One-step alcoholysis of lignin into small-molecular aromatics: Influence of temperature, solvent, and catalyst

Fang Wang[a], You-Zhu Yu[b], Yigang Chen[b,*], Chun-Yu Yang[b], Yuan-Yu Yang[b]

[a] Department of Chemical and Environmental Engineering, Anyang Institute of Technology, Anyang 455000, China
[b] Key Laboratory of Magnetic Molecules and Magnetic Information Material of Ministry of Education, School of Chemistry and Material Science, Shanxi Normal University, Linfen 041004, China

A B S T R A C T

Lignin valorization is a challenge because of its complex structure and high thermal stability. Supercritical alcoholysis of lignin without external hydrogen in a self-made high-pressure reactor is investigated under different temperatures (450–500 °C) and solvents as well as catalysts by using a reactant suspension mode. Small-molecular arenes and mono-phenols (C_7-C_{12}) are generated under short residence time of 30 min. High temperature (500 °C) favors efficient deoxy-liquefaction of lignin (70%) and formation of small-molecular arenes (C_6-C_9). Solvents methanol and ethanol demonstrate much more synergistic effect on efficient deoxy-liquefaction of lignin than propanol. The catalyst Cu-C has the optimal activity and selectivity in methanol (70% of conversion, 83.93% of arenes), whereas Fe-SiC possesses the optimal catalytic deoxygenation in ethanol, resulting in the formation of arenes other than phenols. Further analysis indicates that lignin is converted into arenes by efficient cleavages of C—O ether bonds and C—C bonds under high temperature and pressure.

© 2019 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

Direct conversion of lignocellulosic biomass into hydrocarbon fuels as alternative energy sources has aroused extensive concern [1–3]. However, lignin as one of three main components of lignocellulosic biomass (cellulose, hemicellulose, and lignin) attracts the least attention because of its complex structure and high thermal stability, which makes depolymerization of lignin as a key process in utilizing biomass [4,5]. Lignin accounts for 25–35% of renewable carbon in the world, which is nonetheless used widely as a residue and cheap energy source and often incinerated [6]. Lignin with three-dimensional aromatic biopolymer consists mainly of guaiacyl, syringyl and p-coumaryl alcohol phenylpropane units through several types of C—O—C (β-O-4 as the most common linkage, α-O-4, 4-O-5, and so on) and C—C (5-5, β-1, β-5, β-β) interunit linkages in a random order [7,8]. Since the C—O ether bonds are more fragile than the C—C bonds [9], the cleavage of the C—O ether bonds is always the focus of most depolymerization strategies including catalytic oxidation, catalytic reduction, and acid-catalyzed depolymerization by using different catalysts such as La/SBA-15 [10], H-USY/Raney Ni [11], Pd/C [12], Ru/C [13], Cu/PMO [14], and Ru/N-doped C [15] under mild conditions, which mostly generates oligomers, phenolic monomers and other O-containing compounds [16]. To form simpler monomeric compounds such as mono-phenols and arenes, an additional hydroprocessing step is inevitable.

Supercritical alcoholysis of lignin by hydrogenolysis and hydro-deoxygenation in the presence of hydrogen and/or hydrogen-donor solvents such as methanol, ethanol, and propanol is a promising route [17] because of rapid heat transfer and high solubility [18], which is conducive to higher yields of simple alkylated phenols, arenes or/and aliphatic hydrocarbons and minimal repolymerization reactions [19,20]. Also, solvents play a crucial role in the yield and product distribution as well as depolymerization [21]. The extent of delignification decreases with increasing apolar character of the solvents [22]. For example, supercritical alcoholysis of Asian lignin over Pt/C, Pd/C, Ru/C, and Ni/C at 350 °C with 3.0 MPa H_2 for 40 min indicated that four main monomeric phenols 4-ethylphenol, guaiacol, 4-ethylguaiacol, and syringol were produced [23]. Catalytic hydrocracking (combination of $S_2O_8^{2-}$-KNO_3/TiO_2 and Ru/C) of kraft lignin (0.5 g) at 320 °C with 4.0 MPa H_2 for 6 h in a mixed solution of 30 mL 1,4-dioxane and 6 mL methanol suggested that O-containing monomeric and dimeric degradation products were the main [24]. Supercritical 2-propanol due to great H_2 transfer properties, was considered as one of the best solvent options in conversion of organosolv lignin by using Raney Ni at 300 °C under 7.0 MPa H_2 for 8 h, forming cyclic alcohols, cyclic ketones, and unsaturated products [25]. Besides, simple

monomers such as phenols containing methoxy groups, arenes, or/ and O-containing low-mass oligomers were produced by supercritical liquefaction of lignin in the solvents such as ethanol, propanol, methanol, and water by using the catalysts like Ru/C, NiMo, Ru-Cu/HY, MoC_{1-x}/Cu-MgAlO$_z$, and Ni/Al-SBA-15 [26–30]. The efficient deoxy-liquefaction of lignin remains extremely challenging in order to develop small-molecular arenes used as transportation fuels or additives.

In our previous work [31], deoxy-liquefaction of lignin was first suspended in a self-made high-pressure reactor over nano-SiC catalyst in supercritical ethanol. Lignin depolymerization and deoxygenation for small-molecular arenes were fulfilled at 500 °C. The change of residence time (30–120 min) did not influence distribution of the liquid products. By the reactant suspension mode, some advantages can initially be discovered: first, liquid products and solid residues are naturally separated; second, re-polymerization is further inhibited, and oligomers and solid products are not observed in the liquid products; third, lignin depolymerization and deoxygenation retaining aromatic rings are well performed when the process can be carried out in a short residence time.

Supercritical hydrogen-donor solvents methanol, ethanol and propanol are first used to research the effects of yield and composition of the liquid products under a short residence time of 30 min, different temperatures and catalysts by the reactant suspension mode since temperature, solvent, and catalyst are the factors of prime importance which controls yield and composition of products. In order to accomplish the efficient deoxy-liquefaction of lignin, reasonably high temperature (450500 °C) is essential to do the cleavage of C—O ether bonds and C—C bonds in lignin interunit linkages. The development of highly effective catalysts with low cost should be selected to make this process industrially feasible [32], although noble metals catalysts like Pt, Pd, Re, Rh, or Ru loaded on various supports have high catalytic activities towards hydrogenolysis and hydrogenation of C—O bonds [33–37]. Besides the Fe-SiC catalyst, the Cu-C catalyst with hydrogenation and cracking is first used to fulfill deoxy-liquefaction of lignin. The aim of this study is to determine the optimal technology parameters to perform the efficient deoxy-liquefaction of lignin and the main process mechanisms are explored.

2. Materials and methods

2.1. Materials

Dealkaline lignin as raw material was obtained from Tokyo Chemical Industry Co. Ltd, and the powder has a dark brown color. Compositions of the dealkaline lignin were analyzed on Vario MACRO Cube Elemental Analyzer and oxygen content was calculated by difference. The contents (wt%) of C, H, N, S, and O are 51.43%, 4.71%, 0.35%, 0.18%, and 43.33%, respectively; and empirical formula is $C_{4.29}H_{4.71}O_{2.71}N_{0.025}S_{0.006}$. Nano-SiC with a grain size of 40 nm (99.9%) and nano-C with a grain size of 30 nm (99.5%) were purchased from Aladdin Industrial Corporation. Reduced iron powder with a diameter of 100 mesh (Fe, AR) and copper powder with a grain size of 50 nm (99.9%) were derived from Aladdin Industrial Corporation. All the chemicals were not further treated before use.

2.2. Experimental setup

The experiments of deoxy-liquefaction of lignin without external hydrogen were carried out in an airproof system. Tubular reactor (Φ 35 mm × 90 mm) constructed of hastelloy C-276 was heated in electric furnace. A temperature controller did the adjustments of the reaction temperature and heating rate by a thermocouple inserted in the tubular reactor. The system pressure was shown by a pressure gauge. In a typical process, lignin and catalyst were well blended and the obtained mixture was wrapped up by using double-layer nets of 800 mesh composed of 304 stainless steel, and next, the wrapping like the Chinese dumpling was suspended in the self-made reactor. 22 ml of the solvent (methanol, ethanol, or 1-propanol; AR, Tianjin Kemiou Chemical Reagant) was put to the reactor. Before the experiment, the reactor was emptied three times with argon gas. The sealed reactor was raised to the desired temperature (450 °C or 500 °C) at a rate of 10 °C/min and held for 30 min. The maximum pressure of the system depending on the reaction conditions reached 26–34 MPa for methanol, 15–28 MPa for ethanol, and 10–21 MPa for 1-propanol, respectively. Once the experiment ended, the reactor removed was quenched in cold water. After reaching room temperature, the reactor was opened and gas fraction was collected for the compositional analysis. The wrapping was got out and dried, and solid fraction was weighed and analyzed. The liquid products without solid residue were poured out. Specifically, the Fe-SiC catalyst was obtained by using simply mechanical mixing of Fe powder and nano-SiC with a ratio of 1:1, and also, the Cu-C catalyst with the same amount of Cu and C was achieved. 0.50 g of lignin was evenly mixed with 1.00 g of the Fe-SiC catalyst or Cu-C catalyst. As comparative experiments, deoxy-liquefaction of lignin with no catalyst was performed. The liquid products were marked as OLM for that of methanol, OLE for that of ethanol and OLP for that of 1-propanol. Each experiment was conducted six times and the mean value (the standard deviations under the same conditions were within 7%) was exhibited in the recorded results.

2.3. Product analysis

Analysis of the liquid products was done by using Trace GC Ultra/Polaris Q (GC–MS, Thermo Electron) equipped with a column of TRACE TR-5MS (30 m × 0.25 mm ×0.25 μm). Helium was used as carrier gas. GC programmed temperature: at 45 °C for 3 min, 180 °C at a rate of 5 °C/min, and up to 280 °C for 2 min at a rate of 20 °C/min. The injector temperature was 250 °C with a split ratio of 50:1. After a delay of 2 min, full scan mass spectra in the mass range of m/z 30–400 were produced. The collected data were processed by Xcalibur Data System. The liquid compositions were identified by comparison with the mass spectra with the NIST II (National Institute of Standards and Technology), together with a series of arenes and phenols possessing C_2 to C_5 branched chains as standard compounds to perform more accurate identification of the liquid compositions. FTIR spectra were collected by using KBr pellets in the range 4000–400 cm^{-1} on a Nicolet 5DX spectrometer. Gas compositions were analyzed by a gas chromatograph (GC122, Shanghai, China) with a thermal conductivity detector (TCD) and carbon molecular sieve column TDX-01 (1.5 m × 2.0 mm i.d.) for determination of H_2, CO_2, CO, and CH_4. The solid residue was dried at 120 °C for 12 h, and its analysis was done by the Elemental Analyzer. Higher heating value (HHV) of the liquid products was calculated by Dulong's formula [31]. Due to the solvent reactivity, gas products were negligible, and yields of the liquid product (Y_{liquid}, wt %) and solid residue (Y_{solid}, wt %) were calculated by the following equations, respectively:

$$Yliquid = \frac{weights\,of\,(lignin + the\,catalyst) - weight\,of\,the\,solid\,residue}{weight\,of\,lignin}$$

$$Ysolid = 100 - Yliquid$$

3. Results and discussion

3.1. Conversion of lignin

Conversion of lignin under different conditions (Fig. 1) shows that temperature has a significant influence on the yields. When
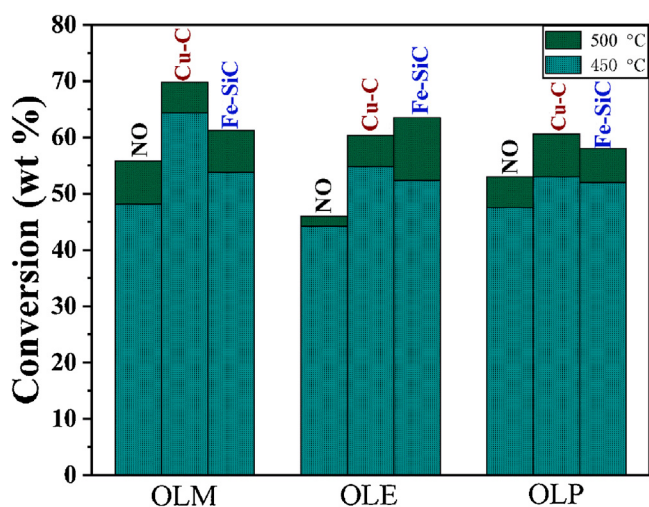
Fig. 1. Conversion (wt%) of liquid products at 450 °C and the increase in conversion at 500 °C under different conditions. OLM, OLE, and OLP represent the liquid products from methanol, ethanol, and propanol, respectively.

the temperature rises from 450 °C to 500 °C, conversion of lignin all increases, indicating that temperature has a marked effect on conversion of lignin [38,39]. Conversion of lignin goes up under the catalysts in comparison with that of no catalyst. Concretely, in methanol, conversion of lignin is in the range 48.2% to 53.8% at 450 °C and 55.8% to 70.0% at 500 °C, respectively. Over the Cu-C catalyst, conversion of lignin reaches a maximum of 70.0% at 500 °C, higher than that of the Fe-SiC catalyst (61.2%), meaning that the Cu-C catalyst has better catalytic cleavage in methanol. In ethanol, conversion of lignin are between 44.2% and 54.8% at 450 °C and between 46.0% and 63.5% at 500 °C, respectively. The Fe-SiC catalyst demonstrates higher catalytic conversion (63.5%) than that of the Cu-C catalyst (60.4%) at 500 °C, indicating that the Fe-SiC catalyst possesses better catalytic cracking in ethanol. In propanol, the conversion changes between 47.6% and 53.0% at 450 °C, and between 53.0% and 60.6% at 500 °C, respectively. A maximum of 60.6% emerges under the Cu-C catalyst, slightly higher than that of the Fe-SiC catalyst (58.0%). The results illustrate that besides temperature and catalyst, solvent exerts a considerable effect on conversion of lignin [16,21]. Propanol exposes the worst synergistic effect on conversion of lignin, implying that conversion of lignin under high temperature and pressure has almost no connection with the apolar character of the solvents, which is different from the reported results [22].

3.2. The effect of temperature on distribution of liquid products

The main components of liquid products are showed in Tables 1–3. The components are classified into four fractions: arenes, phenols, hydrocarbons including alkanes and alkenes, oxygen-containing compounds (O-compounds). Overall, with a rise of temperature, yield of of arenes increases sharply, while yield of of phenols decreases, indicating that high temperature favors the deoxy-liquefaction of lignin. In methanol and with no catalyst, yield of of arenes is only 7.05% at 450 °C, whereas arenes is raised to 40.57% at 500 °C. The arenes is mostly alkylated, including C_6-C_9 and C_{10}-C_{14} arenes. At 500 °C, although the number of arenes jumps, distribution of the carbon number shifts towards the heavier arenes and especially, naphthalenes with high boiling point are evidently formed, meaning that further condensation reaction happens. Yield of phenols increases to 51.65% from 42.21% with the increase of temperature and the alkylated phenols are distributed in the C_7-C_{12} range. Hydrocarbons and O-compounds

reduce from 13.74% and 37.04% to 1.06% and 4.34%, respectively, further demonstrating the advantages of cracking and deoxygenation at high temperature. In ethanol and with no catalyst, yield of of arenes is 37.59% at 450 °C and 46.87% at 500 °C, but yield of of phenols is only 9.08% at 450 °C and no phenols are detected at 500 °C, implying that the deoxy-liquefaction of lignin is well demonstrated and arenes are derived from hydrodeoxygenation of phenol derivatives. Importantly, the increase of temperature only causes the formation of small naphthalenes (1.84%), and thus further condensation reaction is not evident. The results are contrary to that of methanol. Yields of hydrocarbons and O-compounds are 14.82% and 38.50% at 450 °C, 0.36% and 53.11% at 500 °C, respectively. The O-compounds are composed of alcohols, esters, acetal, and ketones. However, at 500 °C the esters disappears, and more stable O-compounds such as alcohols are the main, similar to that of methanol. The formed O-compounds are considered to be from alcohols and alcohols are reactant [31]. In propanol and with no catalyst, yield of arenes is only 6.11% at 450 °C and 27.13% at 500 °C, when yield of phenols is 20.07% at 450 °C and 16.45% at 500 °C. Compared to those of methanol and ethanol, yield of arenes does not change markedly with the rise of temperature. The arenes largely consist of C_6-C_9 hydrocarbons and no naphthalenes are detected. At 500 °C, some esters still exist. Additionally, nitrogen-containing compounds like 2-ethyl-3, 5-dimethylpyridine and sulfur-containing compounds like 3, 4-dimethylthiophene are detected, showing that N and S elements are not removed completely, which is unfavorable as transportation fuels or additives [40].

Although temperature imposes a remarkable influence on distribution of the liquid products, the obtained aromatics are alkylated arenes and mono-phenols with one hydroxyl group and no methoxy groups, and contain no oligomers at 450 or 500 °C, different from the reported lignin depolymerization [23,24,29,41]. The reactant suspension mode holds some advantages. The results mean that during supercritical alcoholysis of lignin, the C—O—C and C—C linkages in the lignin units are cleaved. Compared to 450 °C, the temperature of 500 °C results in much more arenes, reasonably concluding that mono-phenols are further converted into arenes. Under the same temperature, ethanol favors the deoxy-liquefaction of lignin more in comparison with methanol and propanol, and in other words, ethanol provides better liquid products, a little similar to that of the reported results [23,42].

3.3. The effect of catalyst on distribution of liquid products

The catalysts Cu-C and Fe-SiC demonstrate the different catalytic activity and selectivity under different temperatures and solvents (Tables 1–3). Specifically, in methanol, yield of arenes increases from 10.25% at 450 °C to 83.93% at 500 °C over the Cu-C catalyst, while yield of phenols reduces accordingly from 66.79% to 14.76%. In the presence of Fe-SiC, yield of arenes rises from 9.24% at 450 °C to 37.96% at 500 °C, and correspondingly, yield of phenols decreases from 81.45% to 53.66%. With no catalyst, yields of arenes and phenols are 7.05% and 42.21% at 450 °C, and 40.57% and 51.65% at 500 °C, respectively. It can be seen that at 450 °C, catalytic alcoholysis of lignin has no remarkable improvement and efficiency of the catalysts is not presented well, whereas at 500 °C, the catalysts, especially Cu-C, possess high catalytic activity and selectivity. From the standpoint of the component distribution, the catalysts at 500 °C heighten the yield of C_6-C_9 arenes significantly as well as C_{10}-C_{12} arenes. However, it should be noted that Cu-C results in much more naphthalenes (17.98%) such as naphthalene, 1-methylnaphthalene, 1, 7-dimethylnaphthalene and 1, 6, 7-trimethylnaphthalene than that of Fe-SiC (10.14%) and no catalyst (12.57%) at 500 °C. The results indicate that although Cu-C causes high yield of arenes and conversion of lignin (70%), the

Table 1
Content (wt%) of main compounds under different conditions in methanol.

RT	Compound	Molecular Formula	No Catalyst		Fe-SiC		Cu-C	
			450°C	500°C	450°C	500°C	450°C	500°C
2.00	2,3-Dimethylbutane	C_6H_{14}	13.70	1.06	1.42	×	8.67	0.83
2.29	Methyl propionate	$C_4H_8O_2$	3.90	×	4.04	×	3.02	×
2.39	2-Methyl-1-propanol	$C_4H_{10}O$	5.15	1.52	0.36	4.31	5.54	0.48
2.54	Benzene	C_6H_6	×	0.48	×	0.85	×	0.74
2.88	3-Methyl-2-butanol	$C_5H_{12}O$	8.47	2.16	2.37	3.17	3.62	×
4.24	Toluene	C_7H_8	0.47	0.92	0.47	1.37	0.36	3.42
4.46	2-Methylbutanoic acid, methyl ester	$C_6H_{12}O_2$	2.78	0.66	1.11	0.90	2.12	×
6.55	p-Xylene	C_8H_{10}	×	1.81	0.61	2.90	×	5.31
7.47	Ethylbenzene	C_8H_{10}	×	0.70	×	0.82	×	0.91
9.65	1-Ethyl-4-methylbenzene	C_9H_{12}	×	×	×	1.02	×	1.86
9.99	Mesitylene	C_9H_{12}	0.48	1.19	×	1.53	0.30	0.80
10.64	1,2,4-Trimethylbenzene	C_9H_{12}	×	2.53	0.51	3.61	0.42	3.40
12.51	1-Methyl-3-propylbenzene	$C_{10}H_{14}$	0.76	1.65	0.99	3.20	0.42	3.30
13.14	o-Cresol	C_7H_8O	×	1.05	×	1.14	×	2.28
13.46	p-Cymene	$C_{10}H_{14}$	×	1.05	×	1.21	×	1.03
14.20	2-Ethylphenol	$C_8H_{10}O$	×	2.89	2.44	3.39	0.56	1.12
14.55	1,2,3,5-Tetramethylbenzene	$C_{10}H_{14}$	1.75	2.50	0.55	2.67	1.21	×
15.41	2,3-Dimethylphenol	$C_8H_{10}O$	×	6.05	2.36	6.49	×	3.43
15.66	1-Methyl-3,5-diethylbenzene	$C_{11}H_{16}$	1.20	×	×	×	2.19	0.81
15.93	4-Ethylphenol	$C_8H_{10}O$	×	1.08	×	1.00	×	1.39
16.23	2,5-Dimethylphenol	$C_8H_{10}O$	×	1.80	×	1.08	×	×
16.49	Naphthalene	$C_{10}H_8$	×	2.51	×	1.16	×	4.33
16.88	1-Methyl-4-(3-amyl)-benzene	$C_{12}H_{18}$	0.44	0.94	×	2.13	×	×
17.11	2,4,6-Trimethylphenol	$C_9H_{12}O$	1.94	4.67	4.46	4.73	4.21	0.81
17.78	2,4,5-Trimethylphenol	$C_9H_{12}O$	1.63	5.42	5.32	5.94	×	1.35
18.07	1,3,5-Triethylbenzene	$C_{12}H_{18}$	0.44	0.99	×	2.51	3.31	×
18.57	3-Ethyl-5-methylphenol	$C_9H_{12}O$	0.54	0.86	2.61	3.03	0.75	×
18.78	2,6-Diethylphenol	$C_{10}H_{14}O$	0.47	8.45	2.59	4.82	×	2.22
19.14	Pentamethylbenzene	$C_{11}H_{16}$	1.52	1.88	2.05	1.59	1.02	×
19.61	2,4-Diethylphenol	$C_{10}H_{14}O$	1.10	1.33	2.44	1.63	5.08	×
19.87	2,4,5,6-Tetramethylphenol	$C_{10}H_{14}O$	2.11	×	1.05	×	×	×
20.03	1-Methylnaphthalene	$C_{11}H_{10}$	×	5.69	×	2.38	×	6.60
20.42	2,3,4,6-Tetramethylphenol	$C_{10}H_{14}O$	0.47	×	1.32	2.15	0.66	×
21.00	2-Ethyl-5-n-propylphenol	$C_{11}H_{16}O$	0.66	1.48	1.34	1.43	×	2.16
21.34	2,3,4,6-Tetramethylphenol	$C_{10}H_{14}O$	22.38	11.08	25.23	10.09	25.97	×
22.29	1-Ethyl-naphthalene	$C_{12}H_{12}$	×	×	×	1.48	×	2.45
22.64	1,7-Dimethyl-naphthalene	$C_{12}H_{12}$	×	2.89	2.41	1.74	1.01	3.22
23.06	3,5-Bis(1-methylethyl)-phenol	$C_{12}H_{18}O$	10.92	5.49	12.71	4.89	11.91	×
24.82	2,2'-Dimethylbiphenyl	$C_{14}H_{14}$	×	×	×	×	×	2.23
25.08	1,6,7-Trimethylnaphthalene	$C_{13}H_{14}$	×	1.48	1.63	3.38	×	1.38
25.69	o-Isopropylphenetole	$C_{11}H_{16}O$	16.73	2.37	14.53	1.85	15.68	×
26.72	2,4-Bis(1-methylethyl)-phenol	$C_{12}H_{18}O$	×	×	3.04	×	1.96	×
27.01	Fluorene	$C_{13}H_{10}$	×	×	×	×	×	3.15
29.47	2-Methyl-9H-fluorene	$C_{14}H_{12}$	×	×	×	×	×	4.88
31.15	Phenanthrene	$C_{14}H_{10}$	×	2.34	×	2.42	×	4.55
31.60	2,3-Dimethyl-9H-fluorene	$C_{15}H_{14}$	×	×	×	×	×	2.27
32.56	2-Methylanthracene	$C_{15}H_{12}$	×	5.80	×	×	×	6.93
33.46	4,5-Dimethylphenanthrene	$C_{16}H_{14}$	×	×	×	×	×	2.81
34.25	Pyrene	$C_{16}H_{10}$	×	3.23	×	×	×	17.5

condensation reaction is fairly violent and thus Cu-C cannot suppress the formation of naphthalenes effectively. For phenols, phenols are alkylated and carbon number ranges from C_7 to C_{12}, consistent with that of arenes, which can be deduced that arenes stem from hydrodeoxygenation of phenols. So, at 500 °C, Cu-C demonstrates much better performance of catalytic deoxygenation than that of Fe-SiC, resulting in smaller amounts of phenols. Besides, 2, 3-dimethylbutane as hydrocarbons is the main component at 450 °C, but at 500 °C, the compound declines substantially. At 450 °C, O-compounds mainly include esters such as methyl propionate and 2-methylbutanoic acid, methyl ester, and alcohols such as 2-methyl-1-propanol and 3-methyl-2-butanol. At 500 °C, the O-compounds drop drastically.

In ethanol, arenes rises from 45.11% at 450 °C to 63.24% at 500 °C over the Cu-C catalyst, when phenols varies accordingly from 8.59% to 19.40%. In the presence of Fe-SiC, arenes climbs from 25.43% at 450 °C to 58.61% at 500 °C, and 34.24% of phenols at 450 °C is determined while at 500 °C, phenols is not detected. With no

catalyst, arenes and phenols are 37.59% and 9.09% at 450 °C, respectively, and arenes is 46.87% and no phenols is detected at 500 °C. At 450 °C, considerable amounts of arenes are obtained and Fe-SiC has the disadvantage of hydrodeoxygenation resulting in more phenols. However, at 500 °C, two kinds of the catalyst prove catalytic deoxygenation and selectivity, and the difference is that Cu-C produces quite a few alkylated phenols (C_7-C_{12}) whereas Fe-SiC does not, demonstrating better catalytic deoxygenation. As for the product distribution, at 500 °C, Fe-SiC causes almost equal amounts of C_6-C_9 and C_{10}-C_{12} arenes when C_6-C_9 arenes account only for 12.87% of arenes over the Cu-C catalyst. Meanwhile, Cu-C results in more formation of naphthalenes (10.03%) than that of Fe-SiC (2.94%), implying that Cu-C not only makes distribution of the carbon number shift towards the heavier arenes but also favors condensation reaction similar to that of methanol. O-compounds contain alcohols, acetal, ketones, and esters, and at 500 °C, the O-compounds decline markedly. Cu-C makes the O-compounds reduce from 36.12% at 450 °C to 17.37% at 500 °C and Fe-SiC causes

Table 2
Content (wt%) of main compounds under different conditions in ethanol.

RT	Compound	Molecular Formula	No Catalyst		Fe-SiC		Cu-C	
			450℃	500℃	450℃	500℃	450℃	500℃
2.07	2-Butanone	C_4H_8O	3.22	4.39	1.80	6.18	×	2.58
2.22	2-Butanol	$C_4H_{10}O$	6.85	21.06	6.06	7.86	8.00	3.43
2.43	1-Methylcyclopentene	C_6H_{10}	0.36	×	×	0.67	0.38	×
2.54	Benzene	C_6H_6	1.81	1.68	×	6.00	1.86	1.78
2.73	3-Penten-1-ol	$C_5H_{10}O$	×	3.59	8.57	4.86	×	1.55
2.88	3-Methyl-2-butanol	$C_5H_{12}O$	7.65	4.90	1.93	5.47	10.34	1.76
2.93	3-Methyl-hexane	C_7H_{16}	5.77	×	×	×	5.26	×
3.13	2-Pentanol	$C_5H_{12}O$	1.91	4.54	1.95	3.62	1.82	1.18
3.28	3,4-Dimethyl-2-pentene	C_7H_{14}	0.89	×	0.98	0.85	0.64	×
3.48	1,1-Diethoxyethane	$C_6H_{14}O_2$	7.65	13.53	14.20	9.37	2.32	6.05
3.87	1-Cyclohexene-1-methanol	$C_7H_{12}O$	0.80	×	×	×	1.03	0.81
3.98	3-Methyl-2-pentanone	$C_6H_{12}O$	0.70	1.10	×	2.03	0.61	×
4.16	Toluene	C_7H_8	6.91	5.80	3.57	11.36	7.45	7.92
4.71	2-Heptene	C_7H_{14}	1.02	0.41	1.42	2.47	0.89	1.09
4.86	3-Methyl-2-heptene	C_8H_{16}	2.32	0.64	×	0.77	2.44	×
5.04	Butanoic acid, ethyl ester	$C_6H_{12}O_2$	4.82	×	3.65	×	4.43	×
5.69	Ethylcyclohexane	C_8H_{16}	0.59	×	×	0.43	×	×
5.86	2,3-Dimethylcyclohexanol	$C_8H_{16}O$	0.47	×	×	×	0.65	×
6.19	3-Ethylcyclohexene	C_8H_{14}	1.82	×	0.74	0.65	2.81	×
6.55	p-Xylene	C_8H_{10}	2.19	3.40	1.25	3.94	2.15	4.08
6.79	1,3-Dimethylbenzene	C_8H_{10}	4.60	4.22	3.47	4.06	5.05	5.07
7.47	Ethylbenzene	C_8H_{10}	4.93	2.94	2.82	3.86	5.75	3.66
7.80	1-Ethyl-4-methylcyclohexane	C_9H_{18}	2.05	×	2.10	0.57	1.54	×
9.35	Propylbenzene	C_9H_{12}	0.97	×	×	0.63	1.37	1.10
9.65	1-Ethyl-4-methylbenzene	C_9H_{12}	3.57	3.58	2.13	3.40	4.41	5.10
10.17	1-Ethyl-2-methylbenzene	C_9H_{12}	1.21	1.34	1.12	1.07	1.13	2.56
10.64	1,2,4-Trimethylbenzene	C_9H_{12}	×	1.00	×	0.77	×	1.46
10.83	Hexanoic acid, ethyl ester	$C_8H_{16}O_2$	4.43	×	2.18	×	6.91	×
11.54	3-Ethyl-1,5-dimethylbenzene	$C_{10}H_{14}$	0.58	0.82	×	0.87	0.75	×
11.98	1,4-Diethylbenzene	$C_{10}H_{14}$	0.92	1.63	1.37	1.26	1.14	1.71
12.61	2-Ethyl-1,4-dimethylbenzene	$C_{10}H_{14}$	2.87	1.59	1.06	2.89	2.95	3.43
13.14	o-Cresol	C_7H_8O	×	×	1.34	×	×	2.44
13.20	3-Ethyl-1,4-dimethylbenzene	$C_{10}H_{14}$	0.94	0.87	×	0.57	1.15	×
13.46	p-Cymene	$C_{10}H_{14}$	1.75	2.43	1.00	2.90	2.29	×
14.07	1-Propyl-4-ethylBenzene	$C_{11}H_{16}$	1.20	0.81	1.18	0.87	×	1.50
15.00	3-Ethylphenol	$C_8H_{10}O$	×	×	1.84	×	×	1.93
15.15	1,3,5-Trimethyl-2-ethylbenzene	$C_{11}H_{16}$	0.63	2.48	×	1.06	×	1.62
15.38	1-Ethyl-4-methylethylbenzene	$C_{11}H_{16}$	×	1.29	×	0.78	×	3.11
15.74	1-Methyl-3,5-diethylbenzene	$C_{11}H_{16}$	1.42	1.65	×	0.85	1.62	1.00
15.93	4-Ethylphenol	$C_8H_{10}O$	×	×	2.76	×	×	2.09
16.49	Naphthalene	$C_{10}H_8$	×	×	×	×	×	4.15
16.77	1-Methyl-4-(3-amyl)-benzene	$C_{12}H_{18}$	1.08	4.27	×	3.00	1.51	×
17.65	2,3,6-Trimethylphenol	$C_9H_{12}O$	×	×	4.89	×	×	1.20
17.82	1-Propyl-4-isopropylbenzene	$C_{12}H_{18}$	×	2.18	×	1.12	0.77	2.29
17.94	2-Ethyl-4-methylphenol	$C_9H_{12}O$	×	×	1.04	×	×	2.03
18.56	3-Ethyl-5-methylphenol	$C_9H_{12}O$	×	×	3.16	×	×	2.01
19.12	2,5-Diethylphenol	$C_{10}H_{14}O$	3.88	×	1.82	×	1.59	2.11
20.03	1-Methylnaphthalene	$C_{11}H_{10}$	×	1.84	1.22	2.94	×	2.56
21.00	2-Ethyl-5-n-propylphenol	$C_{11}H_{16}O$	4.23	×	9.16	×	3.82	4.27
22.29	1-Ethylnaphthalene	$C_{12}H_{12}$	×	×	×	×	×	3.32
23.14	3,5-Bis(1-methylethyl)-phenol	$C_{12}H_{18}O$	0.97	×	8.22	×	3.17	1.33
25.08	1,6,7-Trimethylnaphthalene	$C_{13}H_{14}$	×	×	×	×	×	4.71

the O-compounds to decrease from 40.33% to 39.39%. Hydrocarbons mainly include paraffins, cycloparaffins and alkenes.

In propanol, arenes change from 4.53% at 450 °C to 29.34% at 500 °C over the Cu-C catalyst when phenols change accordingly from 29.13% to 22.00%. As for Fe-SiC, arenes range from 5.76% at 450 °C to 27.80% at 500 °C, and phenols range from 28.74% at 450 °C to 25.95% at 500 °C. Without catalyst, arenes change from 6.11% at 450 °C to 27.13% at 500 °C, and phenols are from 20.07% at 450 °C to 16.45% at 500 °C. The results indicate that the Fe-SiC/ Cu-C catalysts have much less influence on distribution of products, compared to that of temperature (450 °C or 500 °C). In other words, catalytic activity cannot play an effective role. From the point of view of the components, at 500 °C, C_6-C_9 arenes are in the majority with Fe-SiC/ Cu-C, or rather, high temperature is more conducive to small-molecular arenes. The alkylated phenols (C_7-C_{12}) have a similar effect. At 500 °C, C_7-C_9 aliphatic hydrocarbons are 18.31%

for Cu-C, 17.98% for Fe-SiC, and 18.73% without catalyst, and corresponding O-compounds including C_4-C_9 alcohols, aldehydes, ketones, ethers, and esters are 30.35%, 28.26% and 36.08%, respectively. At 450 °C, C_7-C_9 aliphatic hydrocarbons are 8.88%, 11.13%, and 10.37%, respectively, and O-compounds are 56.06%, 51.89%, and 60.85%, respectively. Besides the increase of aliphatic hydrocarbons and decrease of O-compounds resulting from higher temperature, it may partly be interpreted as hydrodeoxygenation of the O-compounds resulting in more formation of aliphatic hydrocarbons.

For the catalyst influence, the obtained arenes and monophenols are alkylated, and phenols only possess one hydroxyl group and have no methoxy groups like guaiacols by using the Pt/C catalyst [43] or Pt/alumina catalyst [33]. There are not oligomers [41]. The Cu-C catalyst has the optimal catalytic activity and selectivity in methanol, whereas the Fe-SiC catalyst possesses the

Table 3
Content (wt%) of main compounds under different conditions in propanol.

RT	Compound	Molecular Formula	No Catalyst		Fe-SiC		Cu-C	
			450℃	500℃	450℃	500℃	450℃	500℃
2.31	2-Methyl-1-propanol	$C_4H_{10}O$	3.52	3.45	2.61	2.02	3.09	2.59
2.45	Benzene	C_6H_6	×	2.13	×	1.65	×	1.70
2.58	Tert-amylalcohol	$C_5H_{12}O$	2.00	5.02	1.42	2.57	1.03	2.64
2.71	3-Methyl-2-butanol	$C_5H_{12}O$	0.92	3.25	1.01	3.22	0.70	2.75
2.85	3-Methylhexane	C_7H_{16}	2.02	5.64	2.33	3.57	1.55	3.66
3.00	3-Pentanol	$C_5H_{12}O$	3.37	5.22	3.39	2.78	2.36	2.62
3.27	2,4-Dimethyl-2-pentene	C_7H_{14}	×	1.98	×	1.60	×	1.80
3.60	5-Hexen-1-ol	$C_6H_{12}O$	1.67	×	1.81	×	1.55	×
3.74	4,4-Dimethyl-1,2-pentadiene	C_7H_{12}	1.45	4.36	1.20	3.85	1.35	3.96
4.03	Toluene	C_7H_8	2.43	6.01	2.65	4.94	2.02	5.46
4.15	4-Hexen-1-ol	$C_6H_{12}O$	1.33	1.30	1.09	1.72	1.21	1.18
4.28	2-Methyl-3-pentanol	$C_6H_{14}O$	2.30	1.65	1.76	1.75	1.36	1.50
4.46	2-Ethylbutanal	$C_6H_{12}O$	2.95	2.86	2.22	2.53	1.62	2.60
4.79	2-Methylglutaric acid	$C_6H_{10}O_4$	13.32	×	8.79	×	7.35	×
4.88	3-Hexanol	$C_6H_{14}O$	×	5.42	×	5.31	×	4.93
5.07	Propanoic acid, propyl ester	$C_6H_{12}O_2$	5.68	1.61	8.64	1.37	5.76	1.46
5.60	Ethylcyclohexane	C_8H_{16}	2.49	4.45	4.96	4.15	3.99	4.04
5.80	2-Methyl-4-pentenal	$C_6H_{10}O$	11.96	2.81	10.44	1.31	17.13	2.55
6.44	2-Methyl-2-penten-1-ol	$C_6H_{12}O$	1.74	×	2.09	×	3.80	×
6.69	1,3-Dimethylbenzene	C_8H_{10}	×	7.05	×	6.99	×	6.45
6.74	3,5-Dimethyl-1,6-heptadiene	C_9H_{16}	3.51	×	2.64	×	1.98	×
6.91	3,4-Dimethylthiophene	C_6H_8S	2.60	1.62	0.90	×	×	×
7.19	1-Ethyl-4-methylcyclohexane	C_9H_{18}	0.91	2.31	×	2.25	×	2.31
7.32	Ethylbenzene	C_8H_{10}	0.76	1.65	×	1.94	×	1.75
7.57	Butanoic acid, propyl ester	$C_7H_{14}O_2$	1.51	×	1.04	×	1.30	×
7.59	3-Ethyl-2-methyl-1,3-hexadiene	C_9H_{16}	×	×	×	2.56	×	2.54
9.76	1-Ethyl-3-methylbenzene	C_9H_{12}	1.61	4.42	1.79	5.42	1.29	4.78
10.36	1,1-Dipropoxypropane	$C_9H_{20}O_2$	7.09	2.54	5.57	3.7	6.64	5.53
10.54	1,2,4-Trimethylbenzene	C_9H_{12}	×	1.92	×	2.19	×	2.94
10.68	Pentanoic acid, propyl ester	$C_8H_{16}O_2$	1.50	0.94	×	×	1.17	×
12.33	4-Methyl-1-methylethylbenzene	$C_{10}H_{14}$	1.31	1.89	1.33	1.99	1.22	1.80
12.51	1-Methyl-3-propylbenzene	$C_{10}H_{14}$	×	1.04	×	1.39	×	1.23
13.00	o-Cresol	C_7H_8O	1.23	1.58	1.90	2.21	1.62	1.81
13.37	p-Cymene	$C_{10}H_{14}$	×	1.03	×	1.29	×	1.22
13.99	2-Ethylphenol	$C_8H_{10}O$	×	1.31	×	1.59	×	1.40
14.71	2-Ethyl-3,5-dimethylpyridine	$C_9H_{13}N$	×	×	1.58	×	1.39	×
15.01	1,3,5-Trimethyl-2-ethylbenzene	$C_{11}H_{16}$	×	×	×	×	×	2.01
15.21	2,3-Dimethylphenol	$C_8H_{10}O$	2.29	3.21	2.38	4.17	2.04	3.65
15.84	4-Ethylphenol	$C_8H_{10}O$	0.96	1.20	1.65	1.99	1.37	1.55
16.52	2,5-Dimethylphenol	$C_8H_{10}O$	0.70	1.19	×	0.94	0.97	1.02
16.92	2,4,6-Trimethylphenol	$C_9H_{12}O$	2.05	1.51	1.81	1.63	1.26	1.52
17.33	2,3,6-Trimethylphenol	$C_9H_{12}O$	×	0.92	1.45	2.37	1.24	1.14
18.40	3-Ethyl-5-methylphenol	$C_9H_{12}O$	1.20	1.04	2.49	1.91	1.95	1.38
18.67	2,6-Diethylphenol	$C_{10}H_{14}O$	1.39	1.08	1.36	2.54	2.57	3.36
19.87	2,4,5,6-Tetramethylphenol	$C_{10}H_{14}O$	2.71	1.45	1.57	×	1.50	×
20.10	3,5-Diethylphenol	$C_{10}H_{14}O$	×	×	2.45	2.06	1.93	1.68
20.82	2-Ethyl-5-n-propylphenol	$C_{11}H_{16}O$	3.00	×	5.05	1.85	4.66	1.34
21.14	2,3,4,6-Tetramethylphenol	$C_{10}H_{14}O$	2.06	1.95	2.93	2.68	2.83	2.15
22.99	3,5-Bis(1-methylethyl)-phenol	$C_{12}H_{18}O$	2.48	×	3.71	×	5.19	×

optimal catalytic deoxygenation in ethanol. Cu-C and Fe-SiC can not play an effective role in propanol, inconsistent with the reported results [25]. Overall, at 500 °C, although the Cu-C and Fe-SiC catalysts demonstrate high performance of catalytic deoxygenation, Cu-C tends more easily to make distribution of the carbon number shift towards the heavier arenes and favor further condensation resulting in more naphthalenes, whereas Fe-SiC makes further deoxygenation of mono-phenols form more arenes.

3.4. The effect of solvent on distribution of liquid products

Solvent makes a significant impact on alcoholysis of lignin (Tables 1–3). From the product's perspective, at 450 °C, ethanol is much better suited to alcoholysis of lignin than that of methanol and propanol since the obtained products generate more arenes and less phenols. At 450 °C, Cu-C has the optimal catalytic deoxygenation (45.29% of arenes), suggesting that ethanol is more beneficial to catalytic activity and selectivity of Cu-C. At 500 °C, though conversion of lignin and arenes increase markedly in three

kinds of solvent, methanol has the maximum yield of arenes (83.93%) over Cu-C, indicating that methanol has better synergic effect on catalytic deoxygenation and selectivity of Cu-C. It should be pointed out that, in ethanol, the obtained products contain the least yield of phenols and even phenols are not detected under the catalyst Fe-SiC. In propanol, the obtained products do not show high yield of arenes regardless of the existence of the catalyst or no, and thus propanol is unsuited for the catalysts under this conditions.

On the component side, though arenes and phenols are basically alkylated, the difference is that methyl-substituted aromatics in methanol are much more than that of ethanol, and ethyl-substituted aromatics in ethanol are much more than that of methanol. So, solvent molecules participate in the formation of aromatics. In propanol, propyl-substituted aromatics are very small, but there are much more methyl/ethyl-substituted compounds, which can partly be attributed to the fact that propanol is cleaved to methyl and ethyl, and the smaller radicals are easier to attack benzene rings. As for other hydrocarbons and

O-compounds, the marked effect of solvent is that the obtained esters contain methyl groups in methanol, ethyl groups in ethanol, and propyl groups in propanol, respectively. The total amount of hydrocarbons and O-compounds in methanol is much less than that of ethanol and propanol, meaning that condensation of methanol takes place less readily. It deserves noting that the aim of deoxy-liquefaction of lignin is to obtain small-molecular arenes, and thus ethanol is the most suitable for formation of small-molecular arenes. Additionally, since the obtained liquid products have no solid resides and O-containing oligomers in the three solvents, the solvents can all act as a capping agent rather than only ethanol [17,44] to inhibit re-polymerisation reactions. So, under

(a)

(b)

(c)
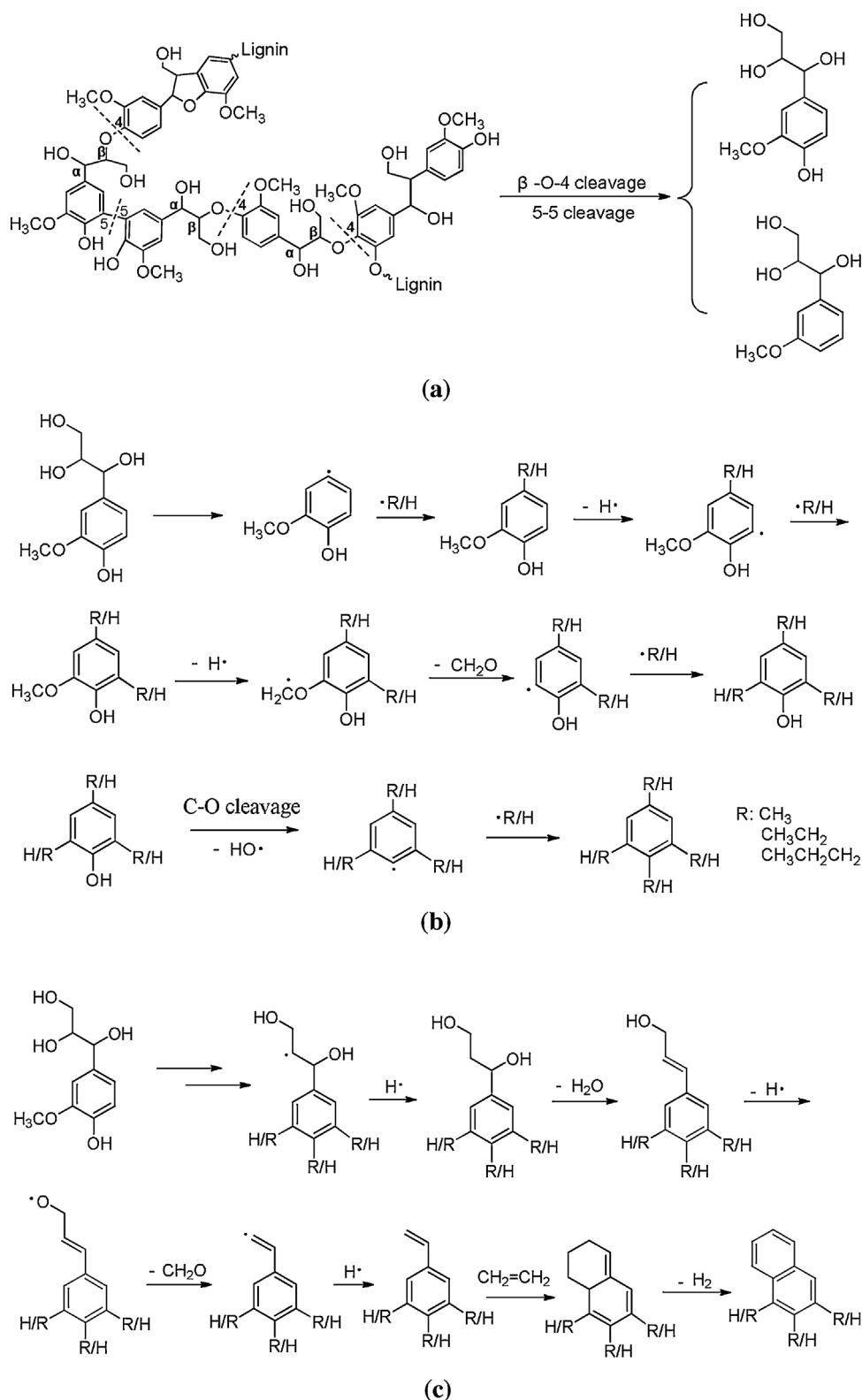
Fig. 2. Main reaction pathways of lignin deoxy-liquefaction under high temperature and pressure.

high temperature and pressure, the reactant suspension mode has the unique process feature. Furthermore, in contrast to the reported results [25], propanol demonstrates the worst synergistic effect on the deoxy-liquefaction of lignin under those conditions.

3.5. FT-IR analysis

The liquid products are analyzed by using FT-IR, indicating that the spectra are mostly identical because they possess almost the same function groups. For example, the peaks in the range 3400-3500 cm^{-1} are assigned to stretching vibration of O—H, when the peaks in the range 2960 and 2850 cm^{-1} are ascribed to symmetric and asymmetric stretching of the C—H bonds. The stretching vibration band near 1640 cm^{-1} is derived from the C=O groups, and the peak near 1120 cm^{-1} is considered to stretching vibration of C—O—C bonds. The intense peaks of Ar-O range from 1260–1180 cm^{-1}. The bending vibration of C—H is observed by a few peaks between 850 and 710 cm^{-1}. The results of FT-IR analysis are in line with that of GC—MS analysis.

3.6. Reaction pathway

Based on the above distribution of arenes and mono-phenols under different reaction temperatures, solvents and catalysts, the main reaction pathway is explored to understand deoxy-liquefaction of lignin. On the whole, first, the obtained arenes and phenols are alkylated, and the phenols only possess one hydroxyl group and contains no methoxy groups, meaning that methoxy groups are removed and alkylation happens during the deoxy-liquefaction process. Second, the phenols belong to small-molecular monomers and have no oligomers. Third, yield of phenols at 450 °C is much higher than that of the corresponding temperature of 500 °C, although higher temperature favors the deoxy-liquefaction of lignin more. In contrast, yield of arenes at 500 °C is much higher than that of the corresponding temperature of 450 °C. Furthermore, carbon number of arenes ranges mostly from C_7 to C_{12}, consistent with that of phenols. Consequently, the main reaction pathway can be reasonably deduced by combining the reactant suspension mode (Fig. 2).

Two-thirds or more of the total linkages in lignin are C—O ether bonds while β—O—4 bonds are the most common linkage, and the rest are C—C bonds such as 5-5 bonds [8]. Since the deoxy-liquefaction of lignin is a complex process, β—O—4 and 5–5 bonds are used as a model of the lignin deoxy-liquefaction. In the first stage (Fig. 2a), the cleavage of β—O—4 and 5–5 bonds occurs by hydrogenolysis, forming aromatic monomers, and the monomers are freed from the named Chinese dumpling and integrate into supercritical fluid. Under high temperature and pressure, free-radical reaction mechanisms are the preferred process [45,46]. In the second stage (Fig. 2b), the monomers are converted into small-molecular mono-phenols which are further converted into small-molecular arenes. Deoxygenation by the cracking of C—C bonds and alkylation/ hydrogenation happen, and then demethoxylation and alkylation/ hydrogenation occur, which results in alkyl-substituted mono-phenols. The formed mono-phenols are further transformed into alkyl-substituted arenes by hydrodeoxygenation and alkylation. During the cleavage, three types of solvents act as a capping-agent to protect reaction intermediates and suppress re-condensation. At higher temperature of 500 °C, hydrodeoxygenation occurs more violently, generating more arenes, and especially, under the catalyst Fe-SiC, mono-phenols are completely transformed into alkyl-substituted arenes. The alkyl radical fragments are obtained from the cracking of lignin and solvent molecules. Hydrogen from solvent reforming is confirmed by gas analysis which shows that apart from CO_2, CH_4, and CO, H_2 is all detected under different reaction conditions. In the third stage (Fig. 2c), a

possible reaction process of naphthalenes is proposed to explain the condensation mechanism especially under the catalyst Cu-C. The formed aromatic monomers undergo a sequence of radical reaction such as hydrodeoxygenation, demethoxylation, alkylation/ hydrogenation, and dehydrogenation, generating benzyl alkenes, and then cyclization such as Diels-Alder reaction and further dehydrogenation occur, finally forming naphthalenes. As the char is observed in the named Chinese dumpling, re-polymerization of lignin causes the char.

3.7. Analysis of the char

The solid residues were dried at 120 °C for 12 h, and their analysis was done by using the Elemental Analyzer. C, H and N contents of the chars at 450 °C are in the ranges of 68.73%–69.52%, 3.74%–3.87%, and 2.67%–2.81%, respectively, and accordingly, the O contents calculated by difference are in the range of 24.86%-23.80%. At 500 °C, C, H and N contents vary between 73.31% and 74.12%, 3.32% and 3.41%, 2.47% and 2.54%, respectively, and the O contents are between 20.90% and 19.93%. The H/C molar ratios at 450 °C are between 0.65 and 0.67 while the H/C molar ratios at 500 °C are between 0.54 and 0.55, indicating that high temperature is conducive to deoxy-liquefaction of lignin. The heating values of the chars are between 24.14 and 26.25 $MJ\,kg^{-1}$, higher than 17.21 $MJ\,kg^{-1}$ of lignin.

4. Conclusion

Small-molecular aromatics (C_7-C_{12}) from efficient one-step alcoholysis of lignin in a self-made high-pressure reactor are produced under different temperatures (450–500 °C), supercritical solvents and catalysts by using a reactant suspension mode. Under the short residence time of 30 min, the temperature 500 °C facilitates conversion of lignin (70%) and formation of C_6-C_9 small-molecular arenes. Methanol has the most synergistic effect on the efficient deoxy-liquefaction of lignin over the Cu-C catalyst. In ethanol, the Fe-SiC catalyst results in the formation of small-molecular arenes rather than mono-phenols. Under high temperature and pressure, the efficient cleavages of the C—O bonds and C—C bonds in lignin eventually generate small-molecular arenes. The results indicate that the reactant suspension mode is a feasible route to perform the efficient deoxy-liquefaction of lignin.

Declaration of Competing Interest

The authors declared that they have no conflicts of interest to this work. We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

Acknowledgement

References

[1] Y.G. Chen, F. Wang, Z.Y. Yang, Preparation and upgrading of hydrocarbon oil from deoxy-liquefaction of oil crop, Bioresour. Technol. 146 (2013) 472–477.

[2] P. Asawaworarit, P. Daorattanachai, W. Laosiripojana, C. Sakdaronnarong, A. Shotipruk, N. Laosiripojana, Catalytic depolymerization of organosolv lignin from bagasse by carbonaceous solid acids derived from hydrothermal of lignocellulosic compounds, Chem. Eng. J. 356 (2019) 461–471.

[3] H.W. Ryu, H.W. Lee, J. Jae, Y.K. Park, Catalytic pyrolysis of lignin for the production of aromatic hydrocarbons: effect of magnesium oxide catalyst, Energy 179 (2019) 669–675.

[4] Q. Ma, Q. Liu, W. Li, L. Ma, J. Wang, M. Liu, Q. Zhang, Catalytic depolymerization of lignin for liquefied fuel at mild condition by rare earth metals loading on CNT, Fuel Process. Technol. 161 (2017) 220–225.

[5] S. Wang, Z. Li, X. Bai, W. Yi, P. Fu, Catalytic pyrolysis of lignin in a cascade dual-catalyst system of modified red mud and HZSM-5 for aromatic hydrocarbon production, Bioresour. Technol. 278 (2019) 66–72.

[6] T. Renders, S. Van den Bosch, S.F. Koelewijn, W. Schutyser, B.F. Sels, Lignin-first biomass fractionation: the advent of active stabilisation strategies, Energy Environ. Sci. 10 (2017) 1551–1557.

[7] H. Wang, Y. Pu, A. Ragauskasd, B. Yang, From lignin to valuable products–strategies, challenges, and prospects, Bioresour. Technol. 271 (2019) 449–461.

[8] C. Liu, S. Wu, H. Zhang, R. Xiao, Catalytic oxidation of lignin to valuable biomass-based platform chemicals: a review, Fuel Process. Technol. 191 (2019) 181–201.

[9] A. Rahimi, A. Ulbrich, J.J. Coon, S.S. Stahl, Formic-acid-induced depolymerization of oxidized lignin to aromatics, Nature 515 (2014) 249.

[10] X. Gu, C. Kanghua, H. Ming, Y. Shi, Z. Li, La-modified SBA-15/H_2O_2 systems for the microwave assisted oxidation of organosolv beech wood lignin, Maderas Cienc. Tecnol. 14 (2012) 31–41.

[11] Y. Jiang, Z. Li, X. Tang, Y. Sun, X. Zeng, S. Liu, L. Lin, Depolymerization of cellulolytic enzyme lignin for the production of monomeric phenols over raney Ni and acidic zeolite catalysts, Energy Fuel 29 (2015) 1662–1668.

[12] F. Gao, J.D. Webb, H. Sorek, D.E. Wemmer, J.F. Hartwig, Fragmentation of lignin samples with commercial Pd/C under ambient pressure of hydrogen, ACS Catal. 6 (2016) 7385–7392, doi:http://dx.doi.org/10.1021/acscatal.6b02028.

[13] L. Shuai, M.T. Amiri, Y.M. Questell-Santiago, F. Héroguel, Y. Li, H. Kim, R. Meilan, C. Chapple, J. Ralph, J.S. Luterbacher, Formaldehyde stabilization facilitates lignin monomer production during biomass depolymerization, Science 354 (2016) 329–333.

[14] D.J. McClelland, P.H. Galebach, A.H. Motagamwala, A.M. Wittrig, S.D. Karlen, J.S. Buchanan, J.A. Dumesic, G.W. Huber, Supercritical methanol depolymerization and hydrodeoxygenation of lignin and biomass over reduced copper porous metal oxides, Green Chem. 21 (2019) 2988–3005.

[15] T. Li, H. Lin, X. Ouyang, X. Qiu, Z. Wan, In situ preparation of Ru@N-doped carbon catalyst for the hydrogenolysis of lignin to produce aromatic monomers, ACS Catal. 9 (2019) 5828–5836.

[16] Z. Sun, B. Fridrich, A. de Santi, S. Elangovan, K. Barta, Bright side of lignin depolymerization: toward new platform chemicals, Chem. Rev. 118 (2018) 614–678.

[17] S. Gillet, M. Aguedo, L. Petitjean, A.R.C. Morais, A.M. da Costa Lopes, R.M. Łukasik, P.T. Anastas, Lignin transformations for high value applications: towards targeted modifications using green chemistry, Green Chem. 19 (2017) 4200–4233.

[18] D.S. Brands, K. Pontzen, E.K. Poels, A.C. Dimian, A. Bliek, Solvent-based fatty alcohol synthesis using supercritical butane: flowsheet analysis and process design, J. Am. Oil Chem. Soc. 79 (2002) 85–91.

[19] X. Ouyang, T. Ruan, X. Qiu, Effect of solvent on hydrothermal oxidation depolymerization of lignin for the production of monophenolic compounds, Fuel Process. Technol. 144 (2016) 181–185.

[20] A. Kloekhorst, Y. Shen, Y. Yie, M. Fang, H.J. Heeres, Catalytic hydrodeoxygenation and hydrocracking of Alcell® lignin in alcohol/formic acid mixtures using a Ru/C catalyst, Biomass (2015).

[21] L. Shuai, J. Luterbacher, Organic solvent effects in biomass conversion reactions, ChemSusChem 9 (2016) 133–155.

[22] W. Schutyser, S. Van den Bosch, T. Renders, T. De Boe, S.F. Koelewijn, A. Dewaele, T. Ennaert, O. Verkinderen, B. Goderis, C.M. Courtin, B.F. Sels, Influence of bio-based solvents on the catalytic reductive fractionation of birch wood, Green Chem. 17 (2015) 5035–5045.

[23] J.Y. Kim, J. Park, U.J. Kim, J.W. Choi, Conversion of lignin to phenol-rich oil fraction under supercritical alcohols in the presence of metal catalysts, Energy Fuel 29 (2015) 5154–5163.

[24] J. Wang, W. Li, H. Wang, Q. Ma, S. Li, H.M. Chang, H. Jameel, Liquefaction of kraft lignin by hydrocracking with simultaneous use of a novel dual acid-base catalyst and a hydrogenation catalyst, Bioresour. Technol. 243 (2017) 100–106.

[25] X. Wang, R. Rinaldi, Solvent effects on the hydrogenolysis of diphenyl ether with raney nickel and their implications for the conversion of lignin, ChemSusChem 5 (2012) 1455–1466.

[26] F. Yan, R. Ma, X. Ma, K. Cui, K. Wu, M. Chen, Y. Li, Ethanolysis of kraft lignin to platform chemicals on a MoC_{1-x}/Cu-MgAlO$_z$ catalyst, Appl. Catal. B Environ. 202 (2017) 305–313.

[27] A. Narani, R.K. Chowdari, C. Cannilla, G. Bonura, F. Frusteri, H.J. Heeres, K. Barta, Efficient catalytic hydrotreatment of kraft lignin to alkylphenolics using supported NiW and NiMo catalysts in supercritical methanol, Green Chem. 17 (2015) 5046–5057.

[28] H. Wang, H. Ruan, M. Feng, Y. Qin, H. Job, L. Luo, C. Wang, M.H. Engelhard, E. Kuhn, X. Chen, M.P. Tucker, B. Yang, One-pot process for hydrodeoxygenation of lignin to alkanes using Ru-based bimetallic and bifunctional catalysts supported on zeolite Y, ChemSusChem 10 (2017) 1846–1856.

[29] I. Kristianto, S.O. Limarta, H. Lee, J.M. Ha, D.J. Suh, J. Jae, Effective depolymerization of concentrated acid hydrolysis lignin using a carbon-supported ruthenium catalyst in ethanol/formic acid media, Bioresour. Technol. 234 (2017) 424–431.

[30] P. Chen, Q. Zhang, R. Shu, Y. Xu, L. Ma, T. Wang, Catalytic depolymerization of the hydrolyzed lignin over mesoporous catalysts, Bioresour. Technol. 226 (2017) 125–131.

[31] Y. Chen, F. Wang, Y. Jia, N. Yang, X. Zhang, One-step ethanolysis of lignin into small-molecular aromatic hydrocarbons over nano-SiC catalyst, Bioresour. Technol. 226 (2017) 145–149.

[32] X. Li, G. Chen, C. Liu, W. Ma, B. Yan, J. Zhang, Hydrodeoxygenation of lignin-derived bio-oil using molecular sieves supported metal catalysts: a critical review, Renew. Sustain. Energy Rev. 71 (2017) 296–308.

[33] A. Yamaguchi, N. Mimura, M. Shirai, O. Sato, Cascade utilization of biomass: strategy for conversion of cellulose, hemicellulose, and lignin into useful chemicals, ACS Sustain. Chem. Eng. 7 (2019) 10445–10451.

[34] K. Zhang, H. Li, L.P. Xiao, B. Wang, R.C. Sun, G. Song, Sequential utilization of bamboo biomass through reductive catalytic fractionation of lignin, Bioresour. Technol. 285 (2019)121335.

[35] P.E. Ruiz, K. Leiva, R. Garcia, P. Reyes, J.L.G. Fierro, N. Escalona, Relevance of sulfiding pretreatment on the performance of Re/ZrO2 and Re/ZrO2-sulfated catalysts for the hydrodeoxygenation of guayacol, Appl. Catal. A Gen. 384 (2010) 78–83.

[36] A. Bjelić, M. Grilca, M. Huš, B. Likozara, Hydrogenation and hydrodeoxygenation of aromatic lignin monomers over Cu/C, Ni/C, Pd/C, Pt/C, Rh/C and Ru/C catalysts: mechanisms, reaction micro-kinetic modelling and quantitative structure-activity relationships, Chem. Eng. J. 359 (2019) 305–320.

[37] H. Wu, J. Song, C. Xie, C. Wu, C. Chen, B. Han, Efficient and mild transfer hydrogenolytic cleavage of aromatic ether bonds in lignin-derived compounds over Ru/C, ACS Sustain. Chem. Eng. 6 (2018) 2872–2877.

[38] S. Farag, B.P. Mudraboyina, P.G. Jessop, J. Chaouki, Impact of the heating mechanism on the yield and composition of bio-oil from pyrolysis of kraft lignin, Biomass Bioenerg. 95 (2016) 344–353.

[39] Y. Zheng, D. Chen, X. Zhu, Aromatic hydrocarbon production by the online catalytic cracking of lignin fast pyrolysis vapors using Mo_2N/γ-Al_2O_3, J. Anal. Appl. Pyrol. 104 (2013) 514–520.

[40] D.C. Rakopoulos, Combustion and emissions of cottonseed oil and its bio-diesel in blends with either n-butanol or diethyl ether in HSDI diesel engine, Fuel 105 (2013) 603–613.

[41] M. Oregui Bengoechea, N. Miletić, M.H. Vogt, P.L. Arias, T. Barth, Analysis of the effect of temperature and reaction time on yields, compositions and oil quality in catalytic and non-catalytic lignin solvolysis in a formic acid/water media using experimental design, Bioresour. Technol. 234 (2017) 86–98.

[42] R. Ma, W. Hao, X. Ma, Y. Tian, Y. Li, Catalytic ethanolysis of kraft lignin into high-value small-molecular chemicals over a nanostructured α-molybdenum carbide catalyst, Angew. Chem. Int. Ed. 53 (2014) 7310–7315.

[43] W. Xu, S.J. Miller, P.K. Agrawal, C.W. Jones, Depolymerization and hydrodeoxygenation of switchgrass lignin with formic acid, ChemSusChem 5 (2012) 667–675.

[44] X. Huang, T.I. Korányi, M.D. Boot, E.J.M. Hensen, Ethanol as capping agent and formaldehyde scavenger for efficient depolymerization of lignin to aromatics, Green Chem. 17 (2015) 4941–4950.

[45] A. Beste, ReaxFF study of the oxidation of lignin model compounds for the most common linkages in softwood in view of carbon fiber production, J. Phys. Chem. A 118 (2014) 803–814.

[46] K.H. Kim, X. Bai, R.C. Brown, Pyrolysis mechanisms of methoxy substituted α-O-4 lignin dimeric model compounds and detection of free radicals using electron paramagnetic resonance analysis, J. Anal. Appl. Pyrol. 110 (2014) 254–263.