



# Biogasoline Production from the Co-cracking of the Distilled Fraction of Bio-oil and Ethanol

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

State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, People's Republic of China

**ABSTRACT:** In view of the severe coke formation and catalyst deactivation during crude bio-oil cracking, an innovative cracking technology based on bio-oil molecular distillation is proposed. The distilled fraction (DF) from bio-oil molecular distillation is enriched with small molecular acids and ketones and has enhanced cracking behavior compared to crude bio-oil. The influence of the reaction temperature, pressure, and the DF/ethanol ratio in the feed was studied. It was found that co-cracking of the DF and ethanol produced a well-defined gasoline phase, and both increasing the reaction temperature and adopting pressurized cracking benefited the yield and quality of this gasoline phase. Using optimum reaction temperature and pressure, co-cracking of the DF and ethanol, with different weight ratios, all generated high-quality gasoline phases. Under 400 °C and 2 MPa, co-cracking of DF and ethanol with a weight ratio of 2:3 produced a high gasoline phase yield of 25.9 wt %; the hydrocarbon content in this gasoline phase was 98.3%.

## 1. INTRODUCTION

Bio-oil, which is produced by the fast pyrolysis of biomass, has the potential to substitute for traditional transport fuels. However, crude bio-oil cannot be directly used as a high-grade liquid fuel because of several inferior characteristics, such as high viscosity, high oxygen and water contents, low heating value, and low pH value.<sup>1,2</sup> Therefore, it is necessary to improve the quality of bio-oil.

Different bio-oil upgrading techniques have been developed, including hydrodeoxygenation, catalytic cracking, esterification, emulsification, and steam reforming.<sup>3</sup> Catalytic cracking is often adopted to reduce the oxygen content in bio-oil using zeolite catalysts. The HZSM-5 zeolite has been proven to be an effective catalyst for cracking, because it has sufficient Brønsted acid sites. These active sites can catalyze deoxygenation reactions, such as dehydration, decarbonylation, and decarboxylation, which can remove the oxygen in bio-oil in the form of CO, CO<sub>2</sub>, and H<sub>2</sub>O. In addition, the aromatization reaction also takes place on Brønsted acid sites, and the special pore structure in HZSM-5 also benefits the formation of aromatic hydrocarbons.<sup>4,5</sup> After catalytic cracking, the upgraded bio-oil becomes richer in hydrocarbons. However, the composition of crude bio-oil is very complicated because it includes acids, ketones, alcohols, aldehydes, phenols, esters, sugars, etc.<sup>6,7</sup> Different compounds in bio-oil have distinct cracking reactivity; therefore, it is difficult to crack bio-oil directly. A previous study showed that the direct cracking of crude bio-oil produced high coke deposition (up to 20 wt %), and the operation had to be terminated after 30 min.<sup>8,9</sup> Alcohol, ketones, and acids were found to have good cracking performance, while phenols showed low reactivity.<sup>10,11</sup> In addition, non-volatile and low-reactivity oligomers in bio-oil (such as sugars and pyrolytic lignin) can easily form coke during the cracking. This deactivates the catalysts and eventually leads to the blockage of the reactor.<sup>12,13</sup> Therefore, proper bio-oil separation pretreatment to enrich those components suitable for cracking is important to ensure the stability of the cracking process.<sup>14</sup>

Current bio-oil separation methods include column chromatography, solvent extraction, and distillation. Bio-oil separation by column chromatography is based on the different adsorption capabilities of components on a stationary phase. For column chromatography, aliphatic compounds, aromatic compounds, and some other polar compounds can be obtained using different eluents. However, these fractions show no outstanding cracking characteristics.<sup>15,16</sup> For solvent extraction, the principle is similarity and intermiscibility; therefore, it will also achieve the enrichment of compounds with similar polarity rather than those suitable for cracking.<sup>6,17</sup> Conventional distillation can be used to separate components according to their evaporation characteristics. However, because there are a lot of high boiling point and thermosensitive compounds in bio-oil, the separation efficiency is low and the residual fraction is easily coked. In a study of conventional bio-oil distillation, the boiling of bio-oil started below 100 °C and stopped at 250–280 °C, leaving a residue formed from polymerization with the yield of 35–50%.<sup>1</sup>

Molecular distillation is a special liquid–liquid separation technology based on the difference of mean free path for various substances. This technology can achieve high separation efficiency at a low temperature; therefore, it is very suitable for the separation of thermosensitive compounds in bio-oil. In our previous study of bio-oil molecular distillation, different operating temperatures (70, 100, and 130 °C) were used at an operating pressure of 60 Pa.<sup>18</sup> The highest yield of the distilled fraction (DF) reached 85.5 wt %, enriched with small molecular acids and ketones. No obvious coking was observed in the residual fraction, even at 130 °C, and almost all of the large-molecular-weight sugars and phenols (pyrolytic lignin) in

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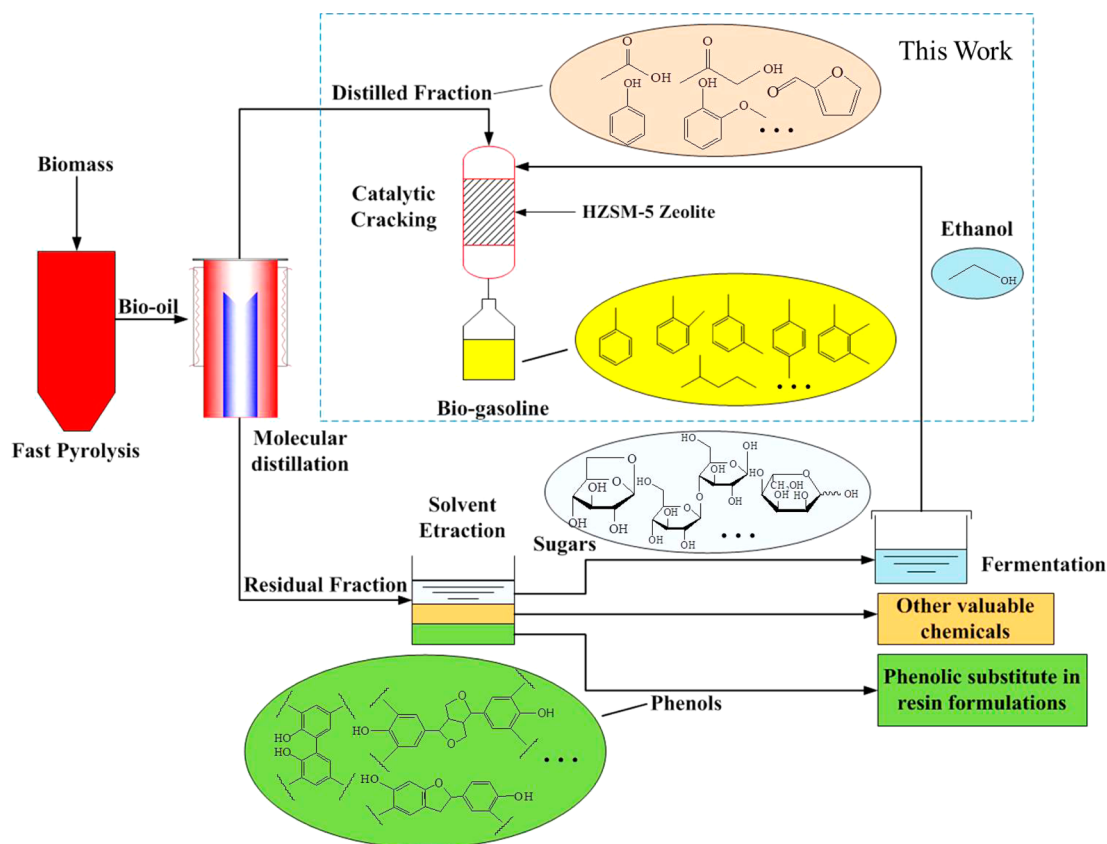


Figure 1. Bio-oil-graded upgrading route based on molecular distillation.

the crude bio-oil were enriched in this fraction. In addition, multiple molecular distillations were also performed to investigate the different separation characteristics of various compounds in bio-oil.<sup>19</sup> On the basis of this high-efficiency separation technology, an innovative bio-oil-graded upgrading route is proposed, as shown in Figure 1. First, bio-oil is separated into a DF and a residual fraction by molecular distillation. The DF has a high proportion of small-molecular-weight acids and ketones with good volatility and high reactivity; therefore, this fraction has better cracking behavior than crude bio-oil and can be co-cracked with ethanol for biogasoline production. The large molecular sugars and phenols rich in the residual fraction can be more easily separated by solvents than crude bio-oil, because phenols and sugars have distinct polarities. Sugars can be fermented to produce ethanol, which could be used as the co-reactant in the cracking process. The phenols obtained in this way can be used as phenolic substitutes in resin formulation or can be further processed for the production of aromatics. This bio-oil-graded upgrading route produces high-quality biogasoline as well as other valuable chemicals, which provides a complete utilization of bio-oil.

Although the DF has better cracking characteristics than crude bio-oil, some coke will still be formed if it is cracked directly. The main reason for this is that the ketones and acids in the DF have a high oxygen content and high degree of unsaturation. This indicates that, if a certain amount of oxygen is removed in the form of water, the hydrogen/carbon ratio of the final products will appear very low, allowing for the easy production of coke. In view of this phenomenon, the concept of an effective hydrogen/carbon ratio  $[(H/C)_{\text{eff}}]$  was introduced

to evaluate the cracking characteristics of different compounds, as shown in eq 1. The symbols  $H$ ,  $O$ , and  $C$  here represent the mole percentages of hydrogen, oxygen, and carbon present in a given compound.<sup>4,20</sup>

$$(H/C)_{\text{eff}} = \frac{H - 2O}{C} \quad (1)$$

A test of bio-oil model compounds showed that catalysts were more easily deactivated during the cracking of compounds with low  $(H/C)_{\text{eff}}$ .<sup>20</sup> The main components in the DF, such as hydroxypropanone and acetic acid, also have low  $(H/C)_{\text{eff}}$  (0.67 for hydroxypropanone and 0 for acetic acid), which is disadvantageous to the stability of the cracking process. Therefore, choosing some compounds with high cracking reactivity and relatively high  $(H/C)_{\text{eff}}$  as the co-cracking reactants can increase the feed  $(H/C)_{\text{eff}}$ , which might be an effective way to improve the cracking stability. Aliphatic alcohols have been proven to be effective co-cracking reactants, because of their high  $(H/C)_{\text{eff}}$  value of 2. Mentzel et al. studied the co-cracking of bio-oil model compounds and methanol and found that the conversion capacity of the catalyst was up to 10 times higher when the bio-oil model compound was diluted in methanol.<sup>20</sup> Valle et al. investigated the co-cracking performance of thermal-treated bio-oil and methanol and achieved a high conversion of reactants up to 90%, with a selectivity of aromatics of 40%.<sup>13</sup> Our previous cracking study of ketones in bio-oil under a HZSM-5 catalyst also showed that the addition of alcohols could promote the conversion of ketones and suppress the deactivation of catalysts. Meanwhile, in comparison to co-cracking of hydroxypropanone and methanol, co-cracking of hydroxypropanone and ethanol was found to

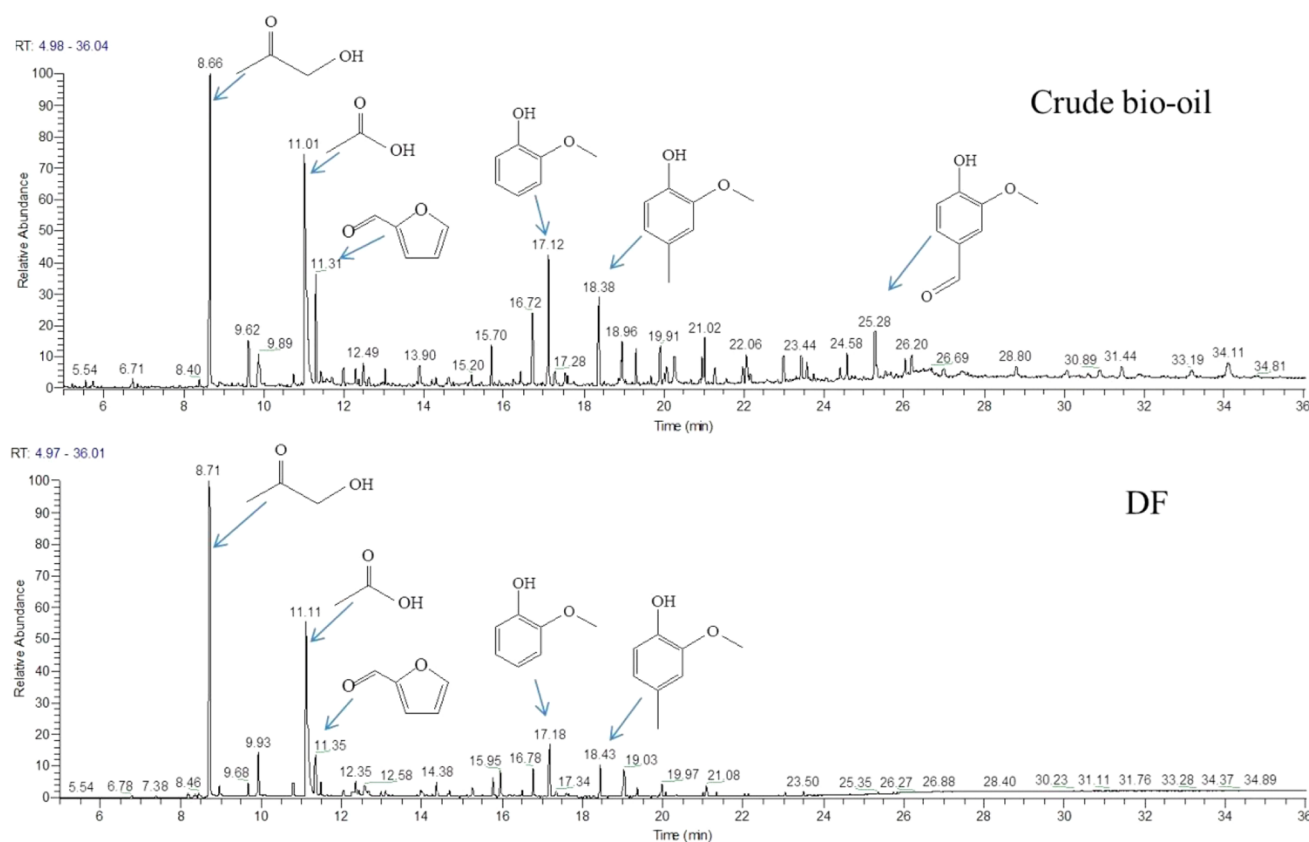


Figure 2. GC–MS total ion chromatograms of crude bio-oil and DF.

generate much more gasoline phase.<sup>21,22</sup> Therefore, a series of experiments was carried out to investigate the co-cracking behavior of the molecular DF from bio-oil with ethanol for biogasoline production.

## 2. EXPERIMENTAL SECTION

**2.1. Bio-oil Molecular Distillation.** Crude bio-oil is produced from rice husk fast pyrolysis, and the ultimate analysis shows that it consisted of 51.4 wt % carbon, 6.7 wt % hydrogen, and 41.9 wt % oxygen. Molecular distillation of crude bio-oil was carried out on a KDL-5 apparatus under a temperature of 90 °C and an absolute pressure of 1000 Pa. This KDL-5 facility, together with the corresponding operation procedure, was discussed in our previous work.<sup>18,19</sup> Using this condition, the yield of crude-distilled fraction (CDF) was 54.6 wt %, with a water content of 57.9 wt %, and the yield of the residual fraction was 45.4 wt %, with a water content of only 4.8 wt %. After molecular distillation, the CDF was further processed by vacuum distillation, using an operating temperature as low as 40 °C to remove the water as much as possible. The processed DF for the subsequent cracking has a low water content of 20.7 wt %.

**2.2. Co-cracking of the DF and Ethanol.** The ethanol used for co-cracking was purchased from Sinopharm Chemical Reagent Co. The HZSM-5 catalyst (Si/Al = 25, purchased from the Catalyst Plant of Nankai University), was calcined in air at 550 °C for 6 h and then sieved to 40–60 mesh.

Catalytic experiments were carried out in a fixed-bed reactor. The reactor was a stainless-steel tube with an inner diameter of 8 mm. About 2 g of catalyst was supported on quartz wool in the reactor. The mixtures of DF and ethanol were introduced by a high-performance liquid chromatography (HPLC) pump. The outlet gas from the reactor passed through a condenser and was separated into liquid products and noncondensable gases. The reaction pressure was regulated by a back-pressure valve using the carrier gas nitrogen at a flow rate of 30 mL/min. The weight hourly space velocity (WHSV) of the reactants was kept at 3 h<sup>−1</sup>. The reaction temperature and pressure

were set within the range of 340–430 °C and 0.1–3 MPa, respectively. The DF/ethanol ratios were 1:4, 1:3, 1:2, and 2:3. The cracking of pure ethanol was also studied.

Most liquid products produced from the cracking consisted of an easily separable crude gasoline phase and an aqueous phase. The yields of the gasoline phase, aqueous phase, and total liquid are defined by eqs 2–4. The symbol “*m*” in these equations represents the mass of the corresponding substance, excluding the water in the DF feed.

$$Y_{\text{gasoline phase}} = \frac{(m_{\text{gasoline phase}})_{\text{collected}}}{(m_{\text{reactants}})_{\text{in}}} \times 100\% \quad (2)$$

$$Y_{\text{aqueous phase}} = \frac{(m_{\text{aqueous phase}})_{\text{collected}}}{(m_{\text{reactants}})_{\text{in}}} \times 100\% \quad (3)$$

$$Y_{\text{total liquid}} = Y_{\text{gasoline phase}} + Y_{\text{aqueous phase}} \quad (4)$$

**2.3. Gas Chromatography (GC) and Gas Chromatography–Mass Spectrometry (GC–MS) Analysis.** The composition of the crude bio-oil, the DF, and the gasoline phase was analyzed by a GC–MS system (Trace DSQ 2) with a 30 m × 0.25 mm × 0.25 μm Agilent DB-WAX capillary column. The GC oven temperature was kept at 40 °C for 1 min and then increased to 240 °C at a ramp rate of 8 °C/min. Data were acquired with Xcalibur software using the National Institute of Standards and Technology (NIST) mass spectral library database. Identified compounds were further quantified by the area normalization method.

The gaseous products were quantified by online GC (Agilent 7890A). Light alkanes and olefins were separated on a HP-Plot Q capillary column with a flame ionization detector (FID). CO and CO<sub>2</sub> were separated on Porapak N, Porapak Q, and Carbon Sieve-11 columns and detected by a thermal conductivity detector (TCD). The GC oven temperature was kept at 50 °C for 1 min and then increased to 180 °C at a ramp rate of 10 °C/min.



### 3. RESULTS AND DISCUSSION

**3.1. Composition of Crude Bio-oil and the DF.** The DF from the molecular distillation was brown in appearance with good fluidity, while the residual fraction was very viscous. The total ion chromatograms of the crude bio-oil and DF are shown in Figure 2. The two obvious peaks in the chromatogram of the DF correspond to hydroxypropanone (retention time of 8.71 min) and acetic acid (retention time of 11.11 min). It was observed that many more components were detected in the crude bio-oil. In particular, more compounds were continually detected in the crude bio-oil at retention times beyond 24 min, while no obvious peaks with these retention times were found for the DF, indicating that there were no compounds with high boiling points in this fraction.

According to the relative contents of different compounds, as quantified by GC-MS analysis, the components in the crude bio-oil and the DF were classified into different chemical families. The major chemical families in the DF were ketones and acids, amounting to 48.6 and 27.5%, respectively. Hydroxypropanone and acetic acid were two typical components in the DF with reactive functional groups (hydroxyl, carbonyl, and carboxyl groups). Compounds with these functional groups can be effectively deoxygenated and converted into aromatic hydrocarbons during cracking, while phenols were found to have low reactivity.<sup>10,11</sup> The content of phenols in the DF was only 14.8%, and most phenols were of the single-ring type, such as guaiacol and phenol, which can be converted into aromatic hydrocarbons by reactions, such as the removal of the phenol hydroxyl and demethoxylation.

The crude bio-oil not only had a higher phenol content of 34.5% but also contained some monosaccharide derivatives, such as levoglucosan. In addition, there are also some compounds in bio-oil that could not be detected by GC-MS because of their rather high boiling points, such as sugars and phenolic oligomers. These non-volatile compounds also have various oxygenated chemical bonds, which make conversion to hydrocarbons very difficult, and they are usually responsible for the coke formation during the cracking. Mohan et al. concluded that only about 40% of components in bio-oil could be detected by GC, and the remaining sugars and pyrolytic lignin were difficult to detect with only GC.<sup>2</sup> Vispute et al. also pointed out that only one-third of the carbon content in the bio-oil quantified by elemental analysis could be identified by GC and HPLC measurements, which also implies the presence of amounts of large-molecular-weight sugars and pyrolytic lignin.<sup>23</sup> Figure 2 shows that the DF had very few high-boiling-point compounds and, in combination with the high viscosity of the residual fraction, it could be inferred that the sugars and pyrolytic lignin in the crude bio-oil were enriched in the residual fraction after molecular distillation. Thus, in comparison to the crude bio-oil, the DF did not contain large-molecular-weight sugars and pyrolytic lignin; therefore, it had better volatility and catalytic cracking behavior.

**3.2. Co-cracking of the DF and Ethanol.** **3.2.1. Liquid Product Distribution.** On the basis of our previous study of the co-cracking of bio-oil model compounds and alcohols, the ratio of DF/ethanol was first set as 1:2 to investigate the influence of the reaction temperature and pressure on the distribution of products. Subsequently, the effect of the DF/ethanol ratio was also studied.

As shown in Table 1, the total liquid yield reached 78.2 wt % when the reaction temperature was 340 °C. However, no

**Table 1. Liquid Products Distribution under Different Conditions**

temperature (°C)	pressure (MPa)	DF/ethanol	liquid yield (wt %)		
			gasoline phase	aqueous phase	total
340	2	1:2			78.2
370	2	1:2	18.5	53.3	71.8
400	2	1:2	27.7	35.8	63.5
430	2	1:2	26.6	33.1	59.7
400	0.1	1:2	5.5	50.6	56.1
400	1	1:2	24.2	41.2	65.4
400	3	1:2	27.8	33.1	60.9
400	2	0:1	29.9	38.8	68.7
400	2	1:4	27.8	42.6	70.4
400	2	1:3	26.8	39.4	66.2
400	2	2:3	25.9	44.3	70.2

obvious separation between the gasoline and aqueous phases was observed. As the reaction temperature increased, the liquid product appeared as two clearly separated layers. The upper layer was a light-yellow gasoline phase product, while the bottom layer was a transparent aqueous phase product, indicating that high temperature benefited the conversion of reactants to hydrocarbons. When the reaction temperature increased from 370 to 400 °C, the yield of the gasoline phase rose from 18.5 to 27.7 wt %. Further increasing the reaction temperature has little effect on the gasoline phase yield, which was 26.6 wt % at 430 °C.

Although the liquid products produced at different pressures all consisted of two separable layers, only 5.5 wt % yield of the gasoline phase was obtained under atmospheric pressure. Pressures above 1 MPa were found to benefit the production of the gasoline phase. This yield increased sharply to 24.2 wt % when the pressure was set at 1 MPa. A further increase of the pressure did not have any obvious influence on the yield, as shown in Table 1. For instance, the gasoline phase yield increased by only 0.1 wt % when the pressure rose from 2 to 3 MPa. Thus, the reaction temperature of 400 °C and the pressure of 2 MPa are considered to be appropriate for high-efficiency and economic cracking.

The influence of the DF/ethanol ratio on the co-cracking behavior is also presented in Table 1. It was found that the DF/ethanol ratio had a smaller effect compared to the temperature and pressure and a higher proportion of ethanol in the feed had some benefit for the production of the gasoline phase. However, a high gasoline phase yield of 25.9 wt % was still obtained even when the DF/ethanol ratio was 2:3.

**3.2.2. Composition of the Gasoline Phase.** The composition of the gasoline phase was measured by GC-MS. As shown in Figure 3, the gasoline phase mainly consisted of aromatic hydrocarbons with a carbon number ranging from 7 to 10, including toluene, xylenes, and methyl ethyl benzenes, which are also important components in commercial gasoline.

To make a clear comparison of the quality of the gasoline phases produced under different conditions, the components of the gasoline phase were classified into nine main groups: aromatic hydrocarbons, aliphatic hydrocarbons, alcohols, esters, ethers, ketones, phenols, acids, and aldehydes, as shown in Figure 4. The reaction temperature had an obvious influence on the deoxygenating efficiency of cracking. As mentioned above, the liquid product from the co-cracking below 340 °C was a homogeneous emulsion. Figure 4a shows that this liquid had a

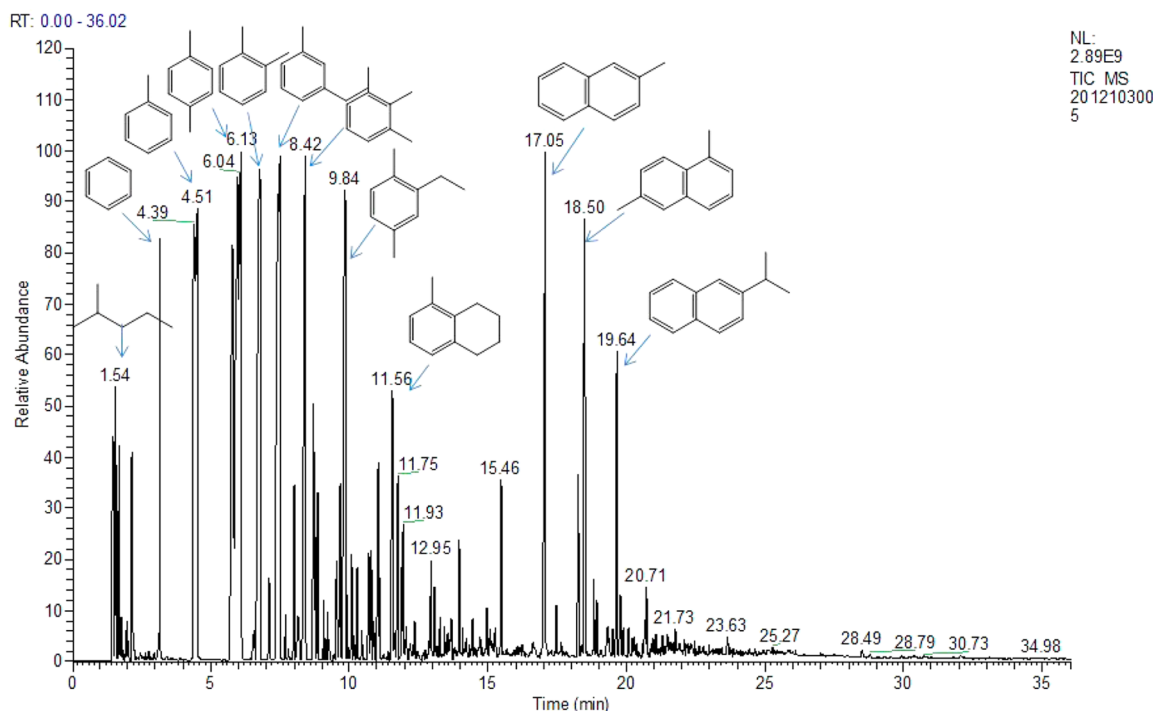


Figure 3. GC-MS total ion chromatograms of the gasoline phase (2:3 DF/ethanol, 400 °C, and 2 MPa).

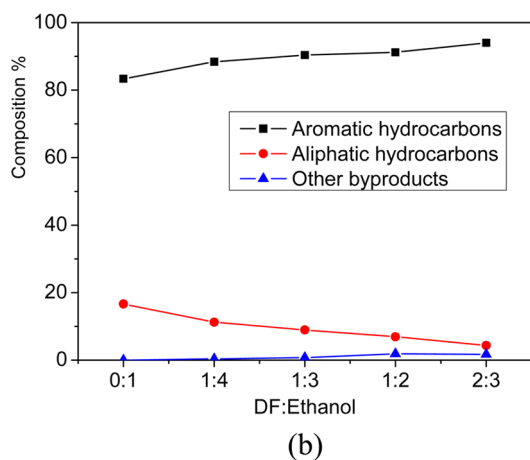
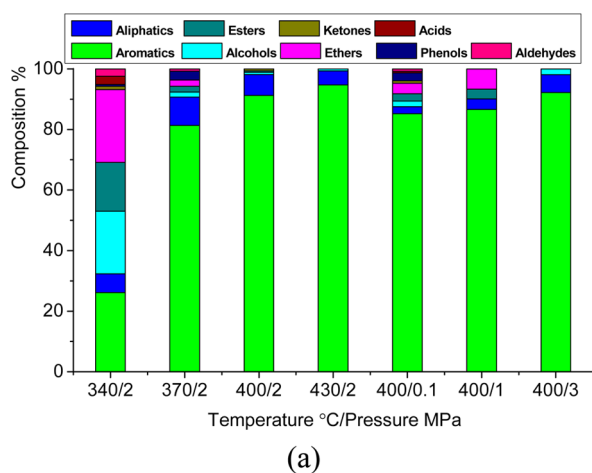


Figure 4. Composition of the gasoline phase under different conditions: (a) effect of the reaction temperature and pressure (1:2 DF/ethanol) and (b) effect of the DF/ethanol ratio.

low hydrocarbon content, only 32.4%, but a high proportion of oxygenated compounds, including alcohols, esters, ethers, ketones, phenols, acids, and aldehydes. Among these compounds, alcohols, esters, and ethers represented the three largest chemical families. The main alcohol was the unconverted ethanol, with a relative content of 18.5% in the mixed liquid, suggesting that ethanol could not be cracked sufficiently at this low reaction temperature. The ethers were mainly ethyl ether and 1,1-diethoxy ethane, which were formed from the etherification of ethanol.<sup>24</sup> A lot of ethyl acetate as well as some ethyl propionate were also produced, indicating the occurrence of esterification of the acids in the DF (acetic acid and propanoic acid) with ethanol. Thus, the high production of oxygenated byproducts showed that side reactions dominated at a low reaction temperature, which consequently lowered the selectivity for the desired hydrocarbons. Meanwhile, because alcohols, ethers, and esters are good solvents, the liquid products appeared as a homogeneous emulsion. Additionally, these intermolecular dehydration reactions occurred without gas release, while the cracking at higher temperature involved the release of more CO, CO<sub>2</sub>, and light hydrocarbons. This explained why the cracking at 340 °C had the highest liquid yield. As the reaction temperature increased to 370 °C, the gasoline phase had a high hydrocarbon content of 90.7%, with a few oxygenated compounds. When the reaction temperature further increased to 400 and 430 °C, the hydrocarbon content reached 98.2 and 99.3%, respectively. This shows that, at temperatures above 400 °C, the intensities of deoxygenation reactions (dehydration, decarbonylation, and decarboxylation) catalyzed by HZSM-5 were high and almost all of the DF and ethanol could be deoxygenated. In addition, the proportion of aromatic hydrocarbons in the gasoline phase was found to increase with the reaction temperature, which reached 91.2 and 94.7 wt % at the temperatures of 400 and 430 °C, respectively, indicating the intensive aromatization reaction on the catalyst active sites. The promotion of aromatization by

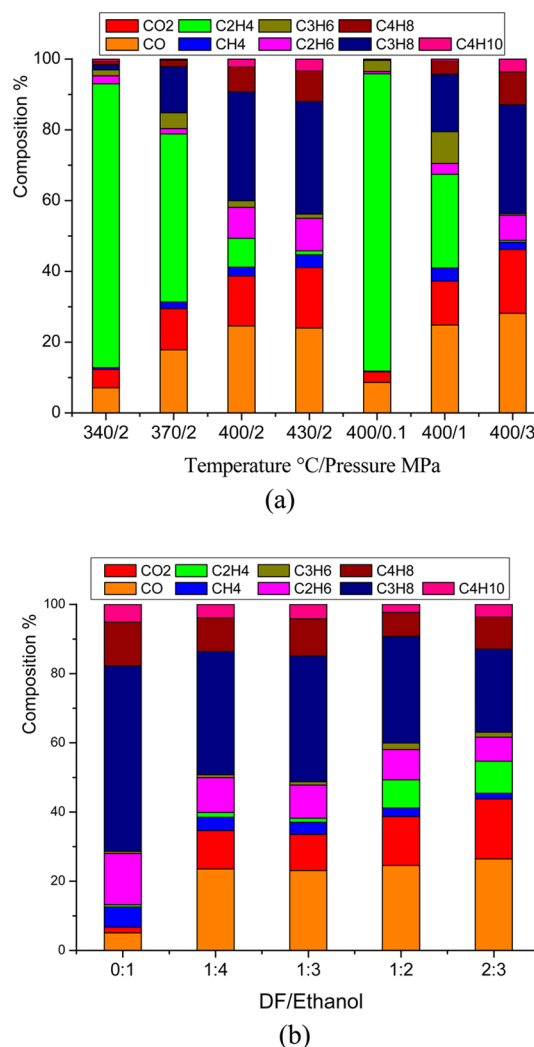
an increasing temperature was also observed by Gayubo et al. in their study of the cracking of ketone model compounds in bio-oil.<sup>11</sup>

The reaction pressure also affected the quantity and quality of the gasoline phase. The gasoline phase produced at atmospheric pressure had a hydrocarbon content of 87.5%, with the remainder being oxygenated products, such as alcohols, esters, ethers, and phenols. For cracking at an increased pressure of 1 MPa, the hydrocarbon content reached 90.1%. Further increasing the pressure to 2 or 3 MPa caused the hydrocarbon content to exceed 98%. The influence of the reaction pressure on the composition of the gasoline phase was weaker than that of the reaction temperature, but considering the clear difference of the gasoline phase yields between atmospheric pressure cracking and pressurized cracking, pressurized cracking significantly promoted the production of liquid hydrocarbons. In the previous cracking study of bio-oil model compounds, light olefins, such as  $C_2H_4$ , were regarded as important intermediates for hydrocarbon production.<sup>11,25</sup> In those reactions that convert light olefins to liquid hydrocarbons, the total stoichiometric number of products was smaller than that of reactants. Therefore, when the reaction pressure increased, the equilibrium of the reaction was shifted to the right, which benefited the conversion of intermediates to the liquid hydrocarbon products.

Figure 4b presents the influence of the DF/ethanol ratio on the composition of the gasoline phase. All of the gasoline phases had high hydrocarbon contents, more than 98%. The main difference among these gasoline phases was the distribution of aliphatic and aromatic hydrocarbons. The gasoline phase from pure ethanol cracking had a relatively high aliphatic hydrocarbon content of 16.6%. With an increase of the DF concentration in the feed, the content of the aliphatic hydrocarbons decreased, while the content of aromatic hydrocarbons increased. The gasoline phase for a DF/ethanol ratio of 2:3 had a low aliphatic hydrocarbon content of 4.3%. These results indicate that introducing ethanol as the co-reactant can also regulate the distribution of products. Most components in the DF have low  $(H/C)_{eff}$ , suggesting that the final cracking products had a low H/C value if oxygen was removed as  $H_2O$ , which is accompanied by hydrogen loss. Because of the inevitable production of water during the DF cracking, the formation of low H/C products was favored, which would consequently promote the production of coke. However, ethanol has a relatively high  $(H/C)_{eff}$ , suggesting that, even if all oxygen in ethanol is removed in the form of water, the average hydrogen/oxygen in the final products can still be as high as 2. If some ethanol is converted to aromatic hydrocarbons, there will be surplus hydrogen that could compensate for the hydrogen requirement for the DF cracking. Because the HZSM-5 zeolite can catalyze hydrogen-transfer reactions,<sup>26,27</sup> the surplus hydrogen produced during ethanol cracking could be offered to the DF cracking, which would shift the DF cracking final products toward more liquid hydrocarbons and restrain the formation of coke. For a DF/ethanol ratio of 2:3, the aliphatic hydrocarbon content was only 4.3%, although the hydrocarbon content in the gasoline phase was 98.3%. Therefore, if the DF/ethanol is increased further, there will not be enough surplus hydrogen for the DF cracking and coking would occur easily. In a similar study of the co-cracking of thermally treated bio-oil and methanol, Valle et al. also pointed out that a mixture of 40% bio-oil and 60% methanol was necessary for successful co-cracking.<sup>13</sup>

When the gasoline yield of co-cracking of DF and ethanol is compared to the weight ratio of 2:3 (25.9 wt %) and pure ethanol cracking (29.9 wt %), it can be inferred that the cracking of DF also contributed a lot to the production of biogasoline. Here, the hydrogen transfer between DF and ethanol might play an important role. The cracking of DF required the surplus hydrogen from ethanol cracking to produce liquid aromatic hydrocarbons, instead of coke. Meanwhile, for ethanol cracking, less gaseous saturated hydrocarbons, such as  $C_3H_8$ , might be produced, while more liquid aromatic hydrocarbons might be generated, because some hydrogen was offered to DF cracking.

**3.2.3. Composition of Vent Gas.** The gaseous products mainly consisted of  $CO_x$  ( $CO$  and  $CO_2$ ) and light hydrocarbons, as shown in Figure 5. The reaction temperature had an



**Figure 5.** Composition of vent gas for different reaction conditions: (a) effect of the reaction temperature and pressure and (b) effect of the DF/ethanol ratio.

obvious influence on the vent gas composition. Figure 5a shows that the  $C_2H_4$  content was 80.2% at a temperature of 340 °C, indicating that the aromatization reactions were suppressed, so that many light olefin intermediates, such as  $C_2H_4$ , were released instead of participating in the subsequent aromatization. In addition, the  $CO_x$  content could be as low as 12.3%, suggesting a low reaction rate for the deoxygenation reactions



involving  $\text{CO}_x$  formation, such as decarbonylation and decarboxylation, which was in accordance with the high content of oxygenated compound in the liquid products. When the reaction temperature rose to  $370^\circ\text{C}$ , the proportion of  $\text{CO}_x$  increased to 29.5% and the proportion of  $\text{C}_2\text{H}_4$  decreased to 47.5%. This showed that the aromatization reaction was enhanced at a higher reaction temperature. Meanwhile, more oxygen was removed by decarbonylation or decarboxylation, which improved the deoxygenation efficiency and increased the hydrogen/carbon ratio of the final products to benefit the production of liquid hydrocarbons. At reaction temperatures above  $400^\circ\text{C}$ , the content of  $\text{CO}_x$  was more than 38% and  $\text{C}_2\text{H}_4$  nearly disappeared. Thus, decarbonylation and decarboxylation were intensive, and almost all  $\text{C}_2\text{H}_4$  underwent aromatization to form liquid hydrocarbons. In addition, more  $\text{C}_3\text{H}_8$  was also formed, possibly from the aromatization reaction, in which light olefins were converted to aromatics with a high degree of unsaturation. The reaction pressure was also found to strongly affect the composition of the vent gas. Cracking at atmospheric pressure produced large amounts of  $\text{C}_2\text{H}_4$ , and the proportion of  $\text{CO}_x$  in the vent gas was low. The massive release of  $\text{C}_2\text{H}_4$  is related to the low intensity of aromatization, in accordance with its low gasoline phase yield. Pressurized cracking produced much less  $\text{C}_2\text{H}_4$  and more  $\text{CO}_x$ , consequently enhancing the gasoline phase production dramatically. Figure 5b shows that  $\text{C}_3\text{H}_8$  is the most abundant alkane in the vent gas for pure ethanol cracking and the proportion of  $\text{CO}_x$  increased with the increase of the DF/ethanol ratio. A higher DF/ethanol ratio would lower the integral  $(\text{H}/\text{C})_{\text{eff}}$  of the feed, which, therefore, requires more oxygen removal in the form of  $\text{CO}$  and  $\text{CO}_2$  to maintain the  $\text{H}/\text{C}$  ratio of the final products.

**3.2.4. Coke Analysis of the Spent Catalysts.** The previous study of crude bio-oil direct cracking usually produced a coke yield of above 20 wt %, which led to the serious catalyst deactivation and was the main reason for the termination of the cracking process.<sup>8,9</sup> The spent catalyst after co-cracking of the DF and ethanol was gray in appearance, indicating that only small amounts of coke were formed on the catalysts. On the basis of thermogravimetric analysis (TGA), the yields of coke from co-cracking for different DF/ethanol ratios were calculated. Pure ethanol cracking had the lowest coke yield of 1.5 wt %. With the increase of the DF/ethanol ratio, the coke yield rose slightly. The highest coke yield was only 3.2 wt % when the DF/ethanol ratio was 2:3. This shows that co-cracking of bio-oil DF with ethanol effectively restrained coke formation.

## 4. CONCLUSION

The co-cracking characteristics of the DF of bio-oil and ethanol were studied using a fixed-bed reactor. The DF from bio-oil molecular distillation achieved the enrichment of light acids and ketones; therefore, it was more volatile and reactive than crude bio-oil. The results from co-cracking of the DF with ethanol showed that increasing the reaction temperature favored the conversion of reactants and increased the deoxygenation efficiency. Pressurized cracking was found to benefit the production of the gasoline phase. Under the reaction condition of  $400^\circ\text{C}$  and 2 MPa, co-cracking of DF and ethanol, with a weight ratio of 2:3, generated a high-quality gasoline phase, with a yield of 25.9 wt %. This gasoline phase had a high hydrocarbon content of 98.3%.  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{C}_3\text{H}_8$  were the main gaseous products, and a low coke yield of 3.2 wt % was

achieved. The hydrocarbons in the gasoline phase were mainly  $\text{C}_7\text{--C}_9$  aromatic hydrocarbons; therefore, this biogasoline is better to be blended with some other high-saturation hydrocarbon fuels (for example, the gasoline from Fischer–Tropsch synthesis) for direct application in engines. In addition, the biogasoline with a high content of aromatic hydrocarbons can also be used as a promising chemical.

## AUTHOR INFORMATION

### Corresponding Author

\*Telephone: +86-571-87952801. Fax: +86-571-87951616. E-mail: srwang@zju.edu.cn.

### Notes

The authors declare no competing financial interest.

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