RENEWABLE GASOLINE PRODUCED BY CO-CRACKING OF METHANOL AND KETONES IN BIO-OIL

Shurong Wang,* Qinjie Cai, Zuogang Guo, Yurong Wang, and Xiangyu Wang

Most research on the upgrading of bio-oil by cracking has been done under atmospheric pressure, which results in a catalyst coke yield as high as 20 wt%. In this paper, pressurized cracking, as well as co-cracking with methanol proved to be an effective solution for relieving catalyst deactivation. HZSM-5 catalyst was found to deactivate rapidly in the cracking process of pure ketones. However, when methanol was used as the co-cracking substance for ketones under 2 MPa, ketones reached a full conversion of 100 % without obvious catalyst deactivation. The highest selectivity of bio-gasoline phase from co-cracking of ketones and methanol reached a value of 31.6%, in which liquid hydrocarbons had a relative content of 97.2%. The co-cracking of hydroxypropanone and methanol had lower bio-gasoline phase selectivity but better oil phase quality (liquid hydrocarbons selectivity up to 99%) than those of cyclopentanone and methanol. Based on the experimental results, the promotion mechanism of methanol on cracking of ketones in bio-oil was illustrated by a co-cracking mechanism model.

INTRODUCTION

Considering the global energy crisis and serious environmental pollution, renewable biomass resources have attracted worldwide attention. Fast pyrolysis of solid biomass waste can produce liquid bio-oil, which is easily stored and transported (Luo *et al.* 2004a). However, when compared with traditional vehicle fuels (gasoline and diesel), the disadvantage of crude bio-oil is a restriction of its direct transport fuel application. Therefore, catalytic upgrading of bio-oil is an essential process to convert it into refined fuels that are miscible with the existing gasoline or diesel (Bridgwater 1996; Czernik and Bridgwater 2004). Hydrodeoxygenation and catalytic cracking are considered two main ways to convert oxygenated bio-oil into pure hydrocarbon fuels (Czernik and Bridgwater 2004; Mortensen *et al.* 2011). Compared with hydrodeoxygenation, zeolite catalytic cracking converts oxygenated bio-oil into pure hydrocarbon fuels without hydrogen consumption, which makes it more economical (Park *et al.* 2011).

The complex compositions of crude bio-oil, including ketones, alcohols, phenols, aldehydes, *etc*., makes its cracking process very complicated (Wang *et al.* 2009, 2012). The catalytic cracking of crude bio-oil has been ongoing for a long time, and some achievements in decreasing oxygen content and conversion of bio-oil into hydrocarbons have been made, but the reasons for catalyst deactivation in cracking of crude bio-oil have not been completely revealed (Adjaye and Bakhshi 1995; Vitolo *et al.* 1999). Some research has investigated the cracking property of bio-oil model compounds and bio-oil fraction. Different compounds in bio-oil were selected and their cracking reactivity was

compared by Gayubo *et al.* (2004a, 2004b). Alcohols and ketones were found to show the best performance during cracking. While aldehydes and acids were easily degraded to coke, phenols showed the lowest reactivity. In our earlier cracking research, the cracking of bio-oil molecular distillation fraction was investigated, and our results indicated that the coke yield on catalyst can be reduced by cracking the bio-oil fraction (Guo *et al.* 2011). To get a deeper understanding in catalyst deactivation and distinguish the cracking characteristics of different compounds in bio-oil, the concept of an effective H/C ratio can be introduced here, as shown in Eq. (1), with H, O, N, C, and S being the mole percents of hydrogen, oxygen, nitrogen, carbon, and sulfur present in the compound (Mortensen *et al.* 2011; Mentzel and Holm 2011). Compounds with low $(H/C)_{eff}$ tend to form carbon deposits and cause deactivation of catalysts (Mentzel and Holm 2011). Therefore, the heavy catalyst deactivation problem in crude bio-oil cracking is explained by its high oxygen content and low $(H/C)_{eff}$, as well as the difference of bio-oil compounds reactivity.

$$(H / C)_{eff} = \frac{H - 2 \cdot O - 3 \cdot N - 2 \cdot S}{C} \tag{1}$$

In this paper, the concept of an effective H/C ratio was further applied. Some compounds with higher $(H/C)_{eff}$ were selected to promote the cracking of bio-oil compounds with lower $(H/C)_{eff}$. As a result, crude bio-oil can be partially converted into refined fuels that are compatible with gasoline or diesel. Cyclopentanone and hydroxypropanone are two typical and dominant ketones in bio-oil as the representatives of ketones containing five-membered rings and hydroxyl groups (Luo *et al.* 2004b; Demirbas 2007; Heo *et al.* 2010). The hydroxypropanone content in olive husk bio-oil was as high as 13.5 wt% by dry basis, while the total content of cyclopentanone and its derivatives was about 3.8 wt% (Demirbas 2007). The study of these two kinds of ketones not only provides insight into the detailed cracking performance of the ketones family in bio-oil, but also has reference value for studies of other compounds containing C=O double bonds, such as acids and aldehydes. Unfortunately, the $(H/C)_{eff}$ values of these two ketones are rather low, 1.2 for cyclopentanone and 0.67 for hydroxypropanone. Methanol is considered an ideal solvent for co-cracking since it has a $(H/C)_{eff}$ of 2 (Keil 1999; Stocker 1999). Hence, it was selected as a co-cracking reactant to promote ketones' cracking.

In the present work, the cracking properties of bio-oil ketones were investigated according to their model compounds (cyclopentanone and hydroxypropanone), and the influences of co-cracking with methanol on ketones cracking properties were also considered. Gasoline phases were successfully produced from the co-cracking of ketones and methanol with almost 100% conversion of ketones.

EXPERIMENTAL

HZSM-5 (Si/Al = 25) zeolite catalyst was activated at 550 °C for 6 h and sieved to 40–60 mesh before reaction. 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 catalyst was supported on quartz wool in the reactor. The liquid reactants were introduced by an HPLC pump, and the reactants entered the catalytic bed after gasification together

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with nitrogen. The nitrogen carrier gas with a flow rate of 30 mL/min was regulated by a flow meter, and the reaction pressures were regulated by a back-pressure valve. More details about the reactor can be found in our early paper (Guo *et al.* 2010). The weight hourly space velocity (WHSV) of the reactants was kept at 3 h^{-1}. The outlet gas from the reactor passed through a condenser and was separated into liquid products and incondensable gases. Each experimental run lasted for 3 h. The conditions of the experiments are shown in Table 1.

Both the gaseous and liquid products were analyzed. Gaseous products were quantified by an on-line gas chromatograph (Agilent 7890A). Light alkanes and olefins were separated on an HP-Plot Q capillary column with a flame ionization detector (FID). CO and CO_2 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 the rate of 10 °C/min. The liquid products obtained consisted of an easily separable crude gasoline phase and an aqueous phase. The crude gasoline phase was determined by a gas chromatography mass spectrometry system (Trace DSQ 2 system, manufactured by Thermal Fisher Company) with a 30m*0.25mm*0.25μm Agilent DB-WAX capillary column. The GC oven temperature was kept at 40 °C for 1 min, and then increased to 240 °C at the rate of 8 °C/min. Data was acquired with Xcalibur software according to the NIST mass spectral library database. Identified compounds were further quantified by the area normalization method. The residual reactants existed in both crude gasoline phase and aqueous phase, and were quantified by gas chromatography with the external reference method.

The BET specific surface areas of blank HZSM-5 and reacted catalysts were measured by N_2 adsorption-desorption at 77 K, using the BET analysis method with an Autosorb-1 Quantachrom BET surface area analyzer.

The conversion of the reactants (X_i) and the selectivity for the liquid components (S_i) are defined by Eqs. (2) to (7). The mass amounts of cyclopentanone (CPO) and hydroxypropanone (HPO) were quantified by GC with the external reference method under the assumption of an ideal instrument condition. In the calculation of selectivity, the unconverted reactants were excluded from the received liquid products. The symbol "m" in the following equations represents mass of the corresponding substances.

$$X_{CPO} = \frac{(m_{CPO})_{in} - (m_{CPO})_{out}}{(m_{CPO})_{in}} \times 100\% \tag{2}$$

$$X_{HPO} = \frac{(m_{HPO})_{in} - (m_{HPO})_{out}}{(m_{HPO})_{in}} \times 100\% \tag{3}$$

$$X_{MeOH} = \frac{(m_{MeOH})_{in} - (m_{MeOH})_{out}}{(m_{MeOH})_{in}} \times 100\% \tag{4}$$

$$X_{Overall(CPO+MeOH, HPO+MeOH)} = \frac{(m_{Reactants})_{in} - (m_{Reactants})_{out}}{(m_{Reactants})_{in}} \times 100\% \tag{5}$$

$$S_{Crude\,gasoline\,phase} = \frac{(m_{Crude\,gasoline\,phase})_{collected}}{(m_{Reactants})_{in} \times X_{Overall}} \times 100\% \tag{6}$$

$$S_{Aqueous\,phase} = \frac{(m_{Aqueous\,phase})_{collected}}{(m_{Reactants})_{in} \times X_{Overall}} \times 100\% \qquad (7)$$

Table 1. Experimental Conditions

Reactants	Temperature (°C)	Pressure (MPa)	WHSV (h^{-1})
100% CPO	370	0.1	3
30% CPO-70% MeOH	370	0.1	3
30% CPO-70% MeOH	400	0.1	3
30% CPO-70% MeOH	400	2	3
30% HPO-70% MeOH	400	2	3

CPO, HPO, and MeOH refer to cyclopentanone, hydroxypropanone, and methanol, respectively.

RESULTS AND DISCUSSION

The cracking performances of pure CPO at 370 °C and of a mixture of 30 wt% CPO and 70 wt% MeOH at different temperatures (370 °C and 400 °C) and pressures (0.1 MPa and 2 MPa) were studied first. Then, the optimal reaction condition for CPO cracking (400 °C and 2 MPa) was adopted for the co-cracking of HPO and MeOH.

Conversion of the Reactants

Figure 1 presents the conversion of pure CPO, 30% CPO, and 30% HPO. Conversion of CPO was low to 23.8% in the cracking of pure CPO at 370 °C and 0.1 MPa. By comparison, in the co-cracking of 30% CPO under the same conditions, the conversion of CPO increased dramatically to 76.3%, accompanied with a high MeOH conversion of 96.9%. This indicated that the existing MeOH strongly promoted the conversion of CPO.

To further investigate the co-cracking performance of CPO and MeOH, the influences of reaction temperature and pressure were studied. The conversion of CPO reached 85.7% under 30CPO-400/0.1, showing that its conversion increased as the cracking temperature increased. However, the conversion of methanol decreased slightly. There might be a competition relationship between CPO and methanol, and CPO exhibited higher reaction ability than methanol at higher temperature. It was seen that both CPO and MeOH completely reacted and had a conversion of 100% under 400 °C and 2 MPa. The BET specific surface areas of spent catalysts were obtained by N_2 adsorption-desorption technology, and the micropore specific surface area was determined by the t-plot method. The BET surface area represents the total surface area including external surface and micropore surface, while the catalytic ability of HZSM-5 was mainly determined by its micropore specific surface. The total BET specific surface area of catalyst under 100CPO-370/0.1 decreased dramatically from 340 (blank HZSM-5) to 20.5 m^2/g, the micropore BET specific surface area of which declined to 3.1 m^2/g. This meant that its micropores were almost totally plugged by the deposited coke, and the catalyst under 100CPO-370/0.1 was deactivated. The BET specific surface area was in accordance with its low conversion of 23.8 %. In contrast, the BET specific surface area of the catalyst under 30CPO-400/2 after the three hour-reaction was still as high as 129.1 m^2/g.

Under the optimal condition of 400 °C and 2 MPa, the co-cracking of HPO and MeOH was also investigated, which led to 100% conversion of HPO and MeOH. Although HPO had a lower $(H/C)_{eff}$ (0.67) than CPO (1.2), it could also be completely cracked with the promotion of MeOH.
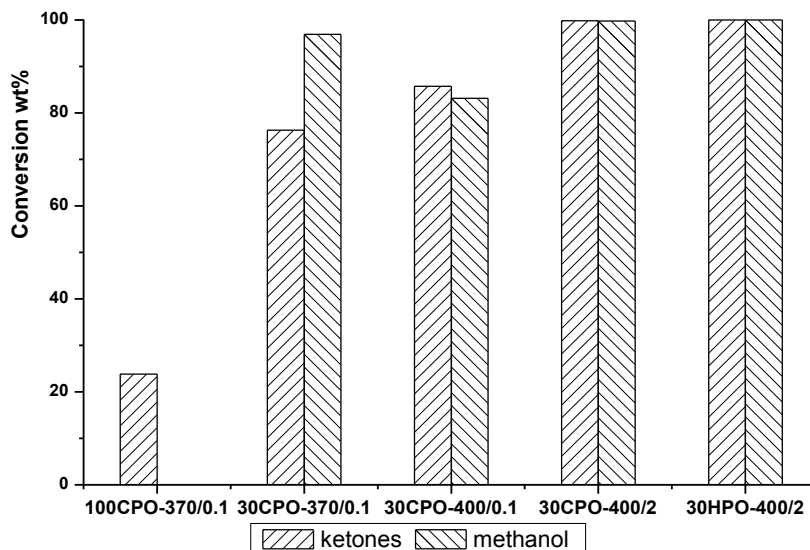

Fig. 1. Effect of reaction parameters on the conversion of ketones and methanol

Liquid Composition

Both an aqueous phase and a crude gasoline phase were obtained from the co-cracking of ketones and MeOH. The compositions of the liquid products, in terms of aqueous phase and crude gasoline phase, are shown in Fig. 2. The catalyst used in cracking of pure CPO was deactivated seriously, and there was only one single-phase liquid collected. The overall liquid selectivity was 71.2 %, and the major component of this liquid was unconverted CPO. For the co-cracking of CPO and MeOH, the upper layer was a light-yellow crude gasoline phase, while the bottom layer was a clear aqueous phase. In the case of the co-cracking of CPO and MeOH, the selectivity of the crude gasoline phase increased with reaction temperature and pressure. The crude gasoline phase accounted for only 6.3% under the conditions of 370 °C and 0.1 MPa, but it increased to 12.3 % when the reaction temperature was 400 °C. The conditions of 400 °C and 2 MPa gave the highest selectivity of crude gasoline phase, up to 31.6 %. The influences of reaction temperature and pressure on the proportion of crude gasoline phase in Fig. 2 were in agreement with those on the conversion of CPO in Fig. 1. In other words, higher CPO conversion favored higher crude gasoline phase selectivity.

In comparison of the results under 30CPO-400/2 and 30HPO-400/2, the selectivity of crude gasoline phase derived from the co-cracking of HPO and MeOH was 18.8%, which was lower than that from the co-cracking of CPO and MeOH. This was due to the higher oxygen content in HPO, which reduced its theoretical gasoline phase value. Based on the difference in catalytic behavior of CPO and HPO, the added amount of methanol can be optimized according to the contents of CPO and HPO in crude bio-oil to improve cracking efficiency.
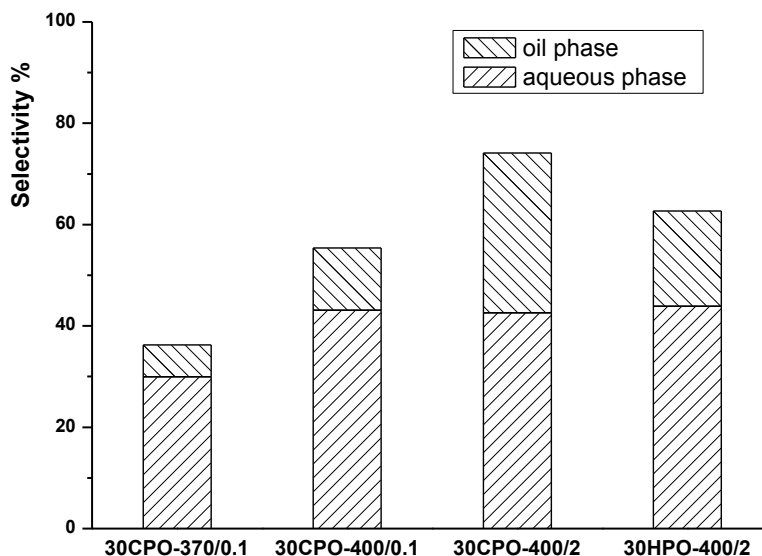
Fig. 2. Selectivity of crude gasoline phase and aqueous phase

Composition of the Crude Gasoline Phase

Crude gasoline phases were obtained under all the conditions of co-cracking of ketones and MeOH. GC/MS technology was adopted to analyze all these crude gasoline phases, and the results indicated that the major components were aromatic and aliphatic hydrocarbons with carbon numbers ranging from 7 to 10. Among these conditions, 30CPO-400/2 and 30HPO-400/2 had higher selectivity of crude gasoline phases, and their main compositions are given in Fig. 3. It was clear that the crude gasoline phases of these two conditions had a similar composition distribution, mainly containing aliphatic hydrocarbons and alkylated aromatic hydrocarbons (xylenes, trimethylbenzene, and so on).

To make a clear comparison on the quality of the crude gasoline phases from different conditions, the components were classified into five groups: aromatic hydrocarbons, aliphatic hydrocarbons, ketones, ethers, and phenols. The classified results are shown in Fig. 4. The case of 100CPO-370/0.1 was a liquid product from the cracking of pure CPO, where the unreacted CPO was excluded. Its hydrocarbon content was quite low, only consisting of 20.4% aromatic hydrocarbons (mainly indane and naphthalene) and 17.3% aliphatic hydrocarbons. The most abundant compounds in this liquid product were new ketone by-products (such as 2-cyclopentylidene-cyclopentanone), which accounted for 55.9%. A by-product of incomplete cracking of CPO was 2-cyclopentylidene-cyclopentanone. The partial deoxygenation between two CPO molecules on the deactivated catalyst formed lots of 2-cyclopentylidene-cyclopenta-none. 2-cyclopentylidene-cyclopentanone had large space structure and easily plugged the HZSM-5 micropores. Then, the catalyst deactivation under this cracking condition was enhanced. The hydrocarbons content in the crude gasoline phase increased dramatically when CPO was co-cracked with MeOH. The contents of aliphatic and aromatic hydrocarbons in the crude gasoline phase obtained under 30CPO-370/0.1 were 11.5% and 79.4%, while those in the case of 30CPO-400/0.1 were 11.5% and 66.9%, respectively. The relative content of hydrocarbons in the crude gasoline phase was a bit lower in 30CPO-400/0.1, but it had a much higher crude gasoline phase selectivity (12.3%) than 30CPO-370/0.1 (6.3%), so its integral selectivity for hydrocarbons was still higher.
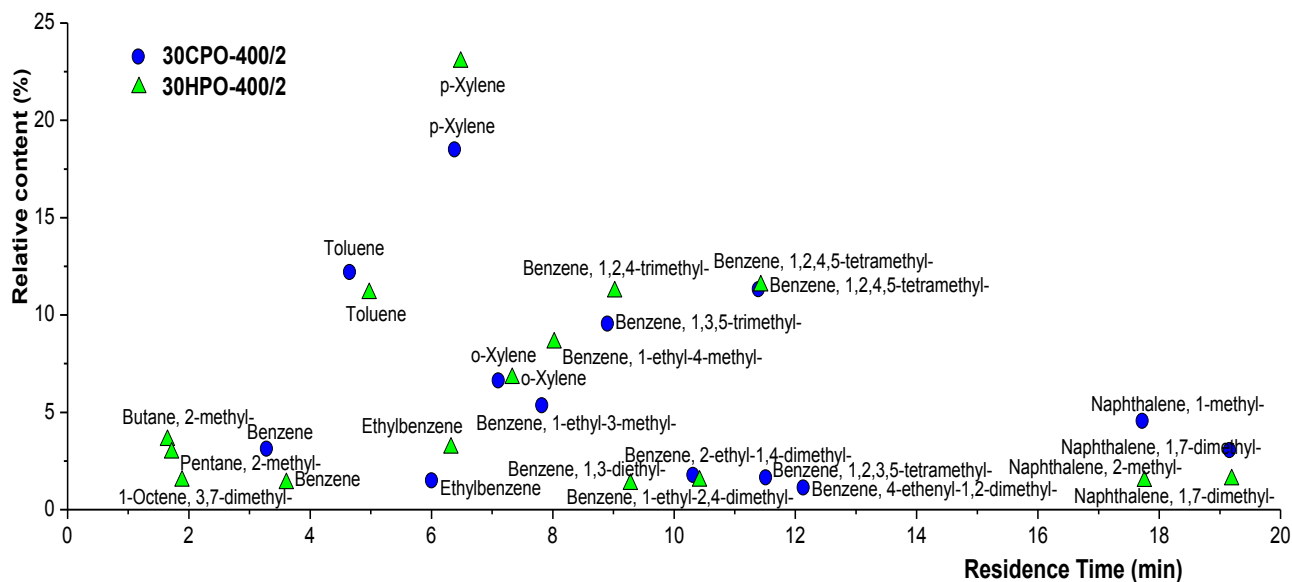
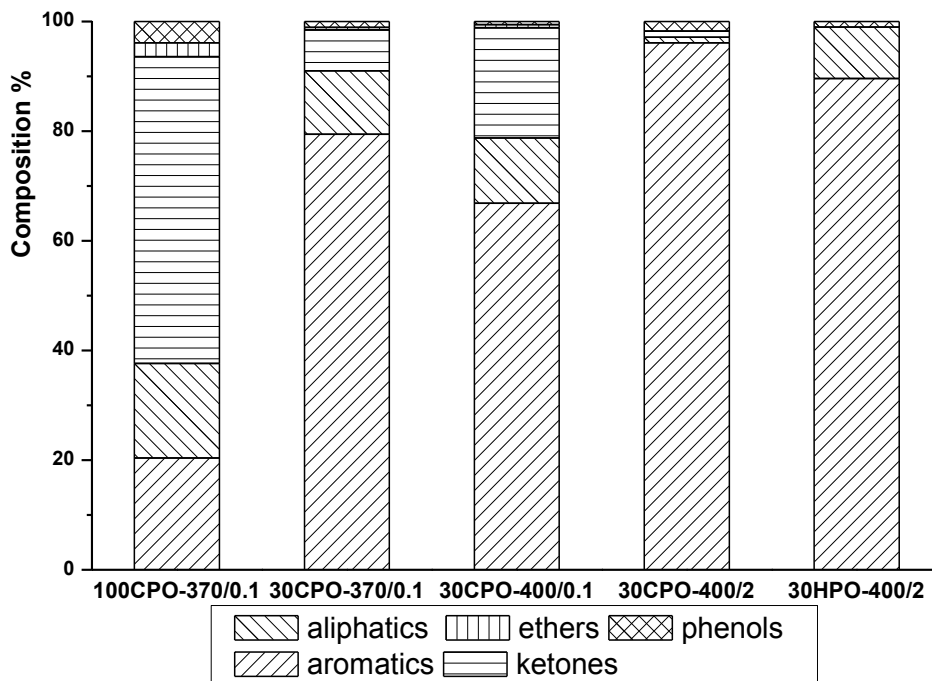**Fig. 3.** Main components in the crude gasoline phase

Fig. 4. Distribution of compositions in crude gasoline phase (reactants excluded)

Besides favoring the conversion of reactants and the selectivity for the crude gasoline phase, increasing the reaction pressure was also beneficial by increasing the selectivity of hydrocarbons production. The relative content of hydrocarbons in the crude gasoline phase obtained under 30CPO-400/2 reached 97.2%, with the relative content of

aromatic hydrocarbons as high as 96.1%. Similar with CPO and MeOH, the high quality of crude gasoline phase was also derived from the co-cracking of HPO and MeOH under 400 °C and 2 MPa. Its total hydrocarbons content reached 99.0% with a higher aliphatic hydrocarbon content of 9.4%. Compared with the co-cracking of ketones and methanol, the cracking of methanol alone under 400 °C/2MPa produced a better quality gasoline phase in which the content of aromatic and aliphatic hydrocarbons were 65.0% and 35.0%, respectively (Zhu *et al*. 2012).

In comparing the results obtained by cracking of pure CPO and co-cracking of ketones and MeOH, it can be concluded that for cracking of ketones, increasing the integral $(H/C)_{eff}$ by co-cracking with MeOH can suppress the catalyst deactivation problem. On the other hand, increasing the reaction pressure also benefited the production of gasoline phase. A similar phenomenon was also observed by Gujar *et al*. (2009), who reported that the yield of gasoline phase from the cracking of methanol almost doubled when the reaction pressure increased from 770 psig to 1710 psig. The improvement of gasoline phase production by pressurized cracking could be explained as follows. As the total reaction pressure increased, the partial pressure of reactant also increased since the concentrations of reactant and methanol were constant in the mixed inlet flow. The partial pressure increased by a certain degree, and this would facilitate the conversion of some light olefins into liquid aromatics as was described in the reference about MTG (Wen *et al*. 2007).

Vent Gas Composition

Besides the liquid products of the crude gasoline phase and the aqueous phase, some incondensable vent gas was also produced during the co-cracking of ketones and MeOH. The vent gas was analyzed by on-line gas chromatography, and the concentrations of CO_x and C_1 to C_4 hydrocarbons were measured by an external standard method. The results are shown in Table 2. In the case of pure CPO cracking, because of early deactivation of the catalyst, only a small portion of the reactant was cracked, and little vent gas was produced. The vent gas from the co-cracking of ketones and MeOH consisted of similar components, with some differences in concentration, indicating that similar reactions occurred under different conditions, such as decarbonylation and decarboxylation.

The vent gases from the co-cracking at 370 °C and 400 °C under atmospheric pressure had similar compositions, in which the concentrations of CO and CO_2 were lower than 4%, while the concentrations of light olefins were up to 40%. These light olefins were released without aromatization under atmospheric pressure. Compared with co-cracking at atmospheric pressure, the concentrations of CO, CO_2, and propane under 30CPO-400/2 increased to 16.77%, 6.67%, and 39.39%, respectively. This may be attributed to the enhancement of decarbonylation and decarboxylation reactions at higher pressure. As a result, deoxygenation of the reactants was enhanced, and more oxygen was released in the form of CO_x, which indirectly decreased the oxygen removal through dehydration, and finally increased the H/C of the crude gasoline phase. It was also observed that the concentrations of light olefins like C_2H_4 were much lower in pressurized condition than atmospheric condition, showing that pressurized cracking could enhance the aromatization of light olefins to produce more liquid hydrocarbons, which was in accordance with the higher selectivity of gasoline phase under pressurized cracking.

Table 2. Concentrations of Gaseous Products in Vent Gas (%)

Conditions	CO	CO_2	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_8	C_4H_{10}
30CPO-370/0.1	1.29	1.01	12.72	44.04	2.51	27.66	7.83	0.00	2.87
30CPO-400/0.1	2.65	3.19	19.82	39.35	3.30	24.78	3.24	3.30	0.24
30CPO-400/2	16.77	6.67	16.06	2.45	5.56	0.67	39.39	8.78	3.63
30HPO-400/2	29.79	11.37	11.97	1.26	4.15	0.92	29.07	8.18	3.25

Proposed Reaction Pathways

The "hydrocarbon pool" mechanism in research on MTG conversion has been widely accepted. This approach emphasized the fact that all the products came from compounds in the hydrocarbon pool, namely active intermediates. Based on the above finding that methanol promoted the cracking of ketones, a double-route mechanism for co-cracking of ketones and methanol was developed here, as shown in Fig. 5.

The first route for the deoxygenation of ketones is direct cracking, where several ketone molecules undergo condensation, decarbonylation, decarboxylation, and dehydration reactions to form olefins, COx, and H_2O. Similar to the decarboxylation mechanism for acetone cracking (Cruz-Cabeza *et al.* 2012), CPO and HPO could undergo aldol condensation and subsequent cracking to produce olefins and carboxylic acids, and then the carboxylic acids intermediates underwent decarboxylation to release CO_2. The decarbonylation of ketones might mainly involve the direct rupture of C-C bonds to form small hydrocarbon fragments and released CO (Wang *et al.* 2012). However, the incomplete deoxygenation by condensation reaction would predominate if the catalyst deactivated. In this case, the condensation of several ketone molecules would result in new ketones by-products, such as the 2-cyclopentylidene-cyclopentanone during pure CPO cracking.

In the second route, ketones are deoxygenated according to the hydrocarbon pool mechanism. The aromatic hydrocarbons accounted for more than 95% in the crude gasoline phase obtained by co-cracking of ketones and methanol, which are considered typical active intermediates in the conversion of methanol. Concerning the hydrocarbon pool mechanism of MTG, some researchers have proposed that either methanol or dimethyl ether interacts with benzene rings by methylation to form methyl-substituted benzenes, which then undergo molecular reforming and side-chain coupling to produce light olefins (Haw *et al.* 2003; Olsbye *et al.* 2005). Some other researchers have assumed that methyl groups on a benzene ring react with methanol to form alkyl groups, the disengagement of which from the benzene ring produces ethylene (Mole *et al.* 1983). Both of these assumptions involve hydration caused by interaction between the hydroxyl groups of the reactants and hydrogen atoms or methyl groups on benzene rings. In view of the high selectivity for aromatic hydrocarbons observed in our results, it can be inferred that there were also some aromatic-like intermediates in the conversion of ketones, which propagated aromatization and other reactions. To make the deoxygenation in cracking similar to that in MTG, hydroxyl or hydroxyl-like groups are required. During the co-cracking of ketones and methanol, on the one hand, hydroxyl groups are provided by the original reactants, such as the hydroxyl groups of methanol and HPO. On the other hand, hydroxyl groups could be borne by intermediates. Enol intermediates formed by chemical adsorption and subsequent hydrogen transfer and molecular reforming of CPO at Brønsted acid sites were identified by NMR by Huang *et al.* (2009). So, it is possible

that ketones are deoxygenated via the hydrocarbon pool mechanism. In the hydrocarbon pool reaction, since the conversion of ketones required an additional step in the formation of enol intermediates compared with the reaction of methanol, the presence of methanol may have provided enough active intermediates in a shorter time. Hence, the methanol added to ketones for co-cracking not only extended the lifetime of the catalyst, but may also have facilitated more efficient conversion of the ketones. Meanwhile, ketones also had great influence on methanol during co-cracking, since much more aromatic hydrocarbons were produced than MTG.

The olefins produced from ketones and methanol underwent aromatization to form primary aromatics, and also underwent polymerization, alkylation, and isomerization to form C_4 to C_6 iso-alkenes. The primary benzene ring could be transformed into active intermediates by alkylation reaction, such as methyl-substituted benzenes, which enriched the hydrocarbon pool and promoted the deoxygenation of ketones and methanol. It could also undergo further aromatization to produce polycyclic arene, such as naphthalene and its derivatives.
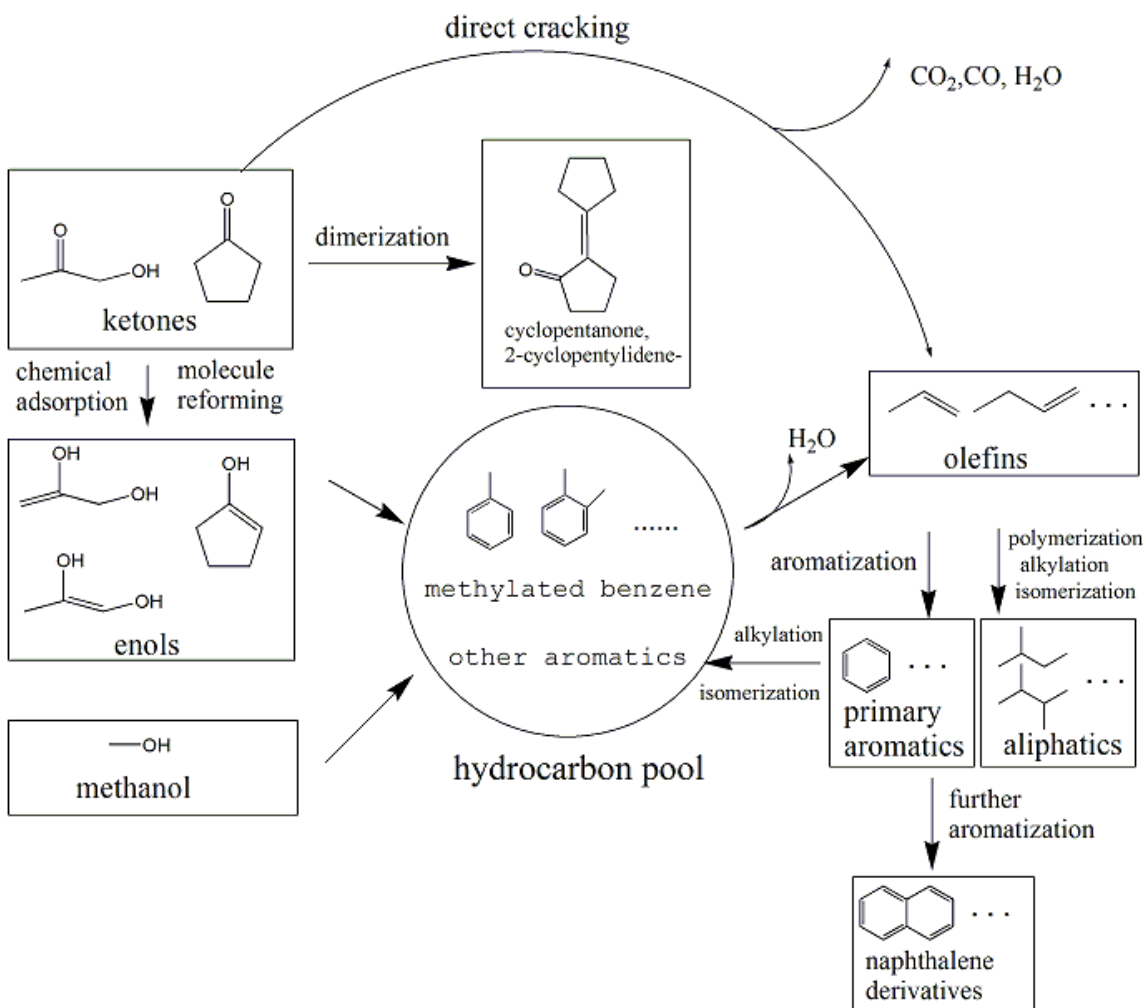

Fig. 5. Co-cracking mechanism model for ketones and methanol

The differences in catalysts' deactivation can also be explained by this reaction scheme. During the cracking of pure CPO, the 2-cyclopentylidene-cyclopentanone was produced by the direct condensation of two CPO molecules. This dimer had a large space

structure so that it could block the pores and eventually lead to the deactivation of catalysts. On the other hand, for the co-cracking of ketones and methanol, hydrocarbons were the main products, and these could go through the catalyst pores easily, indicating that the deactivation of catalysts caused by polyaromatics was very weak. Compared with 2-cyclopentylidene-cyclopentanone, the formation of polyaromatics required more steps, involving complex deoxygenation and aromatization, so the formation rate was lower. Therefore, the deactivation of catalysts by polyaromatics formed by the hydrocarbon pool mechanism was slower than that by ketone condensation, which was in accordance with the experimental results.

CONCLUSIONS

Two ketones (CPO and HPO) were selected from biomass pyrolysis oil, and their cracking characteristics with methanol were investigated. Results indicate that methanol had a positive effect in suppressing the catalyst deactivation problem during ketones' cracking. The highest conversion of ketones reached 100%, accompanied with a crude gasoline phase selectivity of 31.6%. The light-yellow crude gasoline phase mainly consisted of aromatic hydrocarbons and aliphatic hydrocarbons. The highest relative content of liquid hydrocarbons in crude gasoline phase for co-cracking of CPO and methanol was 97.2%, while that for HPO and methanol reached 99.0 %.

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