CHAPTER IV
ENHANCING BIO-KEROSENE AND BIO GAS OIL PRODUCTION FROM BIO-ETHANOL DEHYDRATION USING THE HIERARCHICAL MESOPOROUS MSU-S_{ZSM-5}

4.1 Abstract

HZSM-5 zeolite has been noticed for its potential to convert bio-ethanol to monoaromatics hydrocarbons such as C_6-C_{8s} due to its suitable pore size and shape selectivity. In case of producing heavier hydrocarbons, a catalyst with larger pore sizes is necessary. In this work, the hierarchical mesoporous MSU-S embeded with ZSM-5 seed (MSU-S_{ZSM5}) was employed, aiming to produce heavier hydrocarbon compounds from bio-ethanol dehydration. MSU-S_{ZSM5} was synthesized using TPAOH as a structure directing agent and CTAB as a surfactant. The characterization of catalysts was performed by using XRD with both small- and wide-angle modes, SAA, and XRF. Bio-ethanol dehydration was conducted in a U-tube fixed bed reactor at 450 °C for 8 hours at 0.5^{-1} h LHSV of bio-ethanol. Then, the gaseous products were analyzed by using GC-TCD, and ethanol conversion was examined by using GC-FID. The oil products were analyzed by using SIMDIST GC for petroleum fractions and GCxGC-TOF/MS for oil compositions. As a result, the hierarchical mesoporous MSU-S_{ZSM5}, found to have hexagonal structure, can produce more bio-kerosene and gas oil than conventional HZSM-5. For the oil compositions, C9 and C10+ aromatics hydrocarbons were the majority.

4.2 Introduction

Nowadays, the world is facing the depletion of petroleum sources. Demand of the oil is still rising which is the opposite way with the amount of resources. Therefore, some alternative fuels such as bio-ethanol had been studied. Bio-ethanol can be produced by fermentation process of agricultural feedstocks such as corn, sugarcane, and cassava. It has many advantages such as renewable source, reduce

greenhouse gases. Purified bio-ethanol can be blended with gasoline to be gasohol E10, E20, and E85 for use in the vehicles.

Moreover, bio-ethanol can be used as a feedstock to produce valuable hydrocarbons via dehydration process. The previous research studied on HZSM-5 zeolite catalyst to produce ethylene (Takahara *et al.*, 2005; Zhang *et al.*, 2008) and propylene (Takahashi *et al.*, 2012; Meng *et al.*, 2012). In addition, HZSM-5 also has potential to convert ethanol into liquid hydrocarbons. In 1997, Talukdar *et al.* studied effect of temperature on product distributions. They found that when temperature increased, the liquid yield was decreased via cracking activity. However, aromatic hydrocarbons such as benzene, toluene, xylenes exhibited an increasing trend when increasing temperature. Rownaghi *et al.* (2011) studied the yield of gasoline range hydrocarbons via methanol dehydration ZSM-5 with uniform crystal size. The results showed that light olefins (ethylene and propylene), and paraffins (C1-C4) selectivities were increased when the crystal size of ZSM-5 decreased. Furthermore, nano-size ZSM-5 also gave better catalytic stability than conventional ZSM-5. Not only can methanol dehydration be catalyzed by HZSM-5, but also ethanol dehydration using HZSM-5 had been studied. Viswanadham *et al.* (2012) studied ethanol to gasoline using nano-crystalline HZSM-5. The results showed that nano-crystalline HZSM-5 gave higher gasoline yield than that of micro-crystalline. The nano-crystalline HZSM-5 exhibited the additional mesoporosity by stacking of nano-crystal, which can enhance gasoline production. The obtained gasoline contained a low concentration of benzene, but high concentrations of xylenes, toluene, and isodecane, which was suitable for fuel applications. Bio-ethanol dehydration using HZSM-5 was also studied by Kittikarnchanaporn (2014). The results showed that HZSM-5 had a great potential to convert bio-ethanol into hydrocarbons. Propane was the main component in the gas due to H-transfer to propylene. Moreover, HZSM-5 gave the highest oil yield compared to HY and HBeta, and C_9 and C_{10+} aromatic hydrocarbons were the main composition in oil.

Although, microporous catalysts had potentials to convert bio-ethanol into hydrocarbons, but their small pore size limits the production of heavy hydrocarbons. Liu *et al.* (2001) synthesized MSU-S aluminosilicate mesostructure assembled from ZSM-5 and Beta seeds. MSU-S with hexagonal mesostructure was assembled by

cetyltrimetylammonium bromide (CTAB) as a surfactant. Both of MSU-S with ZSM-5 and Beta seeds had higher hydrothermal stability and higher cumene cracking activity than those of Al-MCM-41. Moreover, MSU-S with ZSM-5 seed (MSU-S_{ZSM-5}) was studied for methanol dehydration by Rashidi *et al.* (2013). In their work, MSU-S_{ZSM5} was used to convert methanol into dimethyl ether (DME). They found that MSU-S_{ZSM5} gave DME selectivity up to 100 % at 320 °C, and the coking rate on MSU-S_{ZSM5} was also slower than the conventional zeolite catalysts because of its larger pore size. Furthermore, bio-ethanol dehydration using MSU-S with Beta seeds as a catalyst was also investigated by Sujeerakulkai and Jitkarnka (2014) aiming to produce more kerosene- and gas oil-range products. The results exhibited that ethylene was the main component in the gas stream, and the oils contained a high amount of C_9 and C_{10+} aromatics due to its large pore size.

Normally, the stability of a hierarchical mesoporous catalyst is higher than a microporous catalyst due to their larger pore size that allows large hydrocarbon molecules to pass throughout. In 2014, Ramasamy *et al.* synthesized nano-size hierarchical HZSM-5 with mesoporore created from stacked nano-crystals, and compared its stability with that of a conventional HZSM-5 at the same Si/Al ratio on ethanol dehydration to hydrocarbons. It was found that the nano-sized hierarchical HZSM-5 gave higher actual/theoretical oil yield and higher olefinic compound than the conventional HZSM-5. Moreover, it exhibited the higher catalytic stability than the conventional one at all Si/Al ratios.

Thus, a hierarchical mesoporous HZSM-5 has great potential and high stability to convert bio-ethanol into fuel range products contaning toluene, and xylenes due to its large mesopore size. In this work, the hierarchical mesoporous MSU-S_{ZSM5}, which is the composite of ZSM-5 and MCM-41 with a large mesopore size, was therefore investigated in the dehydration of bio-ethanol, aiming to produce heavy petroleum fractions such as kerosene and gas oil.

4.3 Experimental

4.3.1 Catalyst Preparation

4.3.1.1 Synthesis of the Hierarchical Mesoporous MSU-S_{ZSM5}

To prepare the ZSM5-seed solution, 10.2 g of tetrapropylammonium hydroxide (TPAOH, 40 %wt) was added into 79.26 g of deionized water. After that, 0.34 g of sodium aluminate and 6.0 g of fumed silica as an aluminum and silicon sources were sequentially added into the solution of TPAOH and deionized water. The solution was kept stirred at 50 °C for 18 hours to form the ZSM5-seed solution. Then, 100 g of deionized water and 9.44 g of CTAB were mixed with the ZSM5-seed solution. The final gel was hydrothermally treated in a Teflon-line autoclave at 150 °C for 2 days to form the mesoporestructure. After the solution was filtered, washed, and dried, the white powder was ion-exchanged with 0.1M NH_4NO_3 in 96 % ethanol at 80 °C reflux temperature for 2 hours. The final catalyst was dried and calcined at 1 °C/min to 550 °C kept for 10 hours to obtain the MSU-S_{ZSM5} (Liu *et al.*, 2001; Rashidi *et al.*, 2013). Then, the calcined sample was pelletized by pelletizer, crushed, and sieved into 20 - 40 mesh particles before use in the reactor.

4.3.2 Catalyst Characterization

The surface area (BET), pore volume (Horvath Kawazoe method), and pore size (Barrett-Joyner-Halenda method) were determined based on N_2 physisorption using the Thermo Finnigan/Sorptomatic 1990. Both of small- and wide-angle modes of XRD patterns of the zeolites were determined by Rigaku SmartLab®. For the small-angle mode, the machine collected the data from $1^o - 7^o$ at 1^o/min. For the wide-angle mode, the machine collected the data from $5^o - 50^o$ at 5^o/min. The Si/Al ratio of the synthesized MSU-S_{ZSM5} was determined by XRF.

4.3.3 Bio-ethanol Dehydration

99.5 % purity bio-ethanol was obtained from Sapthip Co., Ltd. The catalytic dehydration of bio-ethanol was performed in a U-tube fixed bed reactor under atmospheric pressure at 450 °C for 8 hours with 3 g of catalyst using helium as

a carrier gas as shown in Figure 4.1. Bio-ethanol was mixed with helium, and fed at 2 ml/hour and 13.725 ml/min, respectively. The gaseous products were analyzed by using a GC-TCD (Agilent 6890N) for compositions, and a GC-FID (Agilent 6890N) was used to determine the ethanol conversion. The liquid product was condensed in the collector in an ice bath. Then, CS_2 was used to extract the oil from the liquid products. After that, a SIMDIST GC was used to determine the true boiling point curve of oils. The range of boiling point indicates the type of petroleum products: <149 °C for gasoline, 149-232 °C for kerosene, 232-343 °C for gas oil, 343-371 °C for light vacuum gas oil, and >371 °C for high vacuum gas oil (Dũng *et al.*, 2009). The oil composition was determined by using Gas Chromatograph equipped with a Mass Spectrometry of "Time of Flight" type (GC×GC- TOF/MS) (installed with Rxi-5SilMS and RXi-17 consecutive columns). The conditions were set as follows: the initial temperature was set at 50 °C held for 30 minutes, the heating temperature was set at 2 °C/min in range 50-120 °C/min, and 10 °C/min in range 120-310 °C with split ratio of 5.

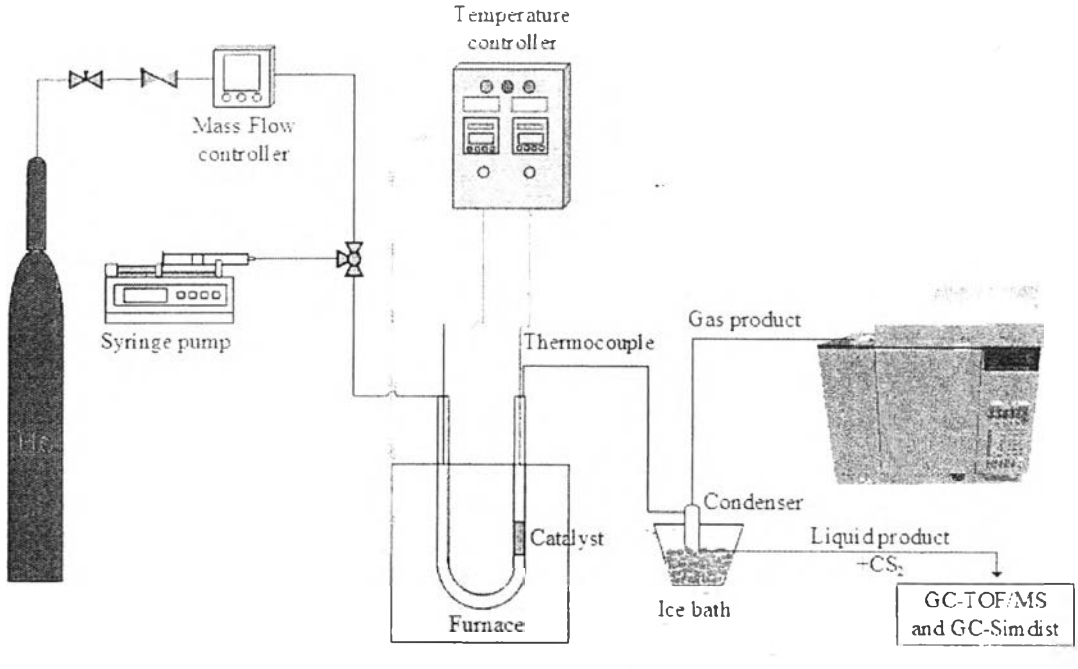

Figure 4.1 Experimental set-up of bio-ethanol dehydration.

4.4 Results and Discussion

4.4.1 Catalyst Characterization

X-ray Diffraction (XRD) pattern in both small-angle (1-7°) and wide-angle (5-50°) modes were derermined by Rigaku Smartlab®. Surface area, pore volume and pore size of the MSU-S_{ZSM5} was determined by using Thermo Finnigan/Sorptomatics 1990. The crystallographic spectra of the hierarchical mesoporous MSU-S_{ZSM5} was determined by using XRD in the small-angle mode (SAX) and wide-angle mode are shown in Figures 4.2 (a) and (b), respectively, which indicate that MSU-S_{ZSM5} semi-crystalline structure was successfully synthesized.

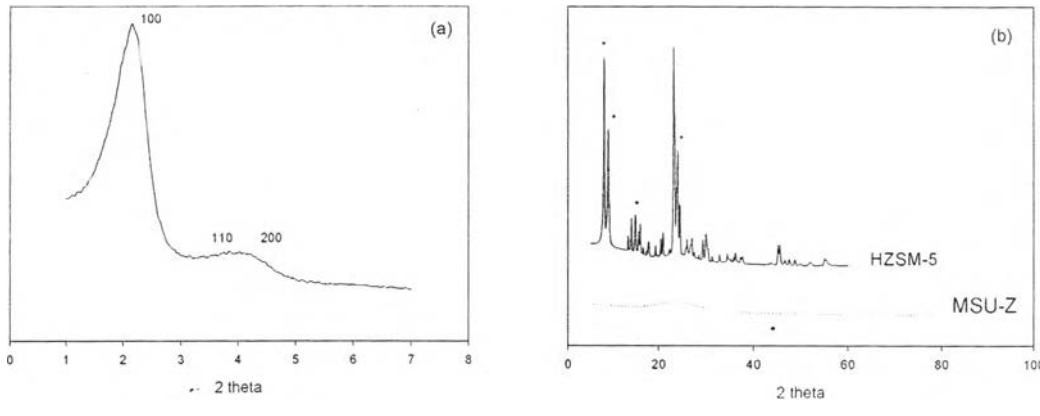

Figure 4.2 (a) SAXS pattern of MSU-S_{ZSM5}, and (b) XRD pattern of HZSM-5 and MSU-S_{ZSM-5}.

From Figure 4.2 (a), the SAX pattern of MSU-S_{ZSM5} exhibited a strongly peak at [100], which confirms that the mesostructure of MSU-S_{ZSM5}. However, two peaks at [110] and [200] were unclearly separated from one another which indicate that the success synthesizing MSU-S_{ZSM5} with a non-uniform hexagonal structure (Schwanke *et al.*, 2013). Figure 4.2 (b) exhibits the characteristic peaks of HZSM-5 zeolite located at 7.94°, 8.89°, 14.77°, and 23.96°. Although MSU-S_{ZSM5} has a broad reflection at about 23°, but it corresponds to the diffraction peak of HZSM-5 (Park *et al.*, 2011). The result from XRF shows that MSU-S_{ZSM5} has the Si/Al_2 ratio of 39.6.

Next, Figure 4.3 (a) exhibits the N_2 adsorption-desorption isotherm of MSU-S_{ZSM5}, which illustrates the same sudden step as Al-MCM-41 at P/P_0 nearby 0.35 (Triantafyllidis *et al.*, 2007). Furthermore, Figure 4.3 (b) shows the pore size distribution of the hierarchical mesoporous MSU-S_{ZSM5}. The micropore and mesopore diameters of MSU-S_{ZSM5} determined by using H.K. and B.J.H methods are at 8.97 and 28.66 Å, respectively. Moreover, the synthesized MSU-S_{ZSM5} also has 3 times higher surface area than the conventional HZSM-5 as shown in Table 4.1.

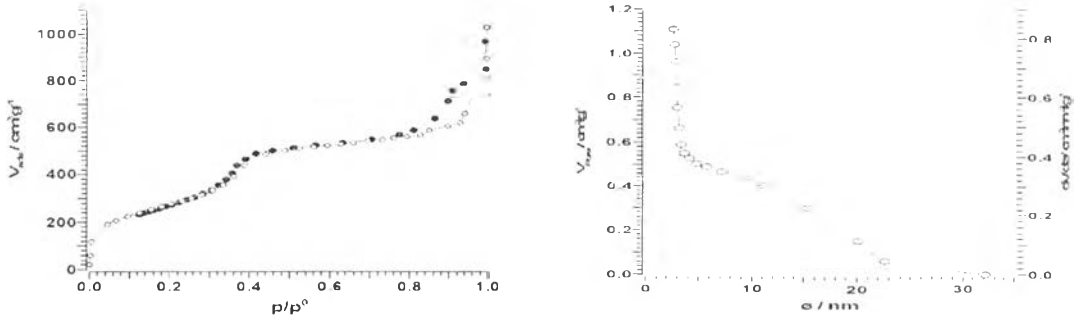

Figure 4.3 (a) N_2 adsorption-desorption isotherm, and (b) Pore size distribution of MSU-S_{ZSM5} using B.J.H method.

Table 4.1 Physical properties of HZSM-5 and MSU-S_{ZSM-5}

Catalysts	Surface Area (m^2/g) [a]	Pore Volume (cm^3/g) [b]	Micropore Diameter (Å)[b]	Mesopore Diameter (Å)[c]
HZSM-5	361	0.159	8.97	-
MSU-S_{ZSM5}	1,028	1.02	5.97	28.66

[a] Determined by BET method
[b] Determined by H.K. method
[c] Determined by B.J.H. method

4.4.2 The Activity of MSU-S_{ZSM5} on Bio-ethanol Dehydration

For the dehydration of bio-ethanol, MSU-S_{ZSM5} exhibited high ethanol conversion about 99.7 %. The large pore size of MSU-S_{ZSM5} tends to produce a high gaseous yield (84.6 %) with a low oil yield (3.7 %). The main component in the gas

products from using MSU-S_{ZSM5} was ethylene (98.7 %), followed by propane and ethane, accordingly. Due to its larger pore size, the hierarchical mesoporous MSU-S_{ZSM5} gives greater quantities of kerosene- and gas oil-range products than the conventional HZSM-5 that yield mostly gasoline, as shown in Figure 4.4 (a). Moreover, the true boiling point curves of HZSM-5 and MSU-S_{zsm5} are compared in Figure 4.4 (b), which indicates that MSU-S_{ZSM5} gives significantly heavier oil.

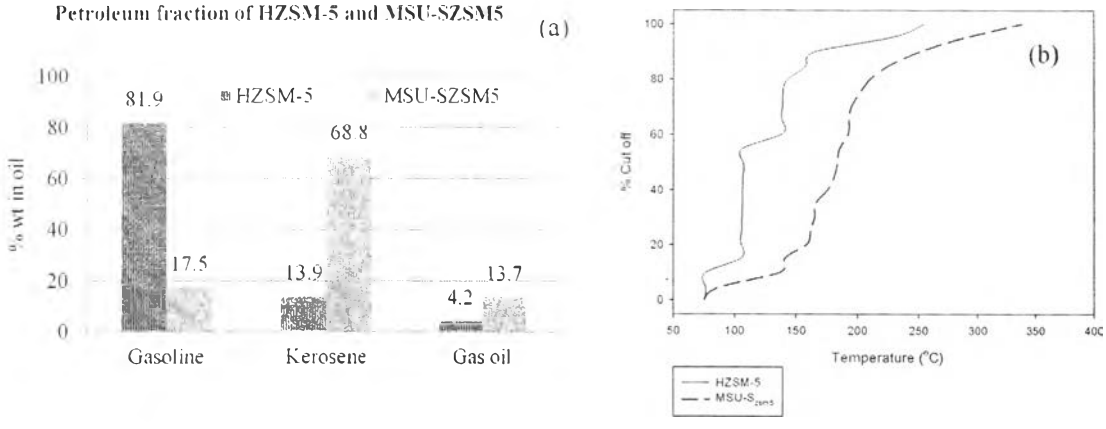

Figure 4.4 (a) Petroleum fractions, and (b) true boiling point curves of HZSM-5 and MSU-S_{ZSM-5}

Furthermore, from GCxGC-TOF/MS results, the large pore size of MSU-S_{ZSM5} favors C_{10+} and C_9 aromatics production in contrast with the medium pore size of HZSM-5 that is proper to produce toluene and xylenes (Vu *et al.*, 2006) because the large pore size of MSU-S_{ZSM5} can also improve the diffusion of large hydrocarbon molecules. However, the result from using MSU-S_{ZSM5} is different from nano-sized hierarchical HZSM-5 (Ramasamy *et al.*, 2014). The mesoporous-stacked nano-sized hierarchical HZSM-5 gave higher olefinic but lower aromatic yield than conventional HZSM-5 whereas the hierarchical mesoporous composite of MSU-S_{ZSM5} provides higher aromatic yield instead. Figure 4.5 illustrates that C_{10+} aromatics are the majority in oil (41.2 %wt), followed by based on C_9 aromatics (22.4 %wt), and xylenes (12.6 %wt). In addition, the boiling points, C_9 and C_{10+} aromatics are in kerosene and gas oil fractions.

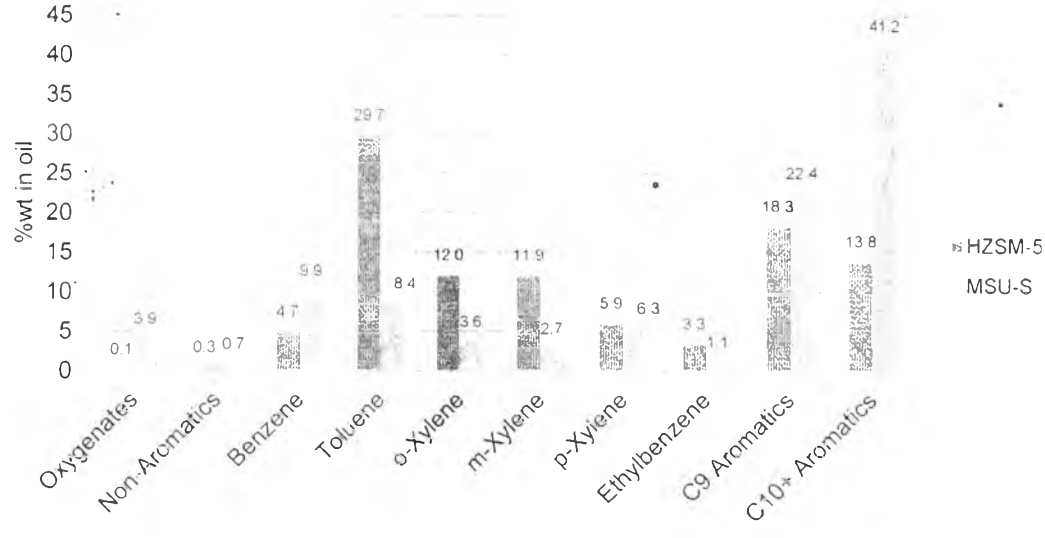

Figure 4.5 Oil composition from using HZSM-5 and MSU-S_{ZSM-5}.

4.5 Conclusion

The hierarchical mesoporous MSU-S_{ZSM5} employed in the dehydration of bio-ethanol was synthesized by using TPAOH as a structure directing agent and CTAB as a surfactant. The hexagonal mesostructure of MSU-S_{ZSM5} was confirmed by using small-angled XRD whereas the wide-angle pattern of XRD assured the semi-crystalline structure. The synthesized MSU-S_{ZSM5} also had 3 times higher surface area than the conventional HZSM-5. For the dehydration of bio-ethanol, MSU-S_{ZSM5} gave a high amount of gaseous product. The obtained oil contained the higher kerosene and gas oil fractions than those obtained from the conventional HZSM-5. C_9 and C_{10+} aromatics are the main components in the oil, which have boiling points in the ranges of kerosene and gas oil.

4.6 Acknowledgements

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4.7 References

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