

Catalytic Reductive Depolymerization of Corncob Lignin to Produce Bio-oil *via* Formic Acid/Ethanol System

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Formic acid (FA) was used for reductive depolymerization of industrial corncob lignin *via* ethanol and Pt/C system. The highest yield of bio-oil obtained was 71.4% when the reaction was conducted at 260 °C with an FA/lignin ratio of 8 for 0.5 h. The bio-oil was composed of oligomers (M_w within 600 Da) and lignin depolymerized fragments (M_w beyond 600 Da). Reaction temperature was the most important factor affecting the properties of bio-oil. Although excessive temperature could increase the C/H ratio and higher heating value (HHV) of bio-oil, it would lead to repolymerization of lignin degraded fragments, thus resulting in a higher molecular weight of bio-oil. Additionally, alkylphenols were major products in bio-oil, and the amount of alkyl phenols could be increased by increasing the temperature and extending the retention time appropriately. This study reveals the effects of various reaction conditions on the yield and properties of bio-oil, providing a theoretical basis for subsequent upgrading of bio-oil to biofuels and aromatic chemicals.

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INTRODUCTION

Corncob, one of the residues from corn crops, is becoming a promising bioresource due to its broad prospects in value-added conversion, responding to the advocacy of agro-forestry residues reuse today. The corn production around the world reached 1.148 billion tons reported in 2019. In most biorefineries, cellulose and hemicellulose are chosen to produce various industrial chemicals (Liu *et al.* 2010; Hu *et al.* 2018; Yong *et al.* 2022). However, lignin, a natural aromatic resource, accounts for 15.7% to 18.8% by weight in corncob, and it is mostly discarded as industrial by-products, resulting in a waste of resources (Takada *et al.* 2018). Lignin is a macromolecule composed of three types of phenylpropane units connected by C-O and C-C bonds. The key to achieving high value application of lignin involves the cleavages of C-C and C-O bonds among lignin units and reserving as much phenylpropane structure as possible *via* thermochemical methods (Sudarsanam *et al.* 2020; Xu and Li 2021). In this way, lignin is degraded into bio-oil rich in phenols, and it is a candidate source for production of aromatic chemicals and biofuels.

Recently, a reduction strategy has attracted increased attention because of its high efficiency on depolymerization of lignin as well as its ability to decrease the complexity of the products. The reduction strategy also provides a good way for value-added utilization of industrial corncob lignin. Bai *et al.* (2019) succeeded in complete liquefaction of lignin from corncob residue in supercritical ethanol, and they achieved a yield of total aromatic phenols as high as 255 mg/g lignin when reaction was conducted at 320 °C, 7.5 h, and 27.6

bar H₂. Wang *et al.* (2019) studied the hydrogenolysis of biorefinery corncob lignin under catalysis of Ni/AC, and the highest yield (12.1 wt.%) of phenolic monomers was achieved at optimum operation conditions. In other cases, lignin extracted from corncob residue was hydrolyzed in the presence of Ni/HZSM-5. The aromatic monomers obtained were principally composed of 4-ethyl phenol and 4-ethyl guaiacol due to the high selectivity of Ni/HZSM-5 (Liu *et al.* 2019).

For reductive depolymerization of lignin, hydrogen can also be supplied by hydrogen donors through its decomposition. Alcohols such as isopropanol, methanol, and ethanol have been widely investigated as hydrogen donors in recent years. When isopropanol was used to degrade organosolv lignin, the yield of bio-oil reached 83.4 wt.%. In addition, isopropanol had excellent performances in promoting hydrodeoxygenation of aromatic monomers and reducing the production of oxygen-containing phenols (Du *et al.* 2020). Kristianto *et al.* (2017) found that ethanol was firstly dehydrogenated into hydrogen and acetaldehyde. Then, acetaldehyde was further dehydrogenated into carbon monoxide and methane during lignin depolymerization. Moreover, ethanol performed better than methanol and propanol in lignin deoxygenation under the same temperature (Wang *et al.* 2019).

Formic acid (FA) is also an excellent hydrogen donor; thus it is widely used in the study of lignin depolymerization. FA may promote the degradation of lignin by *in-situ* generation of hydrogen atoms (Kleinert and Barth 2008a,b). Huang *et al.* (2014) thought that formic acid should be more efficient at supplying hydrogen than H₂, since H₂ needs to dissociate into H atoms before it can participate in reaction. There are two paths of dehydration and dehydrogenation in FA decomposition under high temperature, and the employment of a catalyst might affect the manner of FA decomposition, thus resulting in selective dehydrogenation of FA (Ouyang *et al.* 2015). Riaz *et al.* (2016) showed that as the mass ratio of FA to lignin reached 1.5, the yield of bio-oil reached 92%, which was 25% higher than that without FA. Onwudili and Williams (2014) reported that FA could dissolve lignin, and it took the role of capping agent to inhibit second repolymerization of depolymerized products.

Alcohols are good solvents for lignin depolymerization. Alcohols can be considered as capping agents to inhibit intermediates of lignin from repolymerization (Huang *et al.* 2015). Methanol (Limarta *et al.* 2018; Shao *et al.* 2018), ethanol (Kim *et al.* 2015b; Duan *et al.* 2017; Zhou *et al.* 2018; Hao *et al.* 2022), and isopropanol (Cheng *et al.* 2020; Du *et al.* 2020) are alcohols that have been most studied. Usually, alcohols with shorter carbon chains and stronger polarity show better performance for lignin liquefaction (Duan *et al.* 2018; Wang *et al.* 2020). In addition, noble catalysts, such as Pt, Pd, Ru, and Rh, have attracted increased attention on lignin depolymerization because of their favorable catalytic performances (Yang *et al.* 2016; Guo *et al.* 2017; Bartolomei *et al.* 2021; Gurralla *et al.* 2022; Su *et al.* 2022). The noble catalysts are evenly dispersed over carriers. The surface of noble metals not only can promote the depolymerization of lignin, but also, they can serve as the site of decomposition of hydrogen donors to produce hydrogen, so that lignin and its depolymerized products can be deoxygenated by hydrogen *in situ* (Onwudili and Williams 2014). Studies have shown Pt/C to have excellent ring hydrogenation capabilities (Bjelic *et al.* 2019). The employment of Pt/C in a formic acid system could greatly promote the hydrodeoxygenation of lignin, and thus it could greatly increase the H/C ratio of bio-oil (Xu *et al.* 2012). In addition, the presence of Pt/C during lignin hydrolysis could increase the yield of 4-ethyl phenol and 4-ethyl guaiacol in bio-oil (Ye *et al.* 2012). Kim *et al.* (2015) investigated how the distribution of lignin

depolymerization products is affected by the combination of alcohols and catalysts, and the combination of ethanol and Pt/C showed the highest efficiency in lignin depolymerization.

In this experiment, FA was used for the degradation of industrial corncob lignin in ethanol solvent. Additionally, Pt/C catalyst was employed to fully facilitate FA decomposition. This paper primarily examines the effects of reaction temperature, retention time, and FA/lignin ratio (FA volume/lignin mass, mL/g) on proportions of lignin depolymerized products as well as bio-oil properties. The objectives were to better realize reductive depolymerization of corncob lignin, to obtain bio-oil rich in phenols, and to explore ways for high value conversion of corncob.

EXPERIMENTAL

Materials

The lignin, extracted from corncob residue by alkali and then purified, was provided by Shandong Longli Bio-Technology Ltd., China. The lignin purity was 94%, consisting of 58.7% C, 5.6% H, 31.7% O, and 0.6% N. The raw lignin was screened through a 200-mesh sieve, then dried at 60 °C for 12 h before use. Absolute ethanol (Analytical reagent (AR), 99%), formic acid (AR, 99%), ethyl acetate (Guaranteed reagent (GR), 99.9%), and tetrahydrofuran (GR, 99.9%) were purchased from West Asia Reagent Ltd., China. The Pt/C catalyst (with Pt load of 5 wt.%), tetrahydrofuran (AR, 99%), and potassium bromide (Spectrography, SP) were purchased from McLean Biochemical Technologies Ltd., Shanghai, China. The Pt had a load of 5 wt.%.

Methods

Catalytic depolymerization of lignin

The reaction was completed in a 150-mL batch reactor. For each run, about 0.5 g lignin, 0.1 g catalyst, 25 mL ethanol, and proper amount of formic acid were added into the reactor. Before the reaction, the reactor was deaerated using slow N₂ flow. The reaction system was heated to a preset temperature and maintained at the same condition. After a preset time, the reaction tank was air-cooled to below 80 °C for a period within 1 h, and then naturally cooled down to room temperature. The reactor was opened and the mixture was washed out with ethanol, and then the solid and liquid were separated through suction filtration. After vacuum drying, the solid part was weighed. The ethanol in the liquid phase was removed by rotary evaporation at 40 °C under reduced pressure to obtain crude bio-oil, which is then dissolved with THF, centrifuged to take the supernatant, and finally THF was removed to obtain bio-oil. The procedure used is described in Fig. 1.

The yields of various products are calculated as follows,

$$\text{Yield of bio-oil (\%)} = m_1 / m \times 100\% \quad (1)$$

where m_1 is the mass (g) of bio-oil, and m is the mass (g) of raw lignin;

$$\text{Yield of solid (\%)} = m_2 / m \times 100\% \quad (2)$$

where m_2 is the mass (g) of solid product.

$$\text{Yield of gas products (\%)} = m - (m_1 + m_2) / m \times 100\% \quad (3)$$

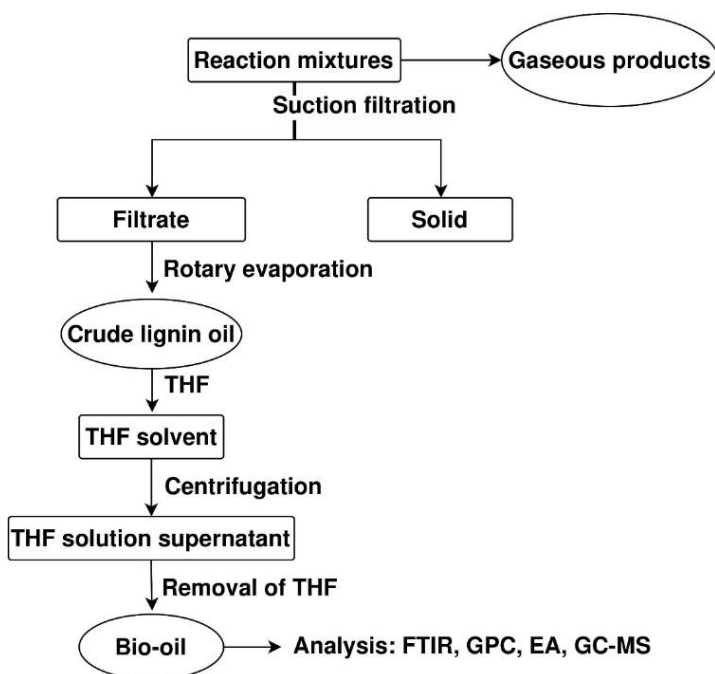


Fig. 1. Flow chart of products separation

In Table 1, experiments performed under different conditions are numbered separately to avoid confusion when different experimental groups are mentioned in subsequent discussions.

Table 1. Experimental Conditions and Numbers of Different Groups (Other Conditions: Lignin 0.5 g, Ethanol 25 mL, and Pt/C 0.1 g)

Numbers	Reaction Temperature (°C)	Retention Time (h)	FA to Lignin Ratio (v/m ^a)
A-1	200	2	8
A-2	230	2	8
A-3 (B-4)	260	2	8
A-4	290	2	8
B-1	260	0	8
B-2 (C-2)	260	0.5	8
B-3	260	1	8
C-1	260	0.5	4
C-3	260	0.5	16

^a "v/m": formic acid volume to lignin mass ratio

Analytical procedures used for bio-oil characterization

Fourier transform infrared (FTIR) spectra of bio-oil and raw lignin were recorded on a Nicolet iS5 FTIR Spectrometer (Shanghai, China). Transparent circular discs were prepared using KBr (SP) powders and trace amounts of samples by hydraulic press before testing. The spectra were recorded in a wavenumber range of 400 to 4000 cm⁻¹ with average scan number of 64 and resolution of 4 cm⁻¹.

Elemental analysis (EA) of bio-oil was performed on an elemental analyzer (Elementer Vario MACRO Cube, Hanau, Germany). The elemental contents of C, H, and N were determined directly in CHNS mode, and the O-content was calculated by difference. The C/O and H/C ratios were calculated by dividing the mass percentages of C, H, and O by their relative atomic masses. The formula used of higher heating value (HHV) is as follows,

$$\text{HHV (MJ/kg)} = 0.338 \text{ C} + 1.428 \times (\text{H\%} - \text{O\%} / 8) \quad (4)$$

where C is the relative atomic mass of C, H% is the mass percentage of H, and O% is the mass percentage of O.

The molecular weight distributions of bio-oil were determined by Shimazu LC-20A equipped with a PL-gel 3 μm MIXED-E 300 \times 7.5 mm column and a UV detector (254 nm). Samples were first dissolved in THF (2 mg/mL); then the solvents were filtered with a 0.2- μm nylon filter. The eluant was also THF at a rate of 1 mL/min. The cylinder was kept at 40 $^{\circ}\text{C}$.

The Shimazu gas chromatograph-mass spectrometer (GC-MS) QP2010 was used for analyses of bio-oil. A HP-5MS (30 m \times 0.25 mm \times 0.25 μm) column was equipped for those experimental procedures. Liquid samples were injected into the chromatographic system at 250 $^{\circ}\text{C}$ with a split ratio of 19:1. The column was first held at 40 $^{\circ}\text{C}$ for 3 min, then heated to 250 $^{\circ}\text{C}$ at a heating ratio of 10 $^{\circ}\text{C}/\text{min}$, and held at 250 $^{\circ}\text{C}$ for 3 min. Full scanning mode in a range of zero to 700 m/z was adopted for the detection of liquid products. The bio-oil was identified based on NIST14 mass spectrometry library and each identified compound was calculated based on the ratio of its peak area to the total peak area.

RESULTS AND DISCUSSION

Influence of Different Factors on Yields of Lignin Liquefaction Products

The influence of reaction temperature on the proportions of various lignin depolymerization products is illustrated in Fig. 2a. Moreover, the yields of lignin degradation products under different reaction conditions are listed in Table A1. Higher temperature was beneficial to increase the bio-oil yield at 200 to 260 $^{\circ}\text{C}$, but the yield of bio-oil notably decreased to 51.6% at 290 $^{\circ}\text{C}$. In addition, increasing temperature also led to a lower proportion of solid, so the maximum solid yield of 26.6% was observed at 200 $^{\circ}\text{C}$ and the minimum was only 4.2% obtained at 290 $^{\circ}\text{C}$. Instead, the gas production would benefit from increasing temperature, especially at 290 $^{\circ}\text{C}$, where gas yield reached 44.1%. These gaseous products were mainly due to the cleavage of benzene ring side chains or functional groups and the further decomposition of depolymerized fragments (Jia *et al.* 2021). The above result revealed that increasing temperature aggravated the liquefaction reaction of lignin and increased the degree of lignin depolymerization, but the depolymerized lignin was inclined to be converted into gases of low molecular weight, so that the yield of bio-oil decreased with a further increase of temperature.

The variation of the yield of different lignin depolymerization products was investigated when the reactions were conducted from 0 to 2 h (Fig. 2b). As shown in Fig. 2b, the solids yield was less differentiating among four groups. Within the range of 0 to 0.5 h, the yield of bio-oil increased from 64.53% to 71.43%, and the gas yield decreased from 23.59% to 18.06%, indicating that part of the gaseous products was converted into bio-oil.

This may be because of the retention time at 0 h that was too short; thus hydrogen produced by FA decomposition did not fully participate in lignin depolymerization. When reactions were conducted at 0.5 to 2 h, the yield of bio-oil continued to decrease, corresponding to a growth of gaseous products. Nielsen *et al.* (2017) found that lignin would undergo decarboxylation and deoxygenation with production of CO₂ during its depolymerization. Therefore, an excessive depolymerization would occur to generate more gaseous products if retention time was too long. Decarboxylation, decarbonylation, demethoxylation, and demethylation also contributed to gas production.

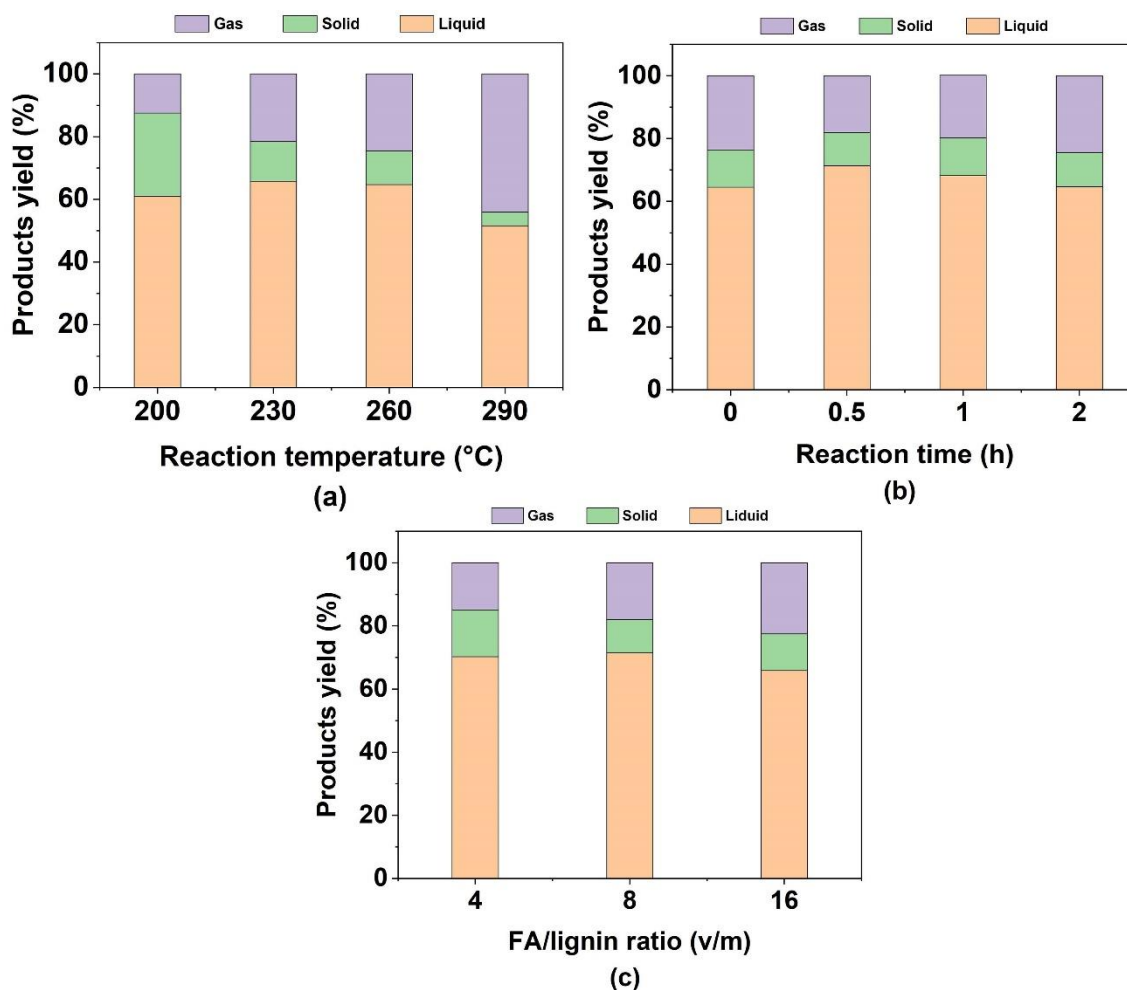


Fig. 2. Investigation of the influence of different factors on yields of lignin depolymerization products: (a) reaction temperature; (b) retention time; (c) FA/lignin ratio

The changes in proportion of each product as FA/lignin ratio increased are concluded in Fig. 2c. It could meet the needs of lignin depolymerization when the FA to lignin ratio was 4, and the yield of bio-oil was up to 70.2%, which was comparable with that of other groups. As FA to lignin ratio reached 8, the solid yield decreased from 14.8% (when the ratio was 4) to 10.5%. However, more depolymerized lignin was converted to gases, resulting in a decline of the yield of bio-oil to only 71.4%. Further increasing the FA/lignin ratio, the solid yield was 11.6%, which showed no notable change compared with FA/lignin ratio of 8. However, the bio-oil yield declined to 65.9%, and the gas yield

was the highest. This indicated that excess usage of FA would promote the cleavage of lignin into low molecular weight gases.

Analysis of Functional Groups and Element Composition of Bio-oil

The infrared spectra of lignin as well as bio-oil are shown in Figs. 3a, 3b, and 3c. These samples exhibited almost the same infrared characteristics. The wide band around 3406 cm^{-1} represents the stretching vibration of $-\text{O}-\text{H}$ bond. Two weak peaks at 2937 and 2842 cm^{-1} are attributed to stretchings of $\text{C}-\text{H}$ in methyl, methylene, and methine groups (Mei *et al.* 2020). The bands found at 2800 to 3000 cm^{-1} in all bio-oils were stronger than those in lignin. The sharp peak at 1701 cm^{-1} observed in lignin indicates the presence of conjugated $\text{C}=\text{O}$ groups. The peak near 1652 cm^{-1} was only observed in bio-oil other than in A-4 group, indicating more conjugated $\text{C}=\text{O}$ is found in bio-oil.

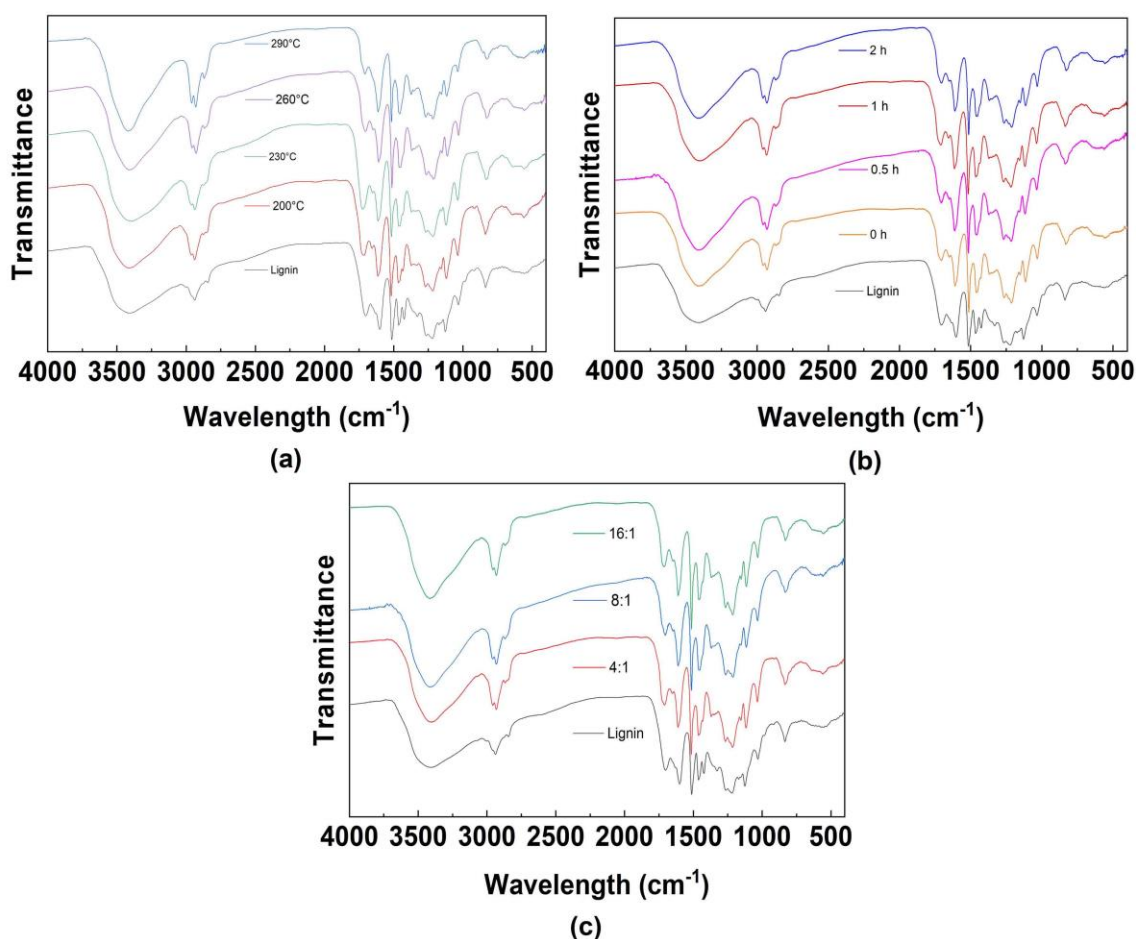


Fig. 3. FTIR spectra of bio-oil under different reaction conditions: (a) reaction temperature; (b) retention time; (c) FA/lignin ratio

A series of strong absorbances around 1600 cm^{-1} , 1514 cm^{-1} , and 1423 cm^{-1} are typical characteristics of benzene rings (Wang *et al.* 2018a). It is notable that the peak near 1423 cm^{-1} was not observed in bio-oil (except for the group of A-4), which might be a signal of excessive reduction, resulting in partial destruction of the benzene rings. The peaks at 1462 cm^{-1} belong to vibrations of $-\text{CH}_2-$ and $-\text{CH}_3$ groups in lignin (Duan *et al.* 2019). The spectra showed that both S-type units (1328 cm^{-1} , 1220 cm^{-1} , and 1125 cm^{-1}) and G-type units (1264 and 1033 cm^{-1}) were present in the raw lignin (Liao *et al.* 2020a;

Liao *et al.* 2020b). However, the infrared characteristics of syringyl units in bio-oil were only detected at 1115 cm^{-1} , but more and stronger peaks representing guaiacyl units (1264 cm^{-1} , 1215 cm^{-1} , and 1033 cm^{-1}) were observed in bio-oil (Wang *et al.* 2018b; Totong *et al.* 2020). Additionally, the peak at 1369 cm^{-1} belonging to Ar-OH was only observed in bio-oil.

The changes of each elemental content in bio-oil with varying reaction conditions are illustrated in Table 2. Reaction temperature was the most important factor promoting ratio of carbon and hydrogen and decreasing the percentage of oxygen. Thus, the HHV of bio-oil increased from 25.13 to 27.66 MJ/kg as the temperature rose from 200 to 290 °C. In addition, prolonged retention time was also favorable to enhancing hydrodeoxygenation (HDO) of lignin, as indicated by the declined ratio of O/C in bio-oil from 0.33 to 0.29 from 0 to 2 h. However, the H/C ratio stayed the same at 1.16 within 1 h, and it only increased to 1.18 at 2 h. On the one hand, it could be inferred that from 0 to 1 h was too short for hydrodeoxygenation of lignin. On the other hand, both the supplemental reactions (such as hydrogenation and hydrogenolysis) and loss (demethylation, demethoxylation, *etc.*) of the hydrogen would occur (Ghoreishi *et al.* 2019), leading to an inconspicuous change in H/C ratio of bio-oil. Moreover, elemental proportions of bio-oil also varied with different FA to lignin ratios. The proportion of bio-oil did not change remarkably when FA/lignin ratio increased from 4 to 8. Until the FA/lignin ratio reached 16 that the O/C ratio declined to 0.33, the H/C ratio and HHV rose to 1.20 and 27.07 MJ/kg in bio-oil, which revealed a higher ratio of FA/lignin would enhance hydrodeoxygenation of the lignin by increasing hydrogen concentration (Kristianto *et al.* 2017).

Table 2. Elemental Analysis and HHV of Bio-oil under Various Conditions

Experimental Groups	Elemental Analysis (%)				O/C	H/C	HHV (MJ/kg)
	C	H	O	N			
A-1	63.78	6.13	29.02	1.07	0.34	1.15	25.13
A-2	64.21	6.26	28.42	1.11	0.33	1.17	25.57
A-3 (B-4)	66.45	6.54	25.80	1.21	0.29	1.18	27.18
A-4	66.69	6.77	25.47	1.07	0.29	1.22	27.66
B-1	64.24	6.20	28.46	1.10	0.33	1.16	25.49
B-2 (C-2)	64.74	6.24	27.92	1.10	0.32	1.16	25.81
B-3	65.52	6.33	27.05	1.10	0.31	1.16	26.36
C-2	64.50	6.31	28.09	1.10	0.33	1.17	25.80
C-3	65.99	6.62	26.29	1.10	0.30	1.20	27.07

Influence of Different Factors on Molecular Weight of Bio-oil

The molecular weight distribution of bio-oil under different reaction conditions was analyzed, and the results are illustrated in Fig. 4. Moreover, the average molecular weights are listed in Table A2. The bio-oil obtained in all cases was composed of a series of compounds whose molecular weight values were continuous, including oligomers, consisting of several benzene rings (M_w within 600 Da) and lignin fragments (M_w beyond 600 Da) that failed to be depolymerized effectively (Bartolomei *et al.* 2021; Kuznetsov *et al.* 2021).

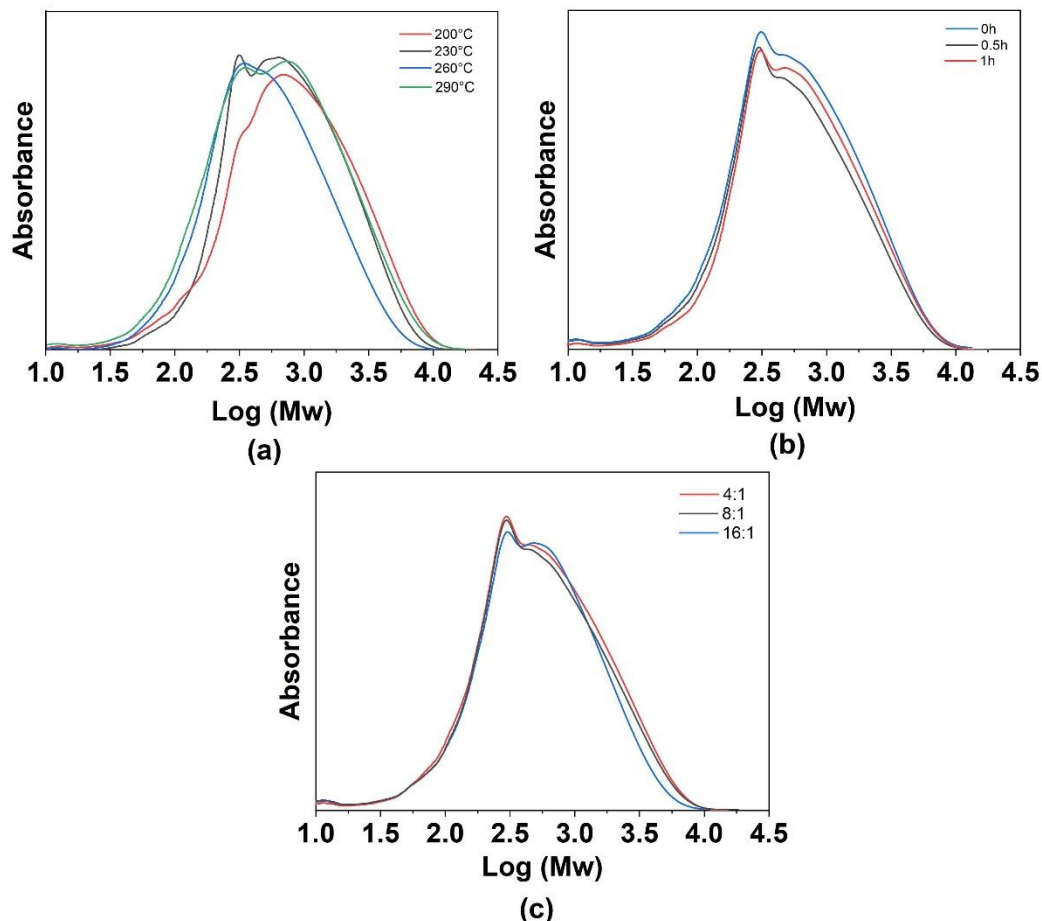


Fig. 4. Different effects on molecular weight distribution of bio-oil: (a) reaction temperature; (b) retention time; (c) FA/lignin ratio

As shown in Fig. 4a, temperature was the most important factor affecting the molecular weight of liquid products. When the temperature increased, the molecular weight curve gradually narrowed and shifted to the left, while at 290 °C, the curve began to develop to the opposite direction, suggesting that increasing the temperature within a certain range was beneficial to depolymerization and thus to reduce the overall molecular weight of bio-oil. However, it would aggravate the reunion of reaction intermediates and hinder lignin depolymerization if the temperature was too high. The bio-oil had similar results of molecular weight distribution in the range of 0 to 1 h. As retention time was prolonged to 2 h, the curve became narrow and shifted to the left, indicating there were fewer large fragments but more oligomers in the bio-oil. Moreover, the least effects on molecular weight distribution of bio-oil were observed when the FA/lignin ratio varied from 4 to 16. Those curves in Fig. 4c illustrated that increased FA/lignin ratio could facilitate the depolymerization of large molecular weight fragments into oligomers, but the proportion of aromatic monomers and dimers changed slightly.

GC-MS Analysis of Bio-oil

In this study, qualitative examination of bio-oil was performed through GC-MS analysis, and the detectable products are summarized in Table 3. It should be noted that some chromatographic peaks were found with no obvious signal. Among the 21 detected

compounds, 19 were aromatic compounds, including phenolic monomers and aromatic acids/esters. The phenolic monomers can be classified into methoxy-containing phenols and alkylphenols according to Kim *et al.* (2015b). Among these phenolic monomers, the alkylphenols (such as 4-ethylphenol and 4-ethylguaiaicol) were in the major part, which is similar to the results from previous studies (Ye *et al.* 2012; Kim *et al.* 2015a; Zhang *et al.* 2022). The aromatic acids/esters are primarily composed of 2-(4-hydroxy-phenyl) ethyl acetate and 3-(4-hydroxy-3-methoxyphenyl) ethyl propionate. According to the structure of aromatic esters, ethanol was possibly esterified with aromatic acid during lignin depolymerization (Huang *et al.* 2014). A certain amount of aliphatic compounds was also detected in the bio-oil of each group (Table 3). It has been speculated that aliphatic compounds were formed by condensation of lignin depolymerized fragments, which have active reaction sites (such as C=O and C-O bond). However, the aliphatic products are more likely to correspond with ring opening of benzene in lignin considering their structure (Kim *et al.* 2013, 2015b). Subsequently, the rules of the proportions of different types of products as the reaction conditions changed are discussed in the next section.

Lu *et al.* (2022) reported that increasing temperature within 240 °C was beneficial to the formation of alkyl guaiacols, but it led to a decrease on proportion of oxygen-containing guaiacols. This result is similar to the present study. As shown in Table 3, the proportion of alkylphenols slightly increased as temperature was elevated at 200 to 260 °C, but it plummeted to 36.7% under 290 °C. In contrast, the content of aromatic acids/esters were increased to 36.9% when reaction temperature was 290 °C. The possible reason was: (i) Alkylphenols repolymerized with molecules that had oxygenic groups, (ii) Increasing temperature accelerated the degradation of lignin to form aromatic acids/esters that were precursors of alkylphenols. However, the alkylphenols further degraded (such as opening and hydrogenation of benzene rings, and demethoxylation, *etc.*) under high temperature. In addition, the ratio of aliphatic products was observed to increase with raising temperature.

When retention time was extended, the total content of phenolic monomers remained almost unchanged within 1 h, but it surged from 40.3% to 58.3% as the retention time was prolonged from 1 to 2 h. This indicated a long enough time was conducive to the formation of phenolic monomers from lignin depolymerization. Meanwhile, the ratio of aromatic acids/esters and aliphatic compounds decreased under prolonged time, among which the aromatic acids/esters were likely to be converted into alkylphenols through deoxygenation. Aliphatic compounds (mainly dimethyl (2E,4E)-2,4-hexadienedioate) continue to cleave due to their unstable structure (Yang *et al.* 2016). It is noteworthy that 2,6-di-*tert*-butyl *p*-cresol was identified in alkylphenols, which could be considered as C-alkylation of the benzene ring (Huang *et al.* 2014). This compound was only found in groups of A-1, A-2, and A-3, indicating that the results of benzene ring C-alkylation seriously occurred under longer retention time.

The effect of FA/lignin ratio on percentages of different products was also investigated. The proportion of phenolic monomers in groups C-1, C-2, and C-3 were 44.6%, 42.1%, and 42.7%, respectively, indicating that a FA/lignin ratio of 4 was sufficient to maintain the content of phenolic monomers. As FA/lignin ratio was raised from 4 to 16, the proportions of aliphatic compounds and aromatic acids/esters increased and decreased, respectively (Table 3). This indicated that hydrodeoxygenation of formic acid was enhanced, leading to further reactions of aromatic acids/esters, such as hydrogenation, deoxygenation, and demethoxylation. In addition, increasing the dosage of FA would aggravate the degradation of lignin, resulting in more small molecular fragments with

active sites, as well as increased cracking of benzene ring in aromatic monomers. Thus, the proportion of aliphatic compounds increased with higher FA/lignin ratio.

Table 3. Identified Compounds by GC-MS in Bio-oil Obtained under Different Reaction Conditions

RT (min)	Identified Compounds, Area (%)	Samples								
		A1	A2	A3 (B4)	A4	B1	B2 (C2)	B3	C2	C3
	Methyl-contained phenols									
7.47	Phenol	3.65	1.32	1.23	- ^b	-	-	1.11	1.70	-
9.74	Guaiacol	6.15	3.00	2.61	4.74	2.25	4.76	4.26	3.76	3.33
13.10	2-Methoxyresorcinol	1.08	-	-	-	-	-	-	-	-
14.67	2,6-Dimethoxyphenol	6.66	3.54	3.30	1.64	1.46	2.15	2.59	4.22	3.65
	Total Alkylphenols Content	17.54	7.86	7.14	6.38	3.71	6.91	7.96	9.68	6.98
9.46	4-Methylphenol	0.83	-	-	-	-	-	-	-	-
11.29	4-Ethylphenol	14.41	16.07	14.99	10.75	12.25	8.36	12.05	12.54	12.65
11.79	4-Methylguaiacol	2.69	2.30	1.94	2.68	2.22	2.22	2.71	3.13	2.13
13.37	4-Ethylguaiacol	13.29	20.28	18.90	16.84	12.52	14.30	11.73	12.47	14.60
14.91	4-Propylguaiacol	2.18	3.72	3.47	4.98	4.29	3.83	3.77	3.35	4.38
16.21	2,6-Dimethoxy-4-Methylphenol	1.89	0.57	0.92	-	-	-	-	1.26	0.39
17.21	Butylated Hydroxytoluene	5.73	7.45	8.49	-	-	-	-	-	-
17.44	5- <i>tert</i> -Butylpyrogallol	2.34	1.86	2.41	1.45	2.66	2.01	2.06	2.17	1.57
27.46	2-(1-methylpropyl)phenol	2.62	-	-	-	-	4.44	-	-	-
	Total content of Aromatic acids/esters	45.98	52.25	51.12	36.7	33.94	35.16	32.32	34.92	35.72
19.32	Ethyl (2-hydroxyphenyl)acetate	8.1	6.64	6.23	10.18	8.61	9.82	12.17	11.88	11.94
19.73	Ethyl homovanillate	1.02	-	-	-	-	-	1.42	-	-
20.66	Ethyl 3-(4-hydroxy-3-methoxyphenyl)propionate	16.84	16.55	16.26	26.72	27.16	24.97	26.40	26.43	19.43
21.69	Syringic acid	-	-	-	-	-	-	-	1.02	-
29.09	Homovanillic acid	1.18	-	2.63	-	2.19	0.99	-	3.47	-
	Total content of Aliphatic compound	27.14	23.19	25.12	36.90	37.96	35.78	39.99	42.80	31.37
18.69	Dimethyl (2E,4E)-2,4-hexadienedioate	7.85	15.59	17.00	16.10	23.75	19.01	16.93	14.84	17.14
27.07	2,7-Dimethyloctane	-	-	-	-	-	-	-	-	0.74
28.11	Hexadecane	-	-	-	-	-	-	-	-	1.86
	Total	7.85	15.59	17.00	16.1	23.75	19.01	16.93	14.84	19.74

^b “-”: the compound was not detected in bio-oil

The detected products in bio-oil are mainly composed of lignin monomers and their oxygenated derivatives. Currently, some research is aimed at upgrading lignin-derived bio-oil into biofuel. One possible approach is to make jet fuel from lignin-derived bio-oil. Jet fuel usually contains 20% aromatics and 20% cycloalkanes (Zhang *et al.* 2021). In this

paper, the bio-oil produced from corncob lignin was a dark brown viscous liquid. Because of its complex composition, high molecular weight and poor combustion performance, the bio-oil cannot serve as biofuel directly. It is necessary to remove macromolecules from bio-oil and retain light parts of bio-oil (such as lignin monomers, monomer derivatives and dimers) (Azadi *et al.* 2013; Cheng and Brewer 2017). Fractionation is considered to be a cost-effective physical method for upgrading bio-oil (Taghipour *et al.* 2019). The light part of bio-oil can be separated by fractionation and then used as a source of aromatics in jet fuel.

CONCLUSIONS

1. Corncob lignin was successfully depolymerized in the presence of formic acid as a hydrogen donor *via* ethanol and Pt/C catalyst system. The highest yield of bio-oil (71.43%) was achieved when the reaction conditions were set at 260 °C and FA/lignin ratio of 8 for 0.5 h.
2. Temperature was the most important factor influencing the properties of bio-oil. Increasing temperature was beneficial to hydrodeoxygenation of lignin, but the depolymerized fragments would repolymerize if reaction temperature was too high, leading to higher molecular weight of bio-oil. Secondly, prolonging the reaction time is beneficial to increase the yield of bio-oil, promote the hydrodeoxygenation of lignin, and reduce the molecular weight of bio-oil. Besides, increasing formic acid/lignin ratio in the range of 4 to 16 could increase the C and H elements ratios in bio-oil, but had little effect on the yield and molecular weight of bio-oil.
3. The bio-oil was primarily composed of alkylphenols and their oxygenated derivative as determined by GC-MS, and elevated proportion of alkylphenols was observed under appropriate high temperature and prolonged retention time. The bio-oil derived from corncob lignin is expected as biofuel through subsequent upgrading.

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APPENDIX

Table A1. The Yields of Lignin Degradation Products under Different Reaction Conditions

Groups	Products Yield (%)		
	Solid Residue	Bio-oil	Gas
A-1	26.61	60.96	12.43
A-2	12.66	65.78	21.56
A-3(B-4)	10.76	64.68	24.56
A-4	4.30	51.63	44.08
B-1	11.88	64.53	23.59
B-2(C-2)	10.51	71.43	18.06
B-3	11.98	68.22	19.80
C-1	14.85	70.25	14.89
C-3	11.63	65.86	22.51

Table A2. Molecular Weight of Different Groups of Bio-oil

Groups	M_n	M_w	M_w/M_n
A-1	406	1374	3.38
A-2	446	1143	2.56
A-3 (B-4)	299	808	2.70
A-4	269	941	3.50
B-1	301	1023	3.39
B-2 (C-2)	288	1067	3.70
B-3	260	915	3.52
C-1	211	950	4.49
C-3	235	821	3.49