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Biogasoline production by co-cracking of model compound mixture of bio-oil and ethanol over HSZM-5

Shurong Wang*, Qinjie Cai, Xiangyu Wang, Li Zhang, Yurong Wang, Zhongyang Luo

State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, Zhejiang, China

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ABSTRACT

Acids and ketones in biomass pyrolysis oil (bio-oil) can be readily cracked to produce hydrocarbons. They can also be enriched in the distilled fraction using molecular distillation techniques. To simulate the actual composition of the distilled fraction, the co-cracking performance of mixtures of hydroxypropanone, cyclopentanone, and acetic acid with ethanol in a fixed-bed reactor over an HZSM-5 catalyst was studied. The influences of reaction temperature and pressure on the reactant conversion, selectivity, and composition of the oil phase were investigated. At a low reaction temperature of 340 °C, the conversions of acetic acid and ethanol were as low as 67.9% and 74.4%, respectively, and the oil phase had a low hydrocarbon content of 59.8%, with large amounts of oxygenated byproducts. Cracking under atmospheric pressure also generated a low-quality oil phase with a very low selectivity of only 10.8%. Increasing the reaction temperature promoted reactant conversion and improved the deoxygenation efficiency, whereas increasing the reaction pressure significantly promoted hydrocarbon production. The optimum conditions for biogasoline production were 400 °C and 2 MPa. Under these conditions, the reactant conversion reached 100% and the oil phase selectivity was 31.5 wt%. This oil phase consisted entirely of hydrocarbons, 91.5 wt% of which were aromatic hydrocarbons, indicating that the HZSM-5 catalyst had high activity for deoxygenation and aromatization reactions during cracking. In addition, characterization of the spent catalysts and stability tests showed that the catalyst was deactivated after a long reaction time. However, the catalytic activity was recovered by catalyst regeneration.

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1. Introduction

With the growing fossil fuel crisis and increasingly severe environmental pollution, the use of renewable and clean biomass is receiving global attention [1–3]. Among methods of using biomass, fast pyrolysis has great potential. Because it can efficiently convert solid biomass to liquid bio-oil [4–6]. However, the inferior properties of bio-oil, such as high oxygen content, high water content, and instability, limit its use as a fuel

for vehicles [7]. It is therefore necessary to upgrade bio-oil for such high-grade uses.

At present, the main bio-oil upgrading techniques are catalytic cracking, catalytic hydrogenation, catalytic esterification, catalytic steam reforming, and emulsification [8]. Catalytic cracking, using a zeolite catalyst, is a promising bio-oil upgrading technique, which can remove oxygen from the bio-oil in the form of H₂O, CO, and CO₂ and convert the bio-oil to high-grade hydrocarbon fuels [9–12].

* Corresponding author. Tel: +86-571-87952801; +86-571-87951616; E-mail: srwang@zju.edu.cn

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The composition of bio-oil is very complicated. It has a high content of oxygenated components such as carboxylic acids, ketones, alcohols, aldehydes, phenols, ethers, esters, and sugars [13,14]. Although direct cracking of crude bio-oil produces some liquid hydrocarbon fuel, serious catalyst deactivation by coking occurs [15]. To investigate the detailed cracking mechanism of each component in bio-oil, the cracking behavior of different model compounds in bio-oil has been studied. It was found that some small-molecule compounds such as alcohols, acids, and ketones have high reactivities, whereas phenols have low reactivities [16,17]. In addition, macromolecules such as sugars and phenols in bio-oil easily form coke deposits on catalysts [18].

To improve the efficiency of bio-oil cracking, it is therefore necessary to enrich components with high cracking activities. Thermosensitive bio-oil can be efficiently separated into the corresponding distilled fraction and a residual fraction using the molecular distillation technique. In our previous studies on the molecular distillation of bio-oil, it was found that the distilled fraction had a high content of small-molecule ketones and acids such as hydroxypropanone (HPO), cyclopentanone (CPO), and acetic acid (HOAc), whereas macromolecules such as sugars and phenols were enriched in the residual fraction [19–21]. The cracking properties of the distilled fraction of bio-oil were therefore better than those of crude bio-oil.

Although the cracking properties of the distilled bio-oil fraction are better than those of crude bio-oil, direct cracking may still cause coking problems because of the high oxygen content and high degree of unsaturation. To evaluate the influence of oxygen content and degree of unsaturation of bio-oil on the cracking performance, some researchers have introduced the concept of the effective hydrogen to carbon ratio, $(H/C)_{\text{eff}}$ [14,22], as expressed in equation $(H/C)_{\text{eff}} = (H - 2O - 3N - 2S)/C$. Mentzel et al. [14] found that catalyst deactivation occurred more easily in the cracking of low $(H/C)_{\text{eff}}$ compounds.

According to the equation, the $(H/C)_{\text{eff}}$ values for HPO, CPO, and HOAc are only 0.67, 1.2, and 0, respectively, suggesting that the catalyst is easily deactivated during cracking of these compounds. The addition of compounds with relatively high $(H/C)_{\text{eff}}$ values as coreactants to increase the overall $(H/C)_{\text{eff}}$ may therefore be an efficient way to improve the stability of the cracking process. Aliphatic alcohols are ideal cracking coreactants because they have a relatively high $(H/C)_{\text{eff}}$ value of 2. In the study of co-cracking of methanol and bio-oil model compounds by Mentzel et al. [14], it was found that the catalyst lifetime was significantly increased and the conversion capacity increased tenfold. Valle et al. [18] used thermally treated bio-oil and then methanol for co-cracking, and the reaction stability was improved. Our previous study of the co-cracking of ketones (HPO or CPO) with alcohols also showed that the addition of alcohols enhanced the deoxygenation of ketones and the production of hydrocarbons [23,24]. In this work, mixtures of HPO, CPO, and HOAc were selected as model compounds to study the co-cracking behavior with ethanol (EtOH). The influences of reaction temperature and pressure on reactant conversion, selectivity, and composition of the oil phase were investigated to determine the most suitable reaction conditions.

2. Experimental

HPO was purchased from Alfa Aesar (Ward Hill, MA, USA), CPO was purchased from Aladdin Industrial Corporation (Shanghai, China), and HOAc and EtOH were purchased from the Sinopharm Chemical Reagent Co. (Beijing, China). In our previous studies, it was found that 70 wt% alcohols mixed with ketones efficiently generated oil phase products [23]. Therefore, mixtures containing 70 wt% EtOH and 30 wt% model compound mixture were again used in this work. Based on the HPO, CPO, and HOAc contents of crude bio-oil and their separation characteristics during molecular distillation [19–21], the weight ratio of HPO, CPO, and HOAc in the model compound mixture was set at 6:1:5, i.e., 15 wt% HPO, 2.5 wt% CPO, and 12.5 wt% HOAc. The HZSM-5 (Si/Al = 25) zeolite catalyst used in the experiments was activated at 550 °C for 6 h and then sieved to 40–60 mesh.

Catalytic cracking experiments were performed in a fixed-bed reactor. The catalyst (about 2 g) was supported on quartz wool in the reactor, which was a stainless-tube with an inner diameter of 8 mm. The mixed reactants were pumped using an HPLC pump and entered the reactor after vaporization with N₂. The reaction pressure was regulated using N₂ at a flow rate of 30 mL/min. The weight hourly space velocity of the reactants was kept at 3 h⁻¹. The outlet gases from the reactor were cooled by a condenser to separate them into liquid products and non-condensable gases. Each experimental run lasted 3 h, and the reaction temperature and pressure were set within the ranges 340–430 °C and 0.1–3 MPa.

The gaseous products were quantified using an online gas chromatograph (Agilent 7890A, Agilent Technologies, Palo Alto, CA, USA). The liquid products had an obviously separable oil phase and an aqueous phase. The oil phase was analyzed using a gas chromatography-mass spectrometry system and quantified using the area normalization method. Finally, the residual reactants in the liquid products were quantified by gas chromatography using the external reference method to calculate the conversion of the reactants based on the feed mass. The selectivities of the liquid products were calculated based on the mass of oil phase and aqueous phase collected (excluding unconverted reactants) and the mass of converted reactants.

The Brunauer-Emmett-Teller (BET) specific surface areas of blank HZSM-5 and spent catalysts were measured by N₂ adsorption-desorption at -196 °C, using an Autosorb-1 Quantachrome apparatus.

3. Results and discussion

3.1. Effects of reaction temperature and pressure

3.1.1. Reactant conversion

The effect of temperature on the conversion of the model compound mixture and EtOH at 2 MPa is shown in Fig. 1(a). At 340 °C, HPO and CPO were almost completely converted, but the conversions of HOAc and EtOH were low, 67.9% and 74.4%, respectively. This might be a result of the low catalytic capacity of the catalyst at low temperature and the low activities of

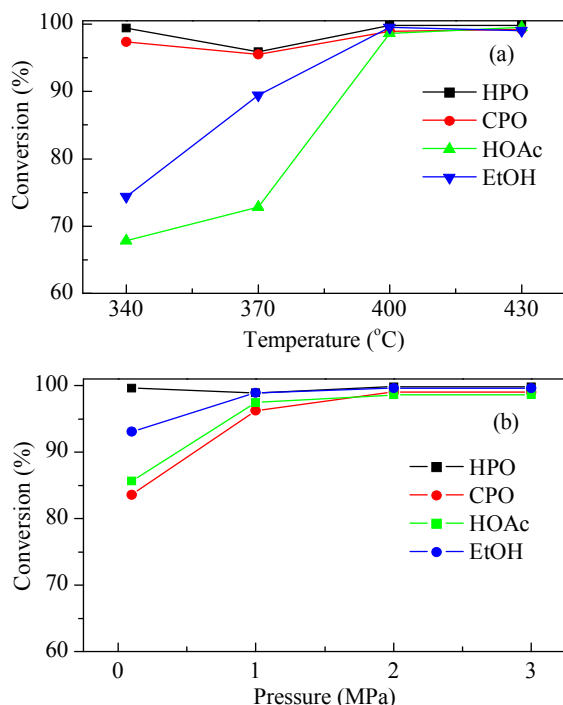


Fig. 1. Conversion of reactants using different conditions: (a) 2 MPa; (b) 400 °C.

HOAc and EtOH molecules, whereas HPO and CPO showed higher activities. However, the converted HPO molecules mainly underwent intermolecular dehydration reactions to form ketones and other oxygenated byproducts at low reaction temperatures [23]. In a study of CPO conversion over acidic zeolites by Huang et al. [25], it was also found that CPO tended to form oxygenated polymers by condensation at low temperatures. Therefore, although the conversion of ketones is very high at low temperatures, the products may not be the desired hydrocarbons. The conversion of HOAc at low temperatures has been proved by Gayubo et al. [17] to be very difficult. They found that acetone, which is produced by ketonization of HOAc

during cracking, was generated in large amounts when the temperature was above 400 °C. As the temperature was reduced to 370 °C, the conversion of EtOH clearly increased to 89.5%, and the conversion of HOAc also increased to 72.8%, but the conversions of HPO and CPO decreased slightly. The main reason for this phenomenon might be that increasing the reaction temperature leads to an increase in the molecular activities of HOAc and EtOH, but the catalytic capacity is not sufficiently high. Consequently, competition occurs among the reactants, leading to an increase in HOAc and EtOH conversions, but has little effect on the HPO and CPO conversions. At 400 °C or above, the catalytic capacity improved further, and not only were the high conversions of HPO and CPO maintained, but HOAc and EtOH were almost completely converted.

Figure 1(b) shows the conversion of the model compound mixture and EtOH at 400 °C at different reaction pressures. HPO, CPO, HOAc, and EtOH all showed conversions of 97% or more under these pressurized conditions and were almost completely converted when the pressure was increased to above 2 MPa. At atmospheric pressure, HPO was also almost completely converted, but the conversions of CPO, HOAc, and EtOH were low, 83.6%, 85.6%, and 93.1%, respectively.

3.1.2. Liquid-product selectivity

The liquid product obtained by cracking consisted of two separable layers. The upper layer was an oil phase product, and the bottom layer was a clear aqueous-phase product, as shown in Fig. 2(a). In addition, the oil phases obtained under different conditions were different colors, as shown in Fig. 2(b), indicating that the compositions of the oil phases were distinct.

Figure 3(a) shows the liquid product selectivities at 2 MPa and different temperatures. At 340 °C, although the oil phase selectivity was 33.1%, the oil phase was brown in appearance, suggesting that it contained many oxygenated byproducts. When the reaction temperature rose to 370 °C, the color of the oil phase changed to fawn. So, although the oil phase selectivity decreased to 27.6%, the actual selectivity for hydrocarbons might be higher. At 400 °C or above, the oil phase selectivity remained above 31%, and the oil phase was light yellow. Based

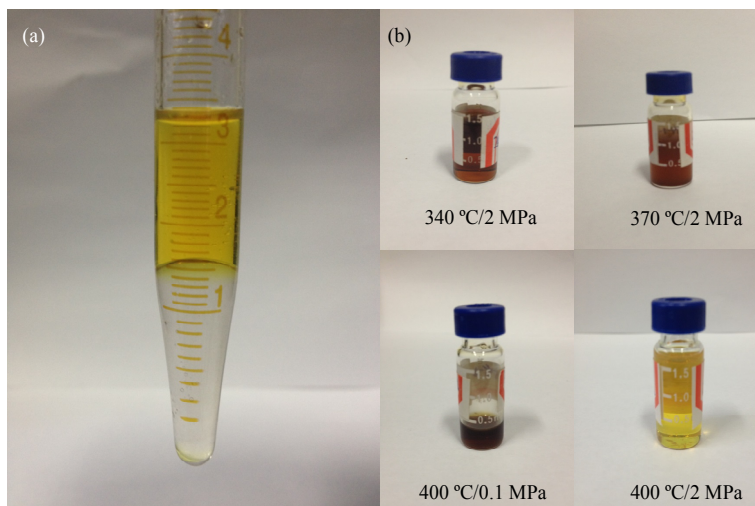


Fig. 2. (a) Photographs of liquid products showing two separable phases at 400 °C/2 MPa; (b) Oil phases obtained under different reaction conditions.

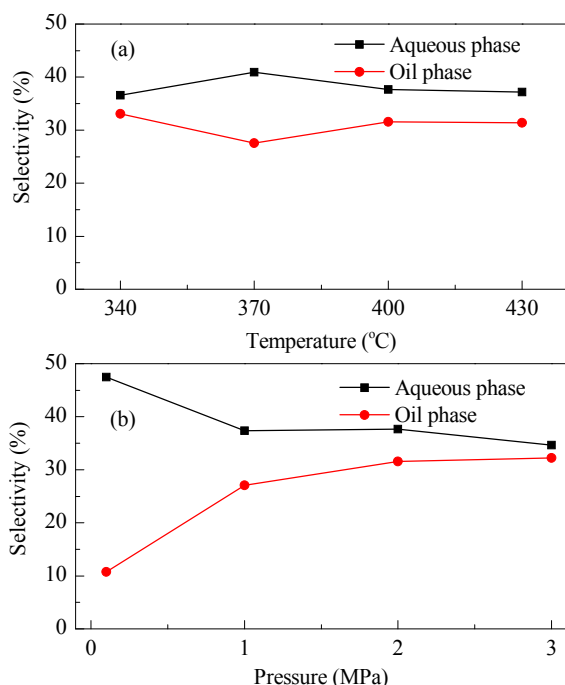


Fig. 3. Reactant selectivities under different reaction conditions: (a) 2 MPa; (b) 400 °C.

on these selectivity variations, we conclude that reaction temperatures above 400 °C are not only conducive to complete conversion of the reactants but also favor oil phase formation. A comparison of the oil phase selectivity in co-cracking of individual ketones (HPO or CPO) with alcohols, which was around 31.8% [23,24], showed that the addition of HOAc did not affect the oil phase selectivity. This showed that HOAc also has good capacity for oil phase generation. This is because HOAc is first cracked to produce acetone, followed by acetone condensation and deoxygenation to produce hydrocarbons [17].

The liquid product selectivities at 400 °C and different reaction pressures are shown in Fig. 3(b). At atmospheric pressure, the oil phase selectivity was only 10.8%, and the product was dark brown, whereas the aqueous phase selectivity was 47.5%. Under pressurized conditions, the oil phase selectivities

reached 27.1%, 31.5%, and 32.2% at 1, 2, and 3 MPa, respectively. This demonstrated that pressurized conditions could also promote oil phase formation.

3.1.3. Oil phase composition

The oil phase composition at 400 °C and 2 MPa is shown in Fig. 4. This oil phase consisted mainly of aromatic hydrocarbons with carbon numbers in the range 7–10; these are also important components of commercial gasoline. To enable a clear comparison of the compositions of the oil phases obtained under different conditions to be made, the compounds in the oil phase are classified into aromatics, aliphatics, ketones, ethers, and esters. The results are summarized in Fig. 5; “340 °C/2 MPa” refers to co-cracking of the model compound mixture and EtOH at 340 °C and 2 MPa.

Figure 5(a) shows the oil phase compositions at different temperatures. At 400 and 430 °C, the oil phase contained high contents of hydrocarbons, greater than 99%. The hydrocarbons were mainly C₇–C₁₀ aromatic hydrocarbons, including toluene, xylene, and methyl-ethyl-benzenes. When the reaction temperature was lower than 400 °C, oxygenated byproducts were generated. Under the conditions 340 °C/2 MPa, the content of oxygenated compounds in the oil phase was 40.2%, and the content of oxygenated byproducts reached 18.2% using the conditions 370 °C/2 MPa. The main oxygenated byproducts were ketones, ethers, esters, and other alcohols. The molecular structures of these oxygenated byproducts suggest that the large-molecule ketones were mainly derived from aldol condensation reactions between HPO, CPO, and acetone [23,26]. The ether content was also high, mainly produced by EtOH etherification. Esters, in particular ethyl acetate, were typical products of the esterification of HOAc and EtOH. To ensure complete deoxygenation of the model compound mixture and EtOH, a reaction temperature above 400 °C is necessary. As the reaction temperature increased, the aromatic hydrocarbon content in the oil phase also increased. This indicates that raising the reaction temperature could promote aromatization reactions; this has also been observed by other researchers [17].

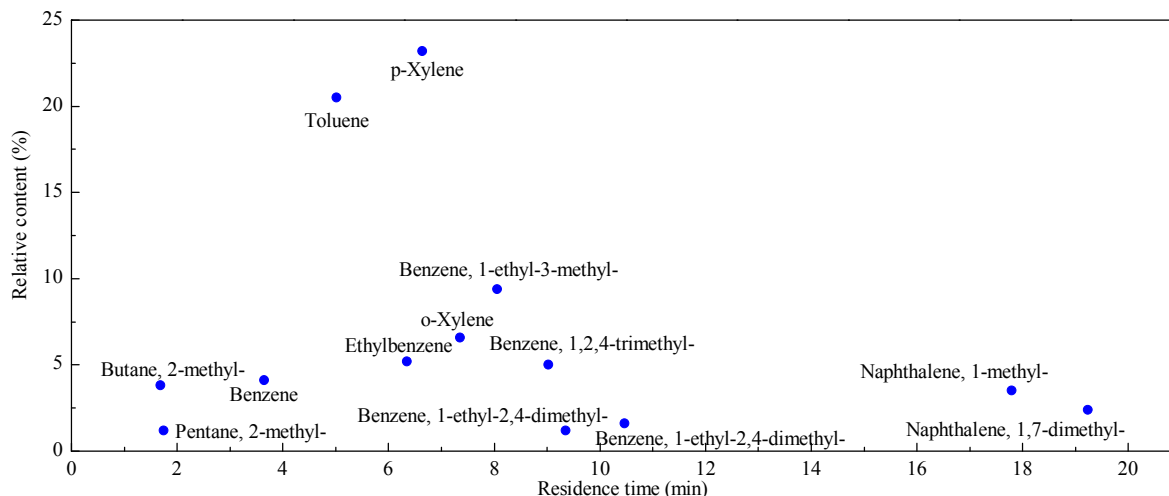


Fig. 4. Oil phase composition at 400 °C and 2 MPa.

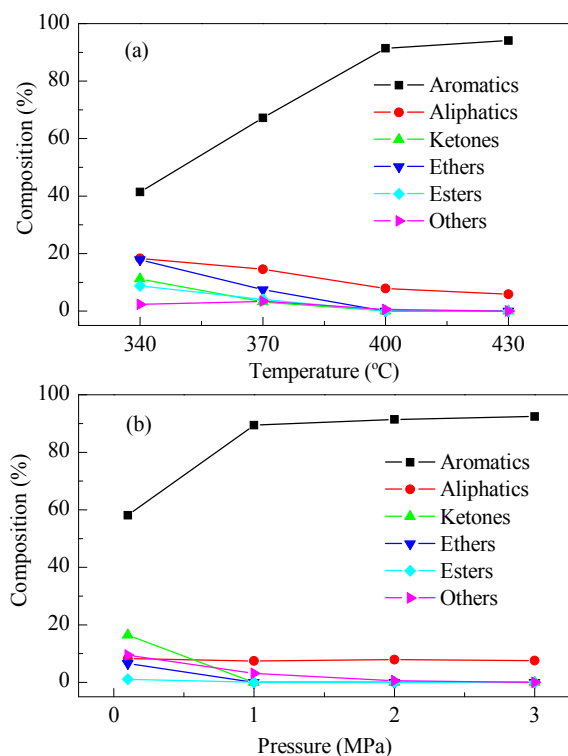


Fig. 5. Oil phase compositions under different reaction conditions: (a) 2 MPa; (b) 400 °C.

The oil phase from co-cracking of the model compound mixture and EtOH had a high content of aromatic hydrocarbons, implying that the reactants might be converted by a double-route transformation mechanism, as proposed in our previous study [23,24]. In the first direct-cracking route, HPO, CPO, and acetone from the primary cracking of HOAc undergo aldol condensation and subsequent decarbonylation, decarboxylation, and dehydration reactions to form olefins, H₂O, and CO_x, and then the olefins undergo further polymerization to form hydrocarbon products [17,26]. The second mechanism, the “hydrocarbon pool” mechanism, is associated with active intermediates such as methyl-substituted benzenes (such as toluene and xylene) [27,28]. HPO, CPO, and the intermediate acetone first undergo hydrogen transfer and molecular reforming on the zeolite acidic sites to form enol intermediates containing hydroxyl groups [25]. The enol intermediates and EtOH then react with the active intermediates and are deoxygenated, forming H₂O and olefins, which ultimately undergo aromatization to generate aromatic hydrocarbons [27,28].

The oil phase compositions at different reaction pressures are shown in Fig. 5(b). The total hydrocarbon contents in the oil phase at 400 °C/1 MPa, 400 °C/2 MPa, and 400 °C/3 MPa were above 97%, and the contents of the corresponding aromatics reached 89.5%, 91.5%, and 92.4%, respectively. However, the hydrocarbon content in the oil phase using conditions 400 °C/0.1 MPa decreased significantly, to 66.3%. Along with low oil phase selectivity, the yield of liquid hydrocarbons was very low. The influence of pressure is related to the reaction equilibrium. Light olefins such as C₂H₄ are important intermediates in bio-oil cracking [19,29]. In the aromatization reac-

tions, where light olefins are converted to liquid hydrocarbons, the total stoichiometric number of the products is smaller than that of the reactants. When the pressure increases, the reaction equilibrium therefore moves to the right, which facilitates the conversion of light olefins to liquid hydrocarbons. When the reaction pressure is increased to 2–3 MPa, as a result of limitation of the catalytic capability of the catalyst, the effect of pressure on the reaction equilibrium is not so obvious, so the hydrocarbon selectivity remains constant.

3.1.4. Vent gas composition

The vent gas compositions under different conditions are shown in Table 1. The general distribution of gaseous products shows that the vent gases generated using good reaction conditions (400 °C/2 MPa, 430 °C/2 MPa, 400 °C/1 MPa, and 400 °C/3 MPa) all had high contents of CO_x and C₃H₈. A high concentration of CO_x in the vent gas indicates extensive decarbonylation and decarboxylation reactions, which are beneficial for the removal of oxygen; C₃H₈, a saturated light hydrocarbon, might come from an aromatization reaction, in which light olefins are converted to highly unsaturated aromatics. As the reaction temperature or pressure decreased, the concentration of CO_x in the vent gas decreased, indicating that deoxygenation reactions such as decarbonylation and decarboxylation were suppressed, and more oxygenated byproducts were produced. In addition, the concentration of C₂H₄ in the vent gas increased significantly when the reaction temperature or pressure dropped, suggesting that a lower temperature or pressure suppressed aromatization reactions, and intermediate olefins were released instead of being involved in aromatization reactions to form liquid hydrocarbons. This is in good agreement with the lower oil phase selectivity at lower reaction temperature or pressure.

3.2. Characterization of spent catalysts

Catalyst stability is important in catalytic cracking processes, and the main cause of catalyst deactivation is coke formation. The spent catalysts were characterized by N₂ physical adsorption and thermogravimetric analysis. The textual properties and coke analysis of the spent catalysts are listed in Table 2.

After reaction for 3 h, the specific surface areas of the spent catalysts all decreased compared with the blank HZSM-5 catalyst, which has a high specific surface area of 340.0 m²/g. Gen-

Table 1
Vent gas compositions under different conditions (%).

Conditions	CO	CO ₂	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	C ₄ H ₈	C ₄ H ₁₀
340 °C/2 MPa	1.6	1.8	0.1	89.1	0.4	3.1	3.4	0.1	0.5
370 °C/2 MPa	4.5	5.4	0.5	69.0	2.3	5.1	11.3	0.6	1.3
400 °C/2 MPa	16.4	15.3	1.8	3.4	8.5	1.8	40.5	10.1	2.2
430 °C/2 MPa	19.7	15.2	4.1	0.2	10.5	0.2	38.4	8.2	3.5
400 °C/0.1 MPa	1.2	1.1	0.1	88.6	0.8	7.8	0.0	0.1	0.4
400 °C/1 MPa	12.7	13.3	1.9	2.9	8.0	2.4	38.4	14.4	5.9
400 °C/3 MPa	19.5	15.4	3.0	0.5	9.4	0.4	38.9	9.2	3.8

Table 2

Textural properties and coke analysis of catalyst.

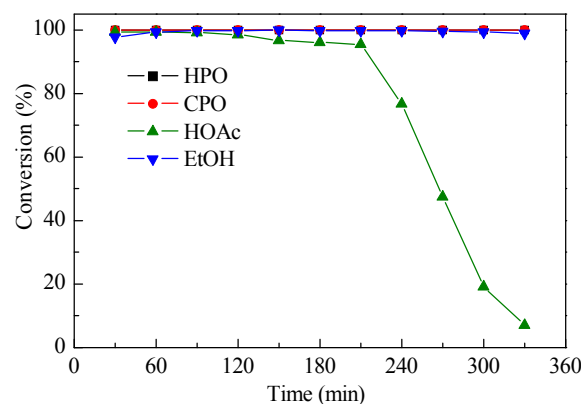
Conditions	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)	C/Cat
400 °C/2 MPa	95.5	0.11	5.42	0.15
430 °C/2 MPa	101.9	0.12	5.21	0.15
370 °C/2 MPa	75.9	0.08	5.89	0.16
340 °C/2 MPa	70.6	0.08	6.02	0.18
400 °C/3 MPa	103.0	0.14	5.32	0.14
400 °C/1 MPa	89.4	0.09	5.66	0.14
400 °C/0.1 MPa	40.9	0.07	6.38	0.18
Blank	340.0	0.26	3.09	—

erally, under conditions that gave gasoline phases of higher selectivity and quality, the corresponding catalyst specific surface areas were higher. For example, the specific surface of the catalyst from 400 °C/2 MPa was 95.5 m^2/g , whereas those from 340 °C/2 MPa and 400 °C/0.1 MPa were 70.6 and 40.9 m^2/g , respectively, showing that the catalytic activity was better maintained under the conditions 400 °C/2 MPa. The coke:catalyst ratio (C/Cat), calculated based on the thermogravimetric analysis, showed the same tendency. The C/Cat was 0.15 for the conditions 400 °C/2 MPa, but those for 340 °C/2 MPa and 400 °C/0.1 MPa both reached 0.18.

In our previous study of co-cracking of HPO and EtOH, the spent catalysts after reaction for 3 h were characterized, and the catalyst from co-cracking of 30% HPO and 70% EtOH under the conditions 400 °C/2 MPa had a specific surface area of 129.3 m^2/g and a C/Cat of 0.12. Compared with these results, the catalyst from co-cracking of the model compound mixture and EtOH had a lower specific surface area but a higher C/Cat, indicating that the decrease in the catalytic activity was more severe. The model compound mixture has only a small proportion of CPO, which might have a similar cracking performance to that of HPO, because they both have carbonyl groups, therefore it can be concluded that the more obvious deactivation tendency was the result of the presence of HOAc. As mentioned above, the $(\text{H}/\text{C})_{\text{eff}}$ values of HOAc, HPO, and CPO are 0, 0.67, and 1.2, respectively. Cracking of HOAc, which has a low $(\text{H}/\text{C})_{\text{eff}}$, would therefore favor production of compounds with low $(\text{H}/\text{C})_{\text{eff}}$ values, such as coke. In the study carried out by Mentzel et al. [14], in which 10% HOAc and 10% acetone, respectively, were cocracked with methanol the catalyst conversion capacities during co-cracking of acetone and methanol were found to be much higher than that of HOAc, indicating that the catalyst lifetime was longer for the co-cracking of acetone and methanol. Coking and catalyst deactivation were therefore higher for cracking of the model compound mixture containing HOAc than those for cracking of individual ketones.

3.3. Catalyst stability tests

The catalyst characterization described in Section 3.2 showed that the specific surface area of the catalyst decreased after reaction for 3 h, and some coke formed on the catalyst surface, indicating that the catalytic activity decreased during cracking. The catalyst stability was therefore tested under the conditions 400 °C/2 MPa.

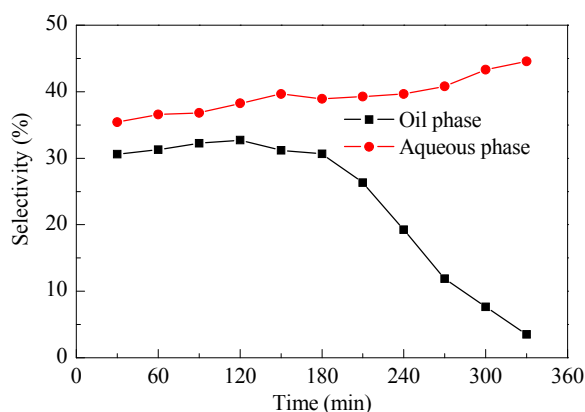
**Fig. 6.** Reactant conversion as a function of time on stream at 400 °C/2 MPa.

3.3.1. Reactant conversion

The changes in reactant conversion as a function of time on stream are presented in Fig. 6. Before 240 min, the four reactants, i.e., HPO, HOAc, CPO, and EtOH, were all converted almost completely. As the reaction continued, the conversion of HOAc began to decrease, from 76.7% at 240 min to 7.2% at 330 min, but the conversions of the other three reactants were still close to 100%. This showed that the decrease in the catalytic activity had a stronger effect on the primary conversion of HOAc than on those of the other reactants, which led to decreased conversion.

3.3.2. Liquid product selectivity

Figure 7 shows the changes in liquid product selectivity as a function of time on stream. In the primary stage of cracking, the oil phase selectivity remained at about 31%. It started to drop at 210 min and reached 3.5% at 330 min. Compared with the changes in reactant conversion, in which only the HOAc conversion decreased, the decrease in oil phase selectivity occurred earlier, and the changes were greater, showing that the decrease in the catalytic activity had a greater effect on the formation of oil phase products. The main components in the oil phase, i.e., aromatic hydrocarbons, were generated by aromatization, so it can be concluded that the aromatization ca-

**Fig. 7.** Liquid product selectivity as a function of time on stream at 400 °C/2 MPa.

capacity of the catalyst was first affected when catalyst deactivation started, and the primary conversion capacity of the reactants was affected to a lesser extent. Unlike the case for the oil phase, the aqueous phase selectivity continued to increase slightly even when the catalyst was deactivated; this also indicated that the primary conversion of reactants involving dehydration was not significantly affected.

3.3.3. Oil phase composition

The changes in the oil phase composition as a function of time on stream are shown in Fig. 8. Prior to 180 min, the oil phase had a stable composition consisting of about 90% aromatic hydrocarbons, 9% aliphatic hydrocarbons, and few oxygenated byproducts. As the reaction continued, accompanied by catalyst deactivation, the aromatic hydrocarbon content decreased, and the aliphatic hydrocarbon and oxygenated by-product contents both increased. At a reaction time of 330 min, the aromatic hydrocarbon content was only 50%, and the contents of aliphatic hydrocarbons and oxygenated byproducts reached 31.6% and 18.4%, respectively. The decrease in the aromatic hydrocarbon content reflected the lower aromatization capacity of the catalyst, and the production of larger amounts of oxygenated byproducts, mainly alcohols and ketones, showed a reduction in the deoxygenation efficiency.

3.3.4. Vent gas composition

The changes in vent gas composition as a function of time on stream are shown in Fig. 9. In general, the concentrations of the gaseous products except C_2H_4 all decreased. In the primary cracking period, the main gaseous products were C_3H_8 , CO, and CO_2 , with concentrations of about 40%, 16%, and 15%, respectively. As the catalytic activity decreased, the concentrations decreased to 33.6%, 13.9%, and 12.3% at 210 min. The concentration of C_2H_4 increased greatly, from 3% to 17.9%, at this time. The discussion of the oil phase selectivity in section 3.3.2 showed that the decrease in the oil phase selectivity also began at 210 min, further proving that this decrease was a result of the weaker aromatization capacity of the catalyst, and the intermediate C_2H_4 was released instead of participating in the subsequent aromatization reaction. When the reaction time

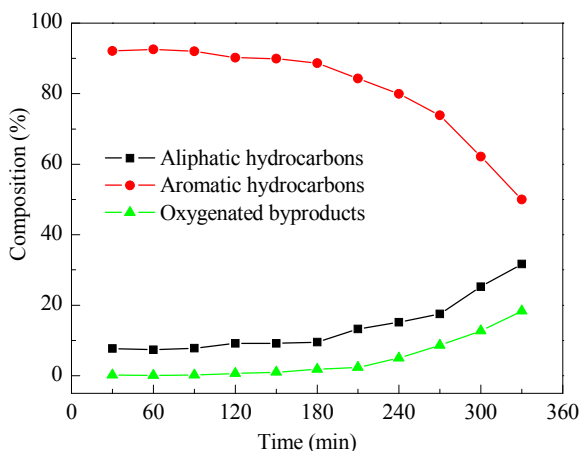


Fig. 8. Oil phase composition as a function of time on stream at 400 °C/2 MPa.

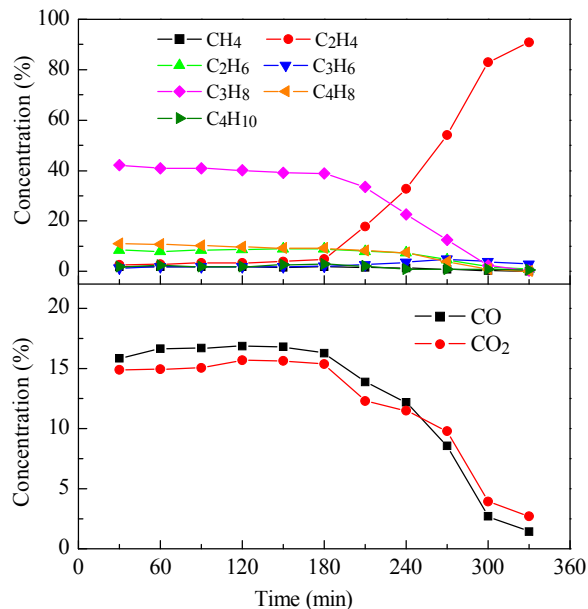


Fig. 9. Vent gas composition as a function of time on stream at 400 °C/2 MPa. (a) Light hydrocarbons; (b) CO_x .

was 330 min, the concentrations of C_3H_8 , CO, and CO_2 declined to 1.9%, 2.4%, and 2.7%, respectively; the concentrations of other gaseous products were lower than 1%, whereas the concentration of C_2H_4 was 90.8%. This indicated the low extent of the aromatization reaction, in good agreement with the very low oil phase selectivity of 3.5% at this point.

3.4. Catalyst regeneration

In the catalyst stability tests, the catalytic activity was found to decrease as the reaction proceeded. Catalyst deactivation was mainly caused by coke formation on the catalyst surface, which would cover the active sites and block the inner pores. The spent catalyst after reaction for 4 h under the conditions 400 °C/2 MPa was regenerated by burning the coke, and the extent of recovery of the catalytic activity was studied. The regeneration temperature was 550 °C based on the study by Valle et al. [18], and the catalyst was regenerated four times.

3.4.1. Reactant conversion

The changes in reactant conversions before and after catalyst regeneration are shown in Fig. 10. During the reaction stage using the fresh catalyst, the conversions of HPO, CPO, and EtOH were close to 100%, but the conversion of HOAc declined to 76.7% at 240 min. After the first regeneration of the catalyst, the conversion of HOAc returned to above 99%, and the conversions of the other three reactants remained above 99%. Similarly, in the subsequent continuous reaction, the regenerated catalysts all achieved good recovery of catalytic activity.

3.4.2. Liquid product selectivity

The changes in liquid product selectivities before and after catalyst regeneration are shown in Fig. 11. Before the first re-

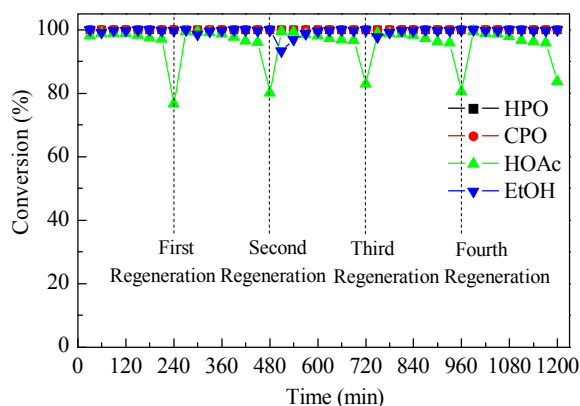


Fig. 10. Reactant conversions before and after catalyst regeneration at 400 °C/2 MPa.

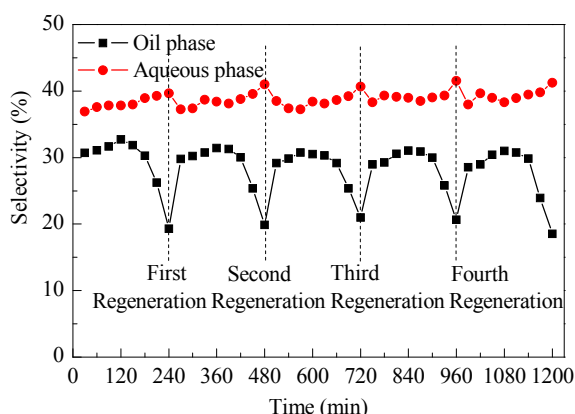


Fig. 11. Liquid-product selectivity before and after catalyst regeneration at 400 °C/2 MPa.

generation, the oil phase selectivity dropped from about 31% at the primary stage to only 19.3%. After catalyst regeneration, the oil phase selectivity was again above 30%. In the subsequent continuous reaction, the catalytic activity recovered well in the regeneration steps and maintained steady generation of the oil phase. In general, the catalyst regeneration extended the catalyst lifetime.

3.4.3. Oil phase composition

Figure 12 shows the changes in the oil phase composition before and after catalyst regeneration. Compared with those in the primary stage, the content of aromatic hydrocarbons declined from 92.0% to 79.1% at 240 min, and the contents of aliphatic hydrocarbons and oxygenated byproducts rose to 15.2% and 5.7%, respectively. After catalyst regeneration, the content of aromatic hydrocarbons returned to above 90%, indicating that the aromatization capacity of the catalyst was well recovered by regeneration.

3.4.4. Vent gas composition

The catalyst stability tests showed that the concentrations of CO, CO₂, C₂H₄, and C₃H₈ changed significantly when the catalyst was deactivated. The concentrations of these four gaseous products before and after catalyst regeneration were therefore monitored; the results are shown in Fig. 13. When the catalyst

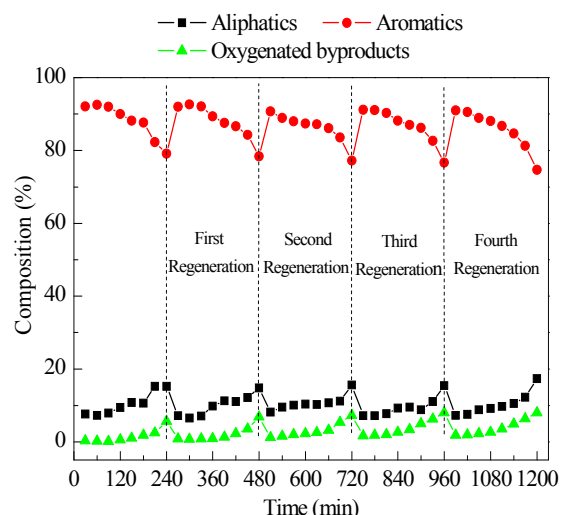


Fig. 12. Oil phase composition before and after catalyst regeneration at 400 °C/2 MPa.

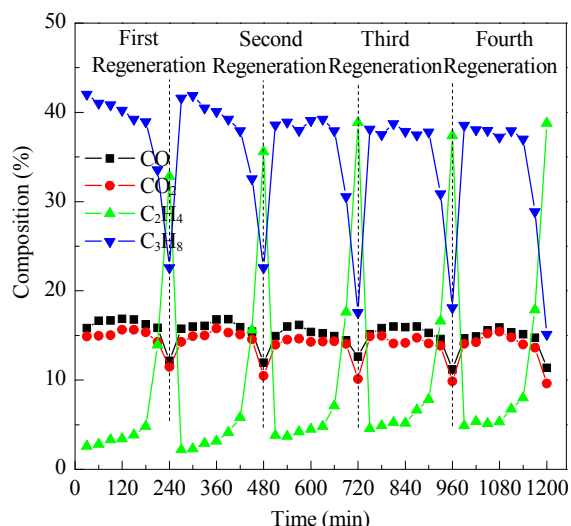


Fig. 13. Vent gas composition before and after catalyst regeneration at 400 °C/2 MPa.

was deactivated, the concentrations of CO and CO₂ decreased, and the concentration of C₃H₈ decreased greatly from 43% to 22.6%, whereas the concentration of C₂H₄ increased significantly from 2.6% to 32.6%. After regeneration, the concentration of C₂H₄ was below 5% again, suggesting good recovery of the aromatization capacity, which favored conversion of the intermediate C₂H₄ to liquid hydrocarbons.

4. Conclusions

The co-cracking performance of mixtures of bio-oil model compounds (HPO, CPO, and HOAc) with EtOH was investigated in a fixed-bed reactor. Higher temperatures and pressures promote conversion of the reactants and generation of liquid hydrocarbons. The optimum reaction conditions were found to be 400 °C and 2 MPa. Under these conditions, acids and ketones were converted completely, and the oil phase selectivity reached 31.5 wt%. This oil phase had a high hydrocarbon con-

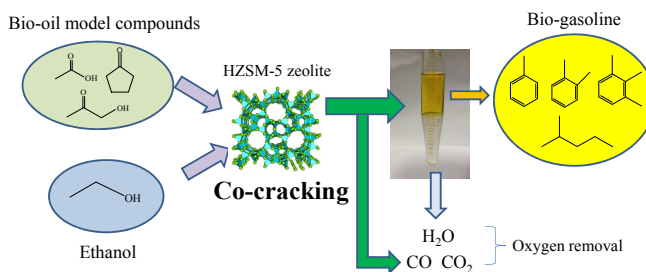
Graphical Abstract

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Biogasoline production by co-cracking of model compound mixture of bio-oil and ethanol over HZSM-5

Shurong Wang*, Qinjie Cai, Xiangyu Wang, Li Zhang,
Yurong Wang, Zhongyang Luo
Zhejiang University

Co-cracking with ethanol using an HZSM-5 catalyst is an efficient method for converting a bio-oil model compound mixture to hydrocarbon fuels.



tent, greater than 99%, and mainly contained C₇–C₉ aromatic hydrocarbons such as toluene, xylene, and methyl- and ethyl-substituted benzenes. Characterization of the spent catalysts showed that the specific surface area decreased after cracking, and some coke formed on the catalyst surface. Stability tests also showed that the catalyst was deactivated after 330 min. The catalyst was regenerated by burning the coke and the regeneration achieved good recovery of the catalyst. Because the bio-oil distilled fraction was rich in small-molecule ketones and acids, the successful conversion of ketones and acids to hydrocarbons proves that the co-cracking of actual bio-oil distilled fractions and EtOH is feasible.

References

- [1] Demirbas A. *Prog Energy Combust Sci*, 2007, 33: 1
- [2] Gu H Y, Zhang K, Wang Y D, Huang Y, Hewitt N, Roskilly A P. *J Energy Chem*, 2013, 22: 413
- [3] Li Q Y, Ji S F, Hu J Y, Jiang S. *Chin J Catal*, 2013, 34: 1462
- [4] Ozbay N, Apaydin-Varol E, Burcu Uzun B, Eren Putun A. *Energy*, 2008, 33: 1233
- [5] Tan S, Zhang Z J, Sun J P, Wang Q W. *Chin J Catal*, 2013, 34: 641
- [6] Wang C, Hao Q L, Lu D Q, Jia Q Z, Li G J, Xu B. *Chin J Catal*, 2008, 29: 907
- [7] Czernik S, Bridgwater A V. *Energy Fuels*, 2004, 18: 590
- [8] Zhang Q, Chang J, Wang T J, Xu Y. *Energy Convers Manage*, 2007, 48: 87
- [9] Gong F Y, Yang Z, Hong C G, Huang W W, Ning S, Zhang Z X, Xu Y, Li Q X. *Bioresource Technol*, 2011, 102: 9247
- [10] Graça I, Lopes J M, Cerqueira H S, Ribeiro M F. *Ind Eng Chem Res*, 2013, 52: 275
- [11] Adjaye J D, Katikaneni S P R, Bakhshi N N. *Fuel Process Technol*, 1996, 48: 115
- [12] Wang W Y, Zhang X Z, Yang Y Q. *Chin J Catal*, 2012, 33: 215
- [13] Guo Z G, Wang S R, Xu G H, Cai Q J. *BioResources*, 2011, 6: 2539
- [14] Mentzel U V, Holm M S. *Appl Catal A*, 2011, 396: 59
- [15] Vitolo S, Seggiani M, Frediani P, Ambrosini G, Politi L. *Fuel*, 1999, 78: 1147
- [16] Gayubo A G, Aguayo A T, Atutxa A, Aguado R, Bilbao J. *Ind Eng Chem Res*, 2004, 43: 2610
- [17] Gayubo A G, Aguayo A T, Atutxa A, Aguado R, Olazar M, Bilbao J. *Ind Eng Chem Res*, 2004, 43: 2619
- [18] Valle B, Gayubo A G, Aguayo A T, Olazar M, Bilbao J. *Energy Fuels*, 2010, 24: 2060
- [19] Guo Z G, Wang S R, Gu Y L, Xu G H, Li X, Luo Z Y. *Sep Purif Technol*, 2010, 76: 52
- [20] Wang S R, Gu Y L, Liu Q, Yan Y, Guo Z G, Luo Z Y, Cen K F. *Fuel Process Technol*, 2009, 90: 738
- [21] Guo X J, Wang S R, Guo Z G, Liu Q, Luo Z Y, Cen K F. *Appl Energy*, 2010, 87: 2892
- [22] Mortensen P M, Grunwaldt J D, Jensen P A, Knudsen K G, Jensen A D. *Appl Catal A*, 2011, 407: 1
- [23] Wang S R, Cai Q J, Wang X Y, Guo Z G, Luo Z Y. *Fuel Process Technol*, 2013, 111: 86
- [24] Wang S R, Cai Q J, Guo Z G, Wang Y R, Wang X Y. *BioResources*, 2012, 7: 5019
- [25] Huang J, Long W, Agrawal P K, Jones C W. *J Phys Chem C*, 2009, 113: 16702
- [26] Cruz-Cabeza A J, Esquivel D, Jimenez-Sanchidrian C, Romero-Salguero F J. *Materials*, 2012, 5: 121
- [27] Haw J F, Song W G, Marcus D M, Nicholas J B. *Acc Chem Res*, 2003, 36: 317
- [28] Olsbye U, Bjorgen M, Svelle S, Lillerud K P, Kolboe S. *Catal Today*, 2005, 106: 108
- [29] Adjaye J D, Bakhshi N N. *Biomass Bioenergy*, 1995, 8: 131