Aromatic Hydrocarbon Generation from a Simulated Bio-oil Fraction by Dual-stage Hydrogenation-cracking: Hydrogen Supply and Transfer Behaviors

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The improvement of the hydrogen-poor composition of bio-oil is important for its cracking to produce aromatic hydrocarbons. In this work, a mild hydrogenation pre-treatment and methanol cocracking were combined to implement proper hydrogen supplementation for cracking. Acetic acid (HAc), hydroxypropanone (HPO), and cyclopentanone (CPO) were selected as model compounds and mixed to prepare a simulated distilled fraction (SDF) of bio-oil. The hydrogen supply and transfer behaviours in hydrogenation-cracking were investigated. For the conversion of individual components: HAc was difficult to be hydrogenated, and therefore in the cracking stage, the conversion and oil phase yield were low; ketones were successfully hydrogenated to alcohols, and thus high aromatic hydrocarbon yields were achieved. Hydrogenation-cracking of SDF showed that the inferior performance of HAc was improved by an internal hydrogen transfer, namely the alcohols produced from ketones supplied hydrogen for HAc conversion. However, because of the high HAc content in SDF, this hydrogen supplement was not sufficient. Therefore, methanol (MeOH) was used as the coreactant for secondary hydrogen supply. The integral efficient conversion of SDF and MeOH to aromatic hydrocarbons was achieved when the MeOH blending ratio was 30%. Finally, a reaction mechanism of hydrogenation-cocracking was proposed.

Keywords: Simulated bio-oil fraction; Hydrogenation-cocracking; Aromatic hydrocarbon; Hydrogen supply; Methanol

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INTRODUCTION

Bioenergy has attracted worldwide attention because it is considered to be a potential substitute of traditional fossil fuels. Biomass wastes, such as straw, can be converted to liquid bio-oil through fast pyrolysis, showing great economic and environmental benefits. However, crude bio-oil has inferior properties, such as low heating value, strong corrosiveness, and high oxygen content, which limit its high-grade utilization (Mohan *et al.* 2006). Therefore, upgrading is required for bio-oil.

Catalytic cracking over zeolite catalysts is an efficient way to transform bio-oil into liquid fuels rich in aromatic hydrocarbons. HZSM-5 is commonly used for catalytic cracking, because the Brønsted acid sites can catalyze deoxygenation reactions such as dehydration, decarbonylation, decarboxylation, and aromatization reactions (Mortensen *et al.* 2011; Saad *et al.* 2015). Aromatic hydrocarbons can be blended with aliphatic hydrocarbons to produce gasoline and diesel fuel, and they can also be used as chemical materials (Wang *et al.* 2014a). However, direct cracking of bio-oil faces problems of low aromatic hydrocarbon yield and severe coking (Vitolo *et al.* 1999). There are two main reasons for the coke (carbonaceous deposit) formation: the presence of large molecular weight compounds in bio-oil, such as phenolic oligomers (pyrolytic lignin), which are nonvolatile and have low cracking reactivity, resulting in easy carbonaceous deposition in the catalytic bed (Valle *et al.* 2010); and the hydrogen-poor composition, namely the high unsaturation degree that leads to the low integral H/C ratios of final products and also favors the formation of coke (Zhang *et al.* 2011).

Therefore, to improve bio-oil cracking, enriching volatile and high-reactivity light components are important. The commonly used bio-oil light fractions for upgrading are an aqueous fraction and a distilled fraction (Vispute *et al.* 2010; Wang *et al.* 2013b). The authors' previous research has shown that the bio-oil distilled fraction could enrich light and active acids and ketones, such as acetic acid (HAc), hydroxypropanone (HPO), and cyclopentanone (CPO) derivatives (Wang *et al.* 2009). However, because the hydrogen-lacking property of this fraction is not improved, proper hydrogen supply is still required to adjust the H/C ratio of the final products. Researchers found that by coprocessing with hydrogen-rich chemicals, such as alcohols, the cracking behaviors of bio-oil components could be improved (Valle *et al.* 2010; Mentzel and Holm 2011). In the authors' previous studies alcohols were also introduced as the coreactants (Wang *et al.* 2012a, 2013a,b; Wang *et al.* 2014b). The results showed that alcohols could supply hydrogen to promote the conversion of components in a distilled fraction to aromatic hydrocarbon; nevertheless, because the hydrogen-lacking characteristic of this fraction is serious, high blending ratios of alcohols (greater than 60%) are often used, which affects the economy of this technique. Therefore, a further improvement is required. Researchers have found that bio-oil could be stabilized by mild hydrogenation, in which some aldehydes and ketones were converted to aliphatic alcohols (Vispute *et al.* 2010; Zheng *et al.* 2015). Transition metals such as Ni and Cu are often used for bio-oil hydrogenation because they can activate H_2 (Mortensen *et al.* 2011), and bifunctional Ni-Cu was found to exhibit high activity in the hydrogenation of bio-oil (Ardiyanti *et al.* 2012). If mild hydrogenation is adopted as the pre-treatment, partial unsaturated oxygenated components can be hydrogenated to substitute the additional alcohol at a relatively low cost (not much hydrogen). As a result, the requisite amount of additional alcohol is lowered and the corresponding economy is improved. However, because the complete saturation of bio-oil components is difficult, the hydrogen supply only by a hydrogenation pre-treatment is not enough and will lead to some coke formation (Vispute *et al.* 2010). Hence, secondary hydrogen supply by cocracking is still required. By combining hydrogenation pre-treatment and alcohol cocracking, the hydrogen supply could be regulated more flexibly and effectively, which is beneficial to the efficient conversion of a bio-oil distilled fraction under a minimum addition of alcohol (Cai *et al.* 2016; Zhang *et al.* 2017).

The above discussion shows that hydrogenation-cocracking is a promising technology to upgrade a bio-oil distilled fraction. In this work, according to the composition of this fraction, a simulated distilled fraction (SDF) containing HAc, HPO, and CPO was prepared, and its hydrogenation-cracking performances with and without methanol (MeOH) were studied. Because the cracking performance of SDF is determined by how much its hydrogen-poor composition is improved, the hydrogen supply and transfer behaviors during hydrogenation-cocracking were investigated. In addition, the acid and ketones in SDF may exhibit different hydrogenation performances (Elliott and Hart 2009) and this will lead to some internal hydrogen transfer from the hydrogenated ones to the unhydrogenated ones. Therefore, the hydrogen supply behavior in the hydrogenation-cracking of individual components were first studied, and the regulation by hydrogenation temperature was revealed. Afterwards, based on a suitable hydrogenation temperature, the interaction between the components in the hydrogenation-cracking of SDF was studied to understand the integral hydrogen supply and transfer behaviors. Finally, MeOH was chosen as the cocracking reactant to achieve the secondary hydrogen supplement aiming at the efficient integral conversion of SDF. Understanding this two-stage hydrogen supplementation not only helps optimize the upgrading of the bio-oil distilled fraction, but also can be useful for operating the conversion of other bio-oil fractions rich in acids and hydroxyketones such as aqueous fraction (Vispute *et al.* 2010).

EXPERIMENTAL

Materials

The hydrogenation catalyst was nickel-copper/silicon dioxide (Ni-Cu/SiO_2). It was prepared in the authors' laboratory, and the detailed preparation method has been described in the author's previous work (Cai *et al.* 2016). The loading amounts of Ni and Cu were both 5%, and before the hydrogenation reaction, the Ni-Cu/SiO_2 catalyst was reduced at 500 °C for 2 h with a hydrogen flow rate of 50 mL/min. The cracking catalyst was Hydrogen Zeolite Socony Mobil-Five (HZSM-5, Si/Al = 25) purchased from the Catalyst Plant of Nankai University (Tianjin, China). It was pretreated in air at 550 °C for 2 h before reaction.

The authors' previous study showed that the major components in the bio-oil distilled fraction were acids and ketones, with the total contents approximately 48.6% and 27.5%, respectively (Wang *et al.* 2013b). In particular, HAc, HPO, and CPO derivatives were the typical compounds, with relative contents of 23.9%, 27.9%, and 5.1%, respectively. Therefore, HAc, HPO, and CPO were selected as model compounds to study their individual hydrogenation-cracking performances, and they were mixed to prepare a SDF and the mixing ratio was set as 5:6:1, respectively (Wang *et al.* 2014a, 2015). Furthermore, MeOH (Sinopharm Chemical Reagent Co., Beijing, China) was used as the cocracking reactant, and the blending ratio of MeOH in the feedstock was 0% to 40%.

Catalytic Reaction

The reaction system and experimental operation have been described in detail in the author's previous work (Cai *et al.* 2016). This reaction system contained two connected tubular reactors, which implement both single-stage hydrogenation and continuous two-stage hydrogenation-cracking. The studied hydrogenation temperatures were 200 °C, 250 °C, and 300 °C, which were typically used in the hydrogenation study of bio-oil chemicals (Elliott and Hart 2009). The cracking temperature was set at 400 °C, which was a suitable cracking temperature for the generation of aromatic hydrocarbons as concluded by a previous study (Wang *et al.* 2013b).

The reaction pressure for hydrogenation and hydrogenation-cracking was 4 MPa, regulated by hydrogen with a flow rate of 50 mL/min. Studies showed that reaction pressure could affect both hydrogenation and cracking processes: the elevation of hydrogen pressure could improve the hydrogenation efficiency of bio-oil components (Mortensen *et al.* 2011); pressurized cracking favored the formation of liquid hydrocarbons, but this influence became insignificant when the pressure was above 2 MPa (Wang *et al.* 2013b). 4 MPa was selected in this work because the author's previous study using this pressure successfully achieved the hydrogenation of aldehyde group (Cai *et al.* 2016), which is also a typical unsaturated functional group in bio-oil, and similar pressures were also used in the mild hydrogenation of bio-oil components (Vispute *et al.* 2010; Chen *et al.* 2016). The weights of hydrogenation and the cracking catalysts were both 2 g. The weight hourly space velocity of liquid feedstock was 2 h^{-1}, in terms of the weight of the hydrogenation catalyst. For the hydrogenation-cocracking of SDF and MeOH, they were mixed as the liquid feedstock and pumped into the reactor together. Each catalytic run lasted for 5 h.

Methods

The gaseous products were analyzed by gas chromatography (GC, Agilent 6820, Agilent Technologies, Palo Alto, CA, USA). The liquid products from hydrogenation were homogeneous, while the liquid products from hydrogenation-cracking contained separable oil phases and aqueous phases.

The liquid products from hydrogenation and oil phases from hydrogenation-cracking were analyzed by gas chromatography-mass spectrometry (GC-MS, Clarus 500, Perkin–Elmer, Boston, MA, USA), and the area normalization method was used to quantify the identified components.

In addition, unconverted reactants in all liquid products were measured by gas chromatography to calculate their conversions. The amounts of carbonaceous deposits on spent hydrogenation catalysts were negligible, and the amounts of carbonaceous deposits on spent cracking catalysts were determined by thermogravimetric analysis (TGA/ SDTA851e, Mettler-Toledo, Greifensee, Switzerland).

The reactant conversions and product yields were defined by the following equations, where *m* represents the mass of the corresponding substance (g). The "liquid" in Eq. 2 refers to the collected liquid after reaction including products and unconverted reactants.

$$\text{Conversion} = \frac{(m_i)_{in} - (m_i)_{out}}{(m_i)_{in}} \times 100\% \;\; (i = \text{HAc, HPO, CPO, MeOH}) \tag{1}$$

$$\text{Yield} = \frac{m_i}{(m_{Liquid\ \ Reactants})_{in}} \times 100\% \;\; (i = \text{Liquid, Gas, Carbonac. deposits}) \tag{2}$$

Hydrogenation-cracking experiments were repeated three times to indicate reproducibility. The mass balances for the hydrogenation and hydrogenation-cracking experiments were all above 95%.

RESULTS AND DISCUSSION

Hydrogenation-cracking of Individual Components in SDF

Understanding the individual hydrogenation-cracking performances of HAc, HPO, and CPO is important for revealing the integral conversion behavior of SDF. Considering that the hydrogenation temperature might affect the hydrogenation degree and thus the subsequent cracking, influences of the hydrogenation temperature on hydrogenation and hydrogenation-cracking of the three components were studied first.

Hydrogenation behavior

The reactant conversions and product yields in hydrogenation of individual components are shown in Fig. 1. For the hydrogenation of HAc, the conversions at 200 °C and 250 °C were very low, but they increased to 21.2% at 300 °C. The gas yield also was clearly increased from 250 °C to 300 °C, and the main gaseous products were CH_4 and CO_2 produced from decomposition of HAc (Elliott and Hart 2009). Correspondingly, the liquid yield decreased from 93.5% at 250 °C to 82.1% at 300 °C. For the hydrogenation of HPO, the conversions were all above 99% at the same three temperatures. However, a substantial increase of gas yield was observed even from 200 °C to 250 °C, while the liquid yield decreased from 94.5% to 82.4%. The main gaseous products were CO and light hydrocarbons from HPO cracking and hydrodeoxygenation (Mortensen *et al.* 2011). For the hydrogenation of CPO, the conversion maintained an increase from 58.5% to 89.3% when the temperature rose from 200 °C to 300 °C. More gases began to be obtained at 300 °C, reaching a value of 18.6%, which were also CO and light hydrocarbons similar to those in HPO hydrogenation.

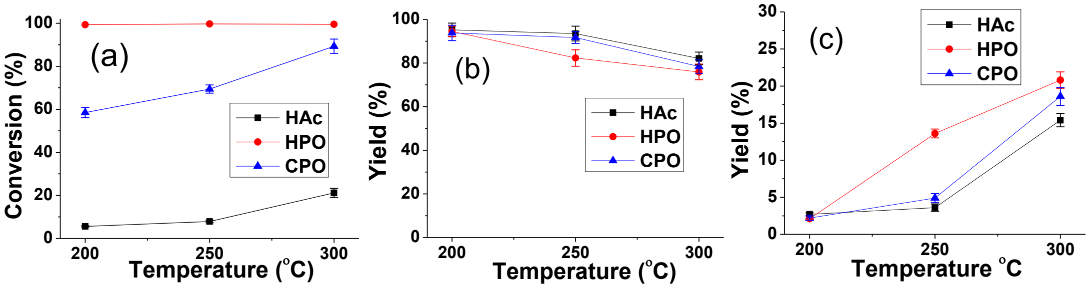

Fig. 1. Hydrogenation of individual SDF components: (a) reactant conversions; (b) liquid yields; and (c) gas yields (P = 4 MPa, WHSV = 2 h^{-1})

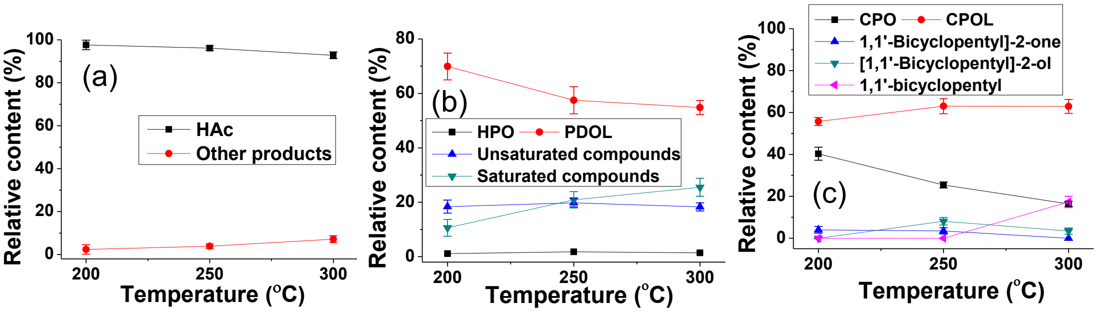

Fig. 2. Compositions of liquids from hydrogenation of individual SDF components: (a) HAc hydrogenation; (b) HPO hydrogenation; and (c) CPO hydrogenation (P = 4 MPa, WHSV = 2 h^{-1})

Figure 2 presents compositions of the liquid products from the hydrogenation of the individual components. In the liquid products obtained from HAc hydrogenation under different temperatures, the contents of the unconverted HAc were all higher than 90%, while the other components included the condensation products of HAc and ethanol. Combined with the reactant conversion and product yields, the relatively high HAc conversion at 300 °C was attributed to the decomposition reaction rather than the hydrogenation reaction.

The liquid products from HPO hydrogenation contained the typical hydrogenation product 1,2-propanediol (PDOL), other saturated products including alcohols and ethers, unconverted HPO, and other unsaturated products, mainly ketones. The variation of the contents of HPO and other unsaturated products indicated the high efficiency of carbonyl group hydrogenation under different temperatures.

As the temperature increased, the content of PDOL decreased while that of the other saturated products increased, which showed that the elevated temperature promoted secondary reactions of PDOL, such as alkylation, hydrodeoxygenation, and etherification. The liquid products from CPO hydrogenation comprised of typical hydrogenation product cyclopentanol (CPOL), unconverted CPO, and some dimers. When the temperature rose from 200 °C to 300 °C, the content of CPO decreased whereas that of CPOL increased, which indicated that higher temperature could facilitate the hydrogenation of carbonyl groups in CPO. From the variation of dimer contents, it was found that increased temperature would promote the hydrogenation of [1,1'-bicyclopentyl]-2-one to [1,1'-bicyclopentyl]-2-ol, and the further hydrodeoxygenation of [1,1'-bicyclopentyl]-2-ol to 1,1'-bicyclopentyl.

Generally speaking, hydrogenation efficiencies of HAc were very low under different temperatures and increased temperature mainly promoted thermal decomposition. Similar results for HAc hydrogenation were obtained by Elliott and Hart (2009). Hydrogenation of HPO to PDOL tended toward saturation at 200 °C, and higher temperature mainly facilitated secondary reactions of PDOL, such as alkylation, hydrodeoxygenation, etherification, and further gasification reactions. Hydrogenation of CPO to CPOL was enhanced to some extent as the temperature increased, in which higher temperature also promoted hydrodeoxygenation, cracking, and gasification reactions. The difference in reactivity of acid and ketones could be attributed to the different activation energies for their hydrogenation reactions (Grange *et al.* 1996).

Hydrogenation-cracking behavior

The hydrogenation study of ketones mentioned above showed that the hydrogenation temperature affected the conversion of ketones from two aspects: it promoted hydrogenation and decreased the liquid product yield. In view of the intensive gasification in the hydrogenation of HPO and CPO at 300 °C, hydrogenation-cracking of HPO and CPO with hydrogenation temperatures of 200 °C and 250 °C were performed. Hydrogenation of HAc at 300 °C also exhibited strong gasification intensity, and hydrogenation behaviors at 200 °C and 250 °C were similar; therefore, only hydrogenation-cracking of HAc with the hydrogenation temperature of 200 °C was studied.

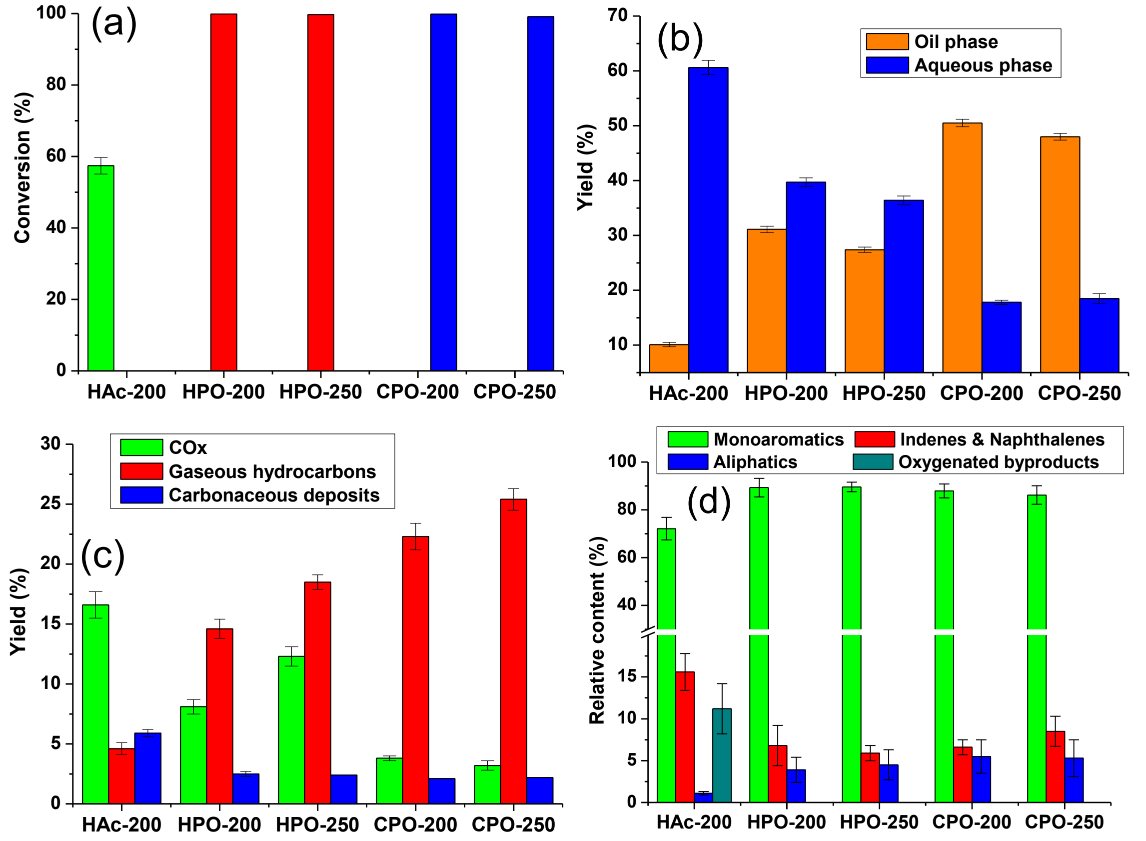

Fig. 3. Hydrogenation-cracking of individual SDF components: (a) reactant conversions; (b) liquid yields; (c) gas and carbonaceous deposit yields; and (d) oil phase compositions (*P* = 4 MPa, T_{cracking} = 400 °C, WHSV = 2 h^{-1})

The conversions of the reactants and the yields of the products in hydrogenation-cracking of individual components are shown in Figs. 3 (a) through (c), in which “HAc-200” represents hydrogenation-cracking of HAc with the hydrogenation temperature of 200 °C and the cracking temperature of 400 °C as mentioned in the Experimental section. The HPO was almost completely converted in both HPO-200 and HPO-250. However, the oil phase yield in HPO-200 reached 31.1%, which was higher than that in HPO-250. An elevated hydrogenation temperature did not greatly affect the oil phase yield in the hydrogenation-cracking of CPO. The HAc had a low cracking reactivity, and the conversion was only 57.4%. Ramasamy *et al.* (2014) also observed a low initial conversion of approximately 50% during HAc cracking. The oil phase yield was as low as 10.1%, whereas the aqueous phase yield reached 60.6%. This was because the unconverted HAc entered the aqueous phase due to its hydrophilic property. Meanwhile, higher yields of carbonaceous deposits and CO_x were observed in HAc-200, which also reduced the carbon selectivity of the oil phase. The carbonaceous deposit yield in HAc-200 reached 5.9%, and according to the conversion of 57.4%, the selectivity of the carbonaceous deposit was up to 10.3%, while the yields and selectivities of the carbonaceous deposits in HPO-200, HPO-250, CPO-200, and CPO-250 were all below 2.5%. In the time-on-stream test of HAc cracking, Ramasamy *et al.* (2014) found that the catalyst activity decreased because of carbonaceous deposit formation and this would further lower the conversion of HAc in long running.

Compositions of oil phases from hydrogenation-cracking of individual components are presented Fig. 3(d). In the oil phase from HAc-200, besides hydrocarbons, some oxygenated byproducts such as phenols were also found, which suggested a relatively low deoxygenation efficiency (Wang *et al.* 2012b). Oil phases from HPO-200, HPO-250, CPO-200, and CPO-250 were all completely composed of hydrocarbons, in which aromatic hydrocarbons predominated. These oil phases also had higher monoaromatic hydrocarbon contents than those from HAc-200. Combined with the oil phase yields, it was concluded that HPO-200 was more favorable for aromatic hydrocarbon production than HPO-250, while CPO-200 and CPO-250 did not show much difference. Therefore, for the hydrogenation-cracking of SDF that contained HAc, HPO, and CPO, 200 °C was a more suitable hydrogenation temperature.

The above results showed that the hydrogen supply behaviors in the hydrogenation stage would substantially affect the subsequent cracking performances. Publications have indicated some inferior cracking characteristics of individual HAc and ketones (Gayubo *et al.* 2004; Wang *et al.* 2012a, 2013a; Ramasamy *et al.* 2014). After the hydrogenation pretreatment at 200 °C, large proportions of ketones, especially HPO, were successfully hydrogenated to alcohols. Therefore, effective conversion to liquid aromatic hydrocarbons was achieved. However, based on the comparison of HPO-200 and HPO-250, the excess hydrogen supply at high temperatures, which promoted the hydrodeoxygenation of obtained alcohols to saturated gaseous hydrocarbons, would consequently decrease the available feedstock for subsequent cracking, and thereby decrease the oil phase yield. As for HAc, because it received almost no hydrogen supplement in the hydrogenation stage, low conversion, low liquid aromatic hydrocarbon yield, and high coking tendency were obtained. These were similar to the results achieved with direct cracking of HAc.

Interaction and Hydrogen Transfer among Components in SDF during Hydrogenation-cracking

The hydrogenation results of individual components showed that the ketones could be transformed into alcohols, which was a potential hydrogen supplier during cocracking (Wang *et al.* 2013b, 2015). Meanwhile, the author's previous study demonstrated that alcohols could promote HAc cracking (Wang *et al.* 2014b). Therefore, during hydrogenation-cracking of a bio-oil distilled fraction, the interaction between acids and ketones may affect their own conversions. To determine this interaction and determine the possibility of hydrogen transfer, the authors conducted hydrogenation and hydrogenation-cracking studies of mixtures, including 50% HAc to 50% HPO and 50% HAc to 50% CPO to investigate the interactions between the HAc and each ketone, and then between the SDF (42% HAc to 50% HPO to 8% CPO). The hydrogenation temperature was 200 °C, as concluded in the previous section.

Hydrogenation behavior

The yields of products and the compositions of liquid products in the hydrogenation of 50HAc-50HPO, 50HAc-50CPO, and SDF are shown in Figs. 4 (a) and (b). The liquid yields in three conditions were all above 90%, while the gas yields were low. The collected liquids contained esters, unconverted HAc, alcohols (mainly PDOL and CPOL), a few ketones, and other compounds. The esters had high contents in all of the collected liquids and mainly included 1,2-propanediol diacetate, 1,2-propanediol acetate, and cyclopentanol acetate, which were produced from esterification of HAc and PDOL/CPOL. Therefore, esterification was the dominant secondary reaction after hydrogenation of ketones. Researchers have found that during cracking, esters could undergo hydrolysis to regenerate acids and alcohols, which were then converted according to their own cracking mechanisms (Ramasamy *et al.* 2014). Furthermore, the formation of esters in the hydrogenation stage would not affect the subsequent cracking. Meanwhile, ester generation under mild conditions could relieve the device corrosion caused by the direct introduction of HAc into the high-temperature cracking reactor. Additionally, the low contents of ketones and other compounds indicated that in the presence of HAc, the integral hydrogenation efficiency was elevated. This was mainly attributed to the occurrence of esterification that consumed alcohols, and thus promoted the hydrogenation of ketones to alcohols.

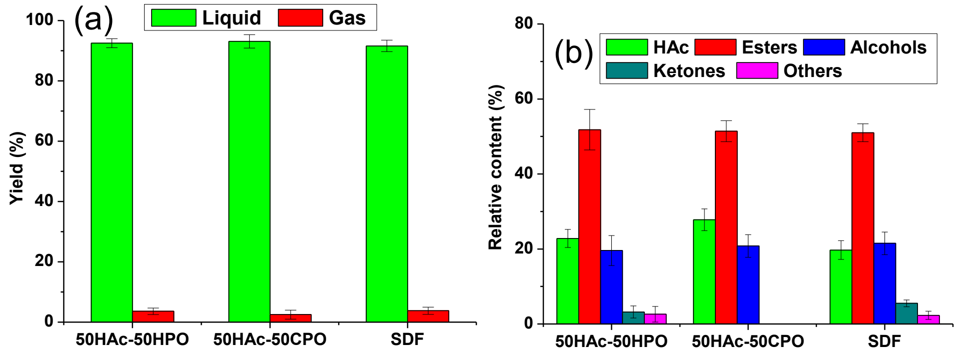

Fig. 4. Hydrogenation of mixed feedstocks: (a) product yields; (b) liquid compositions (P = 4 MPa, $T_{\text{hydrogenation}}$ = 200 °C, WHSV = 2 h^{-1})

Hydrogenation-cracking behavior

Conversions of reactants in hydrogenation-cracking of 50HAc-50HPO, 50HAc-50CPO, and SDF are shown in Fig. 5 (a). In these cases, the conversions of ketones were all above 99%. Meanwhile, by comparing hydrogenation-cracking of 50HAc-50HPO and 50HAc-50CPO with that of individual HAc, it was found that when half of HAc in the feedstock was replaced by HPO and CPO, the conversions of HAc increased from 57.4% to 80.5% and 80.1%, respectively. In the hydrogenation-cracking of SDF, the conversion of HAc also reached 82.7%.

The yields of products are shown in Figs. 5 (b) and (c). To determine the effect of the interaction between ketones and HAc on the formation oil-phase products, theoretical oil phase yields (oil phase-cal) were calculated. This calculation was based on the distributions of components in the feedstocks and the oil phase yields in their individual hydrogenation-cracking. The oil phase yields in the hydrogenation-cracking of 50HAc-50HPO, 50HAc-50CPO, and SDF were 25.8%, 36.8%, and 29.1%, respectively. These were all higher than the corresponding calculated oil phase yields, which indicated that the interaction between HAc and ketones promoted the formation of oil-phase products. However, the aqueous phase yields in these three cases were still relatively high because some of the HAc was not converted. In addition, from the yields of COx and carbonaceous deposits, the formations of COx and carbonaceous deposits in the hydrogenation-cracking of 50HAc-50HPO, 50HAc-50CPO, and SDF were inhibited compared with that in individual HAc hydrogenation-cracking, due to the increase of the integral saturation degree of feedstock. This not only increased the potential carbon selectivity of hydrocarbons, but also better maintained the catalyst activity.

The compositions of the oil phases are presented in Fig. 5 (d). The oil phases from the hydrogenation-cracking of 50HAc-50HPO, 50HAc-50CPO, and SDF had the high aromatic hydrocarbon contents of 94.8%, 95.4%, and 94.4%, respectively. Detailed compositions can be seen in Table 1 and the GC-MS spectrum of oil phase from hydrogenation-cracking of SDF is shown as Fig. 6. Compared with that in individual HAc cracking, besides the promotion of the primary conversion of HAc, ketone also played an important role in HAc deoxygenation during hydrogenation-cracking.

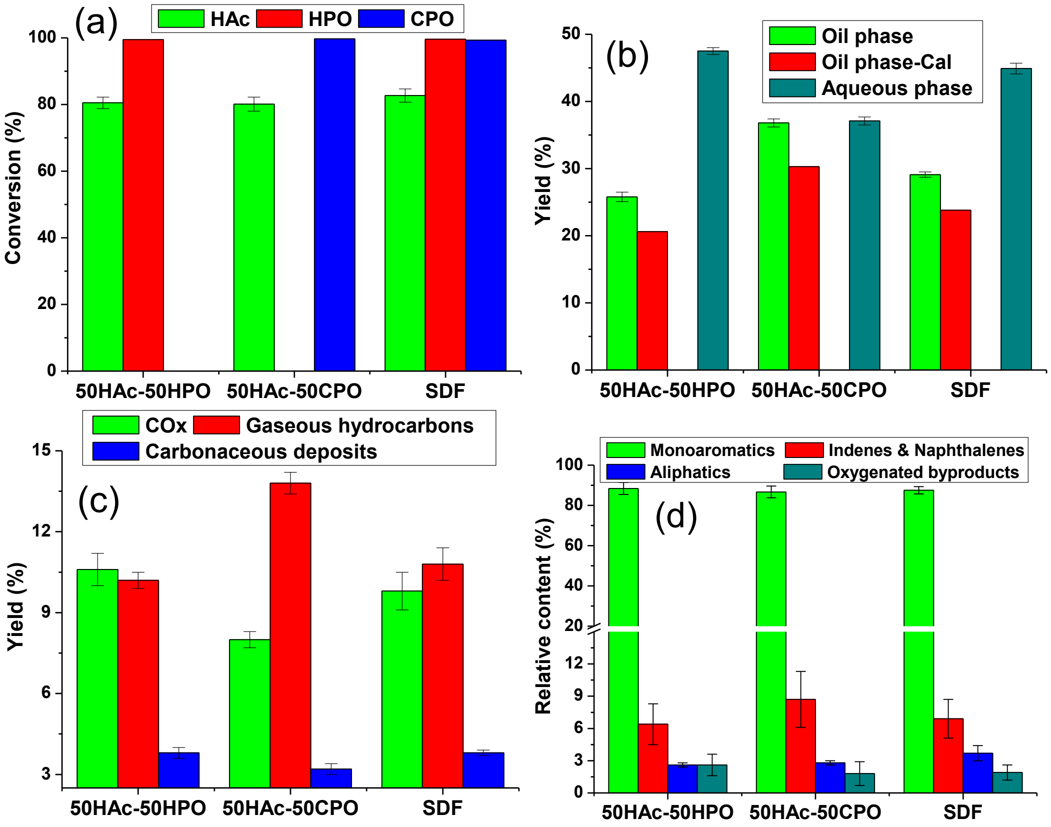

Fig. 5. Hydrogenation-cracking of mixed feedstocks: (a) reactant conversions; (b) liquid yields; (c) gas and carbonaceous deposit yields; and (d) oil phase compositions (P = 4 MPa, $T_{\text{hydrogenation}}$ = 200 °C, T_{cracking} = 400 °C, WHSV = 2 h^{-1})

The results in Table 1 and Fig. 6 showed that during SDF hydrogenation-cracking, the presence of ketones could promote the conversion of HAc to aromatic hydrocarbons. Combined with the author’s previous cocracking study of HAc and alcohol, it was deduced that alcohols formed from ketone hydrogenation acted as the internal hydrogen source to supply hydrogen for the cracking of HAc. However, due to the high content of HAc in SDF, this internal hydrogen supplement was not sufficient. Therefore, a secondary external hydrogen supply was still required for the integrally efficient conversion of SDF.

Table 1. Relative Contents of Compounds in Oil Phases from Hydrogenation-cracking of Mixed Feedstocks (area %). (P = 4 MPa, $T_{\text{hydrogenation}}$ = 200 °C, T_{cracking} = 400 °C, WHSV = 2 h^{-1})

Category	Compound	Feedstock		
		50HAC-50HPO	50HAC-50CPO	SDF
Aliphatics	2-Methyl-Butane	0.9	1.0	1.4
	2-Methyl-Pentane	1.4	1.2	1.9
	Other Aliphatics	0.3	0.6	0.4
Monoaromatics	Benzene	0.3	0.5	0.3
	Toluene	7.5	9.6	3.9
	O-Xylene	6.2	5.2	5.1
	P-Xylene	11.3	9.6	11.0
	Benzene, 1,3-Dimethyl-	7.9	9.5	5.3
	Ethylbenzene	2.5	4.5	1.2
	Benzene, 1,2,3-Trimethyl-	19.5	14.8	30.1
	Benzene, 1-Ethyl-3-Methyl-	12.6	10.2	4.6
	Benzene, 1,2,4,5-Tetramethyl-	12.6	11.9	21.1
	Benzene, 1-Ethyl-3,5-Dimethyl-	1.9	3.3	2.3
	Other Monoaromatics	6.1	7.6	2.6
Indenes & Naphthalenes	1H-Indene, 2,3-Dihydro-4-Methyl-	1.7	2.8	1.6
	1H-Indene, 2,3-Dihydro-1,3-Dimethyl-	1.2	1.1	2.1
	Naphthalene, 2-Methyl-	1.4	1.6	0.6
	Naphthalene, 1,7-Dimethyl-	1.5	1.7	0.9
	Other Indenes & Naphthalenes	0.6	1.5	1.7
Oxygenated Compounds	Phenol, 2-Methyl-	0.3	0.2	0.4
	Phenol, 2,4-Dimethyl-	0.8	0.7	0.5
	Phenol, 2,6-Dimethyl-	0.6	0.8	0.5
	Other Oxygenated Compounds	0.9	0.1	0.5

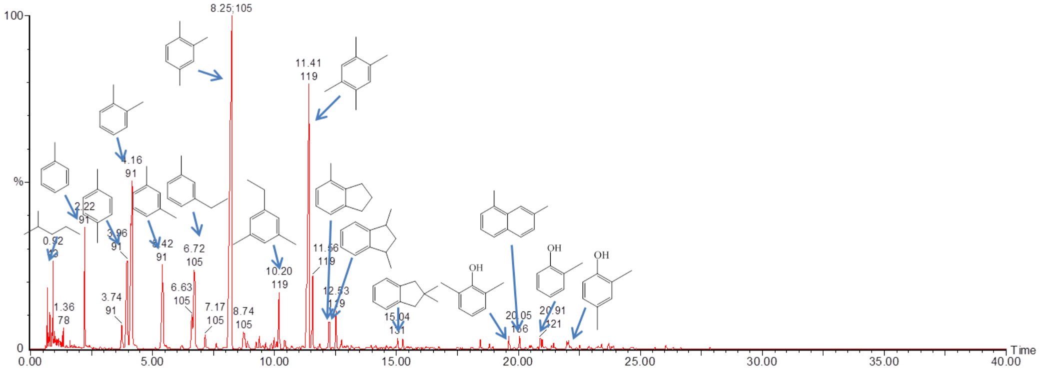

Fig. 6. GC-MS spectrum of oil phase from hydrogenation-cracking of SDF (P = 4 MPa, $T_{\text{hydrogenation}}$ = 200 °C, T_{cracking} = 400 °C, WHSV = 2 h^{-1})

Secondary Hydrogen Supply by Blending MeOH for Hydrogenation-Cracking of SDF

Discussion in the previous section concluded that hydrogen supply by a hydrogenation pretreatment improved the hydrogen-lacking property of SDF to some extent, but a secondary hydrogen supply was still necessary. Therefore, MeOH was used as the cocracking reactant, and the regulation of the secondary hydrogen supply by a varying methanol blending ratio was studied.

Hydrogenation behavior

Figure 7 presents the yields of products and compositions of liquid products involved in the hydrogenation of SDF and MeOH. The influence of the MeOH blending ratio on the liquid and gas yields was not obvious, and the liquid yields were all around 95%. The collected liquids mainly contained esters, unconverted HAc, alcohols (including MeOH, PDOL, and CPOL), ketones, and some other products. The ketones contents were low under different MeOH blending ratios, which indicated the high hydrogenation efficiencies of the carbonyl group. Among the esters, besides 1,2-propanediol diacetate, 1,2-propanediol acetate, and cyclopentanol acetate, methyl acetate was also found as mentioned before, which suggested the esterification of HAc and MeOH.

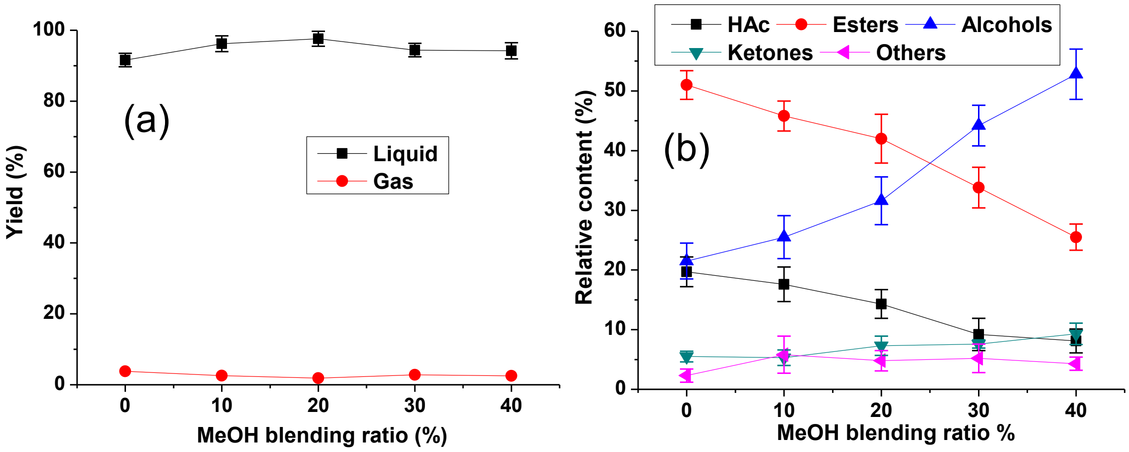

Fig. 7. Influence of MeOH blending ratio on hydrogenation of SDF and MeOH: (a) product yields; and (b) liquid compositions (P = 4 MPa, $T_{\text{hydrogenation}}$ = 200 °C, WHSV = 2 h^{-1})

Hydrogenation-cracking behavior

Conversions of the reactants involved in hydrogenation-cocracking of SDF and MeOH are shown Fig. 8 (a). The conversion of HAc maintained an increase and reached 99.8% when the MeOH blending ratio increased from 0% to 30%, which indicated the promotion effect by MeOH on HAc conversion. Meanwhile, the conversions of HPO, CPO, and MeOH were all above 99% under different MeOH blending ratios.

The yields of the products are shown in Fig. 8 (b) and (c). As the MeOH blending ratio increased from 0% to 30% and 40%, the oil phase yield rose from 29.1% to 36.3% and 36.1%, respectively. A slight decrease of aqueous phase yield was observed, which was due to the increase of HAc conversion. Meanwhile, the carbonaceous deposit yield was decreased with increased MeOH blending ratio and this was beneficial to the catalyst stability.

A similar decline tendency was found for the COx yield, which was attributed to an increased feedstock saturation degree. In addition, the author's previous study showed that the oil phase yield in pure methanol cracking was 22.6% (Zhang *et al.* 2017), showing that cocracking was more favorable for liquid hydrocarbon production.

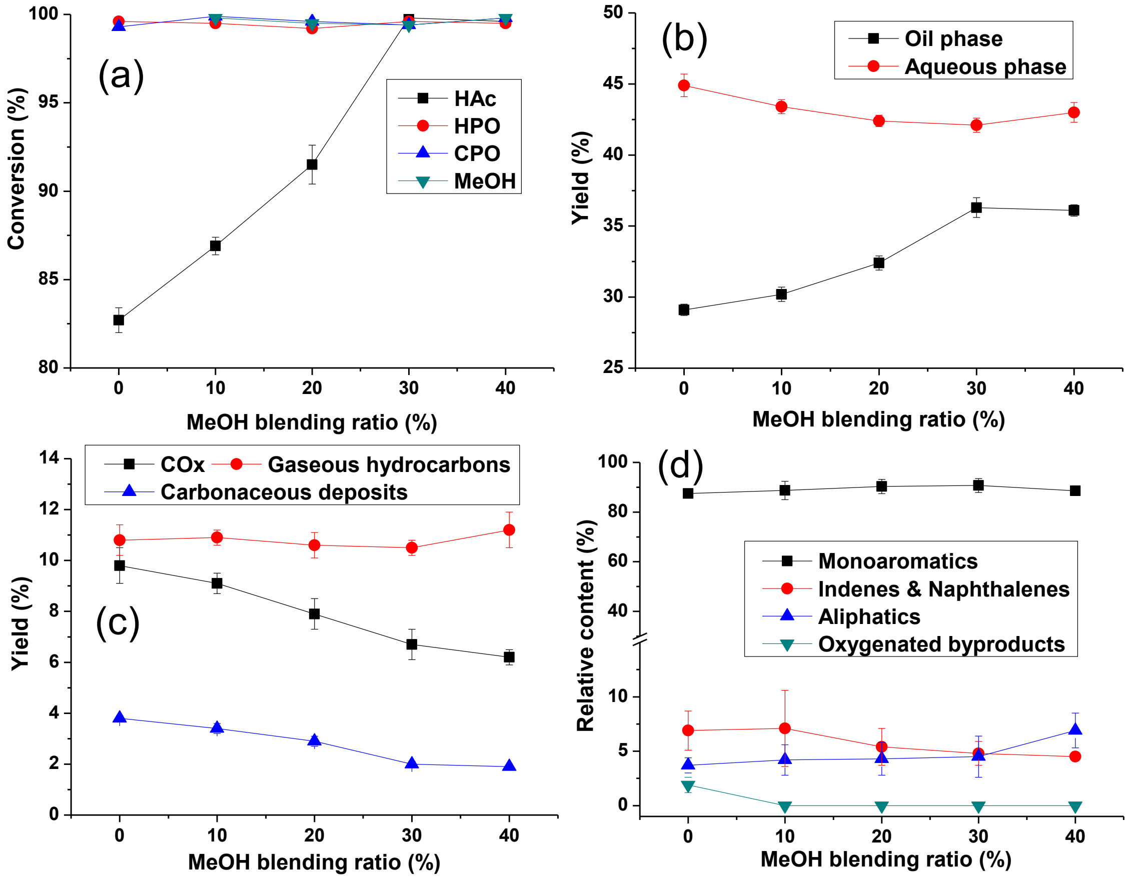

Fig. 8. Influence of MeOH blending ratio on hydrogenation-cocracking of SDF and MeOH: (a) reactant conversions; (b) liquid yields; (c) gas and carbonaceous deposit yields; and (d) oil phase compositions (P = 4 MPa, $T_{\text{hydrogenation}}$ = 200 °C, T_{cracking} = 400 °C, WHSV = 2 h^{-1})

The compositions of the oil phases are presented in Fig. 8 (d). Without MeOH blending, there were a few oxygenated byproducts, such as phenols, in the oil phase. When the MeOH was blended, the oil phases were completely composed of hydrocarbons, which showed that deoxygenation was enhanced. Under the MeOH blending ratio of 30%, the contents of aromatic and aliphatic hydrocarbons were 95.5% and 4.5%, respectively. Further increase of the MeOH blending ratio to 40% resulted in the elevation of aliphatic hydrocarbon content.

Detailed compositions are shown in Table 2. Figure 9 is the GC-MS spectrum of oil phase from hydrogenation-cocracking with the optimum MeOH blending ratio of 30%. Under this optimum condition, according to the GC-MS result and the oil phase yield, the yields of typical monoaromatics, namely toluene, xylenes, 1,2,3-trimethyl-benzene, and 1,2,4,5-tetramethyl-benzene, were 2.1%, 9.2%, 10.0% and 5.8%, respectively.

Table 2. Relative Contents of Compounds in Oil Phases from Hydrogenation-Cocracking with Different Methanol Blending Ratios (area %). (P = 4 MPa, $T_{hydrogenation}$ = 200 °C, $T_{cracking}$ = 400 °C, WHSV = 2 h^{-1})

Category	Compound	Methanol Blending Ratio (%)				
		0	10	20	30	40
Aliphatics	2-Methyl-Butane	1.4	1.5	1.4	1.9	1.6
	2-Methyl-Pentane	1.9	2.4	2.4	2.6	3.5
	Other Aliphatics	0.4	0.3	0.5	0	1.8
Monoaromatics	Benzene	0.3	0.5	0.2	0.4	0.9
	Toluene	3.9	6.6	6.7	5.9	7.5
	O-Xylene	5.1	5.9	5.3	6.5	5.2
	P-Xylene	11.0	12.8	14.4	14.1	16.9
	Benzene, 1,3-Dimethyl-	5.3	5.6	6.2	4.8	6.7
	Ethylbenzene	1.2	2.4	1.5	1.6	2.2
	Benzene, 1,2,3-Trimethyl-	30.1	28.2	25.9	27.5	22.5
	Benzene, 1-Ethyl-3-Methyl-	4.6	2.6	3.9	6.2	6.7
	Benzene, 1,2,4,5-Tetramethyl-	21.1	14.5	17.8	15.9	16.1
	Benzene, 1-Ethyl-3,5-Dimethyl-	2.3	3.8	4.2	2.0	2.5
	Other Monoaromatics	2.6	5.8	4.2	5.8	1.4
Indenes & Naphthalenes	1H-Indene, 2,3-Dihydro-4-Methyl-	1.6	1.6	1.3	0.8	0.5
	1H-Indene, 2,3-Dihydro-1,3-Dimethyl-	2.1	2.3	2.0	1.9	1.1
	Naphthalene, 2-Methyl-	0.6	1.2	0.7	0.6	0.7
	Naphthalene, 1,7-Dimethyl-	0.9	1.3	0.5	0.6	0.6
	Other Indenes & Naphthalenes	1.7	0.7	0.9	0.9	1.6
Oxygenated Compounds	Phenol, 2-Methyl-	0.4	0	0	0	0
	Phenol, 2,4-Dimethyl-	0.5	0	0	0	0
	Phenol, 2,6-Dimethyl-	0.5	0	0	0	0
	Other Oxygenated Compounds	0.5	0	0	0	0

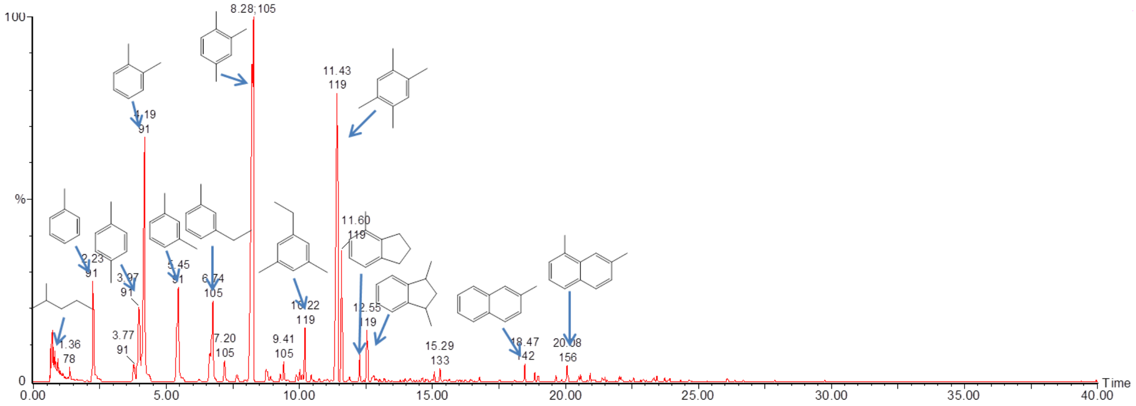

Fig. 9. GC-MS spectrum of oil phase from hydrogenation-cocracking with the MeOH blending ratio of 30%

The above results indicated that using MeOH as the cocracking reactant for the secondary hydrogen supply successfully overcame the problem of partial hydrogen-poor composition in the hydrogenation-cracking of SDF and particularly led to the efficient conversion of HAc. Meanwhile, this hydrogen supply also achieved the regulation of product distribution to decrease the yields of carbonaceous deposits and COx. As a result, the carbon selectivity of hydrocarbons increased and the catalyst activity was also better maintained. By combining the oil phase yield and composition, it was concluded that 30% was the optimum MeOH blending ratio for liquid aromatic hydrocarbon production.

In addition, the comparison of dual-stage hydrogenation-cocracking and single-stage cocracking was also conducted, using the same cracking catalyst (HZSM-5), cracking temperature (400 °C) and methanol blending ratio (30%). It was found that the oil phase yield in single-stage cocracking was only 19.2%, much lower than that of 36.3% in hydrogenation-cocracking. Moreover, oxygenated byproducts was found in the oil phase from single-stage cocracking, with a total relative content of 4.8%. Higher carbonaceous deposit yield of 4.5% was also observed in single-stage cocracking. The more inferior performance of single-stage cocracking compared with hydrogenation-cocracking indicated the necessity of hydrogen supply by hydrogenation pretreatment.

Discussion of Hydrogen Supply and Transfer Behaviors in Hydrogenation-Cocracking of SDF and MeOH Based on a Proposed Reaction Mechanism

Experimental results showed that hydrogenation-cocracking with MeOH was the most favorable method for the conversion of SDF. This process involved two external hydrogen sources, namely hydrogen gas in the hydrogenation stage and MeOH in the cracking stage. Meanwhile, the internal hydrogen transfer in SDF was also important, especially for HAc conversion. Therefore, the hydrogen supply and transfer behaviors in the hydrogenation-cocracking of SDF and MeOH were discussed on the basis of a proposed reaction mechanism, as shown in Fig. 10.

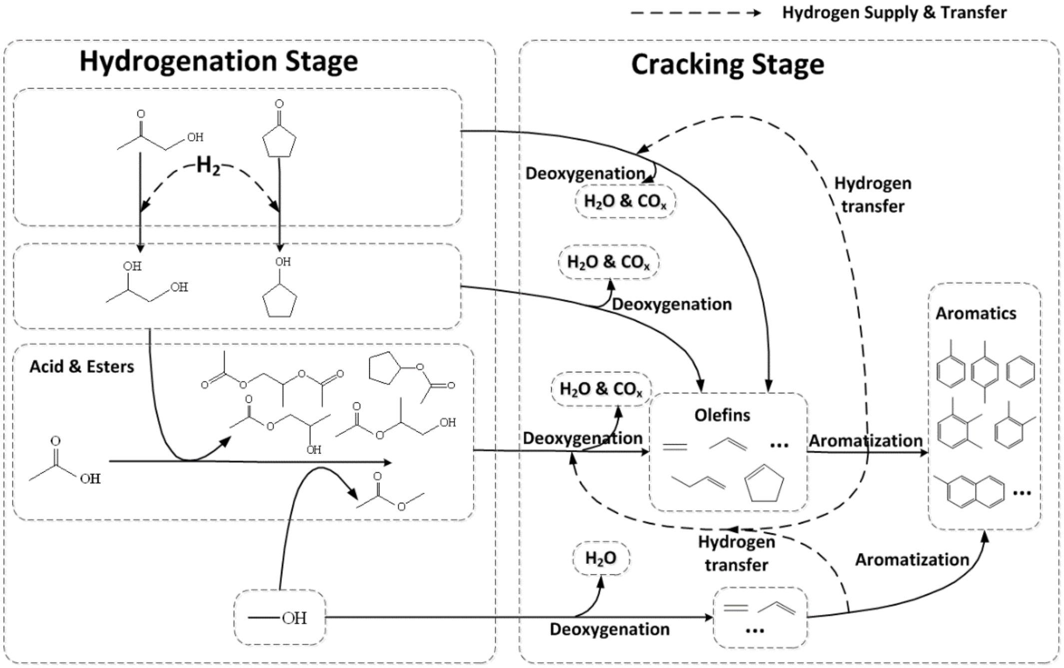

Fig. 10. Reaction mechanism of hydrogenation-cocracking of SDF and MeOH

Based on the hydrogenation results, the components in feedstock exhibited different hydrogenation behaviors. The HPO had a high activity in hydrogenation, and most carbonyl groups were successfully saturated to produce PDOL. The individual hydrogenation activity of CPO was weaker than that of HPO, but it was improved in the presence of HAc and thus a high hydrogenation efficiency was also achieved. The HAc and MeOH showed very low hydrogenation activities. After primary hydrogenation, esterification was the dominant secondary reaction in SDF hydrogenation. Because HAc is a Brønsted acid, it could react with PDOL, CPOL, and MeOH by self-catalysis to produce esters. Besides esterification, ketones could undergo aldol condensation to produce new ketones; alcohols could undergo etherification to generate ethers; and some further deoxygenation and decomposition of alcohols could produce other alcohols and gaseous hydrocarbons. These reactions were weak in SDF hydrogenation at 200 °C.

According to the hydrogenation mechanism, hydrogen supply in the hydrogenation stage mainly contributed to the elevation of saturation degree, but the integral deoxygenation efficiency was low. Therefore, the main available feedstock for subsequent cracking, including alcohols, ketones, acids and esters, were still oxygenated compounds. Deoxygenation reactions and aromatization reactions happened in the cracking stage, which produced the final aromatic hydrocarbons. Research has indicated that the main cracking pathways were through oxygenated compounds first undergoing deoxygenation (dehydration, decarbonylation, and decarboxylation) to produce light olefins, which further underwent aromatization to generate aromatic hydrocarbons (Adjaye and Bakhshi 1995). Although the main reaction pathways were similar, their conversion efficiencies and occurrences of side reactions, such as incomplete deoxygenation and coking, were strongly related to their own chemical characteristics.

Alcohols in the available cracking feedstock mainly included MeOH, CPOL, and PDOL. The MeOH could be efficiently dehydrated to form light olefins, such as C_2H_4 (Haw *et al.* 2003), and then aromatization happened to produce aromatic hydrocarbons. The direct dehydration of CPOL produced cyclopentene and it could be cracked into lighter olefins, which then underwent aromatization. For the conversion of PDOL, because of the double-hydroxyl structure, some decarbonylation and decarboxylation occurred (Zhang *et al.* 2011). However, according to the result of HPO hydrogenation-cracking, dehydration still predominated in the PDOL cracking and complete deoxygenation was achieved to produce light olefins for aromatization. It was noteworthy that in the conversion of light olefins ($H/C = 2$) to aromatic hydrocarbons ($1 \leq H/C < 2$), dehydrogenation reactions occurred and led to the formation of adsorbed hydrogen atoms (Choudhary *et al.* 2001). Therefore, saturated alcohols not only exhibited fine cracking performances but also were potential hydrogen suppliers due to hydrogen-rich properties.

The unsaturated compounds in the available cracking feedstock included ketones, acid, and esters. Unconverted CPO was the main ketone. The decomposition (or decarbonylation) of ketones could produce light olefins (Tago *et al.* 2011). However, according to the author’s previous study, the intensity of decarbonylation was limited, thus some oxygenated byproducts were generated (Wang *et al.* 2012a, 2013a). In the research of CPO conversion over zeolite, Huang *et al.* (2009) found that the conversion started from the adsorption of CPO on Brønsted acid to form an enol intermediate. This intermediate was unstable and easily underwent condensation to produce oxygenated oligomers. Nevertheless, this reaction could have been suppressed by the existence of adsorbed surplus hydrogen that generated from alcohol cracking. In a coprocessing study over zeolite by Xue *et al.* (2016), it was found that the hydrogen produced from hydrogen-rich chemicals could be used to stabilize unsaturated compounds *via* a hydrogen transfer reaction. Therefore, the enol intermediate could be saturated by surplus hydrogen to form alcohols, which could be easily dehydrated to form light olefins, and therefore the integral deoxygenation and aromatic hydrocarbon formation were enhanced.

The acid in the available cracking feedstock was the unconverted HAc. As proposed by Pham *et al.* (2014), for the conversion of HAc over zeolite, it first undergoes dehydration to produce adsorbed acetyl or acylium ion; in the absence of an external hydrogen supply, its ideal conversion pathway was the combination with an adsorbed carboxylate, and then decarboxylation to produce acetone and CO_2. Afterwards, acetone underwent aldol condensation to form diacetone alcohol and mesityl oxide (a dehydration product), which could be further cracked and deoxygenated (decarbonylation or decarboxylation) to generate isobutene (Ramasamy *et al.* 2014). However, because the occurrence of decarboxylation was relatively difficult (Gayubo *et al.* 2004), the primary conversion of HAc was inhibited and some intermediates may not have been completely deoxygenated. Furthermore, the unstable active acetyl or acylium ion may have continuously participated in chain growth and heterocyclic compound formation, which ultimately formed carbonaceous deposits. Therefore, if external hydrogen was supplied, such as the surplus hydrogen generated from alcohol cracking, the highly unsaturated intermediates could be stabilized to form compounds with hydroxyl groups. Consequently, dehydration was strengthened to generate light olefins for aromatization and carbonaceous deposit formation was suppressed. Moreover, for the acetone generated from HAc, according to the discussion on ketone conversion, the surplus hydrogen from alcohol would also promote its deoxygenation.

The esters in the available cracking feedstock included methyl acetate, 1,2-propanediol diacetate, 1,2-propanediol acetate, and cyclopentanol acetate. Because esterification is a reversible reaction, as indicated by Ramasamy *et al.* (2014), in the presence of water, the primary conversion of esters over zeolite is through hydrolysis to regenerate acids and alcohols; afterwards, they are converted according to their own reaction pathways. In this work, the dehydration of alcohols would produce a substantial amount of water, and the experimental results confirmed the high yields of the aqueous phases. Therefore, it was proposed that esters first underwent hydrolysis to produce HAc, MeOH, PDOL, and CPOL. In the subsequent conversion, acetyl or acylium ion and acetone intermediates produced from HAc could receive the hydrogen generated from MeOH, PDOL, and CPOL. However, research showed that the cracking performance of individual ester was not good (Gayubo *et al.* 2004), which indicated that the amount of hydrogen supplied from the ester-generated alcohols was not sufficient for the efficient conversion of ester-generated acids. Consequently, the hydrogen supplied from external alcohols was still required for the conversion of esters.

In summary, the hydrogen suppliers in the cracking stage were saturated alcohols, while unsaturated ketones, acid, and esters were the hydrogen receivers. The hydrogen transfer among them could promote the conversions of ketones, acid, and esters to the desired aromatic hydrocarbons with little effect on the conversion efficiency of alcohols.

The aforementioned mechanism could explain the hydrogenation-cracking performances of individual components, SDF, and SDF and MeOH. Because sufficient hydrogen was supplied for HPO saturation in the hydrogenation stage, the problem of oxygenated byproducts formation was overcome and carbonaceous deposit formation was relieved. This resulted in a high yield and quality of the obtained oil phase. A proportion of CPO was hydrogenated into CPOL in the hydrogenation stage. Because the oxygen content in CPO was low, this hydrogen supplement was also sufficient for its deoxygenation and thus allowed the effective conversion to aromatic hydrocarbons. However, because HAc was not hydrogenated in the hydrogenation stage, the low cracking activity of carboxyl group was not improved. This continued in the cracking stage, leading to the low conversion, low oil phase yield, and more carbonaceous deposits.

For the hydrogenation-cracking of SDF, in the hydrogenation stage, hydrogen was mainly supplied to HPO and CPO for the formations of PDOL and CPOL. Therefore, the unhydrogenated HAc became the main factor that affected the integral hydrogenation-cracking performance of SDF. According to the proposed reaction mechanism, there were some interactions between the HAc and ketones. In the hydrogenation stage, partial alcohols generated from the ketone hydrogenation underwent esterification with HAc to produce esters. In the cracking stage, the alcohols that participated in esterification were rereleased *via* the hydrolysis of esters, and then they together, with the alcohols that did not participate in esterification, acted as the internal hydrogen source to supply hydrogen for HAc conversion. However, due to the high HAc content in SDF, this hydrogen supplement was not sufficient. Therefore, the actual oil phase yield in SDF hydrogenation-cracking was higher than the calculated yield, but some HAc was still not converted. This indicated the potential of an elevated oil phase yield through the promotion of HAc conversion by an enhanced external hydrogen supplement.

Selecting MeOH as the cocracking reactant meant using it as the secondary external hydrogen source. Like PDOL and CPOL, MeOH could undergo esterification with HAc and then be rereleased during the cracking stage. The main function of MeOH was to generate surplus hydrogen during cracking to make the integral hydrogen supplement sufficient. The amount of supplied hydrogen was determined by the blending ratio of MeOH. Therefore, as the MeOH blending ratio increased, HAc conversion and oil phase yield increased while the yield of carbonaceous deposit decreased. When the MeOH blending ratio was 30%, the HAc was completely converted and the oil phase yield reached 36.3%, which indicated the sufficient integral hydrogen supplement for HAc conversion. When the MeOH blending ratio was further elevated, the amount of hydrogen supplied by MeOH was larger than that required for HAc conversion. The excess hydrogen could participate in the saturation of olefin intermediates to produce liquid aliphatic hydrocarbons, which increased the selectivity of liquid aliphatic hydrocarbons and thereby affected the desired aromatic hydrocarbon production. Hence, the optimum MeOH blending ratio was 30%.

Economic Analysis

Based on the experimental results, a simple economic comparison of hydrogenation-cocracking and direct cocracking was conducted. Hydrogenation-cocracking was performed with the obtained optimum MeOH blending ratio of 30%; the aromatic hydrocarbon yield was 34.7% and the estimated weight ratio of consumed hydrogen to SDF was 0.02. Direct cocracking of SDF and MeOH was performed with the MeOH blending ratio of 60% and the obtained aromatic hydrocarbon yield was 32.4%.

The current methanol price is 300 \$/t. The hydrogen price varies depending on location, supplier and natural gas price, and here the relatively cheap one from large steam reformers is used, namely 2000 \$/t (Vispute *et al.* 2010). In the generated aromatic hydrocarbons, xylenes are representative. Therefore, the price of xylene (currently 775 \$/t) is used to represent that of aromatic hydrocarbons.

Based on the above data, for the upgrading of 1 t of SDF by hydrogenation-cocracking: the consumptions of hydrogen and methanol are 0.02 t and 0.43 t, with the total additional chemical cost of \$169.0; the amount of generated aromatic hydrocarbons is 0.50 t and the corresponding product value is \$387.5; the difference of product value and additional chemical cost is \$218.5. For the upgrading of 1 t of SDF by direct cocracking: the consumption of methanol is 1.5 t, with the additional chemical cost of \$450.0; the amount of generated aromatic hydrocarbons is 0.81 t and the corresponding product value is \$627.8; the difference of product value and additional chemical cost is \$177.8. Therefore, hydrogenation-cocracking, which consumes hydrogen to decrease the methanol addition, is more economic than direct cocracking.

CONCLUSIONS

1. A SDF of bio-oil was converted into aromatic hydrocarbons by hydrogenation-cocracking with MeOH. The influence of improvement in the hydrogen-lacking property *via* hydrogen supply and transfer on the corresponding cracking process was studied.
2. Hydrogenation-cracking of individual components showed that ketones could receive sufficient hydrogen in the hydrogenation stage and then be efficiently transformed into aromatics. However, HAc was almost not hydrogenated in the hydrogenation stage and therefore its hydrogenation-cracking had a low conversion of 57.4% and a low oil phase yield of 10.1%, accompanied by some carbonaceous deposits.
3. Hydrogenation-cracking of SDF produced a higher oil phase yield than the calculated one, which was attributed to an internal hydrogen transfer from the alcohols produced by ketone hydrogenation to HAc and facilitated the conversion of HAc to aromatic hydrocarbons. However, some HAc was still not converted, which showed that this hydrogen supplement was not sufficient. Therefore, MeOH was introduced as the secondary hydrogen supplier.
4. The optimum hydrogen supplement was accomplished when the MeOH blending ratio was 30%, under which the oil phase yield reached 36.3% and the aromatic hydrocarbon content was up to 95.5%. This MeOH blending ratio was clearly lower than that used in the direct cocracking of bio-oil distilled fraction and alcohol (commonly ≥ 60%). This indicated that hydrogenation-cocracking could significantly decrease the addition of cocracking alcohol at the cost of a small amount of hydrogen.
5. Hydrogenation-cocracking exhibited superiority in economy for the conversion of a bio-oil distilled fraction to aromatic hydrocarbons. Meanwhile, it also showed potential as an upgrading technology of other bio-oil fractions rich in acids and hydroxyketones such as aqueous fraction.

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