

Pyrolysis of soybean oil with H-ZSM5 and MCM41 catalysts in a fixed-bed reactor

Thanh An Ngo¹, Jinsoo Kim^{1,*}, Sun Kuk Kim², Seung-Soo Kim³

¹Department of Chemical Engineering, Kyung Hee University,
Yongin, Gyeonggi-do, 449-701 South Korea

²Department of Architecture Engineering, Kyung Hee University,
Yongin, Gyeonggi-do, 449-701 South Korea

³Department of Chemical Engineering, Kangwon National University,
Samcheok, Gangwon-do, 245-711 South Korea

ABSTRACT: Soybean oil was pyrolyzed with various catalysts in a fixed bed reactor under nitrogen flow at 420 and 450°C. The H-ZSM5 catalysts (molar ratio SiO₂/Al₂O₃ = 28, 40, and 180) and 2 wt% (Ga, Al or Cu) impregnated MCM41 catalysts were used in order to investigate the effect of catalysts during the pyrolysis process. The gas products in all experiments were mainly methane, ethane and propylene. The liquid products in the presence of H-ZSM5 catalysts were mainly aromatic components while those with metal/MCM41 catalysts were a mixture of alkanes, alkenes, alkadienes, aromatic and carboxylic acids. The highest coke yield of 4.4 wt% was obtained with Ga/MCM41 catalyst at the pyrolysis temperature of 420°C. The effect of catalysts on product yield and composition was systematically investigated.

Keyword: pyrolysis, soybean oil, H-ZSM5, MCM41, acidity.

1. INTRODUCTION

Soybean oil is now considered as a potential source for producing bio-fuel due to its reasonable price and availability compared to other vegetable oils. In recent years, there has been an increasing interest in catalytic pyrolysis to bio-fuel [1]. This method just applies thermal energy combining the usage of appropriate catalysts to cause hydrocarbon cracking, hence it is not necessary to supplement any stages for refining catalyst or separating product. Catalysts for pyrolysis process were usually solid catalysts with a good shape selectivity and proper pore size. H-ZSM5 and metal

impregnated MCM41 catalysts have been used for hydrocarbon cracking [2].

H-ZSM5 and other types of zeolites, such as USZ and beta-zeolite, were synthesized and used for the pyrolysis of palm oil as reported by Farouq et al [3]. However, in their study, they focused on using various zeolites to compare the effect of some specific zeolite structures on catalytic pyrolysis reaction. Although this was a quite typical review for catalytic pyrolysis with zeolite, the role of acidity was not considered for hydrocarbon cracking.

Mbaraka and Shanks [4] reviewed the conversion of oils and fats using various mesoporous catalysts including MCM41.

MCM41 is a typical mesoporous material due to its pore size in the range from 20-50 Å with relatively low acidity. It is the reason why MCM41 is usually modified with some metals to increase its acidic property. Additionally, the pore size of MCM41 is large enough to allow triglyceride molecules or bulky intermediate compounds to diffuse and react in the pore, producing the products with the broad carbon number distribution from gasoline to diesel.

In this study, the pyrolysis of soybean oil was conducted at the pyrolysis temperature of 420°C and 450°C with various catalysts in a fixed bed reactor under nitrogen gas. In order to investigate the effect of catalysts, microporous H-ZSM5 catalysts and mesoporous metal/MCM41 catalysts were synthesized and used for the pyrolysis process. The product yield and chemical composition were mainly characterized by GC and GC-MS. The pyrolysis results were systematically studied in terms of the effect of metal and acidity as well as the catalyst structures.

2. EXPERIMENTAL

2.1 Synthesis of catalysts

For H-ZSM5 catalyst, zeolite ZSM5 with the molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3 = 28, 40$ and 180 were synthesized first following the literature [5]. After calcination at 550°C for 8h, the obtained ZSM5 powder was exchanged twice with 1M NH_4NO_3 solution at 80°C for 3h so as to form the NH_4 -ZSM5. This ammonium zeolite was then calcined at 550°C for 4h to produce the desirable H-ZSM5 catalyst. Corresponding to the ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 28, 40 and 180, the product zeolites were labelled as M28, M40 and M180.

MCM41 was prepared using the method by Caps and Tsang [6]. In order to impregnate 2wt% of Ga, Al and Cu into MCM41, a 30 ml metal nitrate solution with the calculated amount of metal was stirred

and then 2g of MCM41 was added into this solution. This mixture was stirred continuously for 6h at 70°C and subsequently vaporized at the same temperature. The product from vaporization was then dried for 12h at 80°C and finally calcined at 500°C for 5h to obtain the desirable metal/MCM41 catalysts.

2.2 Pyrolysis in a fixed bed reactor

Figure 1 shows a tube reactor ($\varnothing 10\text{mm} \times 300\text{mm}$) set-up for pyrolyzing soybean oil (CJ Food System). For each run, 0.3 g of fresh catalyst ($W_{\text{cat_fresh}}$) with the particle size between 600 and 850 μm was put into the reactor after drying at 120°C for 2h to remove moisture completely. The feed rate of soybean oil was fixed at 2 ml/h by a micro pump and nitrogen at 10 ml/min was used as a carrier gas for all experiments. Before feeding the soybean oil, the reactor temperature was maintained at 420°C or 450°C.

The weight of used feed oil (W_{in}) can be easily calculated by the reaction time. The eutectic solution of NaCl and ice water (76.4 wt% NaCl and 23.6 wt% ice water, at -21.8°C) was used as a coolant for condensing liquid product [7]. The gas-tight bag was used to collect the gas product for GC analysis. After reaction, the liquid product was weighed to calculate the weight of liquid product (W_{liq}). Among the liquid product, the water was separated by a funnel and then weighed to determine W_{water} (weight of water). This water-free liquid was analyzed by GC equipped with the HP-1 column in order to calculate the weight of remaining feed oil in the liquid product (W_{remain}). The weight of used catalyst ($W_{\text{cat_used}}$) was determined by weighing the solid catalyst after filtering, washing with acetone and drying at 80°C for 8h. The yields of the product and conversion are defined as follows:

$$\text{Bio-oil yield} = 100 \cdot \frac{W_{\text{liq}} - W_{\text{water}} - W_{\text{remain}}}{W_{\text{in}}}$$

$$\text{Coke yield (wt\%)} = 100 \cdot \frac{W_{\text{cat_fresh}} - W_{\text{cat_used}}}{W_{\text{in}}}$$

$$\text{Gas yield (wt\%)} = 100 \cdot \left[1 - \frac{W_{\text{liq}}}{W_{\text{in}}} - \text{coke yield} \right]$$

$$\text{Conversion (\%)} = 100 \cdot \left(\frac{W_{\text{in}} - W_{\text{remain}}}{W_{\text{in}}} \right)$$

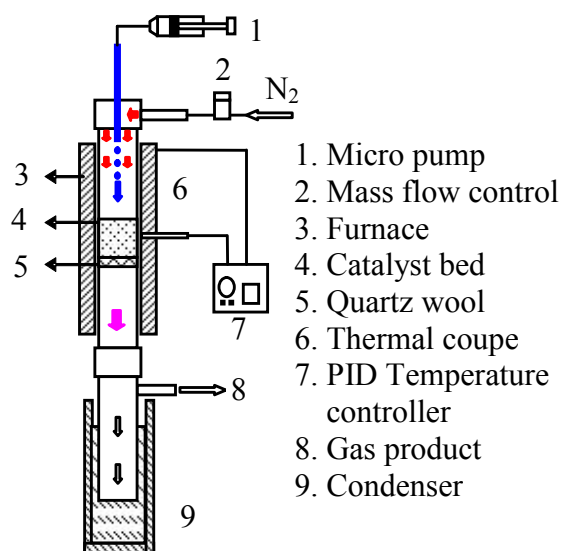


Figure 1: Schematic diagram of a fixed bed reactor set-up.

2.3 Characterization

The composition of soybean oil was determined by an automatic elemental analyzer (EA, Flash EA1112, CE Instruments) with TCD detector. Thermogravimetric analysis of soybean oil was carried out using TGA (TA Instrument, Q50). The sample was heated from room temperature to 800°C with a ramp rate of 10°C/min. The phase composition of the synthesized catalysts was confirmed by XRD (Bruker AXS, Germany).

The gas product of pyrolysis reaction was quantitatively characterized to determine the hydrocarbon fraction by GC-FID (M600D – Younglin Co.) equipped with HP-Plot/Al₂O₃ column (50m × 0.53mm × 15μm). In order to quantify the hydrocarbon composition from C₁–C₆, the peak areas of these

components were calibrated using a standard gas mixture (Supelco – Scotty 14).

The liquid product was analyzed by the same GC above but with HP-1 column (50m × 0.32 mm × 0.52μm). The GC was operated at split mode with the split ratio of 5 in N₂ carrier gas. The oven temperature was programmed from 50°C (10min) to 280°C (10min) with a heating rate of 3°C/min while the injector was maintained at 300°C. In order to prepare the sample for GC analysis, the water-free sample was mixed with solvent CS₂ (Sigma-Aldrich 99.9%) by the volume ratio = 1:7. The pure soybean oil was used for a calibration to determine the quantity of the remaining feed oil after reaction.

The GC-MS (HP 6890 Plus GC/HP 5973 MSD) analysis was also used to identify the composition of the reaction products using each catalyst M28 and Ga/MCM41.

3. RESULTS AND DISCUSSION

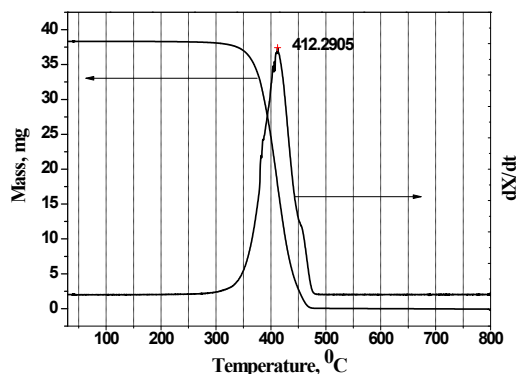
3.1 Elemental and thermogravimetric analysis of soybean oil

Table I shows the result of elemental analysis of soybean oil as well as higher heating value (HHV). The HHV was calculated following the formula in the literature [8]. As the HHV of soybean oil is slightly lower than that of petroleum (43 MJ/kg) and diesel (44.8 MJ/kg) [9], soybean oil can be classified as a promising fuel. However, soybean oil cannot be applied directly in industry due to its high viscosity. Therefore it needs additional process such as pyrolysis to be converted into a proper fuel.

Figure 2 shows TG and DTG curves of soybean oil. The DTG curve indicates that soybean oil is completely decomposed in the temperature range from 300°C to 480°C. In this region, the rate of conversion (dX/dt, where X was defined as conversion and t as the time of decomposing reaction) reached the maximum value at 412°C. Therefore, the pyrolysis temperature should be higher than 412°C.

Table I: Elemental analysis of soybean oil

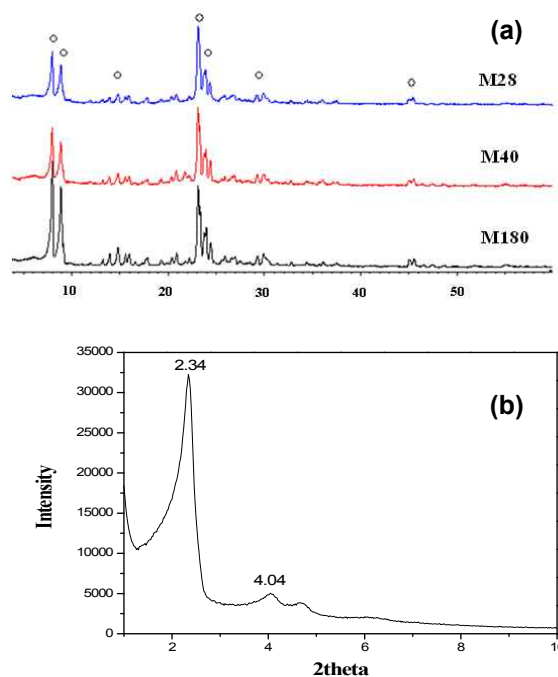
Elemental analysis, wt%				HHV (MJ/kg)
C	H	O	N	
76.2	11.6	10.4	1.9	40.09

**Figure 2:** TG and DTG curves of soybean oil.

If the pyrolysis temperature is above 460°C, on the contrary, the yield of coke would increase significantly resulting in blocking or clinging on the wall of the reactor. More seriously, the acid catalyst would be easily deactivated due to the covering of a large amount of coke on acid sites. Based on this, the pyrolysis temperature was selected to be 420°C and 450°C.

3.2 Phase structure of catalysts

Figure 3 shows the XRD patterns of the synthesized catalysts. The peaks in Figure 3(a) show the XRD patterns of H-ZSM5 catalysts prepared by changing the molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$. All the peaks are in good agreement with the typical peak for ZSM5 structure reported in the literature [10]. Also, it clearly shows that the phase composition is the same regardless of the molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$. The XRD pattern of MCM41 was shown in Figure 3(b). Two typical peaks for mesoporous structure were observed at the 2θ of 2.34° and 4.04°, which is consistent with the literature [11]. This suggests that this MCM41 support is a mesoporous material.

**Figure 3:** XRD patterns of H-ZSM5 catalysts (a) and MCM41 catalysts (b).

3.3 Product yields

Figure 4 shows the effect of various catalysts on the conversion of soybean oil during the pyrolysis process. Also, the product yields of bio-oil, gas and coke were presented in Figures 5(a-c), respectively. In general, higher pyrolysis temperature showed higher conversion.

For H-ZSM5 catalysts, the amount of aluminum participating in the structure of zeolite was known as a source for Lewis acid sites. Consequently, when the molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ of H-ZSM5 increased, the acidity of these catalysts would decrease [2]. When the molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ decreased, the pyrolysis conversion at 420°C and 450°C increased prominently as shown in Figure 4, resulting in increasing simultaneously the bio-oil and gas yields. Moreover, at the same catalyst, increasing temperature also made the cracking reaction occur easier, and hence the conversion was also enhanced. At 450°C, the catalyst M28 had the highest conversion of 98.7% with the highest bio-oil and gas yields of 71.3wt% and 23.1wt%, respectively.

The species of impregnated metal on MCM41 strongly affected the conversion and product yields during pyrolysis process. Among the investigated catalysts, Ga/MCM41 catalyst showed the highest conversion of 98.5% at 450°C, while Cu/MCM41 catalyst had the lowest conversion of 48.7% at 450°C. The highest bio-oil and gas yields of 77.3wt% and 13.6wt%, respectively, were also obtained in the presence of Ga/MCM41 catalyst.

The coke yields during the pyrolysis with H-ZSM5 catalysts were below 2.7wt%. It tends to decrease when either acidity or temperature decreases. The coke product can be ascribed to the reaction of aromatic compounds or the polymerization of light olefins existing in reaction mixture at high temperature [12].

As for metal/MCM41 catalysts, the coke yields were relatively higher, especially Ga/MCM41 catalyst with the highest coke yield 4.4wt% at 420°C. It can be attributed to the difference in pore size of H-ZSM5 (~5 Å) and MCM41 (20-50 Å). The pore size of MCM41 is large enough to let all components diffuse in pore, react with each other and produce large molecules, resulting in making coke and getting block in pores. Additionally, the interaction between metal and triglycerides should be taken into account. These metals may have some affinity with triglycerides, react and also make coke. For example, in the case of gallium, it is a transition metal with an unsaturated orbital d. Hence, it can be easier to accept electrons from the other atoms than in the case of aluminum just with orbital p [13]. When the cracking reaction occurs on the surface of catalyst, gallium can adsorb and interact with reactants more tightly than aluminum. Therefore the active sites of Ga were covered with more adsorbed molecules comparing with those of Al. That is the reason why the coke yield in the presence of Ga/MCM41 catalyst is higher than that in the presence of Al/MCM41.

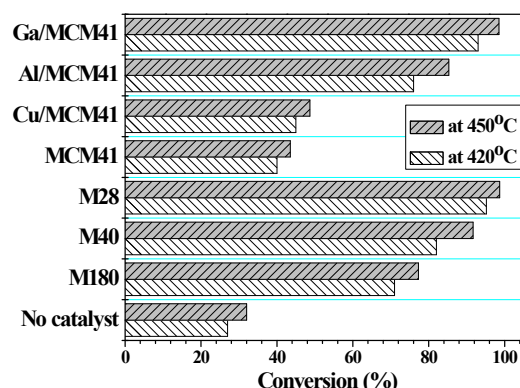


Figure 4: Conversion of soybean oil by pyrolysis in the presence of various catalysts.

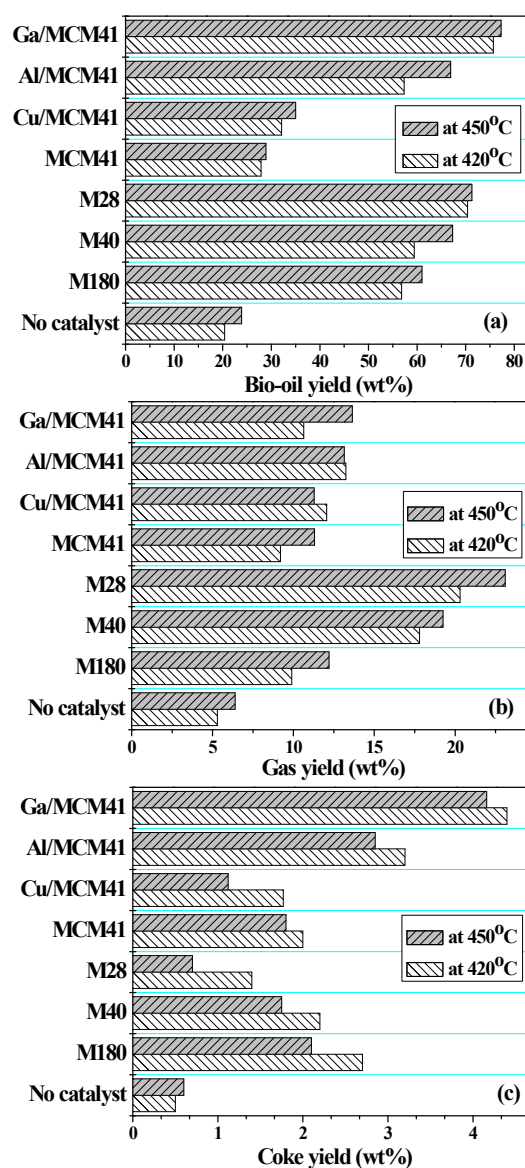


Figure 5: Product yields of bio-oil(a), gas(b), and char (c) by pyrolysis in the presence of various catalysts.

3.4 Chemical composition

The bio-oil products produced by pyrolysis in the presence of H-ZSM5 catalysts were mostly aromatic compounds such as benzene, toluene and xylene as shown in Figure 6. In contrast, the pyrolysis in the presence of metal/MCM41 catalysts produced various hydrocarbon compounds. Especially the bio-oil products produced in the presence of Ga/MCM41 and Al/MCM41 catalysts were very similar as shown in Figure 7, indicating the similar pyrolysis mechanism. The products from Cu/MCM41 were very similar with those from pure MCM41, which indicates that the metal Cu had no effect on the pyrolysis of soybean oil.

Table II shows the major components of the bio-oil products prepared by pyrolysis in the presence of M28 and Ga/MCM41 catalysts. As expected from Figure 6, the major components of the bio-oil products in the presence of M28 catalyst at 450°C were mainly aromatics. In contrast, Ga/MCM41 catalyst produced a mixture of alkanes, alkenes, alkadienes, aromatics and some fatty acids. This suggests that the pyrolysis of soybean oil was induced to different pyrolysis path ways depending on the catalysts used.

The M28 catalyst with a molecular structure of zeolite and strong acidity can facilitate isomerization, cyclization and dehydrogenation reactions, leading to just forming aromatic products. This is in good agreement with Sai et al. [12] who produced similar products by pyrolysis of canola oil with potassium-impregnated H-ZSM5 catalyst. On the contrary, the pyrolysis with Ga/MCM41 catalyst is similar with the work by Shwab et al.[14]. They explained the pyrolysis process by the radical mechanism.

Apart from these results above, the pore size of catalyst also played a crucial role in pyrolysis reaction. Obviously, with the micro pore size (5-6 Å), H-ZSM5 would not allow bulky triglyceride molecules to penetrate into its pore channels. Therefore,

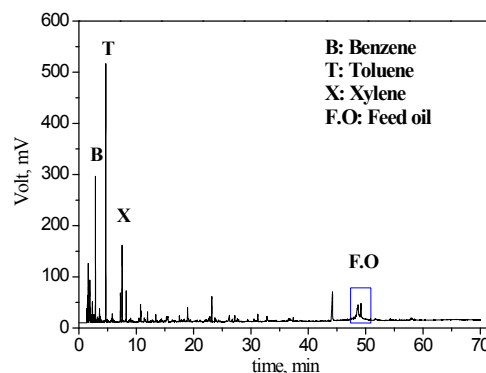


Figure 6: Gas chromatograph for the liquid product by pyrolysis in the presence of M40 at 420°C.

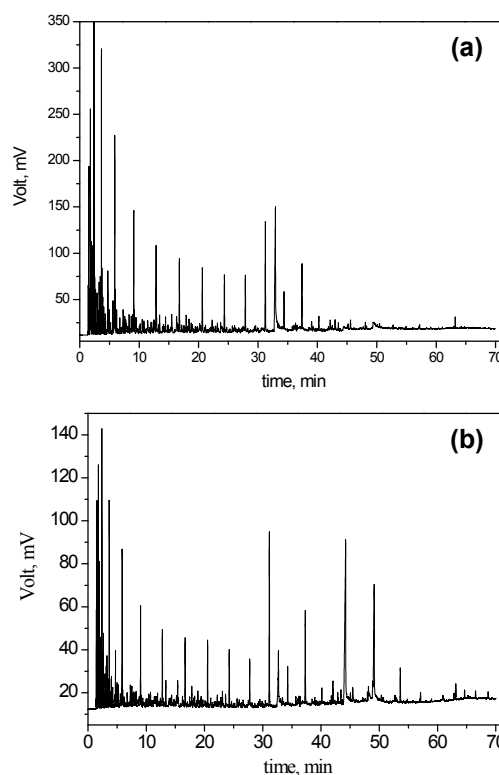


Figure 7: Gas chromatograph for the liquid product by pyrolysis in the presence of Ga/MCM41(a) and Al/MCM41(b) at 450°C.

the cracking triglyceride molecules to shorter hydrocarbon must be initially carried out on the surface of catalyst, and then these hydrocarbons would react with each other in the pore channels to form aromatic compounds. In the case of metal/MCM41 catalysts, large triglyceride molecules could go through the mesoporous channels due to

the comparatively large pore size of MCM41 and interact with acid sites diffused on the channels, as a result there was no selectivity for product and the liquid product was a mixture of different kinds of hydrocarbon.

Although the gas yield changed depending on the species of catalysts, the major components of all gas products were methane (CH_4), ethane (C_2H_6), propane (C_3H_8) and propylene (C_3H_6) as presented in

Table II: GC-MS analysis of bio-oil product prepared by the pyrolysis in the presence of M28 and Ga/MCM41 catalysts at 450°C.

M28 at 450°C	
Component	%
Benzene	6.3
Toluene	12.0
P,o-xylene	17.3
1-ethyl-2-methyl-Benzene	4.9
1-methyl-Naphthalene	9.5
Ga/MCM41 at 450°C	
Component	%
$\text{C}_5\text{-C}_{11}$ (alkanes, alkenes, alkadienes)	16.9
$\text{C}_{12}\text{-C}_{18}$ (alkanes, alkenes, alkadienes)	13.9
Toluene	1.3
Dodecylbenzene	2.2
n-Hexadecanoic acid	1.1

Table III: Composition of gas product prepared by the pyrolysis in the presence of various catalysts at 450°C.

	Gas compositions (%)			
	CH_4	C_2H_6	$\text{C}_3\text{H}_6 + \text{C}_3\text{H}_8$	C_4+
M180	27.7	33	36.8	2.5
M40	30	30	36.3	3.4
M28	24	35	43.7	2.3
Cu/MCM41	40	32.3	20.5	7.2
Al/MCM41	28	40	20	12
Ga/MCM41	20	35.7	25.5	8.4

Table III. In comparison with the gas yield of samples using H-ZSM5 catalysts, those of metal/MCM41 were rather lower. This can be ascribed to the difference in acidity as well as the structure of catalyst, thereby causing difference in reaction pathway. More specifically, in H-ZSM5 structure, both Bronsted (due to proton H^+) and Lewis acid sites (due to Al^{+3} atom) [2] co-participated in the matrix of zeolite structure. Therefore, its acid sites would be well distributed more than those of metal/MCM41 in which the metals were just diffused on the surface (not in the structure as H-ZSM5). From this reason, the acidity in H-ZSM5 may be more effective than that of metal/MCM41, leading to the great effect on the gas yield of pyrolysis on H-ZSM5 catalysts.

4. CONCLUSIONS

In this study, H-ZSM5 and metal/MCM41 catalysts were synthesized and used for the pyrolysis of soybean oil to investigate the effect of various catalysts on the product conversion and yield as well as the chemical composition during the pyrolysis process. The main conclusions from this present work can be given as follows:

(1) The product yield and chemical composition during pyrolysis process was strongly affected by the catalysts used. The highest conversion was obtained in the presence of Ga/MCM41 and M28 catalysts with the highest bio-oil yields of 77.3wt% and 71.3wt%, respectively.

(2) The main liquid products in the presence of H-ZSM5 catalysts were aromatics such as benzene, toluene and xylene, while those in the presence of Ga/MCM41 catalysts were a mixture of alkanes, alkenes, alkadienes, aromatics, and carboxylic acids.

(3) In all experiments, the major components of the gas product were methane, ethane, propane and propylene.

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