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Conversion of lignin oil and hemicellulose derivative into high-density jet fuel

Sichao Yang[a,b], Chengxiang Shi[a,b,*], Zhensheng Shen[a,b], Lun Pan[a,b,c], Zhenfeng Huang[a,b], Xiangwen Zhang[a,b,c], Ji-Jun Zou[a,b,c,*]

[a] Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China
[b] Collaborative Innovative Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China
[c] Haihe Laboratory of Sustainable Chemical Transformations, Tianjin 300192, China

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ABSTRACT

Synthesizing high-density fuel from lignocellulose can not only achieve green and low-carbon development, but also expand the feedstock source of hydrocarbon fuel. Here, we reported a route of producing high-density fuel from lignin oil and hemicellulose derivative cyclopentanol through alkylation and hydrodeoxygenation. HY with SiO_2/Al_2O_3 molar ratio of 5.3 was screened as the alkylation catalyst in the reaction of model phenolic compounds and mixtures, and the reaction conditions were optimized to achieve conversion of phenolic compounds higher than 87% and selectivity of bicyclic and tricyclic products higher than 99%. Then two phenolic pools simulating the composition of two typic lignin oils were studied to validate the alkylation and analyze the competition mechanism of phenolic compounds in mixture system. Finally, real lignin oil from depolymerized of beech powder was tested, and notably 80% of phenolic monomers in the oil were converted into fuel precursor. After hydrodeoxygenation, the alkylated product was converted to fuel blend with a density of 0.91 g/mL at 20 °C and a freezing point lower than −60 °C, very promising as high density fuel. This work provides a facile and energy-efficient way of synthesizing high-performance jet fuel directly from lignocellulosic derivatives, which decreases processing energy consumption and improve the utilization rate of feedstock.

1. Introduction

With the rapid development of aerospace technology, it is increasingly important to explore more efficient power source for advanced propulsion. Due to their ability to significantly increase the range and payload of aerospace vehicles, hydrocarbon fuels with high density and good low-temperature properties (such as low freezing point and low viscosity) have attracted widespread attention [1–4]. Usually, high-density hydrocarbon fuels are synthesized from petroleum-based compounds, but problems such as energy crisis and environmental degradation occur owing to the overuse of fossil energy [5–7]. Accordingly, renewable and environmentally friendly biomass feedstocks are more desirable, among which lignocellulose is the best candidate to replace fossil resources [8–12].

Hydrocarbon fuels with polycyclic structure usually afford high density [13–17]. While most lignocellulosic derivatives are chain or monocyclic compounds, it is necessary to convert them into polycyclic structures. To date, many lignocellulosic derivatives have been converted to polycyclic hydrocarbons via C—C coupling reactions, such as alkylation [18–21], aldol condensation [22], Michael addition [23], and Diels-Alder reaction [24], etc. Among them, alkylation reaction is the most frequently used one. Particularly, lignin derived aromatic oxygenates (such as phenol, guaiacol, cresol, catechol, etc.) and lignocellulose derived cyclic alcohols (such as cyclopentanol, cyclohexanol, methyl-cyclohexanol, etc.) can be easily converted to bicyclic and tricyclic alkanes through alkylation and following hydrodeoxygenation [25–28]. For example, Anand et al. synthesized cyclohexyl phenol by alkylation of phenol with cyclohexanol under the catalysis of HY [29]. Then Liu et al. investigated zeolite-catalyzed alkylation of phenols including phenol, catechol, guaiacol, cresol and anisole, with cyclohexanol and substituted cyclohexanols as feedstock.

Although bicyclohexane and tricyclohexane synthesized from alkylation of phenols with cyclic alcohols afford high density, the

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* Corresponding authors.
E-mail addresses: cxshi@tju.edu.cn (C. Shi), jj_zou@tju.edu.cn (J.-J. Zou).

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low-temperature properties are inferior and cannot meet the requirements of practical application. Recently, our group reported the synthesis of high-density and low freezing point jet-fuel-ranged blend from bio-derived phenol and cyclopentanol [19,30]. Remarkably, the major component, i.e. cyclopentylcyclohexane shows much better low-temperature properties due to its asymmetric structure. Moreover, a mixed feedstock pool simulating lignin oil was used to synthesize blended fuel. However, the ratio of phenols in the feedstock is in equal proportions. In the real lignin oil, the content of different types of phenols is different, and it is very difficult to separate these phenols due to their similar boiling points [30,31]. Therefore, utilizing the real lignin oil directly to synthesize high-performance fuels is more meaningful but challenging.

In this work, we investigated the alkylation of mixed phenols obtained directly from lignin oil and cyclopentanol that can be directly produced from hemicellulose on an industrial scale [32]. Combing with subsequent hydrodeoxygenation (HDO) of the alkylation products, synthesizing high-density fuels from whole lignocellulose was realized. First, we carried out the alkylation reaction using model phenolic compounds to screen the catalysts and explore the reaction conditions. Then, we extended its application in two feedstock pools of phenolic mixture simulating lignin oils from different sources. After that we verified the efficacy of alkylation using real lignin oil. Finally, we carried out HDO reaction to obtain hydrocarbon fuel with high performance mainly ascribed to the polycyclic and asymmetric structures. Specifically, many bicyclic alkanes with branched chains possess relatively low freezing points [33–36], and phenols in real lignin oils mostly have branched chains, which makes the product have lower freezing points. In addition, we studied the competition mechanism of phenolic compounds in the mixed system to reveal which type of phenolic derivatives are preferred in alkylation reactions. This work provides a simple, low-cost and energy-saving method for high-performance fuel synthesis from biomass.

2. Experimental

2.1. Chemicals

Unless stated, all chemicals in this work were used directly without any purification. Cyclopentanol (99%), 2-methoxy-4-(1-propyl)phenol (98%), and sodium hydroxide (NaOH) (98%) were purchased from Meryer (Shanghai) Chemical Technology Co., ltd. Phenol (AR) was obtained from Tianjin Damao Chemical Reagent Factory. 4-Ethylphenol (97%), 2-methoxy-4-methylphenol (97%), 2-methoxy-4-ethylphenol (98%), vanillylacetone (99%), guaiacol (98%), 2,6-dimethoxyphenol (99%), isoeugenol (97%), eugenol (99%), and anhydrous magnesium sulfate were purchased from Tianjin Heowns Biotechnology Co., ltd. Cyclohexane (GR) was gained from Tianjin Yuanli Industrial Corporation. 2,6-Dimethoxy-4-methylphenol (95%), 1-(4-hydroxy-3-methoxyphenyl)propan-2-one (99%), and 2-(4-hydroxy-3,5-dimethoxyphenyl) acetic acid (98%) were obtained from Bide Pharmatech ltd. Ammonium chloride (AR), methanol (HPLC) and dichloromethane (HPLC) were obtained from Tianjin Kemiou Chemical Reagent Co., ltd. Hydrochloric acid (HCl) (GR) was gained from Tianjin Chemical Reagent Supply and Marketing Company. Beech powder was purchased from the local timber factory.

2.2. Catalysts

HY-5.3 (SiO_2/Al_2O_3 = 5.3), HY-20 (SiO_2/Al_2O_3 = 20), HY-40 (SiO_2/Al_2O_3 = 40), Hβ (SiO_2/Al_2O_3 = 25), HZSM-5 (SiO_2/Al_2O_3 = 25) were purchased from Nankai Catalysts Co., ltd. and calcinated in the air at 550 °C for 5 h before use. Al-MCM-41 (SiO_2/Al_2O_3 = 25) was purchased from Tianjin Chemist Technology Development Co., ltd. Pd/C (5 wt%) and Ru/C (5 wt%) were purchased from Tianjin Heowns Biochemical Technology Co., ltd.

2.3. Characterization

Temperature programmed desorption (TPD) of NH_3 was performed under flow conditions with a Micromeritics AutoChem II 2920 analyzer equipped with thermal conductivity (TCD) and mass spectrometer (MS) detectors. The solid catalysts were activated in Ar at 300 °C for 2 h, and then cooled to 100 °C. The samples were adsorbed for 2 h in 2000 ppm NH_3/Ar. Physisorbed NH_3 was removed subsequently with 50 mL min^{-1} Ar for 1 h. For the TPD measurements, the samples were heated up in flowing Ar from 100 to 800 °C with a temperature increment of 10 °C/min. The Brunauer-Emmett-Teller (BET) surface area and pore size distributions of catalysts were obtained on a micrometric ASAP-2460 automated system by N_2 isothermal (77 K) absorption. The samples were degassed at 300 °C for 8 h. The samples were quantified by a gas chromatography (GC, Shimadzu 2010 plus) equipped with a hydrogen flame ionization detector (FID) and a capillary column HP-5 capillary column (30 m × 0.32 mm × 0.25 μm) and structurally analyzed by a GC-MS combination (GC-MS, Shimadzu QP 2010S).

2.4. Reaction

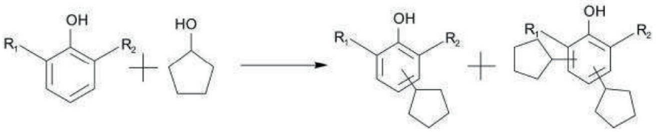
2.4.1. Alkylation of model phenolic compounds

Alkylation of cyclopentanol with phenols (Scheme 1) was conducted in autoclave (EasyChem SLM25) with total volume of 50 mL. First, phenol, guaiacol, and 2,6-dimethoxyphenol were alkylated with cyclopentanol, respectively. For each reaction, 50 mmol of phenolic compound (4.706 g of phenol or 6.206 g of guaiacol or 7.708 g of 2,6-dimethoxyphenol) and 50 mmol (4.306 g) of cyclopentanol were used. The dosage of molecular sieve catalysts was 25 wt% of reactants. The reaction was carried out at 180 °C for 10 h under N_2 atmosphere. Then the reactor was quenched to room temperature, and the sample was drawn for analysis.

Then, three phenolic compounds were mixed in equal proportion for alkylation with cyclopentanol, that is, 25 mmol (2.353 g) of phenol, 25 mmol (3.103 g) of guaiacol, 25 mmol (3.854 g) of 2,6-dimethoxyphenol, 75 mmol (6.46 g) of cyclopentanol and 3.943 g (25 wt% of reactants) of catalysts were used. All other conditions were the same as above.

2.4.2. Alkylation of phenolic compounds pool based on real lignin oil

According to the proportion of phenolic compounds obtained from hardwood lignin (eucalyptus) and softwood lignin (pine wood) depolymerization analysis, two compositions of feedstock pool were used to react with cyclopentanol. 60 mmol of phenolic compound (10 g in total), 60 mmol (5 g) of cyclopentanol, and 3.75 g (25 wt% of reactants) of HY were used at 190 °C for 20 h under N_2 atmosphere. The liquid mixture was sampled and dissolved in dichloromethane for GC-MS analysis. The alkylated prod-



R_1=H, OCH_3; R_2=H, OCH_3

Scheme 1. The scheme of the alkylation of phenols and cyclohexanol.

ucts were filtered to remove catalyst for the further catalytic hydrodeoxygenation.

2.4.3. Alkylation of real lignin oil

The depolymerization of beech powder was carried out in the autoclave (MSG100) with total volume of 100 mL. 3 g beech powder, 0.5 g 5 wt% Ru/C and 60 mL methanol were used for reaction at 230 °C and 3 MPa H_2 for 3 h. After distillation, extraction and filtration, lignin oil was obtained. And then, 0.5 g lignin oil was used to react with 4.5 g cyclopentanol (as both reactant and solvent). And the other reaction conditions were same as the alkylation of phenolic compounds pool. The liquid mixture was sampled and dissolved in dichloromethane for GC-MS analysis.

2.4.4. Hydrodeoxygenation

The hydrodeoxygenation of alkylated products was carried out in autoclave (EasyChem SLM25) with total volume of 50 mL. The reactor was loaded with 10 g alkylated products, 10 g cyclohexane as the solvent, 1 g Hβ and 0.2 g Pd/C as catalyst. The HDO was conducted at 200 °C for 48 h, and the pressure was kept at 6 MPa by continuous inputting hydrogen. The final products were recovered by vacuum distillation to remove solvent and remaining oxygenated compounds for the fuel properties measurements.

2.4.5. Analysis

The conversion, yield and selectivity were calculated by the internal standard method using hexane as an internal standard according to Eq. (1).

$$m_i = \frac{f_i A_i m_s}{f_s A_s} \tag{1}$$

f_i and f_s is the correction factor of the determinand and internal standard, respectively, which was calculated by the effective carbon number method. A_i and A_s is the peak area of the determinand and internal standard, respectively. m_s: the mass of the internal standard.

2.5. Computational details

The molecular structure of all compounds was fully optimized at the B3LYP/6-31+G(d) level of theory using the Gaussian 09 package with tight SCF convergence and ultrafine integration grids [37–39]. The Multiwfn 3.8 program was used to calculate the nucleophilicity index and three-dimensional dimensions using the checkpoint file from the above Gaussian calculations as the input file [40,41].

2.6. Fuel properties measurements

The fuel density was measured by a Mettler Toledo DE40 density meter according to ASTM D4052. The freezing point was measured as outlined in ASTM D2386. Kinematic viscosity was determined using a capillary viscometer (ASTM D445). The volumetric heat value was measured by the IKA-C6000 isoperibol Package 2/10 Calorimeter (ASTM D240-02).

3. Results and discussion

3.1. Alkylation of model phenolic compounds with cyclopentanol

Lignin, one of the main components of lignocellulose and the most abundant natural renewable aromatic resource, consists of phenylpropane units of hydroxyphenyl (H), guaiacyl (G), and syringyl (S). Therefore, in the first part, we focused on the three simplest corresponding phenols: phenol, guaiacol and 2,6-dimethoxyphenol. To begin with, phenol, guaiacol, and 2,6-dimethoxyphenol were alkylated with cyclopentanol respectively. Two catalysts with similar SiO_2/Al_2O_3 molar ratio (Hβ-25 and HY-20) were initially compared under the same reaction conditions. The lower alkylation reactivity of guaiacol and 2,6-dimethoxyphenol than that of phenol in Hβ-25 (Fig. 1a) may be due to the pore constraints (Table 1). This was proved by the fact that HY-20 with a more spacious cavity showed greatly increased conversions of guaiacol and 2,6-dimethoxyphenol even higher than that of phenol. Taking the alkylation of phenol with cyclopentanol as example, cyclopentanol is rapidly combined with phenol to form cyclopentylphenol (**A** in Fig. 1b) through C-alkylation or (cyclopentyloxy)benzene (**B** in Fig. 1b) through O-alkylation. And (**B**) can be rearranged to more stable C-alkylation product (**A**). Besides, some bi- and tri-cyclic compounds are formed from the self-alkylation of cyclopentanol (**C**–**F** in Fig. 1b). Also, some tricyclic compounds (**G** and **H** in Fig. 1b) are produced from the further alkylation of **A**, **C** and **D** [19,32,42–44].

Since real lignin oil is a mixture containing a variety of phenols, after a general understanding of the mechanism of alkylation reaction through single reactant, the three phenolic compounds were mixed to react with cyclopentanol. First, the types of catalysts were screened. From Fig. 2(a), HY-20 showed the highest activity with cyclopentanol conversion of 99%, and the conversion of phenol, guaiacol, and 2,6-dimethoxyphenol were also the highest, which were 75.07%, 74.48%, and 92.58% respectively. The selectivity of the target products (bicyclic and tricyclic hydrocarbons) was higher than 97% under all conditions. And the activity of other catalysts was as follows: Al-MCM-41 > Hβ > HZSM-5, among which HZSM-5 was almost inactive. This result was reasonable according to the acid property and pore size of these catalysts. Although the acidity of HZSM-5 was strong, its pore size was too small (Fig. S1a and Table 1), which limited the formation of rather bulky transition states and the diffusion of products, only allowing the dehydration of cyclopentanol to cyclopentene and inhibiting the alkylation. Hβ was not suitable for guaiacol and 2,6-dimethoxyphenol with greater steric hindrance for the same reason. Although the pore size of Al-MCM-41 was large enough, the conversion of reactants was very low due to the inadequate acid strength and concentration of the acid. Therefore, considering the aspects of acid properties and porous structures, HY was more suitable catalyst.

For HY series molecular sieves, the increase of SiO_2/Al_2O_3 molar ratio decreased their acidic strength and the total acidic amount (Fig. S1b and Table S1). When the SiO_2/Al_2O_3 molar ratio was 5.3, the activity was much better than that when the SiO_2/Al_2O_3 molar ratio was 20 or 40 (Fig. 2b). In addition, the effects of HY dosage, reaction time and reaction temperature on the alkylation reaction were investigated. From Fig. 2(c–e), when the catalyst dosage was 15 wt%, the temperature was 180 °C, and the reaction time was 10 h, the conversion of cyclopentanol reached 99%, and almost all of the intermediates were converted into alkylated compounds. As result, the selectivity of the target product was over 99%, the conversion of three phenols were 85.92%, 83.17% and 94% respectively. On this basis, the conversion increased slightly by continuing to increase the amount of catalyst, raise the temperature, and prolong the reaction time.

3.2. Alkylation of broader feedstock pool with cyclopentanol

The above results have shown that a mixture of simple phenols can be converted at high conversion rate. However, it is still far from the real lignin depolymerization products in terms of component composition and proportion. The preparation, separation and purification of platform compounds often require large energy input and cumbersome process flow, and there are problems such

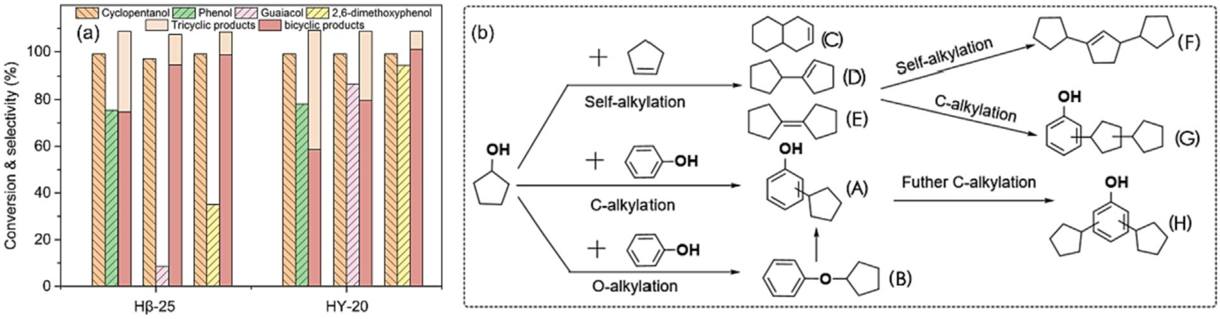


Fig. 1. (a) Performance of catalysts for the alkylations of three kinds of phenols respectively with cyclopentanol at 180 °C for 10 h under 0.5 MPa N_2 atmosphere. (b) Alkylation pathways of phenol and cyclopentanol.

Table 1
Physicochemical properties of molecular sieves.

Sample	SiO_2/Al_2O_3	BET area (m^2/g)	Pore size (nm)	Acid amount (mmol/g)[a]
HY	20	844	0.75	1.35
Al-MCM-41	25	695	3.41	1.27
Hβ	25	559	0.67	2.33
HZSM-5	25	413	0.54	2.52

[a] Quantified by NH_3-TPD.

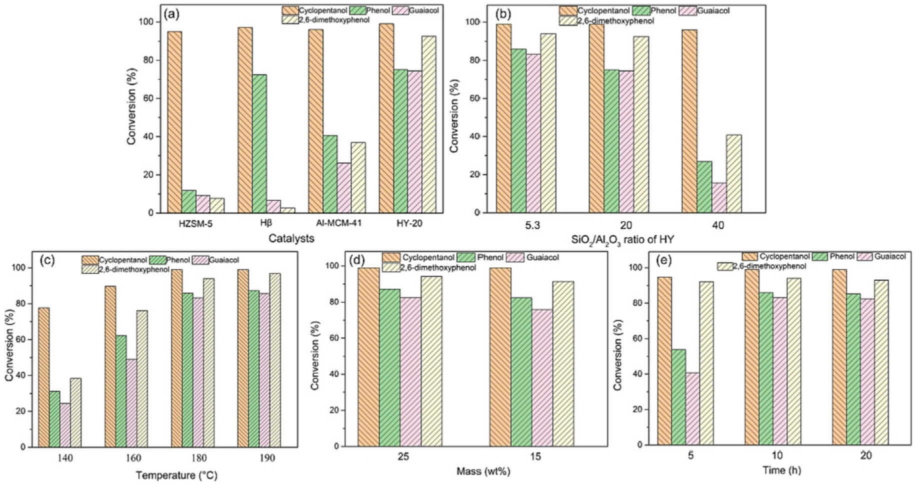


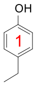
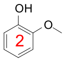
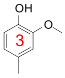
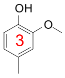
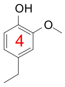
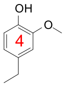
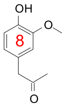
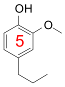
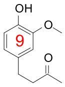
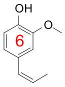
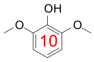
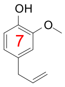
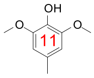
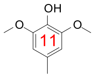
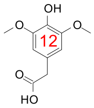
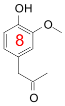
Fig. 2. Effects of (a) different kinds of catalysts, (b) different SiO_2/Al_2O_3 molar ratio of HY, (c) reaction temperature, (d) HY dosage, and (e) reaction time on the alkylation of the phenolic mixture of phenol, guaiacol, and 2,6-dimethoxyphenol with cyclopentanol.

as low utilization rate of feedstock, low product yield, and large energy consumption. Therefore, the feedstock pool according to the proportion of phenolic compounds in the real lignin oil was used.

Lignin can be divided into hardwood lignin, softwood lignin and herbal lignin. The composition of lignin depolymerization products from different sources is also different [45]. Here we studied two typical simulants. Feedstock pool A was obtained from hardwood lignin (eucalyptus) depolymerization products (Table 2, entry 1) [46], containing H-lignin, G-lignin and S-lignin, and one of the S-lignin with no branched chain at the para position of phenolic hydroxyl. Feedstock pool B was obtained from softwood lignin (pine wood) depolymerization products (Table 2, entry 2) [47], only containing G-lignin and S-lignin, and one of the G-lignin with no branched chain at the para position of phenolic hydroxyl. By studying the feedstock pool with different components, the performance of each type of lignin in the competitive reaction was analyzed.

First, in view of the superior performance of HY-5.3 in the simple phenolic mixture system, it was applied in feedstock pool A (Table 2, entry 1). Mass balance evaluation (carbon balance) has been carried out by the internal standard method using hexane as an internal standard, and the carbon balance reached 93%. Notably, very high conversion was obtained, 99% for cyclopentanol and 85.7% for the phenolic mixture (Fig. S2), and the selectivity of bicyclic and tricyclic hydrocarbons reached 99%. In order to examine the regenerability of the catalyst, the solid phase was separated from the reaction mixture by filtration, washed, dried and finally calcined at 550 °C for 5 h before further use. The conversion of phenol decreased slightly from 85.7% to 72.4% after three times of recycling, which showed that the catalyst has good regenerability (Fig. S3).

Table 2
Composition of feedstock pool for alkylation.

Entry 1 (Feedstock pool A)		Entry 2 (Feedstock pool B)	
Monomer	Proportion (wt%)	Monomer	Proportion (wt%)
4-Ethylphenol	 1.85	Guaiacol	 16.05
2-Methoxy-4-methylphenol	 6.77	2-Methoxy-4-methylphenol	 12.35
2-Methoxy-4-ethylphenol	 5.67	2-Methoxy-4-ethylphenol	 10.29
1-(4-Hydroxy-3-methoxyphenyl) propan-2-one	 5.13	2-Methoxy-4-(1-propyl) phenol	 12.35
Vanillylacetone	 2	Isoeugenol	 20.16
2,6-Dimethoxyphenol	 49	Eugenol	 3.7
2,6-Dimethoxy-4-methylphenol	 16.36	2,6-Dimethoxy-4-methylphenol	 9.05
2-(4-Hydroxy-3,5-dimethoxyphenyl)acetic acid	 13.22	1-(4-Hydroxy-3-methoxyphenyl) propan-2-one	 16.05

In addition, we also applied the selected catalyst HY-5.3 for the conversion of feedstock pool B (Table 2, entry 2). The experimental results showed that HY-5.3 can also play a very good catalytic role, and the conversion rate of these phenolic compounds in the alkylation reaction reached 78.5% (Table S2). These results suggested that HY-5.3 can act as an efficient catalyst for co-conversion of lignin derivatives and enable the direct conversion of lignin depolymerization products.

3.3. Competition mechanism of phenolic compounds in mixed system

Fig. 3(a) showed the specific conversion rates of each component in feedstock pool A (Table 2, entry 1). The conversion rates of phenols with different branched chains were different, and they were lower than that of each component alkylation with cyclopentanol alone (Table S2), indicating that there was competition among the components in the complex system. In order to explore this competition mechanism, a series of experiments were conducted and a conclusion was obtained that the conversion rate of each component in the feedstock pool is mainly determined by two factors, i.e. electronic effect and steric hindrance.

Electronic effects are reflected in intrinsic reactivity differences of aromatic rings. These alkylation reactions are electrophilic aromatic substitution reactions. The existing substituents on the benzene ring have an orientation effect on the attack of cyclopentyl carbenium ion. These substituents can be divided into two categories, one is the first type of orientating-group, which activates the benzene ring in the order of hydroxy (–OH) > methoxy ($-OCH_3$) > alkyl ($-C_nH_{2n+1}$), and specifies the positions of the newly introduced groups as the ortho and para positions. But the greater the steric effect, the less the ortho-isomer. The other is the second type of orientating-group, such as carbonyl and alkenyl, which passivates the benzene ring and specifies the position of the newly introduced group as the meta position. When there are multiple substituents, the following orientation rules are followed: if the two original substituents on the benzene ring have the same orientation effect on the introduction of the third substituent, it is still determined by the above two orientation rules, but the yield of substitution products sandwiched between two substituents is generally low due to the high steric hindrance; if the two original substituents have different orientation effects, it is mainly determined by the stronger orientating-group.

The electron effect can be totally measured by the nucleophilic index in the concept density functional theory (CDFT). The nucleophilic index is approximately the negative value of the ionization energy of the material, but with tetrachyanoethylene (TCE) as the reference point, the value is always positive and the expression is $N_{Nu} = E_{HOMO(Nu)} - E_{HOMO(TCE)}$. The higher the N_{Nu} value, the stronger the nucleophile, that is, the stronger the electron-giving ability [48]. The nucleophilic indices of twelve phenolic compounds involved in this work were calculated by Multiwfn (Fig. 3b and d). The order is as follows: **(11)** > **(6)** > **(10)** > **(12)** > **(5)** > **(4)** > **(9)** > **(3)** > **(7)** > **(8)** > **(2)** > **(1)**.

The nucleophilic index can be used as the evaluation index of electronic effect to explain the competition mechanism of some phenolic compounds in this complex system. For example, for 2,6-dimethoxy-4-methylphenol **(11)** and 2-(4-hydroxy-3,5-dimethoxyphenyl) acetic acid **(12)**, the only difference is the branched chain in at the para position of phenolic hydroxyl, the branched chain of **(11)** is methyl, and that of **(12)** is ethyl carboxyl. Due to the electron-withdrawing induction effect of carboxyl group, the electron cloud is biased towards carboxyl group and the electron-giving ability of C directly connected with the benzene ring is weakened. Therefore, the overall electron-donating effect of carboxyl group is weaker than that of methyl group. So, the nucleophilic index of **(12)** is less than **(11)**. The same applies

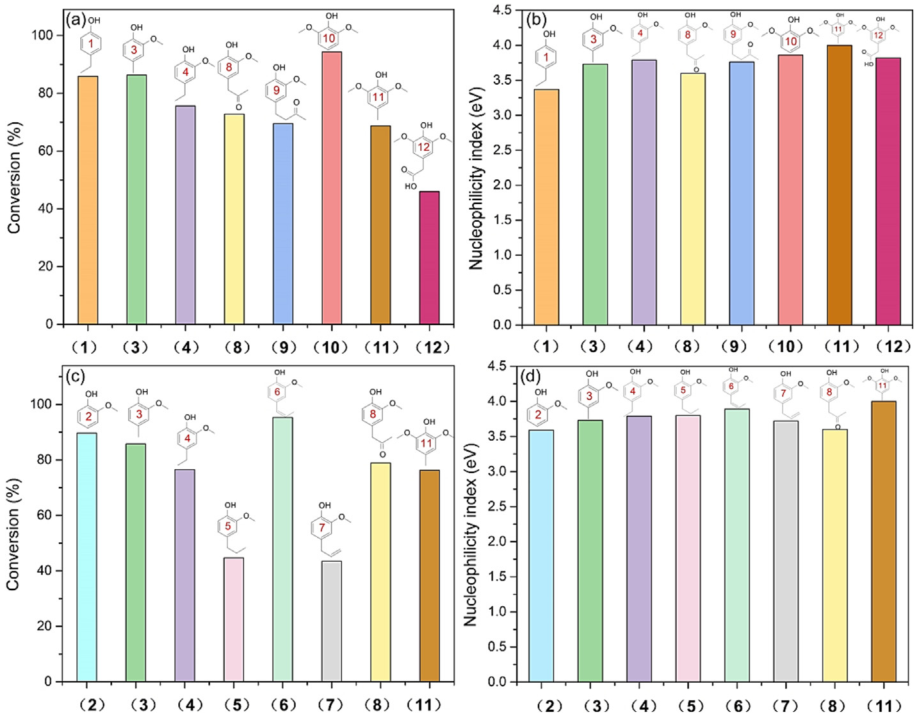


Fig. 3. (a) Conversion of phenolic compounds in feedstock pool A (Table 2, entry 1). (b) The nucleophilicity indices of phenolic compounds in feedstock pool A (Table 2, entry 1). (c) Conversion of phenolic compounds in the feedstock pool B (Table 2, entry 2). (d) The nucleophilicity indices of phenolic compounds in the feedstock pool B (Table 2, entry 2), reaction conditions: 10 g phenolic compounds 5 g cyclopentanol, 3.75 g HY-5.3, 190 °C, 0.5 MPa N_2, 20 h.

Table 3
The three-dimensional dimensions of the phenolic compound molecules.

Phenolic compound	Length (Å)	Width (Å)	Height (Å)	Phenolic compound	Length (Å)	Width (Å)	Height (Å)
(1)	10.258	6.705	4.991	**(7)**	9.977	8.586	6.332
(2)	9.503	7.616	4.19	**(8)**	10.281	8.335	6.372
(3)	9.532	7.903	4.19	**(9)**	11.648	9.351	5.704
(4)	10.622	8.125	4.189	**(10)**	11.066	7.96	4.19
(5)	10.108	8.608	6.145	**(11)**	11.065	8.911	4.35
(6)	10.359	8.933	5.018	**(12)**	10.706	9.902	5.919

to the following groups: 2-methoxy-4-methylphenol **(3)** and 1-(4-hydroxy-3-methoxyphenyl) propan-2-one **(8)**, 2-methoxy-4-ethylphenol **(4)** and vanillylacetone **(9)**.

The effect of steric hindrance is also significant for the groups of phenolic compounds. For phenolic compounds with the same structure but only one branch chain with different groups, the steric hindrance of these different groups can be represented by the three-dimensional dimensions of the whole molecules. We built a rectangular box by Multiwfn and measure the size of the molecule by its length, width, and height (Table 3 and Fig. S3). For example, for **(11)** and **(12)**, the only difference is the branched chain at the para position of phenolic hydroxyl. The steric hindrance of methyl is smaller than that of ethyl carboxyl. In the same way, for **(3)** and **(8)**, the steric hindrance of methyl is smaller than that of acetone, and for **(4)** and **(9)**, the steric hindrance of ethyl is smaller than that of butanone. So, combining electronic effect and steric hindrance, the conversion rate of **(11)** is higher than that of **(12)**, **(3)** is higher than **(8)**, and **(4)** is high than **(9)** (Fig. 3a and c).

Through these two factors, the difference between the conversion rates of phenols with different branches in complex systems can be explained. But in addition to these, there is a situation where the influence of steric hindrance and electronic effects are in opposite directions. For example, for 2-methoxy-4-methylphenol **(3)** and 2-methoxy-4-ethylphenol **(4)**, the only difference is that the branch chain at position 4 is different. In terms of electronic effect, the electron-giving capacity increases with the number of branched carbons, **(4)** is better than **(3)**. But the steric hindrance also increases with the number of branched carbons. So, in terms of steric hindrance, **(3)** is better than **(4)**. In fact, experimental results show that the conversion rate of **(3)** is higher than that of **(4)** in the complex system. It shows that when the steric hindrance and electronic effect are opposite, the steric hindrance is the primary influencing factor. This can also be proved by **(8)** and **(9)**. They are distinguished from acetone and butanone groups. The effect of steric hindrance is more dominant than electronic effect, so the conversion rate of **(8)** is higher than that of **(9)**. The same applies between **(10)** and **(11)**.

This work also provided some suggestions for lignin depolymerization for subsequent fuel synthesis. In order to facilitate further processing such as alkylation, the branched chain at the para position of phenolic hydroxyl should be avoided during depolymerization. If the branched chain can be completely removed, 2, 6-dimethoxyphenol is the most desirable; if not, methoxyl group should be removed as far as possible, para-hydroxyphenyl lignin

Table 4
Physical properties of HY-5.3 treated with different conditions.

Sample	S_{BET} (m^2/g)	S_{micro} (m^2/g)	S_{meso} (m^2/g)	Pore size(nm)	V_{total} (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)
HY-5.3	805	762	43	0.713	0.381	0.289	0.092
HY-5.3-alkali treatment	776	709	67	0.715	0.385	0.267	0.118
HY-5.3-acid treatment	768	707	61	0.716	0.397	0.258	0.139

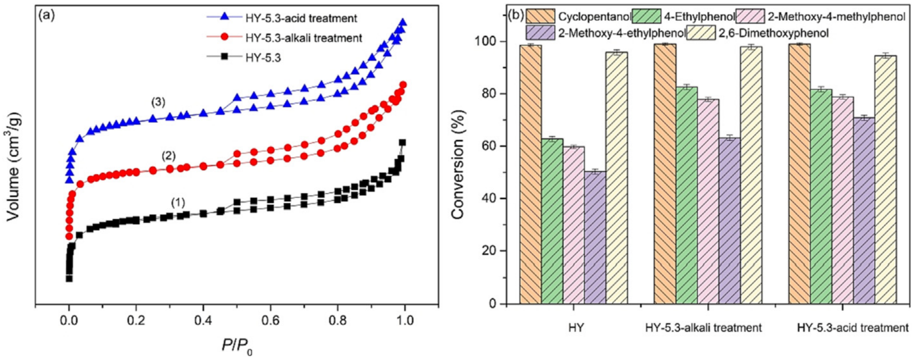


Fig. 4. (a) N_2 adsorption–desorption isotherms along with mesopore size distribution of HY-5.3 treated with different conditions. (b) Effects of catalyst pore reaming on the alkylation of cyclopentanol with the mixture feedstock pool, reaction conditions: 10 g phenolic compounds (4-ethylphenol (**1**): 2.9 %; 2-methoxy-4-methylphenol (**3**): 10.7 %; 2-methoxy-4-ethylphenol (**4**): 9.0 %; 2,6-dimethoxyphenol (**10**): 77.4 %), 5.7 g cyclopentanol, 2.35 g HY-5.3, 190 °C, 0.5 MPa, 10 h.

(H-lignin) without methoxyl group and guaiacyl lignin (G-lignin) with one methoxyl group is better than most syringyl lignin (S-lignin) with two methoxyl groups in further processing. Moreover, for all lignin depolymerization products, the shorter the branched chain, the better for further conversion, and the length of branched chain should not be more than three carbons.

In this way, to further identify the above competition mechanism and improve the catalyst performance, we selected four representative phenolic compounds: 4-ethylphenol (**1**), 2-methoxy-4-methylphenol (**3**), 2-methoxy-4-ethylphenol (**4**), and 2,6-dimethoxyphenol (**10**) to construct the mixture feedstock pool according to their proportion in the actual lignin oil, and treated HY-5.3 by acid treatment (0.2 M HCl) and alkali treatment (0.2 M NaOH) to increase the mesoporous volume for better mass transfer. The result showed that the conversion rate of each phenolic compound increased with the increase of mesoporous volume significantly. As the selectivity of bicyclic and tricyclic hydrocarbons reached 99%, the conversion rate of phenolic mixture reached more than 90% (Table 4, Fig. 4a–b) at 10 h, much higher than those of the above feedstock pools. Moreover, the order of the conversion rate of phenolic compounds was also consistent with the above mechanism. The conversion rate of 2, 6-dimethoxylphenol **(10)** with no branched chain at the para position of phenolic hydroxyl was the highest. The conversion rate of 4-ethylphenol **(1)** without methoxy group was higher than that of 2-methoxy-4-ethylphenol **(4)** with one methoxy group. For the length of the branch chain, the conversion rate of 2-methoxy-4-methylphenol **(3)** was higher than that of 2-methoxy-4-ethylphenol **(4)**.

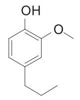
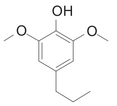
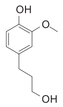
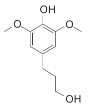
3.4. Alkylation of real lignin oil with cyclopentanol

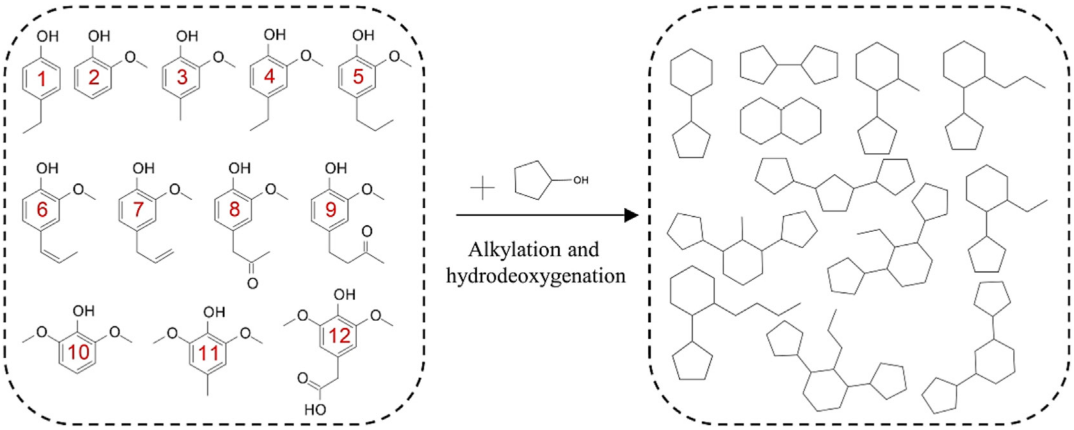
The real lignin oil obtained from the depolymerization of beech powder contained about 70 wt% phenolic monomers consisting four major phenolic compounds [49], and the others were dipolymers. Their composition of real lignin oil and the conversion rate of alkylation reaction were shown in Table 5. The conversion rate of phenolic monomers in real lignin oil was 80%. The ranking of conversion rate of phenolic monomers also accorded with the competition mechanism described above. This result shows that real lignin oil can be used to produce fuel precursors through alkylation with high conversion rate.

3.5. Hydrodeoxygenation of alkylated products and biofuel properties

To evaluate the potential of the fuel blend as high-performance jet fuel, the alkylated products of feedstock pool A (Table 2, entry 1) were hydrodeoxygenated to obtain jet fuel blend. The hydrodeoxygenation required acid Hβ and metal catalysts Pd/C, in which metal sites catalyzed the hydrogenation of unsaturated carbon bonds and acid sites catalyzed dehydration [19]. The yield of the HDO product can reach 95% (Scheme 2). The basic properties of biofuel are shown in Table 6. It can be seen that most of its prop-

Table 5
Alkylation of real lignin oil with cyclopentanol.

Phenolic monomers				
Proportion	13.7 wt%	41.2 wt%	3.7 wt%	11.3 wt%
Conversion	89 %	83 %	86 %	58 %



Scheme 2. Co-conversion of cyclopentanol and phenolic mixtures to jet fuel blend.

Table 6
Properties of bio-jet fuel synthesized in this work and literature.

Fuels	Density (20 °C) (g/mL)	Volumetric heat value (MJ/L)	Freezing point (°C)	Viscosity (20 °C) (mm^2/s)
Fuel blend[a]	0.91	42.89	< −60	5.59
RP-3	0.780	33.89	< −47	1.25

[a] The feedstock composition for synthesizing fuel blend was shown in Table 2, entry 1.

erties, such as density, net heat of combustion and freezing point, are superior to those of RP-3 jet fuel.

4. Conclusions

In this work, we demonstrated a catalytic route to convert lignin oil and hemicellulose derivative cyclopentanol into high-density biofuel by alkylation and hydrodeoxygenation. HY with SiO_2/Al_2O_3 molar ratio of 5.3 is the optimal catalyst and can effectively catalyze the allylation of model phenolic compounds, simulant phenolic mixture of lignin oil and real lignin oil with high conversion rate, among which, the conversion of phenolic monomers in the real lignin oil can reach 80%. The alkylation produced bicyclic and tricyclic products, which was converted to high density fuel blending upon hydrodeoxygenation. Particularly, the fuel derived from phenolic mixture pool of hardwood lignin possessed a density of 0.91 g/mL at 20 °C and a freezing point lower than −60 °C. Also, the competition mechanism of phenolic compounds in the mixed system was studied. This work provides a simple and energy-efficient way of synthesizing high-performance jet fuels by co-conversion of lignocellulosic depolymerization derivatives and suggest a pathway for full utilization of lignocellulose.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jechem.2022.10.050.

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