

## Bio-Ethanol Dehydration to Hydrocarbons Using Ga<sub>2</sub>O<sub>3</sub>/Beta Zeolites with Various Si/Al<sub>2</sub> Ratios

Sakgrit Sujeerakulkai<sup>a</sup>, Sirirat Jitkarnka<sup>\*b</sup>

<sup>a</sup>The Petroleum and Petrochemical College, Chulalongkorn University, 254 Soi Chulalongkorn 12, Phayathai Rd., Pathumwan, Bangkok 10330, Thailand

<sup>b</sup>Center of Excellence on Petrochemical and Materials Technology, 7th floor, Chulalongkorn University Research Building, Soi Chulalongkorn 12, Phayathai Rd., Bangkok 10330, Thailand  
 sirirat.j@chula.ac.th

Recently, oil and petrochemical consumptions are grown up rapidly, but petroleum is a nonrenewable energy. So, biomass is an attractive sustainable energy. From literature review, methanol or ethanol can be converted to gasoline range of hydrocarbons via dehydration and other reactions. It was found that SAPO-34 (8-membered ring) produced more than 70 % ethylene and propylene from methanol and ethanol dehydration. H-ZSM-5 (10-membered ring) was also used as a catalyst for methanol to gasoline process by ExxonMobil Research and Engineering Company because of its shape selectivity. These two examples show that the products from dehydration are controlled by the pore size of zeolites. Therefore, H-Beta (12-membered ring), which has a larger pore size than H-ZSM-5, was used in this work, and it was expected to produce larger hydrocarbons than gasoline range of hydrocarbons. The effects of acid density and acid strength in the product distribution were investigated using various Si/Al<sub>2</sub> ratios of H-Beta zeolites. Gallium oxide was also doped on the H-Beta zeolites by incipient wetness impregnation, since it can enhance single-ring aromatic formation. The catalysts were characterized by using XRD, SAA, and TPD-NH<sub>3</sub>. Then, the dehydration of bio-ethanol was conducted over 3 g of a catalyst in a U-tube reactor. The reaction was performed for 8 h at 450 °C with the LHSV of bio-ethanol at 0.5 h<sup>-1</sup>. Then, the products were analyzed by an online GC, GC×GC-TOF/MS, and SIMDIST-GC. As a result, it was found that the highest oil distribution was produced by using moderate modified H-Beta (Si/Al<sub>2</sub> ratio = 37), and the oil mainly consisted of C<sub>9</sub> aromatics and C<sub>10</sub><sup>+</sup> aromatics, which are in a kerosene range of hydrocarbons.

### 1. Introduction

Asia economy and energy consumption are grown up rapidly. The most anxious problem that crude oil from petroleum is a non-renewable energy should be realized. Biomass is an attractive new sustainable energy. In 2011, 10,000 b/doe (barrels per day oil equivalent) biofuels were produced, which was grown up 0.7 % from 2010 (BP, 2012). In 1970's, ExxonMobil Research and Engineering Company had developed the methanol-to-gasoline process in a commercial scale (ExxonMobil, 2005). HZSM-5 was used as a catalyst in MTG process owing to the suitable pore size (about 5.5 Å). The gasoline range is in the range of C<sub>5</sub>-C<sub>10</sub>. Jiménez-Cruz and Laredo (2004) reported the kinetic molecular diameters of linear and branched C<sub>5</sub>-C<sub>8</sub>, which were between 4.2 Å to 6.2 Å. Therefore, HZSM-5 is very selective zeolite for gasoline production. Not only is methanol converted to hydrocarbons, but ethanol can also be possibly used. Thailand is an agricultural country that has a lot of raw materials used to produce bio-ethanol by fermentation process. Many researchers succeeded to produce light olefins and aromatics from bioethanol. Bio-ethanol was converted to alkanes, olefins and oxygenates by using metal loaded alumina catalyst (Chistyakov et al., 2011). Inaba et al. (2006) studied the ethanol to hydrocarbons process. Ethanol was converted to ethylene and heavier hydrocarbons products. Liquid hydrocarbons products were mainly comprised of C<sub>6</sub>-C<sub>7</sub> hydrocarbons. Talukdar et al. (1997) studied the effect of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios of HZSM-5 on the conversion of ethanol. They found a high amount of Bronsted acid sites on the zeolite with a low SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio tended to convert ethanol to aromatics and paraffins. Aromatic hydrocarbons can be

produced by using medium or large pore zeolite catalysts such as H-ZSM-5, H-Y, H-Beta, etc. Pasomsub (2013) studied two consecutive layers of catalysts for dehydration of bio-ethanol. The first layer was 2 % Ga<sub>2</sub>O<sub>3</sub>/HZSM-5. The addition of 2 % Ga<sub>2</sub>O<sub>3</sub> improved the yield of gas oil, light vacuum gas, and heavy vacuum gas. The second layer was either H-X, H-Y, or H-Beta that was found to promote the formation of heavy aromatic hydrocarbons, like C<sub>9</sub> and C<sub>10</sub><sup>+</sup> aromatics, and the selectivity of p-xylene. The effect of oxide loading was investigated by Wongwanichsin (2013). Aromatics compounds were not observed on the unmodified SAPO-34, but SAPO-34 after modified with Ga significantly improved the aromatics yield, especially C<sub>10</sub><sup>+</sup> aromatics. 5 % loading of Ga<sub>2</sub>O<sub>3</sub> over SAPO-34 significantly improved the oil yield. Other reports also found the same trend with Ga<sub>2</sub>O<sub>3</sub> doping. The physical mixtures of Group 13 oxides (Ga<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub>, Tl<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>) and H-ZSM-5 catalysts (1:1 by weight) have been used and found to enhance aromatics from methanol dehydration. Ga<sub>2</sub>O<sub>3</sub>/HZSM-5 enhanced the aromatic hydrocarbon (C<sub>6</sub> to C<sub>9</sub>) yields up to 46 %, especially C<sub>8</sub>H<sub>10</sub> and C<sub>9</sub>H<sub>12</sub>. However, In<sub>2</sub>O<sub>3</sub>/HZSM-5 and Tl<sub>2</sub>O<sub>3</sub>/HZSM-5 immediately deactivated (Freeman et al., 2002). Hence, this work desires to study the effect of Si/Al<sub>2</sub> ratio on bio-ethanol to hydrocarbons. The acid density and the acid strength were adjusted by using H-Beta, with Si/Al<sub>2</sub> ratio of 27, 37 and 300, modified with Ga<sub>2</sub>O<sub>3</sub> loading.

## 2. Experimental

### 2.1 Catalyst preparation

5.0 wt % of Ga was loaded to calcined zeolites; namely, H-Beta (Si/Al<sub>2</sub> = 27, 37, and 300) using the incipient wetness impregnation technique. The nomenclatures of catalysts are 5GaB27, 5GaB37, and 5GaB300, respectively. After that the catalysts were dried overnight at 120 °C and calcined at 600 °C, 5 h with the heating rate of 2 °C/min. Then, the prepared catalysts were pelletized using a hydraulic pelletizer machine, crushed, and sieved to pellets in 20 to 40 meshes before use in the reactor.

### 2.2 Catalyst characterization

The metal oxide and zeolites structures were analyzed by the Rigaku SmartLab X-Ray Diffractometer (XRD) system equipped with 9 kW rotating anode Cu K $\alpha$  source. The detector scanned for the peak position from the samples as a function of 2 $\theta$  by starting at the 5° to 80° (2 $\theta$ ) range and a scan speed of 5° (2 $\theta$ )/min. The data from XRD were recorded by the SmartLab Guidance software and analyzed by PDXL software.

The Brunauer-Emmett-Teller (BET) technique was employed to determine the specific surface area, the total pore volume and the pore size of catalyst, using Thermo Finnigan/Sorptomatic 1990, which is based on the physical adsorption of nitrogen gas. The sample was initially out-gassed to remove the humidity and volatile adsorbents adsorbed on the catalyst surface under vacuum at 300 °C at least 18 h prior to analysis steps. The specific surface area and the pore size of catalyst were obtained from the twenty-two-point nitrogen adsorption and desorption isotherm plot. The pore size distribution was calculated using the Horvath-Kawazoe (HK) method.

The acidity of catalysts were analyzed using Temperature Programmed Desorption of Ammonia (TPD-NH<sub>3</sub>) with Thermo Finnigan 1100. The catalysts were previously outgassed by using 20 cm<sup>3</sup>/min of nitrogen gas at 500 °C with 10 °C/min for 30 min, and then cooled to 35 °C. After exposed to NH<sub>3</sub> (3 vol.% NH<sub>3</sub> in He; 20 cm<sup>3</sup>/min) at 150 °C for 60 min, the catalysts were treated in nitrogen (20 cm<sup>3</sup>/min) for 30 min at room temperature to remove the physically-adsorbed NH<sub>3</sub>. The sample was then heated from room temperature up to 900 °C with a heating rate of 10 °C/min to perform TPD-NH<sub>3</sub>.

### 2.3 Catalytic reaction

3.0 g of a catalyst was first packed and kept in place by using alumina ball and quartz wool in a stainless steel U-tube reactor. The U-tube reactor was next exposed to assembled in a furnace. The reactor was preheated with helium stream at 450 °C before start. Bio-ethanol was fed into the reactor using a syringe pump at 0.5 h<sup>-1</sup> LHSV with helium as a carrier gas. The reaction testing was performed for 8 h at 450 °C. The product coming out from reactor was separated in two phases, which were gas and liquid. The gaseous product was passed through a condensing flask, and then analyzed by using an online gas chromatograph (GC-FID). The condensable liquid product was subsequently analyzed by using a SIMDIST-GC and a GCxGC-TOF/MS.

### 2.4 Product analysis

Online gas chromatograph (Agilent Technologies 6890 Network GC system) was equipped with a thermal conductivity detector (TCD) to detect hydrocarbons by using the HP-PLOT Q column: 30 m x 0.32 mm ID and 20  $\mu$ m film thicknesses, and a flame ionization detector (FID) to detect oxygenates by using the DB-WAX column: 30 m x 0.32 mm ID and 20  $\mu$ m film thicknesses. The conditions were set as follows: initial temperature of 40 °C, time at initial temperature of 10 min, Ramp 1: heating rate of 10 °C/min, final

temperature of 120 °C, 10 min holding time, Ramp 2: heating rate of 10 °C/min, final temperature of 200 °C, 10 min holding time, and Ramp 3: heating rate of 10 °C/min, final temperature of 220 °C, 2 min holding time.

The extracted oil was analysed by using a gas chromatograph equipped with a Mass Spectrometry of Time of Flight type (GC×GC-TOF/MS), Agilent 7890. Helium was used as the carried gas, and nitrogen was used in the cooling system. The conditions were set as follows: initial temperature of 80 °C, time at initial temperature of 2 min, 4 °C/min heating rate, final temperature of 270 °C held for 5 min, and split ratio at 1:50.

Moreover, the petroleum fractions were determined using a Varian CP-3800 Simulated Distillation Gas Chromatograph (SIMDIST-GC) conformed with ASTM D2887 method for true boiling point curves. The different boiling point ranges were used to classify petroleum fractions; namely, Gasoline (< 149 °C), Kerosene (149 - 232 °C), Gas oil (232 - 343 °C), Light Vacuum Gas oil (LVGO, 343 - 371 °C), and Heavy Vacuum Gas Oil (HVGO, > 371 °C). An oil sample was injected to the SIMDIST-GC after dilution with carbon disulphide (CS<sub>2</sub>) at the ratio of 1:100. The conditions were set as follows: initial temperature of 30 °C, time at initial temperature of 0.01 min, heating rate of 20 °C/min, final temperature of 320 °C, and 8.50 min holding time.

### 3. Results and discussion

#### 3.1 Catalyst characterization

X-ray Diffraction (XRD), Surface Area Analyzer (SAA), and Temperature Programmed Desorption of Ammonia (TPD-NH<sub>3</sub>) were used to identify the specific characteristics of zeolites, and metal oxides, and the physical properties of catalysts. The XRD results are shown in Figure 1. The specific peaks of H-Beta zeolites, shown in Figure 1 (a), are located at 2 theta of 7.6°, 14.6°, and 22.4° (Omegna et al., 2004). Moreover, Figure 1 (b) shows gallium oxide's characteristic peaks at 52.3°, 56.1°, 61.9°, and 68.1°. However, the specific peaks of H-Beta zeolite are still present in the XRD patterns after loaded with gallium oxides, that means the metal oxide loading does not destroy the zeolite structures.

The physical properties of catalysts are presented in Table 1. Surface area, pore volume, and pore diameter were determined using the Braunaer-Emmet-Teller (BET) and Horvath Kawazoe techniques. Gallium oxide loading reduces the surface area and pore volume of unloaded zeolites because of pore blocking by the oxide as shown in Table 1. Moreover, the increasing Si/Al<sub>2</sub> ratio extremely reduces the surface area and pore volume of zeolites. 5GaB27, 5GaB37, and 5GaB300 have the surface area of 495.7 m<sup>2</sup>/g, 354.0 m<sup>2</sup>/g, and 236.8 m<sup>2</sup>/g, respectively, and pore volume reduces with the same trend.

The acidity of modified zeolites with various ratios of Si/Al<sub>2</sub> were analysed using TPD-NH<sub>3</sub>. The area of each peak represents the amount of acid sites as shown in Figure 2. Total acidity is ranked as follows: 5GaB37 > 5GaB27 > 5GaB300. Moreover, the NH<sub>3</sub> desorption temperature also indicates the acid strength of zeolites; that is, 5GaB27 has the highest acid strength, followed by 5GaB37 and then 5GaB300.

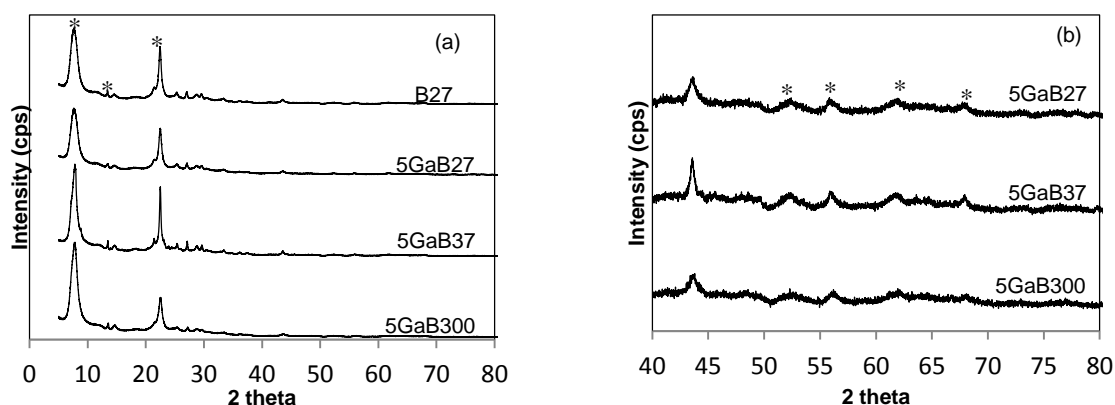
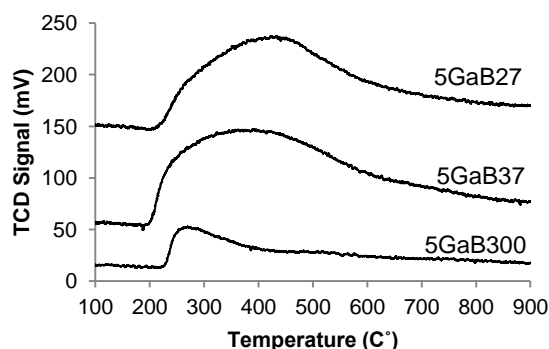


Figure 1: XRD patterns of H-Beta supports and 5 % wt gallium oxide loaded H-Beta catalysts: (a) characteristic peaks of H-Beta, and (b) characteristic peaks of gallium oxide

Table 1: Physical properties of H-Beta supports and 5 % wt gallium oxide loaded H-Beta catalysts

Catalysts	B27	5GaB27	B37	5GaB37	B300	5GaB300
Surface area (m <sup>2</sup> /g)	554.9	495.7	502.7	354.0	425.9	236.8
Pore volume (cm <sup>3</sup> /g)	0.27	0.24	0.26	0.18	0.20	0.13
Pore diameter (Å)	7.68	7.75	7.93	8.02	8.67	7.52

Figure 2: TPD-NH<sub>3</sub> profile of 5 % wt gallium oxide loaded H-Beta catalysts

### 3.2 Catalytic activity

More than 97 % ethanol conversion is achieved over all Si/Al<sub>2</sub> ratio of modified H-Beta. Ethylene is first produced from ethanol dehydration, and then ethylene is converted into various hydrocarbon products, which is governed by acidity or Si/Al<sub>2</sub> of H-Beta zeolite. From Table 2, all modified H-Beta catalysts produce gas as the main product. Only 6.48 % oil is obtained from 5GaB37, that is the highest among those obtained from the other catalysts. For the gas composition, the major gaseous component in all catalysts is ethylene, which is 73.8 % to 95.5 % in the gas product. 5GaB37 gives a noticeable gas composition; that is, 13.4 % C<sub>3</sub> and 5.40 % C<sub>4</sub> are produced. The lower acid density of 5GaB300 produces ethylene mainly; on the other hand, the high acid density of 5GaB37 tends to convert ethylene to larger hydrocarbons.

Table 2: Product distribution over 5GaB27, 5GaB37, and 5GaB300

Catalyst	5GaB27	5GaB37	5GaB300
Bio-ethanol conversion (%)	97.4	97.4	97.4
Product distribution (wt %)			
Gas	83.7	75.4	78.6
Oil	3.92	6.48	3.11
Water	12.4	18.1	18.3
Gas composition (wt %)			
Methane	1.34	1.28	0.00
Ethylene	87.1	73.8	95.5
Ethane	5.27	6.16	1.53
C <sub>3</sub>	5.10	13.4	2.27
C <sub>4</sub>	1.22	5.40	0.41

For the oil phase, 3.11 to 6.48 % of oil is attained from secondary reactions in the reaction pathway (Inaba et al., 2006). 5GaB27 produces the oil that consists of 66.5 % BTEX, 26.9% C<sub>9</sub> aromatics, and a little amount of other hydrocarbons products as shown in Figure 3 (a). However, in Figure 3 (b), the oil composition from 5GaB37 shows that 15.6 % C<sub>9</sub> aromatics, 39.0 % C<sub>10</sub><sup>+</sup> aromatics, and 18.8 % non-aromatics are mainly produced, but BTEX are produced in a low amount.

Acid density and acid strength of 5GaB27 and 5GaB37 are compared in Figure 2. 5GaB27 has lower acid density, but higher acid strength, whereas 5GaB37 has higher acid density, but lower acid strength. So, the protons on 5GaB27 can more easily protonate small hydrocarbons to short chain aromatics than those on 5GaB37; however, a less acid density on 5GaB27 does not allow long-chain aromatic hydrocarbons to grow as much as on 5GaB37 that has a higher acid density. That is the reason why 5GaB27 produces more BTEX, less oil yield, and less long-chain aromatics (C<sub>9</sub><sup>+</sup>). For 5GaB37, the larger amount of weaker

acid sites protonates ethylene, and allows longer chain hydrocarbons to grow. It can be explained that ethylene, which is the major component in the gaseous phase, can be further converted to benzene via oligomerization and aromatization reactions. After that, the alkylation of benzene with ethylene generates ethylbenzene. A large amount of benzene, C<sub>9</sub> aromatics, and C<sub>10</sub><sup>+</sup> aromatics are formed from disproportionation and transalkylation reactions. On the other hand, 5GaB300, which has the lowest acid density and acid strength, produces 83.7 % gas and only 3.11 % oil. Moreover, it produces a large amount of 45.1 % oxygenates (cyclopropanenonanoic acid, methyl ester, tridecanoic acid, methyl ester, 2-pentanone, and 10-undecyn-1-ol) and a low amount of hydrocarbons.

The true boiling point curves (TBPs) of the extracted oils are cut based on the boiling point ranges of petroleum fractions. 5GaB37, which produces the highest amount of oil and heavy products, gives 33.1 % kerosene, which is the highest among the other catalysts. The oil from 5GaB27 has a high boiling point in gas oil range because the catalyst has the highest acid strength. 5GaB300 produces 84.4 % gasoline that is the fraction containing BTEX and oxygenate compounds.

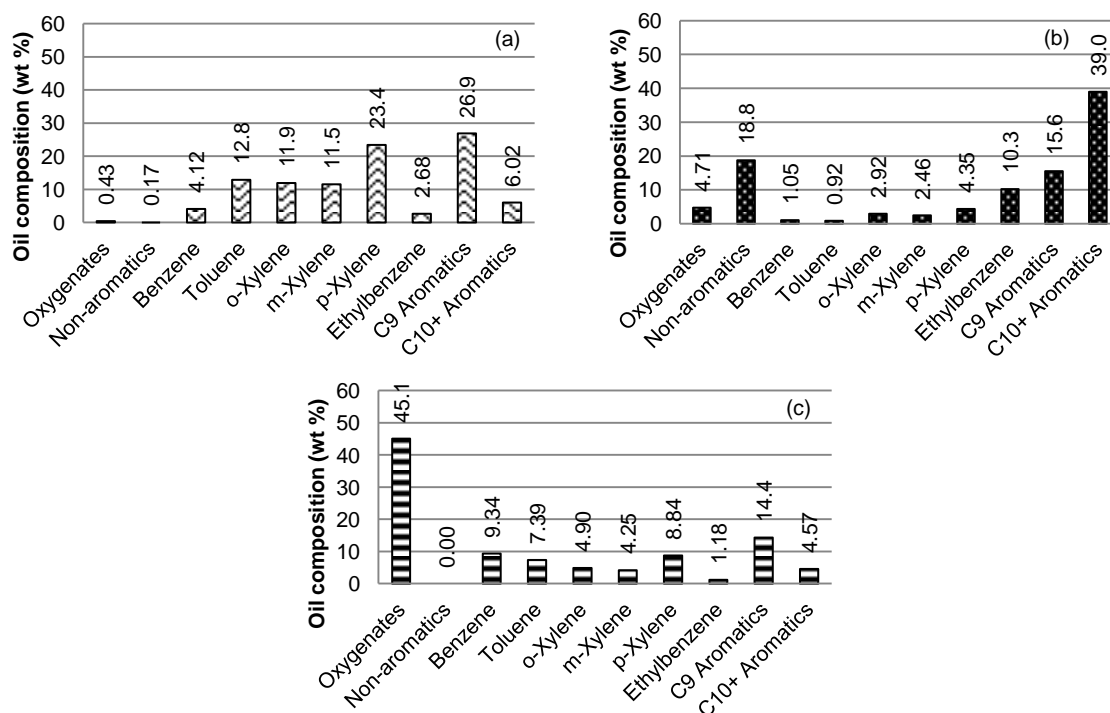


Figure 3: Composition of extracted oil from (a) 5GaB27, (b) 5GaB37, and (c) 5GaB300

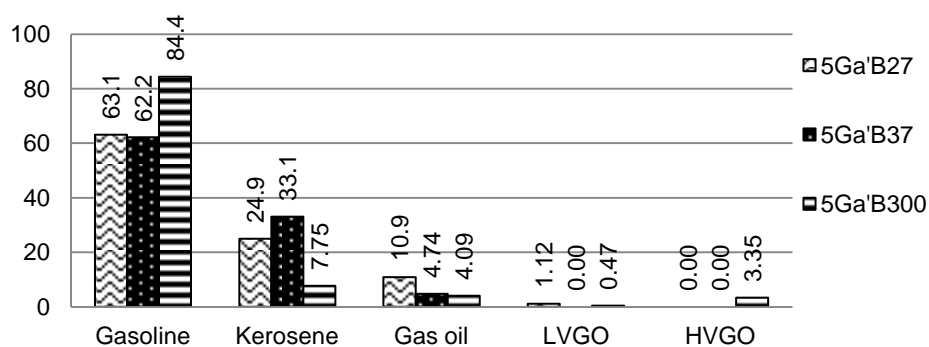


Figure 4: Petroleum fractions in oils derived from using gallium oxide-modified catalysts

#### 4. Conclusions

5GaB37 has the highest acid density whereas 5GaB27 has the highest acid strength. In the other word, 5GaB300 has the lowest acid density and strength. The different acidity of catalysts affected the product distribution. The results showed that acid density is very important for the conversion of small hydrocarbons to aromatics and heavy hydrocarbons. 5GaB27 has a high acid density but too high acid strength, leading to the high production of 66.4 % BTEX and 26.9 % C9 aromatics, whereas 5GaB37 produced the highest oil quantity of around 6.48 % because of the highest acid density and moderate acid strength. However, 5GaB300 produced 95.5 % ethylene mainly because of the lowest acid density and acid strength. So, the acidity affected the production of hydrocarbons since it governs the extents of oligomerization, aromatization, H-transfer, cracking, disproportionation and transalkylation reactions.

#### Acknowledgements

The authors would like to thank The Petroleum and Petrochemical College, Chulalongkorn University, and The Center of Excellence on Petrochemical and Materials Technology, Thailand for the mutual financial support. The authors also thank Sapthip Company Limited for providing bio-ethanol used as the feed.

#### References

- BP, 2012, BP Statistical Review of World Energy <[www.bp.com/liveassets/bp\\_internet/globalbp/globalbp\\_uk\\_english/reports\\_and\\_publications/statistical\\_energy\\_review\\_2011/STAGING/local\\_assets/pdf/statistical\\_review\\_of\\_world\\_energy\\_full\\_report\\_2012.pdf](http://www.bp.com/liveassets/bp_internet/globalbp/globalbp_uk_english/reports_and_publications/statistical_energy_review_2011/STAGING/local_assets/pdf/statistical_review_of_world_energy_full_report_2012.pdf)> accessed 19.05.2013
- Chistyakov A., Tsodikov M., Chudakova M., Gekhman A., Moiseev I., Luk F., 2011, New Aspects of Bioethanol One-step Catalytic Conversion to Fuel Components, *Chemical Engineering Transactions*, 24, 175-180, DOI: 10.3303/CET1124030
- ExxonMobil. 2005, Methanol to gasoline (MTG) production of clean gasoline from coal <[www.exxonmobil.com/Apps/RefiningTechnologies/files/sellsheet\\_09\\_mtg\\_brochure.pdf](http://www.exxonmobil.com/Apps/RefiningTechnologies/files/sellsheet_09_mtg_brochure.pdf)> accessed 19.05.2013
- Freeman D., Wells R.P., Hutchings G.J., 2002, Methanol to hydrocarbons: enhanced aromatic formation using composite group 13 oxide/H-ZSM-5 catalysts., *Catalysis Letters*, 82(3-4), 217-225.
- Inaba M., Murata K., Saito M., Takahara I., 2006, Ethanol conversion to aromatic hydrocarbons over several zeolite catalysts. *Reaction Kinetics and Catalysis Letters*, 88(1), 135-141.
- Jiménez-Cruz F., Laredo G.C., 2004, Molecular size evaluation of linear and branched paraffins from the gasoline pool by DFT quantum chemical calculations., *Fuel*, 83(16), 2183-2188.
- Omegna A., Vasic M., van Bokhoven J.A., Pirngruber G., Prins R., 2004. Dealumination and realumination of microcrystalline zeolite beta: an XRD, FTIR and quantitative multinuclear (MQ) MAS NMR study. *Physical Chemistry Chemical Physics*, 6(2), 447-452.
- Pasomsub S., 2013, Bio-Ethanol dehydration to liquid hydrocarbons. MSc thesis, The Petroleum and Petrochemical College. Bangkok, Thailand, Chulalongkorn University.
- Talukdar A.K., Bhattacharyya K.G., Sivasanker S., 1997. HZSM-5 catalysed conversion of aqueous ethanol to hydrocarbons, *Applied Catalysis A: General*, 148(2), 357-371.
- Viswanadham N., Saxena S.K., Kumar J., Sreenivasulu P., Nandan D., 2012. Catalytic performance of nano crystalline H-ZSM-5 in ethanol to gasoline (ETG) reaction., *Fuel* 95, 298-304.
- Wongwanichsin, P. 2013, Modified SAPO-34 for dehydration of bio-ethanol to light olefins in comparison with KOH-treated HZSM-5., MSc Dissertation, The Petroleum and Petrochemical College. Bangkok, Thailand, Chulalongkorn University.