mL of alcohol and 6 mL of water) in a 250 mL flask, and 1 g of [Bmim][HSO$_4$] was also added as catalyst. Subsequently, the flask was immersed

into a 200 °C oil bath for 1 h with reflux condensation and magnetic stirring. After cooling to room temperature, the solution was filtered with a nylon membrane (0.4 μm) under vacuum to obtain the cellulose-rich material (CRM). The CRM was washed three times with 50 mL distilled water each time and dried. Next, 100 mL of distilled water was added to the combined filtrate to precipitate the lignin. Lignin was also obtained by vacuum filtration and washed with water three times. The CRM and lignin yields were obtained by weighing the dry mass of CRM and lignin and calculating with Eqs. 1 and 2, respectively.

$$\text{CRM Yield} = m_C/m_B \times 100\% \tag{1}$$

$$\text{Lignin Yield} = m_L/m_B \times 100\% \tag{2}$$

where m_B, m_C and, m_L stand for the mass of original biomass, CRM and lignin, respectively.

Autoclave process

In a typical run of the autoclave process, 1 g of ground coir, 30 mL of aqueous glycerol solution (24 mL of glycerol and 6 mL of water), and 1 g of [Bmim][HSO$_4$] were mixed thoroughly by a magnetic stirring in a 50 mL stainless steel autoclave. Subsequently, the autoclave was immersed into a 200 °C oil bath for 1 h. After processing, CRM and lignin were obtained in the same way as the atmospheric process. Figure 1 demonstrates the main procedures of the atmospheric and autoclave processes.
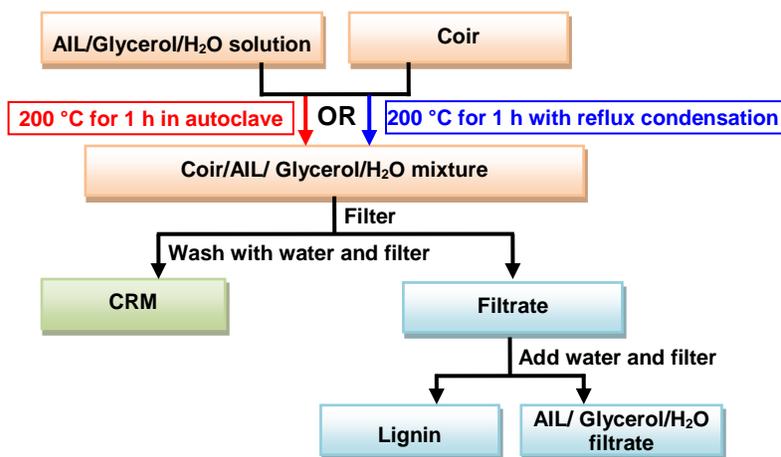
Fig. 1. Flowchart for biomass fractionation with the atmospheric and autoclave processes

Lignin Depolymerization Process

In a typical run of the lignin depolymerization process, 0.5 g of coir lignin extracted with the autoclave process, 10 mL of glycerol, and 0.5 g of [Bmim][HSO$_4$] were mixed thoroughly by magnetic stirring in a 50 mL stainless steel autoclave. Subsequently, the autoclave was immersed in a 240 °C oil bath for 1 h with magnetic stirring. After cooling, 100 mL of water was added to precipitate the non-degraded lignin, and the mixture was filtered. The obtained lignin was washed three times with 50 mL of distilled water each time and dried.

Characterizations

All filtrates were combined and concentrated by rotary evaporation at 60 °C under reduced pressure to remove most of the water. And then the concentrated filtrate was mixed thoroughly with 20 mL ethyl acetate. After standing for 0.5 h, a biphasic system could be

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obtained, and the top ethyl acetate phase was carefully taken out from the system. After repeating the process three times, the ethyl acetate solutions were combined and concentrated to about 0.5 mL by rotary evaporation. The potential conversion products and lignin depolymerization products in the filtrate were then identified with gas chromatography-mass spectrometry (GC-MS), using an Agilent 7890A gas chromatograph (Santa Clara, USA) equipped with a HP-5MS column (30 m long, 250 μm I.D., 0.25 μm film thickness) and Agilent 7000B mass spectrometer (Santa Clara, USA) with helium as the carrier gas. In a typical run, 1.0 μL of ethyl acetate solution was injected using a split mode in a split ratio of 20:1. The column was initially kept at 70 °C for 1 min, then was heated at a rate of 20 °C min^{-1} to 250 °C and maintained at that temperature for 20 min. The ionization mode used was electronic impact at 70 eV, and spectra were acquired from *m/z* 30 to 400. The composition percentage of conversion products was determined by analyzing the GC peak areas. Identification of the products was done by comparing and matching the mass spectra with the standard spectra in the NIST2010 mass spectral library (NIST 2010).

The chemical composition of the original coir and CRM were determined by a combined method reported previously (Datta 1981; Cheng *et al.* 2014). Briefly, 0.1 g of biomass was combined with 30 mL of 0.5 M H_2SO_4 solution, and the mixture was refluxed for 2 h. The hemicellulose content was obtained by the difference in weights of the biomass after drying. The above dried residue was further treated with 2 mL of 72 wt. % H_2SO_4 for 2 h. The solution was diluted to 3% with water and subsequently refluxed for 4 h. The acid insoluble lignin was weighed after drying, and the acid soluble lignin was then determined by ultraviolet (UV) spectrum at 205 nm. The cellulose content was calculated after the determination of hemicellulose and lignin content.

RESULTS AND DISCUSSION

Fractionation Efficiency Analysis

The glycerol organosolv process allows fractionating biomass under atmospheric pressure, which is one of its most important advantages (Sun and Chen 2007). Herein, the glycerol processes were performed in an autoclave or with reflux condensation to analyze the effects of reaction conditions on the fractionation efficiency. The reaction system and conditions were described previously (Cheng *et al.* 2018). The glycerol organosolv process was conducted at 200 °C in aqueous glycerol solution for 1 h with AIL as the catalyst. It is important for the fractionation process to remove as much lignin as possible (Zhao *et al.* 2009). Thus, coir with a high lignin content of 32.64% was chosen as the raw material so that the delignification efficiency of the system could be verified.

CRM yield and lignin yield were determined to evaluate the fractionation efficiency of the AGAIL process. Figure 2(a) shows the CRM yield and lignin yield of the glycerol processes that were carried out under autogenerated pressure and *vs.* atmospheric pressure. It is shown that higher reaction pressure resulted in much lower CRM yields (46.6% *vs.* 68.6%) and slightly higher lignin yields (4.86% *vs.* 3.88%) when they were carried out at 200 °C for 1 h. Also, almost half of the lignocellulose components (48.5%) were degraded into low-molecular-weight compounds during the autoclave process, and a much lower mass loss of 27.6% was achieved during the atmospheric process. Thus, it can be concluded that the conversion of lignocellulosic components can be easily converted into degradation products under elevated reaction pressure.

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Similar results have been reported that an atmospheric aqueous glycerol pretreatment of wheat straw carried out at 220 °C for 3 h led to a CRM yield of 61% (Sun *et al.* 2015), while an aqueous glycerol pretreatment of bagasse in an autogenerated pressure at 190 °C for 3 h resulted in a CRM yield of 57.8% (Novo *et al.* 2011). The aqueous glycerol process of beech wood in an autoclave at 205 °C to 300 °C for 0.5 h led to mass losses of 36.6% to 38.0% (Demirba 1998). Compared with these processes, the presence of AIL in this study facilitated the conversion of lignocellulose and led to a higher mass loss.

The component comparisons of the original coir and the CRMs obtained in the processes are demonstrated in Fig. 2(b). The autoclave process resulted in a higher delignification rate than that of the atmospheric process (57.7% *vs*. 34.5%), while the lignin content in CRM (29.6% and 31.2% for CRM of the autoclave and atmospheric processes, respectively) was still close to that of the original biomass (32.6%). This result indicated the deep removal of hemicelluloses in the process. The autoclave and atmospheric processes gave hemicellulose removal extents of 94.2% and 75.4%, with extremely low hemicellulose contents in CRM (just 2.65% and 7.60%, respectively). Finally, 68.3% and 90.8% of the original cellulose remained in CRM after the autoclave and atmospheric processes, respectively. Compared with the atmospheric process, the autoclave process presented much higher delignification efficiency and more effective lignocellulose conversion capacity. Considering the low lignin yield of the autoclave process, the glycerol-based system may exhibit a promising capacity on lignin depolymerization. Thus, the lignin depolymerization in the glycerol/AIL system was subsequently tested in the present study.
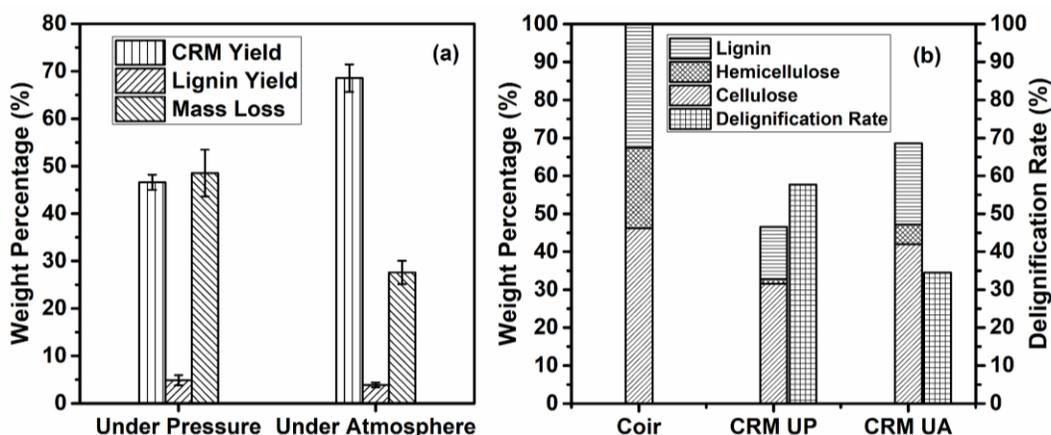
Fig. 2. Results for biomass fractionation: (a) component yields and mass loss; (b) Component and delignification analyses of the original coir and CRMs. (CRM UP: CRM under pressure; CRM UA: CRM under atmosphere)

Analysis of Conversion Products

To analyze the conversion products of lignocelluloses during biomass pretreatment processes, the catalytic degradation products of carbohydrates and lignin were extracted with organic solvent and then identified by GC-MS. Ethyl acetate, a low environmental impact and low toxicity chemical, was chosen to form a biphasic system with the filtrate obtained in the AGAIL process and extract the potential conversion products.
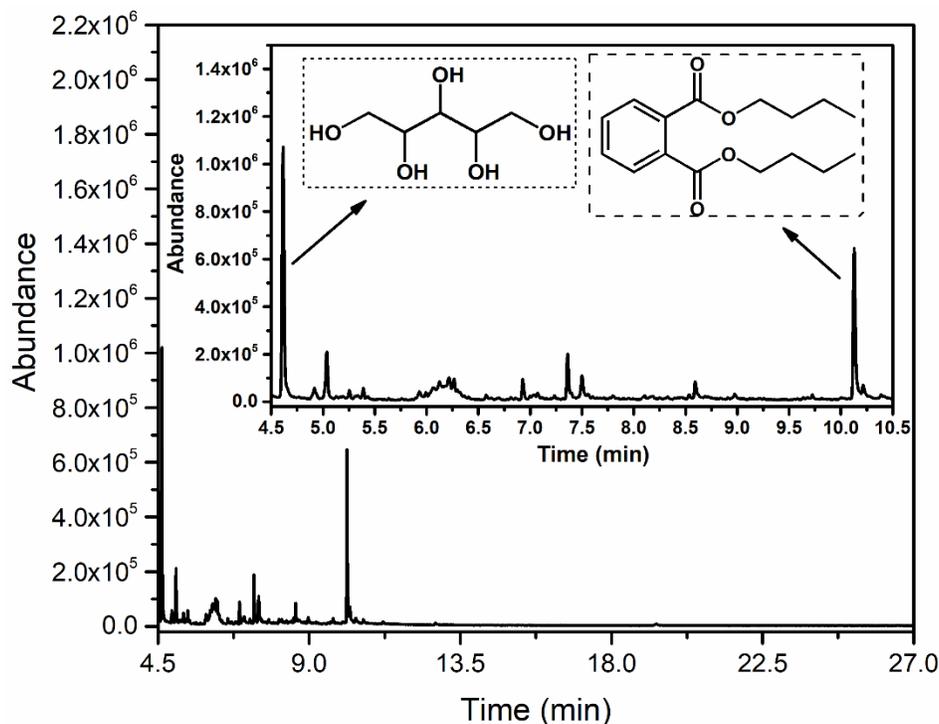
Fig. 3. GC chromatogram of the conversion products generated in the AGAIL process

The GC chromatogram and peak assignments for the conversion products are summarized in Fig. 3 and Table 1, and the main products are also marked in Fig. 3. The biomass conversion products of both carbohydrates and lignin generated in the process can be identified, which was in accordance with the results of component analysis. The main conversion products corresponding to carbohydrates (mainly hemicellulose) degradation were tentatively identified by matching with the NIST 2010 library (NIST 2010) as ribitol, 1-(2-ethoxypropoxy)-2-propanol, methyl 2-(2-(2-butoxyethoxy)ethoxy) acetate, and 4-oxo-pentanoic acid butyl ester. The conversion products of carbohydrates accounted for more than half of the total peak area, which indicated the more effective conversion capacity of the AGAIL system on the carbohydrates than that on the lignin. The major product generated from the carbohydrates degradation was ribitol, which had a retention time of 4.61 min and accounted for 39.4% of the total peak area (Fig. 3). It is reported that hydrothermal liquefaction of barley straw with K_2CO_3 at 280 °C to 400 °C can also generate ribitol from the degradation of cellulose and hemicellulose (Zhu *et al.* 2015). Furthermore, the glycosidic bond in hemicellulose can be broken during the ethylene glycol process to generate xyloside, and the xyloside may continue to generate ribitol through a ring-opening reaction (Zhang *et al.* 2012).

In the GC chromatogram, many kinds of lignin degradation products, mainly monomeric phenolic products, were identified. These products accounted for 32.9% of the total peak area, which indicates the effective degradation capacity of AGAIL system on lignin. According to the chemical structural analysis, the above-mentioned monomeric phenolic products mainly came from the degradation of syringl (S) units, guaiacyl (G) units, and *p*-hydroxyphenyl (H) units in lignin.

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Table 1. Conversion Products of the AGAIL Process as Identified by GC-MS

Entry	Retention Time (min)	Compound Name	Peak Area (%)
1	4.614	Ribitol	39.36
2	4.919	1,4-Anhydro-D-Glucitol	2.58
3	5.037	1-(2-Ethoxypropoxy)-2-Propanol	7.43
4	5.132	Arabinitol	0.21
5	5.254	1-(2-Ethoxypropoxy)-2-Propanol	0.99
6	5.316	6-Desoxy-L-Gulitol	0.14
7	5.335	Methyl 2-(2-Butoxyethoxy)Acetate	0.21
8	5.390	Ethyl Ester Octanoic Acid	1.09
9	5.633	5-Hydroxymethylfurfural	0.22
10	6.266	Methyl 2-(2-(2-Butoxyethoxy)Ethoxy) Acetate	5.19
11	6.575	4-Hydroxy-Benzaldehyde	0.59
12	6.928	Vanillin	2.91
13	6.998	6-Desoxy-L-Gulitol	0.19
14	7.039	Glyceraldehyde Diethylacetal	0.34
15	7.072	D-Mannose	0.51
16	7.234	4-Hydroxy-3-Methoxy-Mandelic Acid	0.38
17	7.363	4-Oxo-Pentanoic Acid Butyl Ester	5.39
18	7.499	3-Phenoxy-1,2-Propanediol	3.40
19	7.771	1-(4-Hydroxy-3-Methoxyphenyl)-2-Propanone	0.09
20	7.801	1,4-Diethoxy-2-Butene	0.37
21	8.537	4-Hydroxy-3,5-Dimethoxy-Benzaldehyde	0.55
22	8.596	1-O-Octanoyl- Xylitol	2.76
23	8.912	*β*-Sedoheptitol	0.14
24	8.975	3-(4-Hydroxy-3-Methoxyphenyl)-2-Propenal	0.97
25	9.722	4-(1-Methylpropyl)- Phenol	0.48
26	10.127	Dibutyl Phthalate	23.51

Dibutyl phthalate, a very common plasticizer for plastic products (Gimeno *et al.* 2014), has also been identified in the GC chromatogram, which may be transferred from the plastic containers or instrument. However, the fractionation and extraction processes were conducted in stainless steel autoclave and glassware, respectively. Considering the common utilization of dibutyl phthalate in plastic, there was possibility for the GC-MS sample to be contaminated by accidental touching of plastic products. It was still impossible for dibutyl phthalate to take the dominated proportion in the GC chromatogram, because the plasticizer in plastic products can't be extracted so easily with organic solvent (Shen 2005).

There was a consensus that dibutyl phthalate may be derived from lignin during the processing of biomass. Yuan *et al.* (2009) has reported that dibutyl phthalate can be obtained by the pyrolysis of lignin during the thermochemical liquefaction of straw by hot, compressed water. Fan *et al.* (2015) have also confirmed that dibutyl phthalate was one of the three main products of photocatalysis degradation of lignin through NMR and GC-MS determinations. It is known that lignin is an irregular macromolecular network of phenylpropane units (Gallezot 2012), which is intended to transform into methoxy phenolic propane or methoxy phenol (*e.g.* guaiacol) during the biomass degradation process (Pandey

and Kim 2011). This means that even if the methoxy phenol can be further transformed into catechol, the possible product would be a catechol-based diester, rather than phthalate. Thus, it seems impossible that lignin was able to be converted normally into dibutyl phthalate through thermochemical reactions.

MS is an analytical technique that measures the molecular masses of individual compounds and atoms precisely by converting them into charged ions, and the structure of a molecular can be deduced by matching its MS spectrum with the standard MS libraries (Dass 2006). It may not be able to accurately discriminate between different compounds having the similar composition based on mass-to-charge ratios of ions (*m/z*). In this case, the target compound can be arranged in different ways through matching with the standard library, and other characterizations are needed to ensure the correct identification among them. Based on the above analyses, further investigations are needed to be conducted to determine whether dibutyl phthalate truly exists in the reaction system and understand the potential mechanism for dibutyl phthalate production.

All the above results indicated that the AGAIL system can lead to the degradation of both carbohydrates and lignin and, as a result, only a small amount of lignin was able to be isolated. Therefore, the glycerol-based process was suitable for the catalytic conversion of lignocelluloses, which is in accordance with the above-mentioned inference.

Lignin Depolymerization with Glycerol and AIL

Lignin, an important part of lignocellulosic biomass resources, is the only renewable feedstock that can be used to produce aromatic chemicals (Roberts *et al.* 2011). Therefore, lignin depolymerization processes have been developed to prepare aromatic chemicals. Because the AGAIL system was shown to be able to degrade lignin to a certain extent during the fractionation process in the above section, the depolymerization of coir lignin was also attempted with the glycerol-based system. The glycerol/AIL system without water and with an elevated temperature of 240 °C was selected to achieve promising lignin depolymerization efficiency due to the results of other works (Lu *et al.* 2013; Song *et al.* 2013). After the depolymerization reaction of 0.5 g coir lignin in the glycerol/AIL system, 0.3595 g of non-degraded lignin were obtained, resulting in a lignin depolymerization rate of 28.1%. In the proposed mechanism for lignin depolymerization with AIL, the imidazole-based acid ionic liquid, as a promising acidic catalyst, is able to effectively fracture the β-O-4 linkages in lignin (Jia *et al.* 2010).

To analyze the depolymerization products, the resulting reaction liquid was extracted with ethyl acetate and then analyzed with GC-MS. The results of the GC chromatogram and the corresponding main lignin depolymerization products are shown in Fig. 4. The products identified by matching with the NIST 2010 library (NIST 2010) can be classified into two categories: polyether ester that may be derived from glycerol and monomeric aromatic products generated from lignin depolymerization. The lignin depolymerization products were mainly monomeric aromatic compounds, which consisted of 2,6-dimethoxy-phenol (6.568 min), 2-methoxy- 4-propyl-phenol (7.315 min), and 1-(4-hydroxy-3-methoxyphenyl)- 2-propanone (7.771 min). These products may be derived from S units and G units of lignin according to the chemical structure analysis. The content of monomeric phenolic compounds, according to their peak area in the GC chromatogram (Fig. 4), was small. Dibutyl phthalate (10.127 min) was the dominant component identified in the GC chromatogram, which was also needed to be further investigated as discussed above. Finally, it should be noted that, due to the difficulty of matching the various products with the corresponding compounds in the NIST library (NIST 2010), the peak area

percentage of GC chromatogram was not provided here. In sum, these results confirmed that the glycerol-AIL system could effectively degrade coir lignin into a variety of depolymerization products.
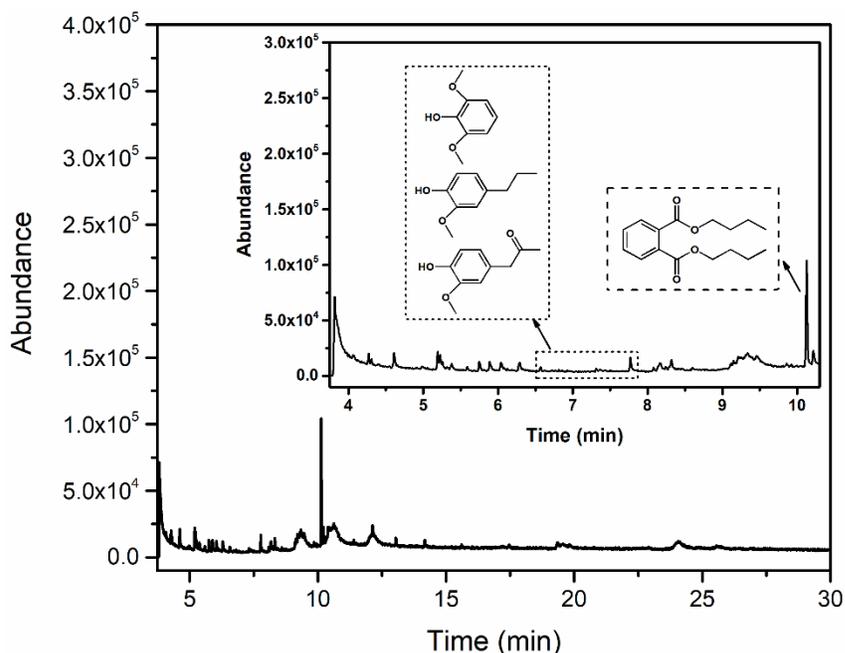
Fig. 4. GC chromatogram of the lignin depolymerization products

As reported previously, technical lignins, including organosolv lignin, were selectively degraded to alkylated phenols over Pt/C, Pd/C, Ru/C, and Ni/C in supercritical t-BuOH at 350 °C for 40 min, and 42.4-60.7 wt% of the lignin can be degraded in the system (Kim *et al.* 2015). Combining lignin with formic acid and water under high temperature (280 to 300 °C) and pressure resulted in a lignin depolymerization rate of 26 to 64%, and lignin was converted to a bio-oil rich in alkylated phenols and aliphatic hydrocarbons in the process (Løhre et al. 2018). Compared with these processes, the present system exhibited higher availability and recyclability on solvent and catalyst and lower requirements on reaction conditions, although further studies are needed to optimize the lignin depolymerization efficiency.

CONCLUSIONS

1. The AGAIL process of coir conducted in an autoclave exhibited better capacity for the removal of hemicellulose and lignin than did the atmospheric AGAIL process. After the process under autogenerated pressure, 57.7% of the original lignin and 94.2% of the original hemicellulose can be removed, and 68.3% of the original cellulose remained in the CRM.

2. Carbohydrates and lignin can be partially converted into degradation products during the AGAIL process under autogenerated pressure, and ribitol and monomeric aromatic compounds were identified as the main conversion products of carbohydrates and lignin.

3. The glycerol/AIL system was able to depolymerize coir lignin and the main lignin depolymerization products were monomeric aromatic compounds.

ACKNOWLEDGMENTS

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