Catalytic Depolymerization of Alkali Lignin in Sub- and Super-critical Ethanol

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The effects of reaction parameters on catalytic depolymerization of alkali lignin in sub- and super-critical ethanol were investigated using a high pressure autoclave, and the liquid oil and solid char products were characterized. The experimental data indicated that Rh catalysis, controlling reaction conditions at ethanol critical temperature (240 ºC) and pressure (7.0 MPa), high ethanol/water ratios (100/0), and the medium reaction time (4 h) enhanced the depolymerization of alkali lignin to liquid oil and decreased the char formation. A gas chromatography/mass spectroscopy (GC/MS) analysis showed that the main compositions of liquid oils were phenols, esters, ketones, and acid compounds, and the supercritical state favored the formation of bio-phenols, but the subcritical state improved the generation of bio-esters. Scanning electron microscopy (SEM) and Fourier transform infrared spectrometer (FTIR) spectra analysis showed that the addition of the Raney/Ni and Rh/C catalysis could inhibit the re-fusion of alkali lignin micron-sized spheres in the supercritical ethanol, which led to an increase in the occurrence of the depolymerization reactions.

Keywords: Alkali lignin; Sub- and super-critical ethanol; Depolymerization; Catalytic

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INTRODUCTION

Compared with the currently depleting stocks of fossil fuels, bio-oils and bio-chemicals derived from renewable resources are promising alternatives to petrochemical products (Azadi *et al.* 2013; Devappa *et al.* 2015; Ullah *et al.* 2015). Meanwhile, lignin is one of the main constituents of these abundant renewable resources, and this cheap feedstock has the potential to aid in the production of liquid fuels and bio-chemicals (Yoshikawa *et al.* 2013; Singh *et al.* 2014; Strassberger *et al.* 2014). However, the efficient conversion of lignin into bio-chemicals is challenging because of the high structural heterogeneity of lignin biopolymers and their recalcitrance to depolymerization. More and more researchers have been trying to find efficient methods for depolymerization of lignin to produce bio-based mono-phenol chemicals and other value-added chemicals (Jiang *et al.* 2015; Kim *et al.* 2015a; Yao *et al.* 2015).

There has been much previous research for the depolymerization of lignin, involving thermochemical, biological, catalytic oxidation, *etc.* (Pandey and Kim 2011; Wang *et al.* 2013; Peng *et al.* 2014; Liu *et al.* 2016). However, the authors' previous research (Guo *et al.* 2014, 2017) indicated that the phenols yields obtained from alkali lignin pyrolysis were approximately 60% liquid oil, while the solid product yield also reached 30%. Thus, it is difficult to improve the liquid oil yield of lignin solely by a pyrolysis reaction.

In recent years, supercritical solvent is considered to be a reaction system with the capability to prevent the condensation reactions (Gosselink *et al.* 2012; Kim *et al.* 2015b), and increase the oil yield of lignin. Based on related research (Mahmood *et al.* 2015; Güvenatam *et al.* 2016a), the abundant hydrogen radicals released from the supercritical solvent can couple with the intermediate products generated from the lignin depolymerized process, thereby preventing the condensation reaction between the intermediate products. A number of studies have illustrated the strong effects of the reaction conditions on the product properties of lignin depolymerized in sub- and super-critical ethanol. Cheng *et al.* (2012) found that an 89% yield of degraded alkali lignin was achieved as alkali lignin was depolymerized in 50/50 (v/v) water-ethanol at 300 ºC for 2 h under 5 MPa H_2. Riaz *et al.* (2016) proposed that the effective liquefaction associated with supercritical ethanol resulted in a high conversion of 92% and high bio-oil yield of 85 wt.% at 350 ºC in a short reaction time of 30 min. Kim *et al.* (2013) concluded that the yields of liquid oil and solid char were directly influenced by reaction conditions, and the depolymerization reaction was significantly accelerated by increasing the reaction temperature, which led to lignin-derived phenols in the oil fraction.

Similar phenolic compounds were observed in the depolymerization of Norway spruce lignin in a supercritical ethanol/formic acid mixture at 380 ºC for 54 h (Kleinert and Barth 2008), non-catalytic cracking of pyrolytic lignin in supercritical ethanol at 260 ºC for 8 h (Tang *et al.* 2010), hydro-processing of organosolv lignin in supercritical ethanol using Ru/C-Al_2O_3 as a catalyst at 260 ºC for 8 h (Patil *et al.* 2011), depolymerization of kraft lignin in supercritical ethanol using CuMgAlOx as a catalyst at 300 ºC for 4 h (Huang *et al.* 2014), and catalytic ethanolysis of kraft lignin using Mo_2C/AC at 280 ºC for 6 h (Ma *et al.* 2014). Based on this research, the use of a catalyst can reduce the reaction temperature of lignin depolymerized in supercritical ethanol, while the regulation mechanisms of the catalyst on the depolymerization reaction of lignin in sub- and super-critical ethanol are not clearly understood.

For this purpose, alkali lignin was first prepared. Secondly, alkali lignin was depolymerized in sub- and super-critical ethanol at different conditions, including catalysis (Raney/Ni and Ru/C), solvent ratios (100:0, 75:25, 50:50, 25:75, and 0:100), temperatures (180 ºC, 210 ºC, 240 ºC, 270 ºC, and 300 ºC), and times (1 h, 2 h, 4 h, and 8 h) by using a laboratory autoclave to obtain the depolymerization products (solid char and liquid oil). Finally, the component of the liquid oil were analyzed by gas chromatography/mass spectroscopy (GC/MS); the morphology of the solid char was characterized by scanning electron microscopy (SEM), Fourier transform infrared spectrometer (FTIR) spectra, and elemental analysis. A comparison of the product formation laws of alkali lignin depolymerized with and without a catalysis in sub- and super-critical ethanol is also presented.

EXPERIMENTAL

Material

Alkali lignin was separated from wheat straw *via* soda-AQ pulping black liquor in accordance with previous research (Hu *et al.* 2013; Guo *et al.* 2014). The detailed AL extraction process was as follows: black liquor was acidified to a pH value of about 2.0 with 10 wt.% H_2SO_4, and stirred for 1 h at 60 ºC in a constant temperature bath. Then the acidified black liquor was filtrated under centrifugation and vacuum-dried at room temperature for 48 h. The isolated lignin was extracted with 1, 4-dioxane/water (9/1, v/v) for 1.5 h, once the mixed solution was evaporated to 3 mL to 5 mL. Lastly, the solution was put into a vacuum drying oven (Xiamen Yunsong Industrial & Trade Co., Ltd., Fuzhou, China) and then the alkali lignin sample was obtained. The solvents used in the study were purchased from Hangzhou Mike Chemical Instrument Co., Ltd. (Hangzhou, China) and used as received.

Methods

The depolymerization of alkali lignin was conducted in a 100-mL SenLong parallel high pressure autoclave (Beijing Century Senlong experimental apparatus CO., Ltd., Beijing, China). The autoclave has a maximum working pressure of 12 MPa. In a typical run, 0.6 g alkali lignin was first loaded into the reactor with 30 mL anhydrous ethanol with or without catalysis. Raney/Ni and Ru/C catalysts were purchased from Sigma-Aldrich, and the catalyst is added in a physically mixed manner. Next, the reactor was sealed and allowed to run a pre-specified temperature of 180 ºC to 300 ºC, with a reaction time of 1 h to 8 h, the reactor was then stopped. Until the reactor cooled to room temperature, the depolymerization products were poured into a beaker, and the reactor was rinsed with anhydrous ethanol. Thirdly, the mixture of depolymerization products and ethanol washing liquid was filtered through 0.2 μm microporous filtering film under vacuum. The retentate was dried at 50 ºC for 8 h and washed with tetrahydrofuran to remove undegraded lignin, and then the solid char product was obtained. The permeating liquid product was diluted to 500 mL with anhydrous ethanol, and then 100 mL of the diluted liquid product was dried at 78 ºC for 24 h. The dried liquid product was designated as liquid oil products. Three replicates were conducted for each condition and the average values were reported. The liquid oil yield and the lignin conversion yield were calculated using the following equations,

$$\text{Liquid Oil Yield (wt.\%)} = \frac{\text{Weight of liquid oil}}{\text{Weight of dry ash free lignin}} \times 100 \tag{1}$$

$$\text{Solid Char Yield (wt.\%)} = \frac{\text{Weight of solid char}}{\text{weight of dry ash free lignin}} \times 100 \tag{2}$$

Measurements

The liquid oil was dehydrated by anhydrous sodium sulfate, filtrated by Millipore filtration, and then detected on a GC/MS (Agilent 6890N GC equipped with a 5973I MSD using a 30 m × 0.25 mm × 0.25 μm DB-5ms column). The GC/MS programming was as follows: a 5 min hold at an initial oven temperature of the GC was 40 ºC followed by an increase of 5 ºC min^{-1} up to 200 ºC, and then the temperature was raised to 280 ºC for 5 min. The solvent delay was set at 5 min. The carrier gas was the highest purity helium with a flow rate of 0.8 mL/min. The separated components were determined by using a NIST08, and the relative concentrations of specific compounds identified by the methods of areas of peak normalization.

The surface morphology of the solid char products was performed by using a scanning electron microscope (VLTRA55, Carl Zeiss SMT Pte. Ltd, Jena, Germany). The chemical bonds of solid char were analyzed by Fourier transform infrared spectroscopy (NICOLET5700, Madison, USA). The measurement was performed by the KBr method for their functionality changes in the range of 400 cm^{-1} to 4000 cm^{-1} (scans = 32). The carbon, hydrogen, nitrogen, and sulfur weight percentages of solid char were determined using an elemental analyzer of Elementar Analysensysteme (Vario MICRO Cube, Langenselbold, Germany). The oxygen content was obtained as a difference.

RESULTS AND DISCUSSION

Effect of Reaction Conditions on the Yields of Depolymerization Products

The yields of liquid oil products, in which the main depolymerization chemical compounds, such as phenols, aromatics, and heavy aliphatic hydrocarbon, are important determines the degree of lignin depolymerization (Kim *et al.* 2013; Lee *et al.* 2016). Results indicated that the composition of lignin-degraded products was clearly affected by the pyrolysis conditions (Guo *et al.* 2014, 2017). To investigate the effect of the reaction condition on the depolymerization products of alkali lignin in sub- and super-critical ethanol, a series of experiments were firstly performed at the ethanol-to-water ratios of 100:0, 75:25, 50:50, 25:75, and 0:100. The yields of depolymerization products as a function of the solvent ratio are shown in Fig. 1.

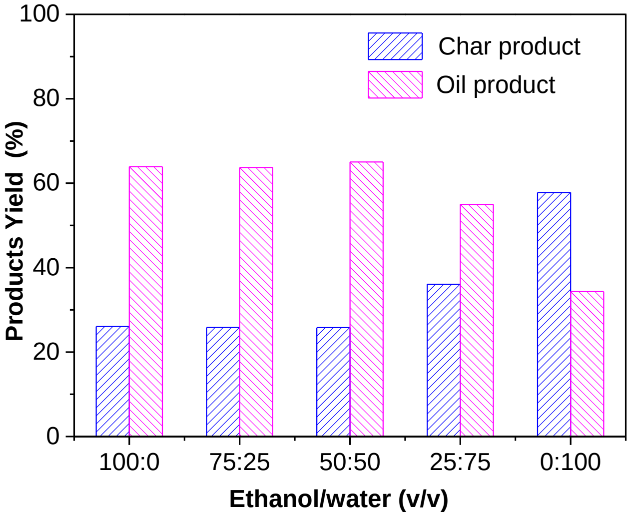

Fig. 1. The effect of ethanol/water ratio on the product yields of alkali lignin depolymerized at 240 °C, 4 h

The yields of char and liquid oils remained unchanged as the ethanol ratio of the solvent decreased from 100:0 to 50:50 (Fig. 1). Conversely, the yield of oil clearly decreased but the yield of char dramatically increased by decreasing the ethanol ratio of the solvent from 50:50 to 0:100. This indicated that higher ethanol ratios enhanced the depolymerization of lignin to liquid oil and decreased the char formation. This phenomenon may have been caused by the hydrogen radicals formed by the homolysis of ethanol that were involved in the coupled reactions among the lignin depolymerization intermediates, and the inhibition of repolymerization reaction intermediates, preventing char formation (Güvenatam *et al.* 2016b; Riaz *et al.* 2016). Based on the characteristics of the depolymerization liquid products (Table 1), the possible coupled reaction patterns are presented in Fig. 2. So, to obtain a high yield of liquid oils, the ethanol-to-water ratios should remain in the range of 100:0 to 50:50.

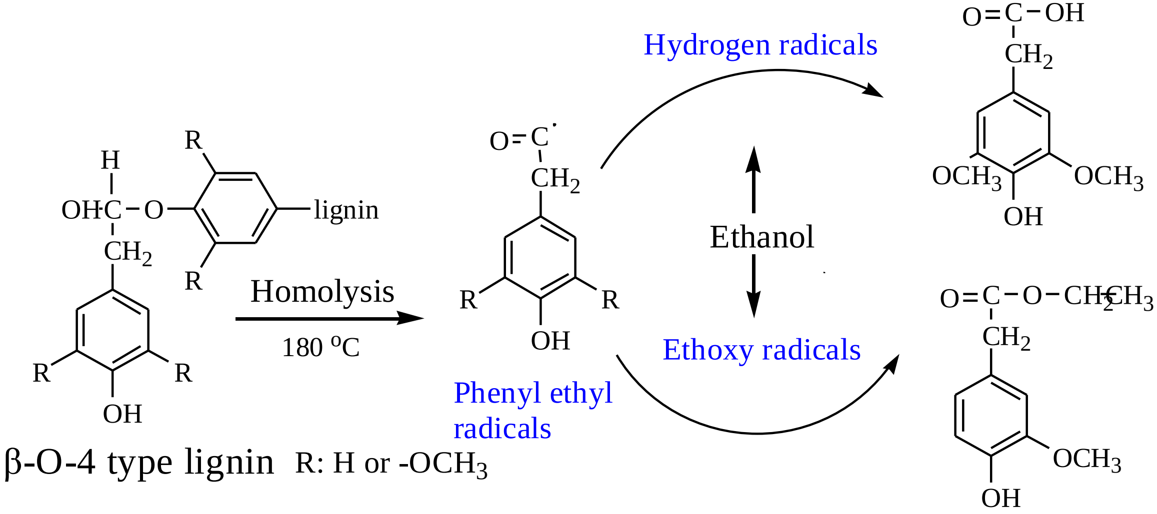

Fig. 2. The coupled reactions mechanism of lignin depolymerization intermediates in sub- and super-critical ethanol

The yield of liquid oil products, with and without catalysis (Raney/Ni and Rh/C), varied with reaction temperatures (180 ºC, 210 ºC, 240 ºC, 270 ºC, and 300 ºC) and time (1 h, 2 h, 4 h, and 8 h), as shown in Figs. 3a and b, respectively. Figure 3a shows that for catalysis or non-catalysis depolymerization processes, the yield of liquid oils all increased with increasing the reaction temperature from 180 ºC to 240 ºC, and the oil yield decreased when the reaction temperature increased from 240 ºC to 300 ºC. However, at each depolymerization temperature, the yield values of the liquid products for catalysis depolymerization process were higher than for the non-catalyzed process, and the liquid product yield for the Rh catalysis process was higher than the Raney/Ni catalysis process. Specifically, the maximum yield of the liquid oil product (75.38%) appeared as the Rh catalyzed alkali lignin depolymerized at 240 ºC for 4 h. These results indicated that the oil yield increased and then decreased as the depolymerization temperature increased from 180 ºC to 300 ºC, and the maximum yield of oil occurred at the critical temperature of ethanol. Thus, to obtain a high yield of liquid oils, the depolymerization temperature should be controlled at around 240 ºC. The reason for this phenomenon may have been that the low temperature depolymerization process led to the depolymerization reaction being inadequate (Cheng *et al.* 2010; Kim *et al.* 2013). As the reaction increased to 240 ºC, the high heat transfer efficiency and high content of the hydrogen radical of the supercritical ethanol system could ensure the energy needed for the depolymerization reaction and inhibit the repolymerization reaction (Riaz *et al.* 2016). However, as the depolymerization temperature increased to 300 ºC, the depolymerization reaction rate occurred too quickly, and formed a large amount of depolymerization intermediate radicals, leading to a higher probability of the repolymerization reaction occurring, and a decrease in the liquid oil yield (Yao *et al.* 2015). As the Raney/Ni or Rh/C catalysts were added to the depolymerization system, the hydrogenation of the depolymerization intermediates was promoted, which led to the decreased probability of the repolymerization reaction (Zhang *et al.* 2014). Moreover, the oil yield of the Rh catalysis process increased 8.34% and 11.46%, compared to the Raney/Ni catalysis and non-catalyzed process, respectively. Therefore, the Rh catalysis was an effective way to improve the depolymerization efficiency of alkali lignin in sub- and super-critical ethanol.

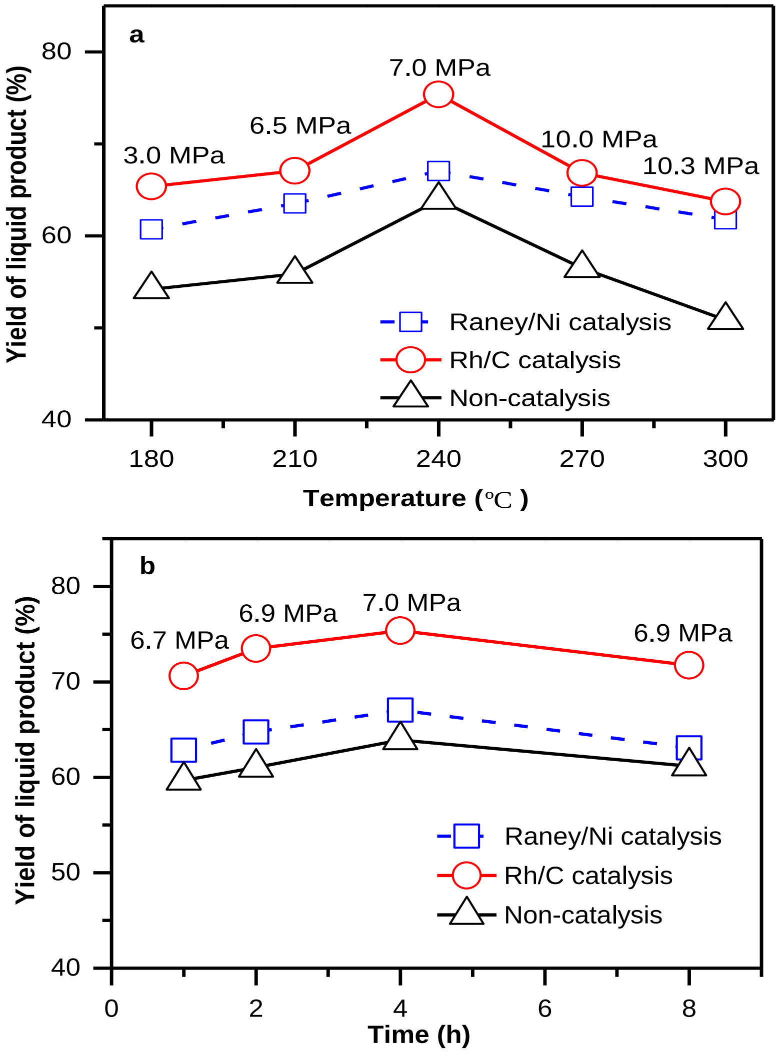

Fig. 3. Effect of reaction temperature and time on the yield of liquid oil products

As shown in Fig. 3b, following catalysis or non-catalysis depolymerization, the yield of liquid oils all slightly increased, and then they gradually decreased with increased reaction time from 1 h to 8 h. The maximum yield of liquid oil also occurred at 4 h during the Rh-catalyzed depolymerization process. This result corresponded with the effect of the reaction temperature. This indicated that a lengthy reaction time was not conducive to the depolymerization of alkali lignin in sub- and super-critical ethanol. A longer reaction time could lead to the mass of char was due to carbonization and recondensation between lignin-degraded products (Yuan *et al.* 2010; Pińkowska *et al.* 2012).

Effect of Reaction Conditions on the Components of Liquid Oils

The main compositions of liquid oils produced from the different conditions were analyzed by GC/MS. The representative GC/MS chromatograms obtained from the alkali lignin depolymerized at 240 ºC for 4 h are shown in Fig. 4. As shown in Fig. 4, the oil GC/MS chromatogram for Raney/Ni- and Rh/C-catalyzed depolymerization had similar main characteristic peaks with a non-catalytic process, which indicated that the main oil consisted of various types of chemicals all including phenols, esters, ketones, and acids compounds.

The chemical compositions of liquid oils obtained from alkali lignin depolymerized at 180 ºC, 240 ºC, and 300 ºC for 4 h were categorized depending on their structure and chemical functionalities, and the results are listed in Table 1. From Table 1, for catalysis or un-catalysis depolymerization processes, the components of liquid oil prepared at 180 ºC mainly were esters and ketones compounds, especially esters, while the components of liquid oil for 240 ºC and 300 ºC were phenolic compounds. Therefore, it was necessary to control the depolymerization conditions in supercritical states for the production of bio-phenols, while it was necessary to control the reaction conditions in subcritical states for the formation of bio-esters.

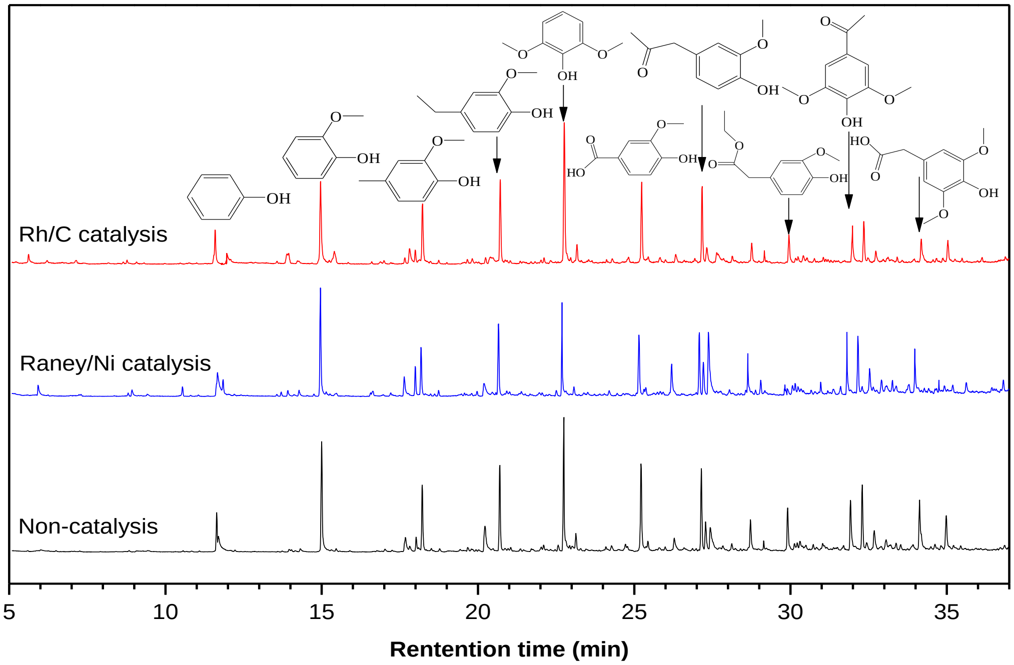

Fig. 4. GC/MS chromatogram of liquid oil obtained from alkali lignin depolymerized at 240 ºC for 4 h in supercritical ethanol

As shown in Table 1, the common features of ether compounds were all ethyl ether. This indicated that the ester products were generated by the esterification reaction between the depolymerization intermediates and ethoxy radicals ($CH_3CH_2O\cdot$) released from the homolytic cleavage reaction of ethanol. Specifically, the ester bond of the structure unit occurred during the homolytic cleavage reaction as the alkali lignin depolymerized at 180 ºC. This generated phenyl methyl radicals, then part of the phenyl methyl radical was coupled with ethoxy radicals that released from the homolytic cleavage reaction of ethanol, mainly forming benzoic acid, 4-hydroxy-3-methoxy-, and ethyl ester. This conclusion is consistent with previous literature (Güvenatam *et al.* 2016b; Riaz *et al.* 2016). Meanwhile, the molecular formula of benzoic acid, 4-hydroxy-3-methoxy-, ethyl ester; 2-propanone, 1-(4-hydroxy-3-methoxyphenyl)-, and benzoic acid, 4-hydroxy-3-methoxy- all have the same aromatic structure and methoxy substituent groups. These findings indicated that the formation of these compounds should be correlated. Based on the above discussion, the ethers compounds were generated from the esterification reactions between the depolymerization intermediates and ethoxy radicals, which indicated that the ketones compounds may have been formed by the coupled reaction between the phenyl methyl and hydrogen radicals, while the acid compounds were mainly produced by the hydrolysis reactions of ester compounds.

Table 1. The Main Components of Liquid Oils Obtained from Alkali Lignin Depolymerized at Different Temperature

Products Name		Relative content (%), 180 ºC			Relative content (%), 240 ºC			Relative content (%), 300 ºC		
		Non-	Raney /Ni	Rh/C	Non-	Raney /Ni	Rh/C	Non-	Raney /Ni	Rh/C
Phenols	Phenol	1.28	1.95	2.5	3.59	3.02	4.4	10.68	14.78	15.23
	Phenol, 2-methoxy-	2.78	3.69	3.77	9.46	10.66	12.35	12.57	12.64	14.74
	Phenol, 4-ethyl-	1.47	2.34	2.25	1.23	3.32	3.81	8.34	11.5	14.02
	Phenol, 2-methoxy-4-methyl	1.25	2.45	3.21	4.61	5.05	5.64	8.38	8.78	8.24
	Phenol, 2-ethyl-4-methyl-	1.50	4.32	3.94	3.45	6.32	7.2	3.09	3.64	3.28
	Phenol, 4-ethyl-2-methoxy-	2.11	4.85	5.48	4.9	5.56	6.03	9.26	10.2	9.09
	Phenol, 2,6-dimethoxy	4.46	8.28	8.45	10.27	14.16	15.14	17.27	13.83	13.46
Acids	Benzoic acid, 4-hydroxy-3-methoxy-	9.9	6.17	4.12	17.13	9.11	10.5	7.57	6.52	5.93
	3-Domethoxy-4-hydroxy phenylacetic acid	15.25	11.46	10.14	8.32	3.32	2.43	1.20	1.66	1.44
Ketones	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-	4.66	11.09	12.37	7.96	10.83	11.65	6.23	5.57	5.32
	Ethanone, 1-(4-hydroxy -3,5-dimethoxyphenyl)-	17.88	20.5	21.95	10.75	13.76	11.08	4.43	4.21	3.66
Esters	Benzoic acid, 4-hydroxy -3-methoxy-, ethyl ester	16.7	10.49	10.56	8.21	6.48	2.95	4.24	2.61	1.84
	4-Hydroxy-3-methoxyphenylacetic acid, ethyl ester	15.73	9.48	8.41	6.57	3.78	3.09	3.74	1.36	1.41
	Ethyl-β-(4-hydroxy-3-methoxy- phenyl)-propionate	5.03	2.93	2.85	3.55	4.63	3.73	3.00	2.7	2.34

As shown in Table 1, phenols were the main products of the liquid oil. This was attributed to the fact that alkali lignin with or without the catalysis depolymerizes in supercritical ethanol, which can be naturally expected because phenol is the basic entity of the lignin structure (Tang *et al.* 2010; Patil *et al.* 2011; Huang *et al.* 2016). Meanwhile, the content of phenolic compounds that contained methyl, methoxy, and ethyl groups bonded to the aromatic ring were clearly high, which indicated that the ether linkages of the methoxy groups and the C-C linkages of alkyl groups in the lignin structural unit were difficult to break compared to the ether linkages among the lignin structural units. Because of this, demethoxylation and demethylation reactions did not occur easily during the alkali lignin depolymerization in subcritical ethanol. Therefore, the bio-phenols obtained from alkaline lignin depolymerized in sub- and super-critical ethanol were mainly substituents of phenolic compounds.

The components of the liquid oil obtained from alkali lignin with and without catalysis depolymerization varied with reaction temperature, time, and catalyst amount, and the results are presented in Figs. 5a, b, and c, respectively.

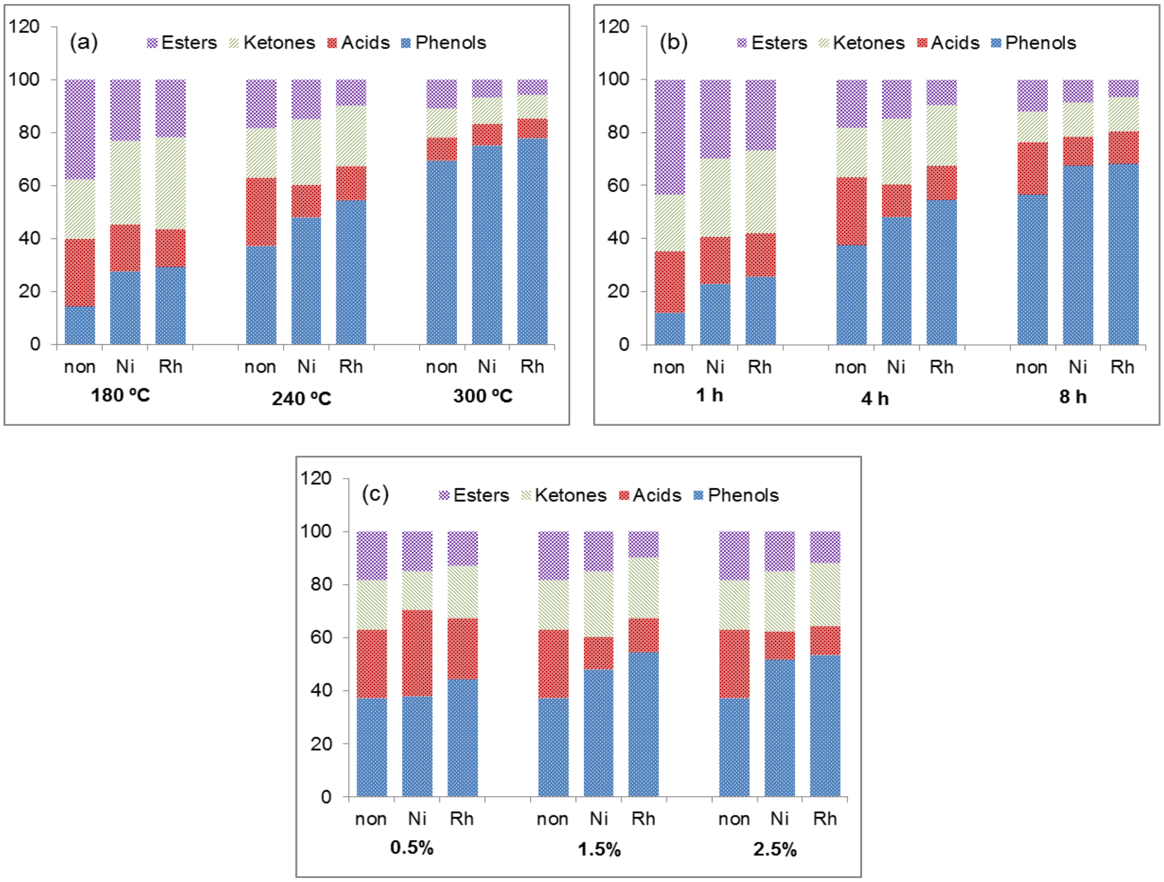

Fig. 5. Effect of reaction conditions on the components of liquid oils

As shown in Fig. 5a, the addition of the Raney/Ni and Rh/C catalysis led to the phenols and ketones content increasing, but the esters and acids content decreased during the alkali lignin depolymerization at 180 ºC, 240 ºC, and 300 ºC. The difference was that the increase in the amount of phenols and decrease in the amount of esters for 180 ºC and 240 ºC were clearly greater than the changes associated with 300 ºC. Meanwhile, as the reaction time was reduced from 4 h to 1 h or increased from 4 h to 8 h, the effects of the Raney/Ni and Rh/C catalysis on the increasing of phenols or the decreasing of esters were all inhibited (Fig. 5b). This indicated that the effect of the Raney/Ni and Rh/C catalysis on the component of liquid oil was also affected by the reaction temperature and time. This phenomenon may have been due to the fact that the depolymerization reaction rate of alkali lignin was so fast that too many depolymerization intermediate radicals were formed as the depolymerization temperature rose to 300 ºC, which led to an increase in the probability of the repolymerization reaction, and an increase in the hydrogenation reaction of the Raney/Ni and Rh/C catalyst inhibition. As the reaction time was extended from 4 h to 8 h, the secondary reactions may have resulted in the decreasing capacity of the Raney/Ni and Rh/C catalyst. As the amount of Raney/Ni and Rh/C catalysis increased from 1.5% to 2.5%, the content of phenols slightly increased for the Raney/Ni catalysis process, while the content of phenols remained largely unchanged (Fig. 5c). These observations indicated that the amount of the catalyst had a slight effect on the composition of the liquid oil. In conclusion, the effect of temperature and the type of catalysis on the compositions of liquid oil products during alkali lignin depolymerized in sub- and super-critical ethanol were more salient than those for the reaction time and catalysis amount.

Effect of Reaction Conditions on the Properties of Solid Chars

The SEM micrographs of char prepared by sub- and supercritical ethanol depolymerization are shown in Fig. 6.

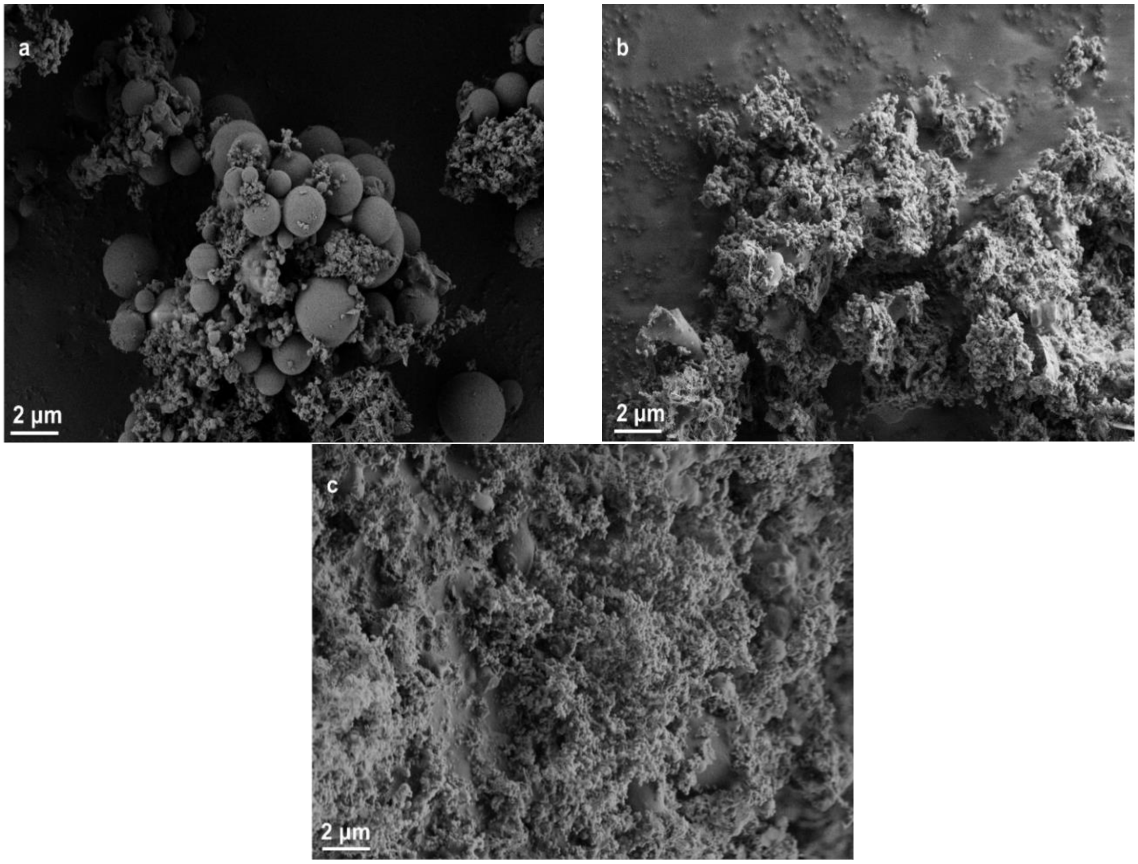

Fig. 6. Char SEM micrographs of alkali lignin depolymerized at 240 ºC and 4 h in sub- and supercritical ethanol: (a) non-catalysis, (b) Raney/Ni, and (c) Rh/C

In previous studies, the alkali lignin has been shown to have an irregular polygonal, smooth surface (Hu *et al.* 2014). The morphology of char obtained from alkali lignin depolymerized at 240 ºC without catalysis displayed plenty of micron-sized spheres on the surface of the char (Fig. 6a). The accumulation intensity of the micron-sized spheres increased, but the particle volume of micron-sized spheres decreased following the Raney/Ni and Rh/C catalysis process (Fig. 6b and c). This finding indicated that the sub- and super-critical ethanol depolymerization process of alkali lignin first softened, melted, and then fused into a mass of matrix and micron-sized spheres on the surface of lignin (Sharma *et al.* 2004). For the non-catalysis depolymerization process, the formation and depolymerization rate of micron-sized spheres was similar, but all were lower than the repolymerization rate, so the microspheres, which did not undergo the depolymerization reaction, were fused together to form larger size spheres. For the Raney/Ni- and Rh/C-catalysis depolymerization process, the hydrogenation reaction rate was fast enough to prevent the repolymerization reaction, which then inhibited the melting of the microspheres. Therefore, the addition of the Raney/Ni and Rh/C catalysis could inhibit the re-fusion of lignin micron-sized spheres in the supercritical ethanol; thus it accelerated the occurrence of the depolymerization reactions, which thereby enhanced the yield of the liquid oil products.

The distribution of functional groups on the surface of lignin chars were affected by the reaction conditions (Kang *et al.* 2012); thus the functional groups of chars could reflect the effect of the Raney/Ni and Rh/C catalysis on the depolymerization process of alkali lignin in sub- and super-critical ethanol. The FTIR spectra of chars obtained from alkali lignin depolymerized at 240 ºC (4 h) and the Rh/C catalysis alkali lignin depolymerized at different temperatures in sub- and super-critical ethanol are presented in Fig. 7a and b.

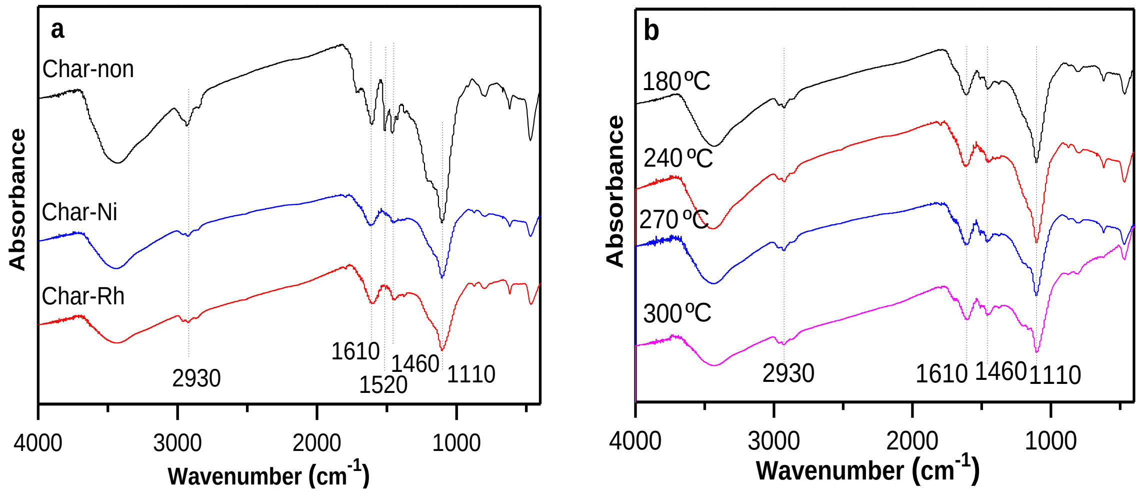

Fig. 7. Char FTIR spectra of alkali lignin depolymerized in sub- and super-critical ethanol; (a) 240 ºC, 4 h; (b) 1.5% Rh/C, 4 h

As shown in Fig. 7a, the chars prepared with and without catalysis had similar IR absorptions but had different intensities. The chars obtained from the alkali lignin depolymerized at 240 ºC with the Raney/Ni and Rh/C catalysis contained less methyl and methylene groups (alkyl groups) as the intensity of absorptions near 2930 cm^{-1} and 1460 cm^{-1} were relatively stronger. These results indicated that the alkyl groups in the side chain of the phenylpropane unit were markedly removed during the catalysis depolymerization process. Meanwhile, the bands at 1610 cm^{-1} and 1110 cm^{-1} originated from the aromatic skeleton and C-O linkage stretching, respectively (Cheng *et al.* 2010). The absorption intensity of the aromatic skeleton and C-O linkage for the Raney/Ni and Rh/C catalysis process were weaker than those for the non-catalysis process. This indicated that the addition of the Raney/Ni and Rh/C catalysis not only helped the breakage of ether linkages lead to a decrease of the C-O bond, but they also promoted the carbonization reaction, which resulted in a decrease in the aromatic ring structure. Therefore, the Raney/Ni and Rh/C catalysis could efficiently break the ether linkages of lignin and selectively depolymerize the lignin, and could also promote the carbonation reaction of depolymerization chars. From Fig. 7b, as the reaction temperature increased from 180 ºC to 240 ºC, the absorption intensity of the C-O bond remained essentially constant, while the absorption intensity of the C-O bond slightly reduced as the reaction temperature increased from 240 ºC to 300 ºC. Meanwhile, the absorption intensity of the methyl groups and the aromatic skeleton were similar. This indicated that reaction temperature had an effect on the ether bond of chars, but little effect on the aromatics ring for the Rh/C catalysis alkali lignin depolymerized in sub- and super-critical ethanol.

The elemental compositions of chars obtained from the Rh/C catalysis of alkali lignin depolymerized for 1 h, 4 h, and 8 h in sub- and super-critical ethanol are presented in Table 2, respectively. As shown in Table 2, for the Rh/C catalysis depolymerization process, the content of C increased but the content of O and H declined as the temperature increased from 180 ºC to 300 ºC due to the dehydration and fracture of ether linkages as the alkali lignin depolymerized at high temperatures (Huang *et al.* 2016). The C/O and C/H ratios of the solid chars gradually increased when the reaction temperatures increased from 180 ºC to 300 ºC, which indicated a mass loss of O and H and a gradual enrichment of C (Mahinpey *et al.* 2009). The difference was that the increased rate of C/O and C/H ratios for supercritical ethanol were clearly faster than those for subcritical ethanol. It indicated that the supercritical ethanol was more favorable for the cleavage of ether linkages than subcritical ethanol.

Table 2. Elemental Compositions of Alkali Lignin Chars

Sample	Elemental Composition (wt.%)					Atomic Ratio	
	C (%)	H (%	N (%)	S (%)	O^{a} (%)	C/O	C/H
Char-Rh/C-180 ºC	51.11	4.89	0.63	1.29	42.08	1.21	10.45
Char-Rh/C -240 ºC	52.15	4.73	0.64	1.24	41.24	1.26	11.03
Char-Rh/C -270 ºC	57.87	4.01	0.71	0.89	36.52	1.58	14.43
Char-Rh/C -300 ºC	59.72	4.01	0.97	0.76	34.54	1.73	14.89

[a] Stands for subtraction method

CONCLUSIONS

1. The addition of Rh/C as a catalysis, under controlled reaction conditions at ethanol's critical temperature (240 ºC) and pressure (7.0 MPa), with high ethanol/water ratios (100/0), and a medium reaction time (4 h) enhanced the depolymerization of alkali lignin to liquid oil and decreased the char formation.
2. The main composition of liquid oil obtained from the alkali lignin depolymerized in sub- and super-critical ethanol were phenols, esters, ketones, and acids compounds. The supercritical state favored the formation of bio-phenols, while the subcritical state improved the generation of bio-esters. The effect of temperature and the type of catalysis on the liquid oil compositions were more salient than those for the reaction time and catalysis amount.
3. The addition of a Raney/Ni and Rh/C catalysis could inhibit the re-fusion of lignin micron-sized spheres in the supercritical ethanol, which led to an increase in the occurrence of the depolymerization reaction, thereby enhancing the yield of liquid oil products. The Raney/Ni and Rh/C catalysis could efficiently break the ether linkages of lignin and selective depolymerized lignin.

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