

Recovery of useful chemicals from oil palm shell-derived oil using zirconia supporting iron oxide catalysts

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Abstract—The possibility for recovering methanol, acetic acid and phenol from oil palm shell-derived oil was investigated. Thermal cracking mainly produced a solid residue and was not a suitable method for recovering these three target chemicals. When zirconia supporting iron based catalyst (Zr/FeOx, Zr-FeOx or Zr-Al-FeOx) was applied, the “others”—unidentified hydrocarbons—were satisfactorily removed without formation of a solid residue while these target compounds were considerably stable over these catalysts. Zr-Al-FeOx showed the highest activity for oxidation of the oil to CO₂. Effect of operating parameters (steam to oil ratio, temperature and time factor) on its performance was further investigated. In order to gain insight into the reaction path, the reaction using model compounds (methanol, acetic acid, acetone, ethyl acetate and phenol) was performed.

Key words: Biomass Utilization, Renewable Chemicals, Catalytic Cracking, Iron Oxide Catalyst, Oil Palm Shell

INTRODUCTION

Recently, energy consumption in South East Asia has continuously increased due to high economic growth rate. Limited fossil resources will not be enough for serving this demand in the near future. In Thailand, the process for production of biodiesel, as an alternative energy, from palm oil has been rapidly developed. Beside the massive production of palm oil, huge amount of biomass wastes are disposed from palm oil mills, approximately 12.7 million tons in 2003 [1]. This amount has continuously increased. Although these wastes have been mainly used for on-site energy production, the combustion with low energy efficiency causes air pollution. An alternative way for utilizing these excessive palm wastes should be, therefore, established rapidly.

The solid wastes from palm oil mills are classified into shell (3.25%), fiber (11.79%), empty fruit bunch (51.36%) and kernel (33.6%). Shell, fiber and empty fruit bunch mainly consist of lignin, cellulose and hemi-cellulose. Thermochemical conversion, especially pyrolysis, of these three chemicals produces a liquid mixture of several valuable hydrocarbons (e.g., alcohols, aldehydes, ketones, carboxylic acids, phenol and its derivatives) [2,3]. Acetic acid is an important raw material for chemical and petrochemical industries. Its applications are mainly in polymer and textile synthesis. Phenol is widely used in the production of plastic resins. Methanol is an important raw material in the chemical industry, and it can be used as a bio-fuel, feedstock in fuel cell application and production of gasoline. Thus, these palm wastes should be a promising chemical

resource if a suitable process for recovery of these useful chemicals is economically established. In order to purify these target chemicals from the pyrolyzed liquid mixture, the unstable chemicals existing with only small amount and having closed physical and chemical properties should be removed in the early step.

Our group previously reported that ZrO₂ supporting FeOOH shows high performance for recovery of phenol and acetone from the oil waste obtained from the production of activated carbon [4]. This catalyst was further improved and applied for ketone production from domestic sewage sludge-derived black water [5]. The activity of the catalyst was affected by its preparation method. The durability of the catalyst was successfully improved by loading Al₂O₃ into the lattice of FeOx in the application for ketone production. The catalysts may be suitable for the recovery of our target chemicals from pyrolyzed liquid mixture obtained from the solid palm wastes. However, ZrO₂ and Al₂O₃ themselves also have catalytic activity for several reactions with hydrocarbons [6,7]. Difference of compositions and concentrations between the black water and oil palm shell-derived oil may result in undesired side reactions. It is worthwhile to investigate the performance of the catalysts for the process using palm waste-derived oil as a feedstock.

Among those solid wastes from palm oil mills, oil palm shell has the lowest water content. It was selected as a model for the investigation in order to evaluate the possibility of the process for recovery of methanol, acetic acid and phenol. In this study, the oil palm shell was pyrolyzed to produce bio-oil under the condition giving the highest yield of a liquid mixture. The oil palm shell-derived oil was used as a feedstock in the reaction for recovering three target chemicals: methanol, acetic acid and phenol. The performance of several zirconia supporting iron based catalysts was examined. Effects of operating parameters on the performance of the most active catalyst were further clarified.

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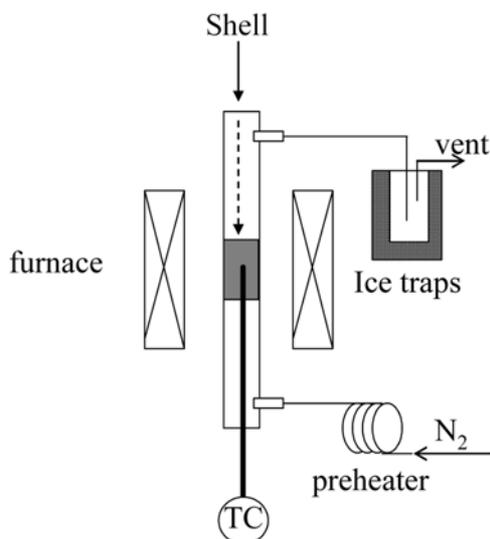


Fig. 1. Schematic diagram of the pyrolysis reactor.

EXPERIMENTAL

1. Preparation of Oil Palm Shell-derived Oil

Oil palm shell taken from a typical palm oil mill in southern of Thailand was ground and sieved to a particle size between 500-850 μm . The ground oil palm shell was dried in air at 383 K overnight to remove humidity. A schematic diagram of the experimental apparatus used for the pyrolysis is illustrated in Fig. 1. Nitrogen was introduced into the reactor for carrying the liquid product out of the reactor. The dried oil palm shell was dropped into the reactor after the temperature of the reactor was constant at 773 K, then kept for pyrolysis at this temperature for 1 h. The liquid product was collected in a series of ice traps.

2. Catalyst Preparation and Characterization

Three types of zirconia supporting iron-based catalyst were prepared and tested for their performance. Impregnated catalyst (Zr/FeOx) was prepared from FeOOH and ZrOCl₂ by the method previously described in detail elsewhere [4]. Zr-FeOx and Zr-Al-FeOx were prepared by the co-precipitation method described in the previous work [5]. The amount of zirconia in the catalysts was fixed at 7.7 wt%. The structure of the catalyst was analyzed with an X-ray diffractometer (JDX-8020, JEOL).

3. Catalytic Cracking Test

The apparatus used in this study was similar to the one used previously [5]. The oil palm shell-derived oil and water were separately introduced into the reactor by using micro syringe pumps. Flow rate of the oil palm shell-derived oil was fixed constant at 0.5 $\text{g}\cdot\text{h}^{-1}$ for all experimental runs. The catalyst with a particle size of 300-850 μm was packed in the fixed bed reactor. The reaction temperature varied in the range of 623-723 K. Time factor (W/F) varied in the range of 0.5-12 h. Composition of gas and liquid products were analyzed by using GC-TCD and GC-FID as described in the previous work [8].

Reaction experiment using the most active catalyst (Zr-Al-FeOx) was also conducted using model compounds (methanol, acetic acid, acetone, ethylacetate and phenol) in order to gain more information about possible reaction paths. The mixture of the interested model

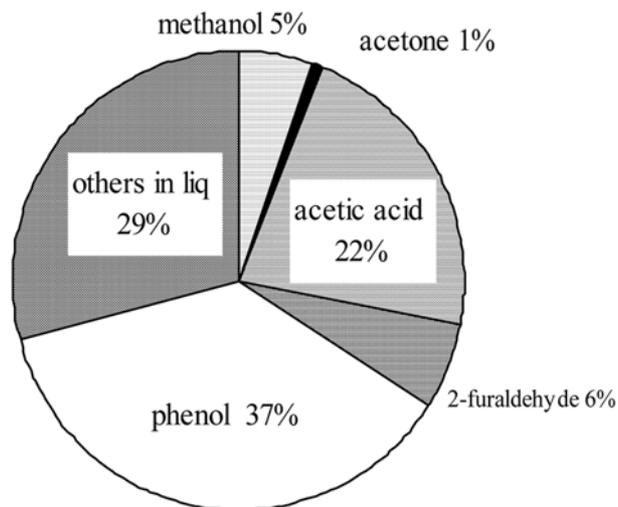


Fig. 2. Composition of oil palm shell-derived oil obtained by pyrolysis at 773 K.

compound and water ($C_{\text{model compound}}=20\%$ vol diluted in water) was introduced into the reactor with a flow rate of 0.5 $\text{g}\cdot\text{h}^{-1}$. All the experiments were conducted under the same condition ($T=673\text{ K}$, $W/F=3\text{ h}$).

RESULTS AND DISCUSSION

1. Composition of Oil Palm Shell-derived Oil

By varying the pyrolysis temperature, we found that yield of the liquid product reached the highest value of 55 wt% at 773 K. Fig. 2 shows the composition of the oil palm shell-derived oil obtained under this condition. Although the oil derived from pyrolysis of lignocellulose is a mixture of water and several hydrocarbons [9], we gave special interest to the composition of hydrocarbons. Therefore, the composition of the oil was reported based on the total carbon in the liquid mixture (dried basis). This oil mainly consisted of phenol (ca 37% C), acetic acid (ca 22% C) and methanol (ca 5% C). The chromatogram from gas chromatograph showed that there are

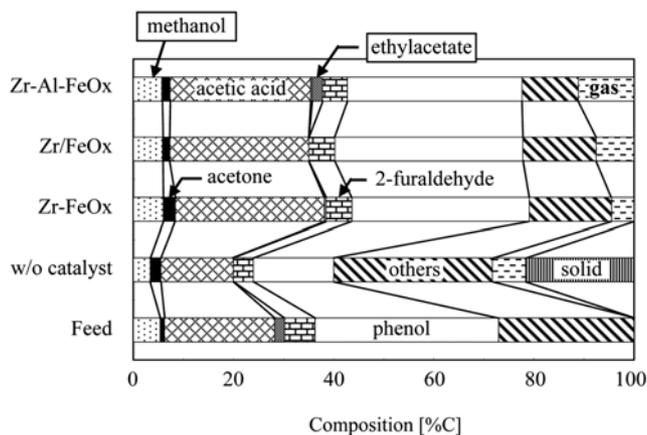


Fig. 3. Product yields obtained by thermal cracking and catalytic cracking over different catalysts ($W/F=2\text{ h}$, $T=673\text{ K}$, $F_{\text{Ino}}:F_{\text{out}}=2:1$).

more than 20 hydrocarbons existing in this oil. For further discussion, we denoted these unidentified chemicals as “others”. Based on the information reported in several previous works [3,9], these “others” are chemicals such as small alkanes, alkenes, carboxylic acids, ketones, aldehydes, alcohols, esters, aromatics. Since several chemicals are thermally unstable [3,10,11] and make the utilization of this oil palm shell-derived oil become uneconomical, it is necessary to upgrade this pyrolyzed oil by removing these “others” as much as possible. It should be noted that the amount of total carbon in the oil palm shell-derived oil obtained in this study (ca 12 wt%) was much higher than the sewage sludge derived black water (ca 2 wt%, [5]).

2. Oil Upgrading and Catalyst Screening

Fig. 3 shows the product distributions from thermal and catalytic cracking of oil palm shell-derived oil under typical operating condition. When a catalyst was not used for the reaction, only thermal cracking occurred. The amount of acetic acid and phenol in the product significantly decreased while a solid residue was produced as a main product. Moreover, the amount of the “others” was nearly unchanged. Therefore, thermal cracking is not an effective method for recovering the target useful chemicals from this oil palm shell-derived oil.

We have previously reported that zirconia supporting iron oxide catalysts show suitable activity for recovering useful chemicals from biomass derived-black waters with high stability [4,5]. The roles of ZrO_2 and Al_2O_3 were previously examined. Optimum amount of ZrO_2 was added into the $FeOx$ catalyst in order to accelerate the generation of active oxygen and hydrogen species from H_2O . The active oxygen species spills into the hole in the structure where the oxygen was consumed by the reaction. As a result, the zirconia supporting iron oxide catalyst has activity and stability higher than $FeOx$ catalyst. Addition of Al_2O_3 into the catalyst could reduce the size of $FeOx$ lattice. Consequently, stability of the catalyst was improved by reduction of the deactivation by shrinking and expansion of the lattice during the reaction [12]. These three catalysts should also be applicable in the catalytic cracking of oil palm shell-derived oil. However, ZrO_2 and Al_2O_3 themselves also have catalytic activities for several reactions (e.g., dehydrogenation, dehydration and catalytic cracking). Formation of mixed metal oxides may form strong

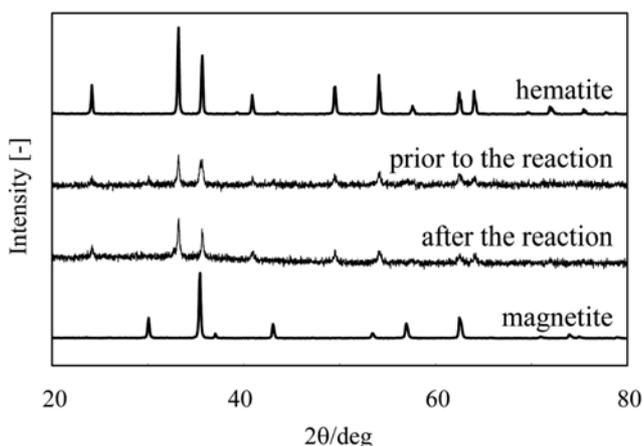


Fig. 4. XRD pattern of the Zr-Al-FeOx before and after the catalytic cracking (W/F=2 h, T=673 K, $F_{H_2O} : F_{oil}=2 : 1$).

acid sites [13]. On the other hand, the oil palm shell-derived oil had carbon content and the amount of “others” much higher than the sewage sludge derived black water. Therefore, the addition of these two components may affect the performance of the catalyst for recovering target compounds from the oil palm shell-derived oil. It is interesting to investigate their performance towards our recovering process. The results in Fig. 3 show that all of the catalysts may be used to recover the target compounds (methanol, acetic acid and phenol) since the target compounds were not reacted over the catalysts while “others” was converted to gas. The main product in gas was CO_2 (more than 90%). This result confirmed that complete oxidation of “others” to CO_2 mainly occurred during the reaction. By comparing the amount of CO_2 , the activity of the catalysts was in the order of $Zr-Al-FeOx > Zr/FeOx > Zr-FeOx$. Fig. 4 shows the XRD patterns of the most active catalyst (Zr-Al-FeOx) prior to and after the reaction. The spectra reveal that no phase transformation from hematite to magnetite occurred after the reaction test. This confirms no deactivation of the Zr-Al-FeOx during the reaction. These results indicate high possibility for applying the Zr-Al-FeOx to upgrade this oil palm shell-derived oil. In order to obtain information for process and catalyst design, the performance of Zr-Al-FeOx was further investigated under various operating conditions.

3. Effect of Operating Condition

As mentioned in section 3.2, water is necessary for the catalytic cracking of hydrocarbons over Zr-Al-FeOx. The relative amount of water to total carbon during the reaction should be a key factor for the performance of the catalyst. Fig. 5 obviously shows that dilution of hydrocarbons in feed stream reduced the methanol decomposition and increased the yield of acetic acid. The difference in the product yields was clearly observed when the steam to oil palm shell-derived oil increased from 0 : 1 to 2 : 1 and insignificant when the ratio increased from 2 : 1 to 2.5 : 1. This result indicates that the water existing in the oil palm shell-derived oil was not enough for the cracking of hydrocarbons. Furthermore, adding water into system by the ratio of 2 : 1 could be considered as water in excess condition. Although the performance of Zr-Al-FeOx for recovering the target chemicals was improved by addition of water, the large excess steam will cause wasteful of energy. The ratio of 2 : 1 was chosen

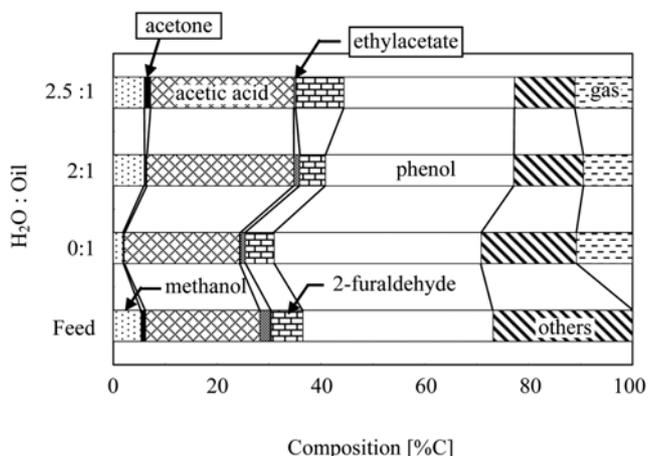


Fig. 5. Effect of steam concentration on the product yields obtained from catalytic cracking over Zr-Al-FeOx (T=623 K; W/F=2 h).

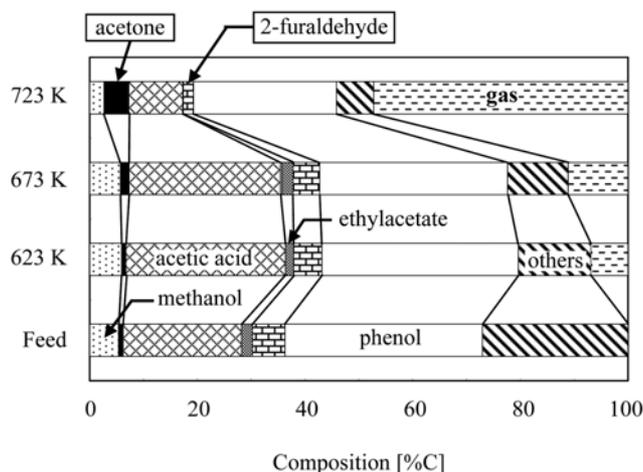


Fig. 6. Effect of cracking temperature on the product yields obtained from catalytic cracking over Zr-Al-FeOx (W/F=2 h; $F_{H_2O} : F_{oil}=2 : 1$).

and set for further investigation.

Fig. 6 shows that increasing of reaction temperature accelerated the complete oxidation of hydrocarbons in the oil palm shell-derived oil to CO_2 . At 723 K, the yield of gaseous product was nearly 50% C so that the recovery of the target compounds in liquid is not efficient. This result indicated that the reaction temperature should not be as high as 723 K. In the lower range, the yield of acetic acid increased by the reaction while the amount of “others” decreased. This implies that under mild operating condition, some of “others” were converted to acetic acid.

Fig. 7 shows effect of time factor on product yields at 623, 673 and 723 K. In this temperature range, the yield of “others” decreased with increasing of W/F while the yield of gas increased. This behavior implied that oxidation of “others” finally produced gases. This effect was more obvious when the reaction temperature was high. In the tested range of time factor, the yield of methanol was nearly constant at $T=623$ K and decreased with the time factor at higher temperature ($T \geq 673$ K). This result reveals that the decomposition of methanol over Zr-Al-FeOx occurred only when the temperature was high enough. The yield of acetic acid showed the maximum at W/F=2, 2 and 1 h when the temperature was 623, 673 and 723 K, respectively. This result shows the possibility of production of acetic acid from some amount of “others” in the oil and simultaneously decomposition of acetic acid over this catalyst. At low temperature or W/F, the amount of acetic acid produced from the reaction was higher than that was decomposed. The dependence of phenol yield on the time factor was similar to that of methanol. In addition, it was interesting that the amount of acetone increased with increasing of W/F for all the tested reaction temperatures. This reaction route for the formation of acetone will be examined in the next section. At the highest temperature ($T=723$ K), the amount of all components in liquid product sensitively decreased with increasing of W/F and only gas product was produced. This result reveals that the reaction at 723 K was too severe for recovering all target compounds. Since the decreasing of the amount of the “others” with respect to W/F was more significant compared to those of the target compounds at $T=673$ K, it is reasonable to recover these target com-

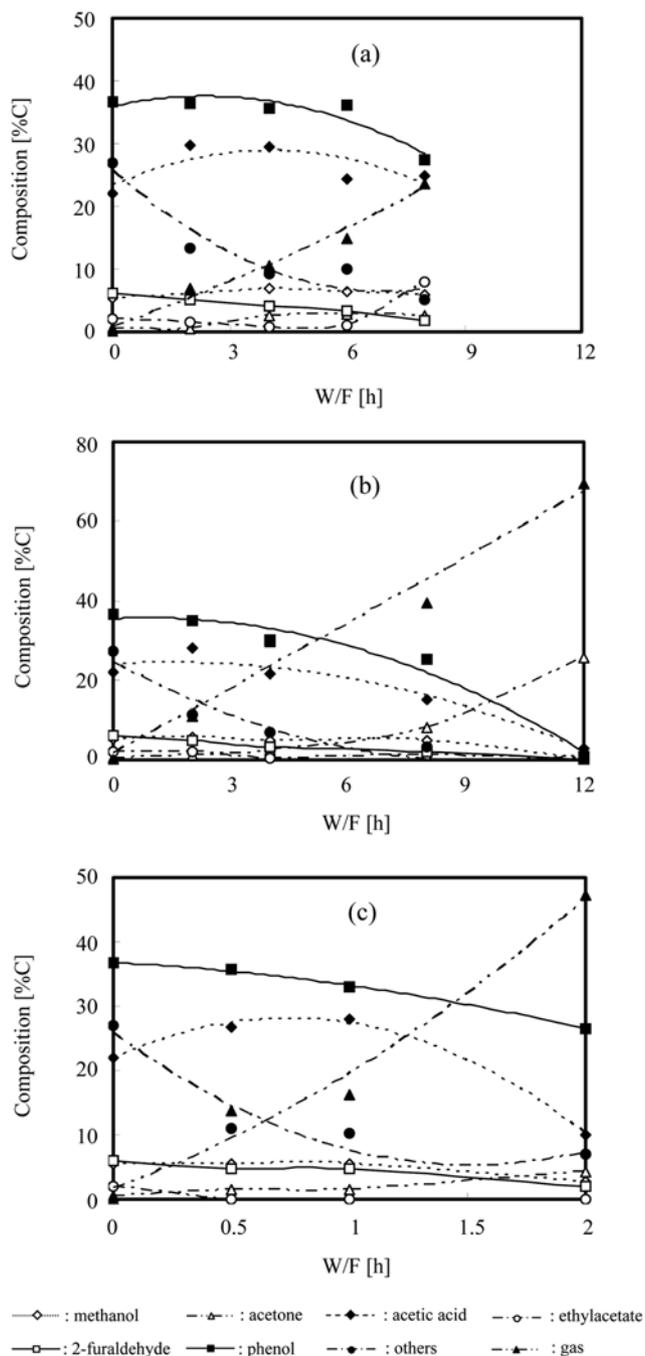


Fig. 7. Effect of W/F on the product yields obtained by catalytic cracking over Zr-Al-FeOx at (a) 623 K, (b) 673 K and (c) 723 K ($F_{H_2O} : F_{oil}=2 : 1$).

pounds at 673 K. A mixture of methanol 6% C, acetic acid 24% C, acetone 3% C and phenol 36% C was obtained at W/F=6 h; $T=623$ K. This liquid mixture contained a reasonable amount of the target compounds with small amount of “others”. This condition (W/F=6 h and $T=623$ K) was considered as the optimum condition for the process in this study.

4. Catalytic Cracking of Model Compounds

The reaction over Zr-Al-FeOx was tested for five model compounds (methanol, acetone, acetic acid, phenol and ethyl acetate) in order to gain information on the reaction route. Fig. 8 shows the

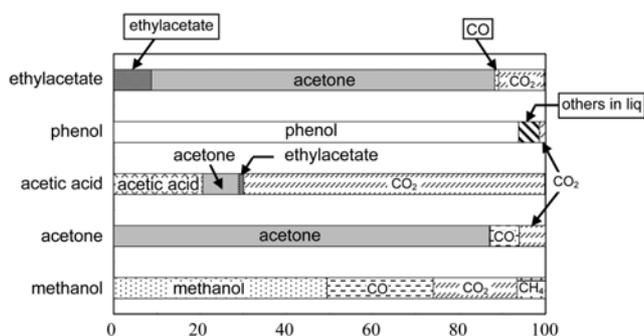


Fig. 8. Product yields obtained from catalytic cracking of model compound over Zr-Al-FeOx at 673 K, W/F=3 h, C_{model} =20%vol diluted with water.

Table 1. Composition of gaseous products obtained from the catalytic cracking of each model compound

Products compound	CO	CO ₂	CH ₄	Others
Methanol	48.6	38.3	13.0	0
Acetone	52.5	47.5	0	0
Acetic Acid	0	99.8	0.2	0
Phenol	0	100	0	0
Ethyl acetate	8	89.5	0	2.5

product yields obtained from each model compound. Composition of the gaseous products is summarized in Table 1. Methanol was converted to gaseous product mainly consisting of CO, CO₂ and CH₄. Acetone was converted to gaseous product mainly consisting of CO and CO₂. Phenol was quite stable under the reaction condition; only small amount of CO₂ was formed due to the reaction. Acetic acid was easily converted to acetone, ethyl acetate and gases (mainly CO₂). The reaction of ethyl acetate mainly produced acetone with small amount of gaseous products. According to the results from three model compounds (acetic acid, acetone and ethyl acetate), it should be concluded that acetic acid was firstly converted to ethyl acetate and then successively transformed into acetone. In the final step, acetone decomposed to gaseous products.

CONCLUSION

This research proved that oil palm shell could be considered as a new resource for methanol, acetic acid and phenol. The process for recovery consists of two steps: pyrolysis of oil palm shell and

catalytic upgrading over Zr-Al-FeOx catalyst. Pyrolysis of oil palm shell at 773 K in nitrogen stream produced a liquid oil containing 12 wt% of C. For the catalytic upgrading, it was found that the activity of the tested catalysts was Zr-FeOx < Zr/FeOx < Zr-Al-FeOx. Performance of the most active catalyst (Zr-Al-FeOx) under various operating condition was investigated. The results showed that addition of water was useful for selective stabilizing methanol and phenol and for production of acetic acid from "others". The suitable temperature for the reaction should not be higher than 623 K. Under the optimum condition (W/F=6 h; T=623 K) for recovery of these target compounds, a mixture of methanol 6%C, acetic acid 24%C, acetone 3%C and phenol 36%C was obtained.

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