Effect of Pd/C Catalytic Extraction on the Hydrothermal Depolymerization Properties of Ethanol Organosolv Lignin (EOL) in Supercritical Ethanol

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This study investigated the effect of a Pd/C catalytic extraction process on the hydrothermal depolymerization product properties of ethanol organosolv lignin (EOL) in supercritical ethanol. Phenolic products were separated and analyzed by gel permeation chromatography (GPC) and thermogravimetric (TG) analyses. The gas chromatography–mass spectrometry (GC-MS) analyses of obtained liquid oil products from depolymerized EOL confirmed the presence of value-added phenolics. Scanning electron microscopy (SEM) was used to observe the morphology of the char product. During ethanol organosolv lignin extraction, 90.5% purity of EOL was obtained. A high yield of EOL up to 39.6% from bamboo without catalysts and with higher yield of EOL up to 44.0% from 1% Pd/C catalyst under 200 °C. A high yield of liquid oil products, up to 65.4%, was recovered from EOL depolymerization under conditions of 240 °C, 240 min, 100 vol % ethanol, and 2% EOL, with only 24% solid residue. The main phenolic products were 2-methoxyphenol, 4-ethylphenol, 4-methoxy-2-methylphenol, 4-ethyl-2-methoxyphenol, 2,6-dimethoxy-phenol, and 2-methoxy-4-propylphenol.

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INTRODUCTION

Lignin is the second-most abundant organic material in nature after cellulose. Due to its aromatic macromolecular structural characteristics, lignin has the most potential to replace fossil resources in the production of bio-based phenolic platform chemicals (Margellou and Triantafyllidi 2019; Toledano *et al.* 2014). The lignin in the cell wall of plant fibers is an aromatic polymer composed of phenylpropane units that are connected through C-C and C-O bonds (Jiang *et al.* 2017). The β-O-4 bond is the most frequent coupling linkage, which accounts for 50% of all connections (Jiang *et al.* 2017). The preparation of bio-based monophenol chemicals requires the depolymerization of lignin macromolecular structures into small molecular monomers. Due to its vast heterogeneous structure, the depolymerization reactivity and reaction selectivity of lignin macromolecules are very poor (Agarwal *et al.* 2018). In addition, the intermediate radicals generated in the course of the lignin depolymerization process undergo a repolymerization reaction, leading to a low yield of monophenol products (Qiu *et al.* 2018). Breaking the chemical bond between lignin monomers, especially the β-O-4 bonds, is very important for the selective depolymerization of lignin.

The structure of lignin changes during its isolation, especially in the course of pulp cooking. Due to physical and chemical reactions, the obtained alkali lignin or lignosulfonate undergoes extensive condensation reactions, and the proportion of C-C bonds between monomers becomes significantly higher than in the original lignin, leading to the difficult depolymerization of isolated lignin into smaller phenolic molecular units. In view of such difficulty, previous research proposed that the macromolecular structure of alkali lignin that is autocatalytically depolymerized by organic bound sodium can optimize the distribution of depolymerization products (Guo *et al.* 2014, 2012). Based on these studies, the formation of phenolic anions in the monomer structure by the catalysis effect of organic-bound sodium improves the homogeneity of monophenol products. However, the total liquid monophenol yield obtained from lignin pyrolysis between 150 and 300 °C is maintained within 40%, while the pyrolysis solid product yield reaches 45%.

To improve the liquid product yield, Kotake's (2014, 2013) study showed that abundant hydrogen free radicals of diphenoxybenzene and 1,2,3,10b-tetrahydro-fluoranthene mixed solvent coupled with lignin depolymerization intermediate free radicals and inhibited the repolymerization reaction of lignin depolymerization intermediates, leading to an increase in the yields of the monomers and oligomers. Similarly, Cheng *et al.* (2012) reported that for the degradation of alkali lignin (AL) for the production of bio-phenolic compounds, hydrothermal treatment of AL in 50/50 (v/v) water-ethanol at 300 °C for 2 h under 5 MPa H_2 without a catalyst led to an 89% yield of degraded lignin (DL). Riaz *et al.* (2016) investigated process parameters (pressure, time, and formic acid) for producing high-yield and high-calorific bio-oil from concentrated sulfuric acid hydrolysis lignin (CSAHL) with formic acid as an in-situ hydrogen source in supercritical ethanol (scEtOH) and concluded that the effective deoxy-liquefaction nature associated with scEtOH with aid of formic acid resulted in high conversion of 92% and high bio-oil yield of 85 wt% at 350 °C for 30 min. Depolymerizing lignin under the condition of hydrogenation and high reaction temperature (above 300 °C) can improve the yield of liquid monophenol products to some extent. However, excessive reaction temperature limits the application of lignin in the preparation of bio-based monophenol products. Guo *et al.* (2017) previously studied the catalytic depolymerization process of alkali lignin by organic bound sodium in supercritical ethanol and found that the liquid oil yield increased to 63.92% at 240 °C, but the solid char yield remained at approximately 20%. To enhance the liquid oil yield from alkali lignin depolymerization at lower reaction temperatures, Guo *et al.* (2017) studied the effect of Raney/Ni, Ni_7Au_3, and Rh as a catalyst on the process of alkali lignin depolymerization in a critical ethanol system. The yield of liquid oil product of alkali lignin in the presence of a metal catalyst was increased by 4 to 10%. The depolymerization reaction solvent increases the yields of the monomers and oligomers. For industrial lignin, due to the condensation reaction of the β-ether linkages in the separation process, the liquid mono-phenol product yield is difficult to reach the theoretical value. The large number of C-C linkages formed in industrial lignin makes it hard to use supercritical hydrogen systems or catalysts to improve the liquid product yield.

It is difficult to isolate lignin with high purity and reactivity using a single dissolution mechanism because cellulose, lignin, and hemicellulose are closely cross-linked to form a 'natural degradation barrier' in the supramolecular structure of the natural plant. Consequently, Guo *et al.* (2019) previously tried to obtain ethanol organosolv lignin (EOL) with high reactivity by using a formic acid-catalyzed subcritical ethanol process. This was done to limit the formation of C-C linkages. They found that the extractions yields of EOL were up to 59.9% and the liquid yield of EOL depolymerized in supercritical ethanol solvent system was 89.6% which was significantly higher than industrial alkali lignin. Similarly, Michelin *et al.* (2018) separated lignin by a two-step method combining liquid hot water (LHW) and ethanol organosolv (EO). They found that the yield of lignin was 6.23% to 17.48%, while the purity of the lignin was 86.7 to 93.1%. To improve the yield of separated EOL, Yao *et al.* (2018) found that the yield of lignin was improved (40.3 to 71.5%) with the increase of separation reaction time (5 to 60 min). However, the increased weight-average molecular weight (M_w) of the separated lignin with increasing pretreatment time through GPC analysis indicated that some repolymerization reactions probably occurred. In sum, the separation by pure ethanol enhances the yield of lignin, but the long reaction time increases the molecular weight while decreasing the content of phenolic hydroxyl groups. Kim *et al.* (2015) studied the effect of palladium on the characteristics of EOL by acid-catalyzed organosolv pretreatment of yellow poplar. The yield and purity of EOL were enhanced, and pretreatment with palladium at higher temperatures preserves ether linkages of EOL. However, the effect of Pb/C catalyzed extraction for EOL on the depolymerization process in supercritical ethanol and the characteristics of mono-phenol products remain unclear.

This study investigated the effect of palladium catalyzed extraction process on the depolymerization behaviors of EOL in supercritical ethanol and the properties of depolymerized products. Thirteen kinds EOL were fractionated by palladium-catalyzed extraction of bamboo, and the structural properties of fractionated EOL were investigated by GPC, FT-IR, and TG. The EOL was depolymerized in super-critical ethanol using a laboratory autoclave to obtain the depolymerization products (solid chars and liquid oils). The morphology of the solid chars was characterized by SEM, and the liquid oils was analyzed by GC-MS. Finally, the relationship between palladium catalyzed extraction and depolymerization products properties was evaluated.

EXPERIMENTAL

Extraction of Lignin

Extraction of lignin produced from bamboo was performed in a 500 mL high-pressure reaction kettle (KCF-0.5), equipped with a mechanical stirrer. In a typical run, 20 g of bamboo powder, palladium on carbon (0, 0.5, 1, 2, or 4 g), and 400 mL of ethanol-water were loaded in the reactor and sealed. Then the reactor was heated to the desired temperature (160, 180, and 200 °C) at a heating rate of 5 °C/min and extraction time (60 min). Cooling water is always injected into the kettle during the process of reaction. The the power is turned off at the end of the reaction and cooling water is injected into the insulation layer. The extraction time and the ratio of extraction of 70 vol % ethanol-water was set at constant 60 min and 8/2 (v/v, mL/mL), respectively. After the reaction and cooling, the extracted materials were filtered through a previously weighed filter paper and divided into a pretreated solid fraction and liquid fractions. The solid was washed with 10 mL of ethanol that was heated to 60 °C. The solid was oven-dried at 105 °C. The liquid phase and washing liquid were mixed in a round-bottom flask, subjected to rotary evaporation under 45 °C concentrate to 30 mL, and then the concentrated extractive solution was poured into a1L acid deionized water of pH = 2.0. This was left to stand for 8 h, then filtered with a sand-core funnel. The EOL obtained by the filter was then freeze-drying for 24 h. The initially dried lignin was used for characterization and depolymerization.

Depolymerization of Lignin

The depolymerization experiments were conducted in a 100 mL SLP high-pressure autoclave (Beijing Century Senlong experimental apparatus CO., Ltd). In a typical run, the lignin powder extracted in the previous section was loaded into the reactor. The reactor condition was the raw material and ethanol (95%, analysis level) at a solid-liquid ratio of 1:50 (w: v), and a reaction time of 4 h. Sample temperatures were 180 and 240 °C. The heating speed control was set to 8 °C/min, with a hold of 4 h after reaching the reaction temperature, respectively. The device was heated to the indicated reaction temperature (40 min in total for the heating process) for the indicated reaction times, after which it was rapidly cooled by immersion in a water bath. The degradation product of EOL was firstly filtered by a sand core filter, the solid product was washed with isopropyl ethanol 2 to 3 times (about 50 mL in total). The sample was then dried to constant weight at 50 °C. The weight of the solid char product was recorded. The liquid oil was shaken well in a volumetric flask with isopropyl alcohol as the solvent, left for 4 hours, poured into two separately weighed Petri dishes, dried in a 50 °C oven to constant weight, and the mass data of the liquid oil was recorded. The depolymerization product content of liquid was examined with respect to degradation products by GC-MS. The lignin extraction and degradation process are shown in Fig.1.

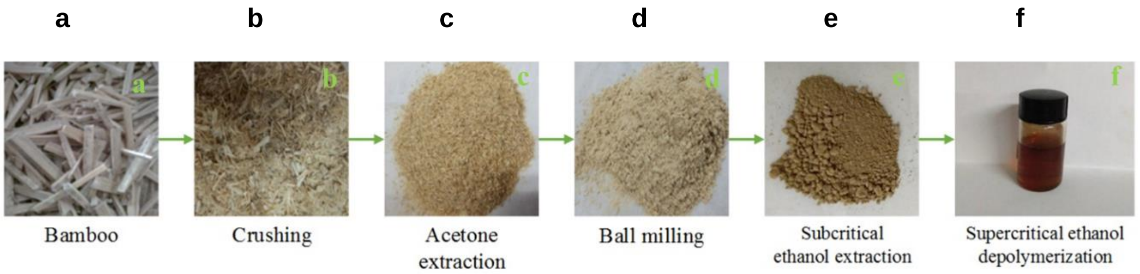

Fig. 1. Schematic representation of the experimental process, a: bamboo materials, b: crush bamboo materials, c: crush bamboo materials after acetone extraction, d: bamboo materials after ball milling, e: ethanol organosolv lignin (EOL), f: EOL depolymerization liquid oil products

Characterization Methods

FT-IR analysis

FT-IR spectroscopy of the ethanol organosolv lignin was carried out using a spectrophotometer (Thermo Nicolet, USA). The ethanol organosolv lignin for analysis was prepared by mixing material power with KBr. Data were recorded from 4000 to 400 cm^{-1} with 32 scans.

TG analysis

TG was performed by simultaneous thermal analysis (Dennis Bergkamp-Elmer, USA) under nitrogen atmosphere, and the gas velocity was 40 mL/min. The ethanol organosolv lignin of about 5 mg was heated from 20 to 600 °C at a rate of 10 °C/min.

GPC analysis

The gel permeation chromatography analysis of EOL was obtained using a PL-GPC 50 plus type gel permeation chromatography analysis system. 10 mg of acetylated EOL was firstly dissolved in 10 mL tetrahydrofuran (chromatography grade). Then GPC analysis was conducted at 40 °C, using tetrahydrofuran as the solvent, with a solvent flow rate of 0.1 mL/min. Standard polystyrene (Polystyrene) was used for the calibration gel column. Millenium 32 GPC software was used for data processing.

SEM analysis

Lignin depolymerized carbon was analyzed by thermal emission scanning electron microscopy (Zeiss Semiconductor, Germany). The samples were coated with gold, then vacuumed for 10 min, with distinguishability at 1.0 kV.

GC-MS analysis

The liquid product tar specimens were firstly adjusted to constant volume of 100 ml by using isopropanol. Secondly, the diluted liquid products were dehydrated with anhydrous sodium sulfate, and then the supernatant sample was prepared by using a millipore filtration. Lastly, the components of the samples were detected on a GC/MS analyzer (Agilent). The chromatographic column is DB-5ms (30 m x 0.25 mm x 0.25 µm), and chromatography-grade isopropyl alcohol was used as the diluent. Upon evaporation, it served as a carrier gas. The flow rate was 0.8 mL/min with a shunt ratio of 5:1. The sample quantity was 1 µL, and the automatic sampling method is adopted. The oven heating procedure was as follows: the initial column temperature was 40 °C, keeping constant for 5 min, heating up to 200 °C in steps of 5 °C/min, then heating to 280 ºC with 20 °C/min, keeping constant for 5 min, and with a solvent delay of 5 min. The compound similarity was compared with the NIST08 database (Pan *et al.* 2006).

RESULTS AND DISCUSSION

Effect of Pd/C Catalyst on the Yields of EOL

The moso bamboo (*Phyllostachys edulis*) sample was received from Zhejiang, China, and the refiner was milled to the specified mesh size. The chemical composition of the bamboo powder was as shown in Table 1.

Table 1. Fundamental Chemical Component Analysis of Bamboo Sample

Chemical Components	Content (%)
Acid insoluble lignin	30.02
Acid soluble lignin	0.24
Ash	1.36
Hot water extract	14.93
Acetone extract	8.81
Ethanol cellulose nitrate	38.16
Holocellulose	67.09
Poly-pentose	11.18

The effect of Pd/C catalyst on the extraction yields of EOL is presented in Table 2. The extraction yield of EOL was 8.66%, 11.01%, and 20.65%, corresponding to the extraction temperatures of 160, 180, and 200 °C, respectively. With 0.5% Pd/C catalyst, the extraction yields of EOL were increased by 5.83%, 10.7%, and 16% with increasing temperature from 160 to 200 °C, respectively. When the additional amount of Pd/C catalyst was increased up to 1%, the extractions yields of EOL were obviously increased by 9.34%, 11.58%, and 22.91%, respectively. The addition of Pd/C catalyst enhanced the extraction yields of EOL, and the effect of Pd/C catalyst on the EOL yield became more evident at higher temperatures. The addition of Pd/C catalyst in extraction reduced cleavage of ether linkages, resulting in EOL yield enhancement due to alleviation of the re-distribution and condensation of lignin to the surface of cellulosic fiber (Pan *et al.* 2006).

Table 2. Effect of Pd/C Catalyst on the Yields of EOL

Temperature (°C)	Time (min)	Catalyst Amount (%)	Residue Yield (%)	Lignin Yield (%)
160	60	-	89.23	8.66
180	60	-	78.62	11.01
200	60	-	69.93	20.65
160	60	0.50	83.17	14.49
180	60	0.50	75.13	21.73
200	60	0.50	64.36	36.65
160	60	1.00	82.75	18.00
180	60	1.00	73.03	22.59
200	60	1.00	56.09	43.56
200	60	2.00	61.61	43.81
200	60	4.00	63.76	43.84
200	120	1.00	56.09	43.61
200	120	2.00	61.57	41.52

For the 2% and 4% Pd/C catalyst extraction process, the extraction yields of the EOL were 43.8% and 43.8% at an extraction temperature of 200 °C, respectively. This result indicated that the enhanced effect of Pd/C catalyst on the EOL yield was slight, as the catalyst amounted up to 2%. With increasing reaction time from 60 min to 120 min, the extraction yields of EOL remained similar. When both the reaction time and catalyst amount were raised simultaneously, the extraction yield of EOL decreased from 43.8% to 41.5%. Excessive degradation of lignin structure occurred at long reaction time and resulted in the formation of small fragments of the lignin. The fragments of lignin were highly soluble in ethanol and unable to be recovered by the precipitation operation, leading to low EOL yield (Pan *et al.* 2006).

Effect of Pd/C Catalyst on Chemical Properties of EOL

Table 3 presents that effect of Pd/C catalyst on the molecular weight of lignin. The molecular weight distribution value of lignin dissolved at 160 °C was 3.2, which was significantly higher than that of lignin dissolved at 180 °C (1.3) and 200 °C (1.5). At the same time, the molecular weight of EOL-160, EOL-180 and EOL-200 samples increased first and then decreased. A possible reason for this phenomenon may be that the dissolution ability of EOL at low temperature is small. Only the lignin with smaller molecular weight can be dissolved, and with the increase of dissolution temperature, the lignin with larger molecular weight is dissolved in large quantities, resulting in the increase of EOL molecular weight. When the dissolution temperature continues to increase to 200 °C, the reaction system conditions are already in the subcritical conditions of ethanol, resulting in the depolymerization of EOL, which in turn leads to a decrease in the molecular weight of EOL.

Table 4 shows that with the increase of Pd/C catalyst content, the molecular weight of lignin increased from 8294 to 9925 and then decreased to 9273, while the molecular weight distribution increased from 1.59 to 1.68. Thereafter it tended to be relatively stable, indicating that the molecular weight of lignin first increased and then decreased, and the width of molecular weight distribution first became wider and then tended to be relatively stable.

Table 3. GPC Analysis of the Obtained Lignin Samples

Sample		M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	Molecular Weight Distribution
No catalyst	EOL-160 °C	1146	3776	11805	3.2
	EOL-180 °C	6873	9380	12896	1.3
	EOL-200 °C	5203	8294	12240	1.5
1% Pb/C	EOL-160 °C	1023	3555	10047	3.17
	EOL-180 °C	6633	9042	11430	1.29
	EOL-200 °C	5342	8773	13479	1.64

Table 4. Effect of Pd/C Catalyst Content on Molecular Weight and Molecular Weight Distribution of EOL

Sample	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	Molecular Weight Distribution
No catalyst	5203	8294	12240	1.59
1% Pb/C	5342	8773	13479	1.64
2% Pb/C	5894	9925	15546	1.68
4% Pb/C	5561	9273	15471	1.67

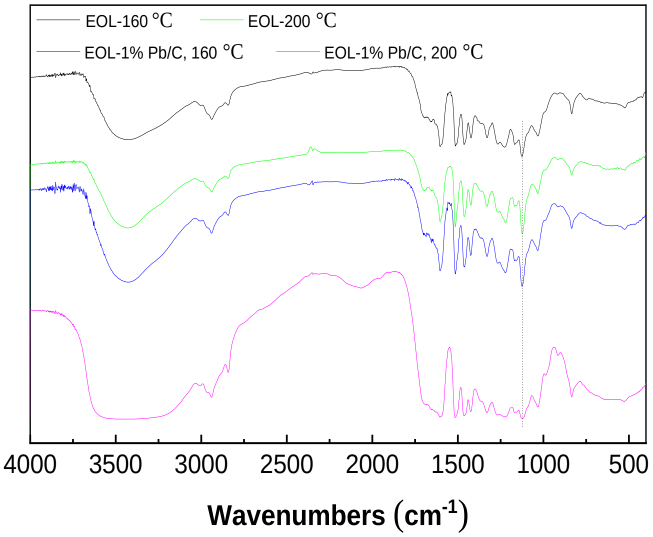

Fig. 2. FTIR analysis of the obtained lignin samples

Changes in bonding types and chemical structures of EOL were investigated by FT-IR. As shown in Fig. 2, the infrared absorbance peaks of four kinds of lignin were similar, but the absorbance intensities were different. The peak at 1703 cm $^{-1}$ was attributed to C=O stretching vibration in the non-conjugated carbonyl, carboxyl, and ester groups. The peaks at 1593 cm^{-1} and 1507 cm^{-1} were generated by the vibration of benzene ring skeleton, and the peaks at 1236 cm^{-1} were generated by the stretching vibration of C-O-C bond in aryl ether bond directly connected with benzene ring. Those peaks did not change significantly depending on the pretreatment temperature and addition of Pd/C catalyst.

As shown in Fig. 3a, when the temperature reached 600 °C, the residual mass percentages of the three compounds were 35.2%, 37.1%, and 38.4%, respectively. When the temperature was below 200 °C, the lignin quality decreased due to the volatilization of the water in the lignin, and when the temperature was between 200 and 400 °C, the lignin quality decreased.

The loss of lignin quality was mainly caused by the pyrolysis of lignin organic structure to form volatile matter. Therefore, the dissolution temperature of lignin has an effect on the pyrolysis process of lignin. At the same time, the thermogravimetric curves of EOL-200 were basically above EOL-160 and EOL-180 in the temperature range of 200 to 400 °C. It can be inferred from Fig. 3a that the thermal stabilities of EOL-160 and EOL-180 were lower than that of EOL-200.

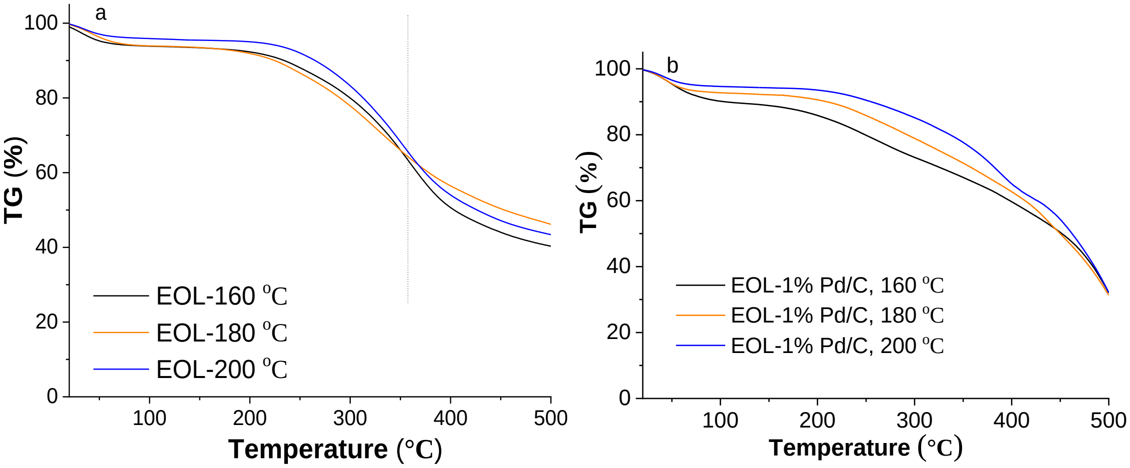

Fig. 3. Thermogravimetric analysis of obtained lignin samples

According to Fig. 3b, the thermogravimetric curves of Eol-1%Pd/C -200 °C were basically above EOL-1%Pd/C-160 °C and EOL-1%Pd/C-180ºC in the temperature range of 200 to 400 °C for the depolymerization of EOL. Thus, the thermal stability of Eol-1%Pd/C-160 °C and EOL-1%Pd/C-180 °C was lower than that of EOL-1%Pd/C-200 °C.

Effect of Pd/C Catalyst on Depolymerization Properties of EOL

Effect of Pd/C catalyst on lignin conversion

The effect of extracting temperature and Pd/C catalysis on EOL conversion are summarized in Fig. 4. When the extracting temperature was raised from 160 to 200 °C, lignin conversion slightly increased. The highest lignin conversion was obtained at 200 °C. In this temperature range, the adjustment of extracting temperature did not notably affect lignin conversion. Addition of 1% Pb/C notably affected lignin conversion at 160 to 200 °C. When the extracting temperature was raised from 160 to 200 °C, the effect of 1% Pb/C was more noticeable.

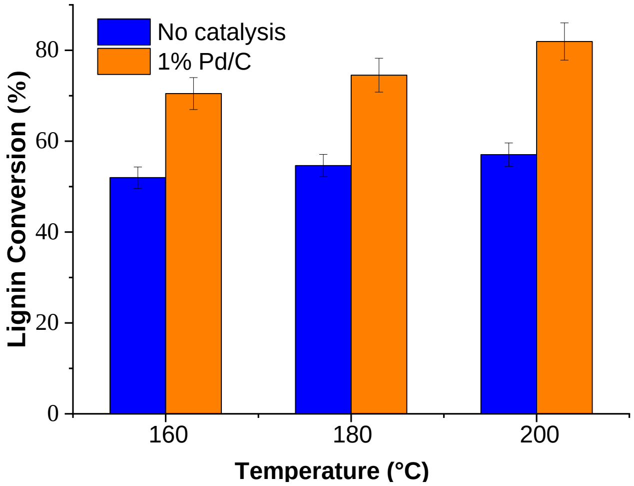

Fig. 4. Effect of extracting temperature and Pd/C catalysis on EOL conversion

Effect of Pd/C catalyst on liquid products components

GC/MS was employed to analyze the chemical composition, and the detected compounds and their relative content are summarized in Table 5.

Table 5. Composition of the Lignin Depolymerized in Supercritical Ethanol

Component	Relative Content (%)					
	160 °C		180 °C		200 °C	
	No	**Pd/C**	No	**Pd/C**	No	**Pd/C**
Phenol	0.66	6.12	1.04	1.11	-	3.11
Phenol, 4-ethyl-	13.49	0.15	9.96	3.15	2.33	-
Phenol, 2-methoxy-	3.73	7.66	5.94	15.08	-	0.47
Phenol, 4-methyl-2-methoxy-	5.38	3.85	4.21	10.95	12.04	-
Phenol, 4-ethyl-2-methoxy-	6.40	1.62	5.00	6.60	2.25	4.58
Phenol, 4-vinyl-2-methoxy-	-	3.4	-	-	0.76	5.46
Phenol, 4-propyl-2-methoxy-	6.47	1.09	4.68	2.27	3.24	4.54
Phenol, 4-propenyl-2-methoxy-	2.00	3.58	1.40	5.78	7.26	6.48
Phenol, 2,6-dimethoxy	12.60	0.91	17.57	5.25	1.24	5.66
Phenol, 4-propyl-2-methoxy-	6.47	1.09	4.68	2.27	3.24	4.54
Benzaldehyde,3-hydroxy-4-methoxy-	-	1.59	-	3.00	1.91	15.54
Benzoic acid, 4-hydroxy-3-methoxy-	13.20	13.23	12.52	16.04	12.52	20.59
Ethanone,1-(3-hydroxy-4-methoxy phenyl)-	-	4.77	0.60	0.30	3.30	1.05
3-tert-Butyl-4-hydroxyanisole	-	4.22%	-	0.41%	3.79	-
2,6-Di-tert-butyl-4-methylphenol	5.35	-	1.45	-	3.16	-
Benzene,1,2,3-trimethoxy-5-methyl-	-	-	7.02	0.57	4.91	2.03
4-(2-Hydroxyethyl)-2-methoxyphenol	1.23	7.73	0.80	7.04	-	1.06
4-Hydroxy-3,5-dimethoxybenzaldehyde	-	7.39	-	6.46	1.56	6.06
Benzoic acid,4-hydroxy-3-methoxy-,ethyl ester	20.30	19.26	17.93	8.52	17.69	9.56
Phenol,2,6-dimethoxy-4-(2-propenyl)-	0.88	4.96	2.74	0.71	4.98	5.02
Ethanone,1-(4-hydroxy-3,5-dimethoxy)-	2.19	3.15	1.88	4.22	14.29	7.59
Ethyl-β-(4-hydroxy-3-methoxy-phenyl)-propionate	4.34	0.82	4.62	2.93	1.77	1.20
3,5-Dimethoxy-4-hydroxyphenylacetic acid	1.45	4.50	-	-	-	-
Total Phenols Yields	106.14	101.09	104.04	102.66	102.24	104.54

Based on the molecular formula properties, the liquid oils obtained from EOL depolymerized in subcritical ethanol (180 °C) were mainly ester compounds, while the components of liquid oils prepared in supercritical ethanol (240 to 300 °C) were mainly phenolic compounds. The total phenols yields of EOL depolymerized at 180, 210, 240, 270, and 300 °C were 9.66%, 52.73%, 53.72%, 56.94%, and 68.21%, respectively. The liquid oils obtained from EOL depolymerized at 180 ºC included benzoic acid, 4-hydroxy-3-methoxy-, ethyl ester; phenylacetic acid, 4-hydroxy-3-methoxy-, ethyl ester; phenylacetic acid, 3-methoxy-4-hydroxy; and phenylacetic acid, 3,5-dimethoxy. The liquid oils products prepared at 300 °C included phenol; phenol, 2-methoxy; phenol, 4-ethyl-2-methoxy-; phenol, 2-methoxy-4-methyl; and phenol, 2, 6-dimethoxy.

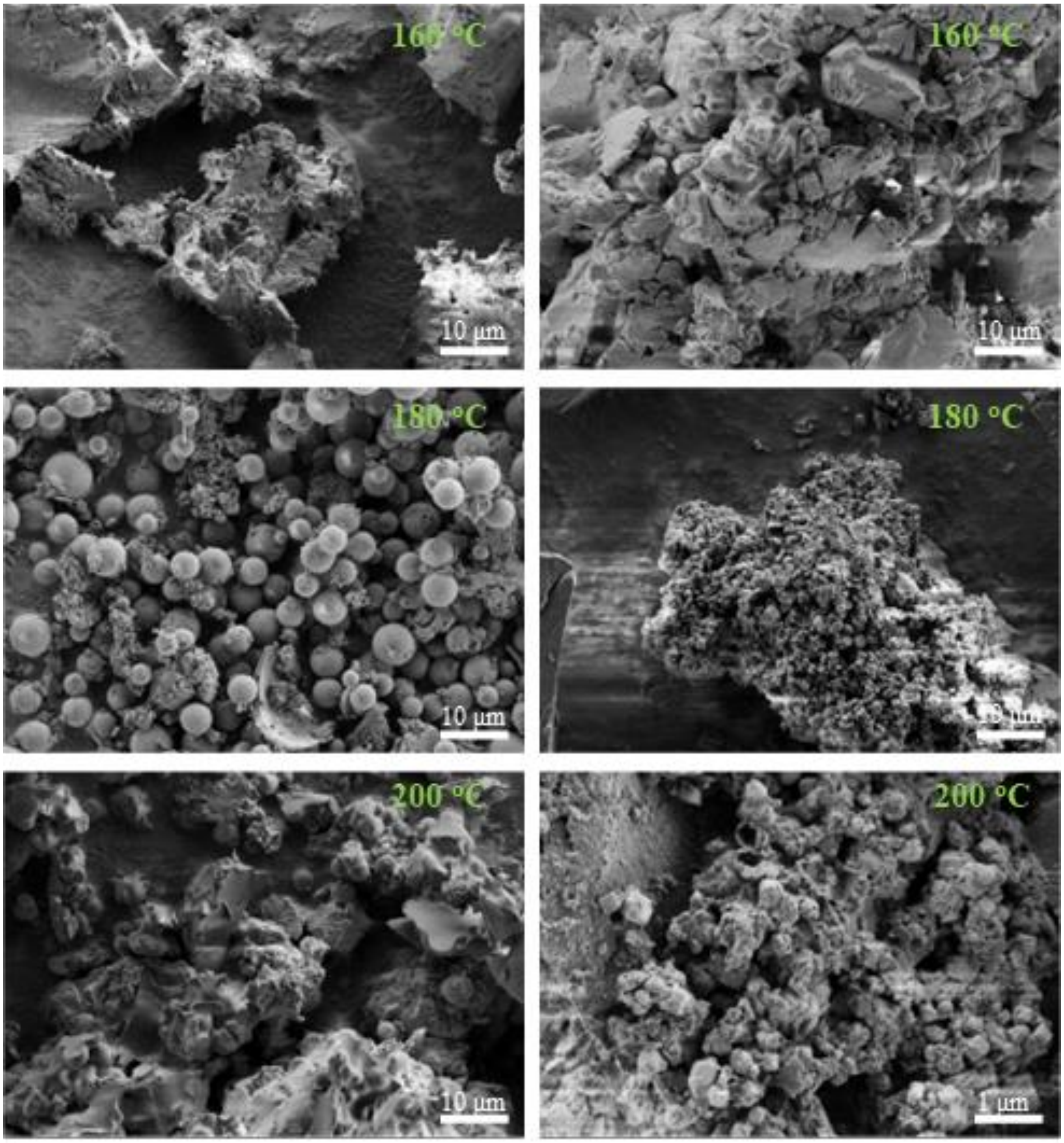

Fig. 5. SEM analysis of the obtained lignin depolymerization char

According to the composition of liquid oils, it can be inferred that the β type ether bonds of lignin units were involved in the homolytic cleavage reaction, and that they generated phenyl methyl and phenyl ethyl radicals, respectively. Then part of phenyl methyl and phenyl ethyl radical was coupled with propionyl radicals being released from the homolytic cleavage reaction of ethanol, mainly forming phenol and phenol, 2-methoxy, respectively. Phenolic compounds were the primary products of liquid oils as EOL was being depolymerized in supercritical ethanol, which can be naturally expected since phenol is the basic entity of the lignin structure.

Effect of Pd/C catalyst on char surface topography

SEM micrographs of chars obtained from lignin depolymerized after extracted at 160, 180, and 200 °C with different addition amounts of Pd/C catalyst are shown in Fig. 5. When the extraction temperature was increased from 160 to 200 °C, the char morphology obtained after lignin depolymerization could be described as a large number of micron-sized spheres at 180 °C without Pd/C, while the presence of 1% Pd/C catalyst reduced the micron-sized spheres. The trend of char morphology may be illustrated by noting that the addition of Pd/C catalyst had an obvious effect on the sphere size of the char products. The different size char spheres underwent different depolymerization or repolymerization reactions, and the incidence of the depolymerization or repolymerization reaction was determined by the reaction conditions. Especially, the number of micron-sized spheres and the particle size of micron-sized spheres decreased with increasing temperature from 180 to 200 °C. Moreover, as the additional amount of Pd/C catalyst increased from 1% to 4%, corresponding to the extraction temperature of 200 °C, the gap spacing of the matrix on the char surface increased.

CONCLUSIONS

1. Through comparison of the experiments of other groups in this study, it was concluded that the most favorable process conditions for the ethanolic solvent lignin of bamboo powder were 200 °C reaction temperature, 60 min reaction time, and 1% Pd/C content of catalyst. A high yield of EOL up to 39.6% without catalysts under mild conditions, and higher yield of EOL up to 44.0% were obtained from bamboo in Pd/C catalyst at 1% content at 200 ºC. The ethanol organosolv lignin extracted at 180 °C had the highest thermal stability without the addition of catalyst, and with the addition of Pd/C catalyst, the lignin extracted at 200 °C had the highest thermal stability.
2. The degradation products of ethanol organosolv lignin in supercritical ethanol process were main phenolic products, including 2-methoxyphenol, 4-ethylphenol, 4-methoxy-2-methylphenol, 2-methoxy,1,4-benzenediol, 4-ethyl-2-methoxyphenol, 2,6-dimethoxyphenol, 2-methoxy-4-propylphenol, 2,6-ditert-butyl-4-methylphenyl, and 2,6-dimethoxy-4-(2-propenyl)phenol.
3. The morphology characteristics of the char product was changed with the addition of a Pd/C catalyst. The morphology obtained from the supercritical ethanol degradation process gave evidence of a bulging phenomenon. With the increase of the degradation temperature, volatility production releasing rate increased, whereas the bubble volume shrinkage and pore size decreased. For Pd/C catalyst EOL, the char bubbles were reduced, and the crosslinking structure of coke faded away.

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