

EVAPORATED PALM OIL CRACKING TO GASOLINE OVER ZEOLITE CATALYSTS

TIRENA BAHNUR SIREGAR¹ & NOR AISHAH SAIDINA AMIN²

Abstract. The catalytic cracking of palm oil to gasoline over H-ZSM-5 and H-Beta was studied in fixed bed reactor operated at atmospheric pressure and weight hourly space velocity (WHSV) of 2.5 h⁻¹. The reaction temperature was varied between 450°C to 525°C. The calcined catalysts were characterized using X-Ray Diffraction (XRD), Pyridine Adsorption-Infrared Spectrophotometry (Py-IR) and Nitrogen Adsorption (NA) methods. The liquid and gaseous products were analyzed using (FID) and (TCD) gas chromatography respectively. Increase in reaction temperature led to higher palm oil conversion. The highest conversion and gasoline selectivity obtained at 525°C were 96.12 wt% and 29.92 wt% respectively with H-ZSM-5. Although the conversion and the gasoline selectivity of both catalysts was high, but H-ZSM-5 performed better than H-Beta at all temperature range. Gasoline produced using H-ZSM-5 consisted mainly of naphthenes beside isoparaffins, olefins, aromatics and a small amount of paraffins, while the gasoline obtained by using H-Beta contained olefins, naphthenes, paraffins and aromatics. Gas was the major side product, which consisted mainly of C₁-C₃ for using H-ZSM-5 and C₃-C₄ compounds for using H-Beta.

Keyword: Zeolite; H-ZSM-5; H-Beta; cracking, palm oil; gasoline

Abstrak. Peretakan bermangkin minyak kelapa sawit kepada gasolin menggunakan H-ZSM-5 dan H-Beta dijalankan pada tekanan atmosfera dan kadar alir mengikut berat 2.5 jam⁻¹. Suhu tindak balas ditetapkan dalam julat 450°C hingga 525°C. Mangkin yang dikalsinkan telah dicirikan menggunakan teknik pembelauan sinar X, penyerapan piridina-spektrofotometri inframerah dan penyerapan nitrogen. Hasil cecair dan gas dianalisis menggunakan kromatografi gas (FID) dan (TCD). Peningkatan suhu tindak balas meninggikan penukaran minyak kelapa sawit. Penukaran minyak kelapa sawit dan pemilihan gasolin tertinggi diperolehi dengan mangkin H-ZSM-5, masing-masing ialah 96.12 %berat dan 29.92 %berat. Walaupun penukaran minyak kelapa sawit dan pemilihan gasolin untuk kedua-dua mangkin adalah tinggi, tetapi H-ZSM-5 menunjukkan hasil yang lebih baik berbanding H-Beta pada semua suhu. Gasolin yang dihasilkan menggunakan H-ZSM-5 mempunyai kandungan naftena yang tinggi, diikuti oleh isoparafin, olefin, aromatik dan sedikit paraffin, manakala gasolin yang terhasil menggunakan H-Beta mengandungi olefin, naftena, paraffin dan aromatik. Hasil sampingan utama adalah gas yang terdiri daripada komponen C₁-C₃ menggunakan H-ZSM-5 dan C₃-C₄ menggunakan H-Beta.

Kata kunci: Zeolit; H-ZSM-5; H-Beta; peretakan; minyak kelapa sawit; gasolin

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1.0 INTRODUCTION

Zeolites have been creating a growing interest because of their application as catalysts in various industries. The conversion of hydrocarbons to valuable chemicals such as gasoline and aromatic compounds via catalytic processes have been investigated and progressively improved. Currently some researchers are concentrating on developing alternative and renewable sources of environmental friendly liquid fuel.

Conversion of vegetable oil to fuels has been investigated in the past decade [1–5]. Various kinds of vegetable oils such as castor, corn, jojoba and palm oil were reported to successfully form gasoline and other useful chemicals after the catalytic conversion process [1, 2]. Study conducted by Prasad and co workers [3] showed that about 60 to 95 wt% of canola oil was converted to gasoline over H-ZSM-5, which contained about 60 to 70 wt% of aromatic hydrocarbons, light gas and water. They continued their study by adding steam in the feed stream with canola oil and obtained liquid hydrocarbon products with less aromatic compounds [4]. Further research on canola oil cracking over H-ZSM-5 was carried out by Katikaneni *et al.* [5]. They obtained the highest amount of organic liquid product (OLP) of 63 wt% at 1.8 WHSV and 400°C. The hydrocarbon content of this OLP product was 83.8 wt%.

Malaysia is the largest producer of palm oil in the world. In 2004, the palm oil production was about 13,416 million tons [6]. Palm oil can be converted to clean liquid hydrocarbon fuels and chemicals by using shape selective catalyst [7]. Salam and co-workers [8] studied catalytic cracking activity on crude palm oil using H-ZSM-5 in fixed bed reactor, at 450°C with a WHSV = 2 h⁻¹. They gained about 23 wt% gasoline enriched with aromatic compounds. Tan and co-workers [9] carried out conversion of RBDPO using H-ZSM-5 in fixed bed micro reactor at 383°C with WHSV = 2 h⁻¹. They obtained a conversion of about 67 wt% with 21.30 wt% gasoline yield. Furthermore, Twaiq and co-workers [10] investigated H-ZSM-5, H-Beta and H-USY as catalysts on RBDPO in a fixed bed micro reactor. Among the three zeolite catalysts, H-ZSM-5 gave the best performance in terms of conversion, gasoline yield and highest selectivity for aromatics, with the lowest coke formation. The second best catalyst was H-Beta, followed by H-Y. At 450°C and WHSV of 2.5 h⁻¹, conversion was 91.6 wt% and gasoline yield was 22.9 wt% using H-ZSM-5.

Activity and selectivity of the catalysts were governed by several factors, such as their surface area, pore size and acidity. Temperature has important role in catalytic activity [11]. Preheating of palm oil at below palm oil cracking temperature has purpose to obtain an evaporated palm oil and to prevent a sudden boiled palm oil. The objective

of present study is to investigate the effects of surface area, pore size and acidity of H-ZSM-5 and H-Beta for evaporated palm oil cracking. The effect of temperature on the gasoline selectivity over H-ZSM-5 and H-Beta is also studied.

2.0 EXPERIMENT

2.1 Materials

The raw material was a refined, bleached and deodorized (RBD) commercial grade palm oil “Vesawit” that was purchased from the local market. Chemicals used in this research were hydrogen gas and nitrogen gas from SIG company; while catalysts were ammonium form of ZSM-5 (Si/Al = 30, code no. CBV 3024 E) and Beta (Si/Al = 25, code no. CP 814 E) purchased from Zeolyst International. Catalysts were dried overnight at 120°C and followed by calcination at 550°C, 5 h for ZSM-5 and at 450°C, 6h for Beta. The cooled catalyst was finally sieved to about 35 mesh particle size.

2.2 Catalyst Characterization

The calcined and hydrotreated catalysts were characterized with XRD, Py-IR and NA. XRD measurements were performed using a Philips 1840 with CuK α radiation with $\lambda = 1.54056 \text{ \AA}$ at 40 kV and 30 mA in the 2θ range of 5° to 50° at a scanning speed of 0.05° per second, with a vertical goniometer at room temperature (20°C). The sample was placed on a mountain sample holder, and then grounded before mounting on a glass slide. Py-IR was used to identify types of acid sites in the catalysts. About 10 mg of samples were pressed at 5 ton for a minute to get a 13 mm die. The samples were introduced in the infrared cell with calcium fluoride, CaF₂ windows and were heated at 400°C under vacuum condition for four hours. The samples were then cooled to room temperature before pyridine was adsorbed for a minute, which was then desorbed at 150°C for an hour under vacuum. The infrared spectra were collected at room temperature using a Shimadzu 2000 FTIR spectrometer with 2 cm⁻¹ resolution. The infrared spectra were monitored at room temperature in the wave number range of 1400–1700cm⁻¹. Adsorption and desorption of nitrogen was performed using a Micromeritics Accelerated Surface Area and Porosimetry (ASAP) 2010 at 120°C under vacuum conditions for six hours prior to the adsorption-desorption process. The data obtained included the Brunauer-Emmet-Teller (BET) surface area, pore size, micropores volume and micropores area. The type of pores was determined by comparing the sample’s isotherm with the standard isotherm from the literature [12].

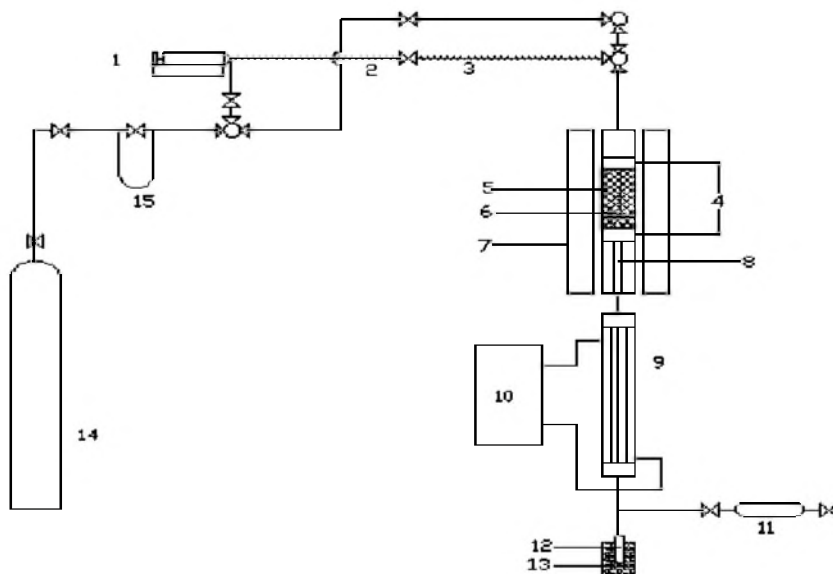
2.3 Experimental Setup

The catalytic performance of each catalyst (with respect to palm oil conversion and product distribution) was carried out in a fixed bed stainless steel reactor (30 cm length with 0.83 cm inner diameter). An electric furnace is used to heat the reactor and the temperature was managed by Carbolite temperature controller. The palm oil was fed to the reactor by a variable speed syringe pump with a pumping rate of 0.25 ml/hr to 13 ml/hr. The palm oil was preheated and evaporated using heating tape with TOP temperature controller before being fed to the reactor. The reaction products were condensed in a condenser, which was connected with a water bath. It was then separated into liquid and gas products. To ensure that the lighter liquid product did not escape to gas sampling port, the liquid products were trapped in an ice trap.

2.4 Experimental Procedure

All the experiments were conducted in a fixed bed reactor as at atmospheric pressure shown schematically in Figure 1. The catalytic cracking and analytical procedure are shown in Figure 2. Initially, the reactor was loaded with 1 g of catalyst that was plugged by 0.2 g of glass wool, which was supported by a stainless steel pin. The reactor was preheated at 450°C for 1 hour. It was then flushed with N₂ at 100 ml/min for 15 minutes. Later, the reactor was heated to the desired temperature. Palm oil was injected into the system by a syringe pump at a WHSV = 2.5 h⁻¹. It was preheated at 120°C to decrease a viscosity of palm oil and then evaporated at 250°C to prevent a sudden boiled palm oil before entering the reactor. The experiments were conducted for 4 h with the N₂ flowing at 1 L/h. After that, the syringe pump was turned off, while the N₂ was flowed for another 1 h to continue the reaction. The reactor was then flushed with N₂ for 30 minutes at 30 ml/min.

The products exiting the reactor were cooled to 40°C with a condenser system to prevent solidification of the residual oil. It was then separated into liquid and gas fractions. The liquid fraction was collected in a liquid collecting flask while the gas fraction was collected in a gas sampling port. The aqueous phase was separated from the condensed liquid product using a syringe. It consisted mainly of water and some organic components that are soluble in water. Among the components that are soluble include alcohols and acid carboxylic chains [13]. The organic liquid product (OLP) was then distilled in a micro distillation unit at atmospheric pressure and at gasoline boiling point range of 40–170°C for an hour and heavy liquid product (which contains kerosene, jet oil and diesel) boiling point range from 171 to 250°C for another hour. The products remaining after the distillation were termed as residue.



REFERENCES

- | | | | | | |
|---|--------------|----|-------------------------|----|-------------------|
| 1 | SYRINGE PUMP | 6 | CATALYST | 11 | GAS SAMPLING PORT |
| 2 | HEATING COIL | 7 | VERTICAL FURNACE | 12 | LIQUID COLLECTOR |
| 3 | HEATING COIL | 8 | SUPPORTING ROD WITH PIN | 13 | ICE TRAP |
| 4 | GLASS WOOL | 9 | CONDENSER | 14 | NITROGEN GAS TANK |
| 5 | REACTOR | 10 | WATER BATH | 15 | MANOMETER |

Figure 1 The palm oil cracking rig

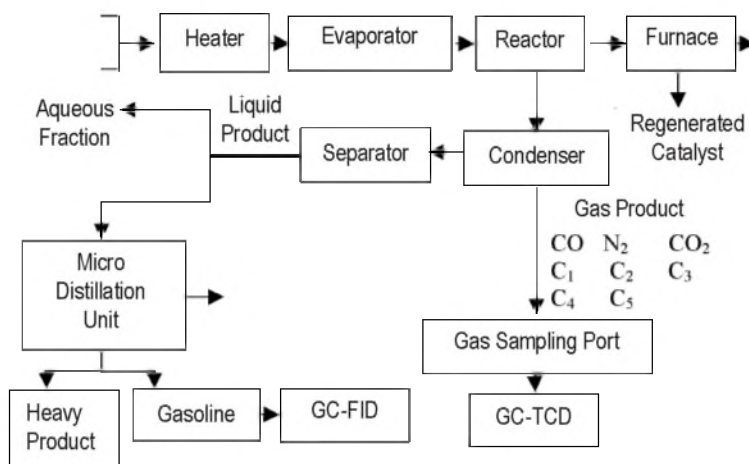


Figure 2 Schematic diagram for the catalytic cracking and analytical procedure

The gaseous products (C_1 – C_5 , CO and CO_2) were analyzed with a Hewlett Packard Agilent 6890N GC system equipped with a thermal conductivity detector (TCD) and 4 series column (UCW 982, DC 200, Porapak Q and Molecular Sieve 13A). The gasoline product was analyzed with a gas chromatograph (Perkin Elmer, Auto System) using capillary column (100 m long \times 0.25 mm width, model no: SGE 100QC2.5 BPI PONA) with a flame ionization detector (FID).

A substantial amount of coke was accumulated on the catalyst after each experiment. The spent catalyst was weighed using a microbalance. It was then heated to 500°C in a furnace for five hours. The spent catalyst was then re-weighed. The difference in the weight of the spent catalyst before and after heating was termed as the weight of coke that was burned off.

3.0 RESULTS AND DISCUSSION

3.1 Catalyst Characterization

3.1.1 XRD Measurement

The XRD pattern of H-ZSM-5 and H-Beta are shown in Figures 3. Two high intensity diffractograms at $2\theta = 7$ – 9° and three high intensity diffractograms at $2\theta = 22$ – 25° for H-ZSM-5 (Figure 3a), which was similar to simulated ZSM-5 pattern [13, 14]. For H-Beta, the XRD pattern (Figure 3b), showed two high intensity diffractogram at $2\theta = 7.9^\circ$ and $2\theta = 22.5^\circ$, which was also similar to simulated Beta pattern [13, 15]. It concluded that H-ZSM-5 and H-Beta had the crystalline form.

3.1.2 Py - IR Measurement

The pyridine adsorption infrared (Py-IR) spectrum of H-ZSM-5 and H-Beta after evacuation at 150°C is shown in Figure 4. The IR frequencies of coordinated pyridinium at 150°C correspond to Brønsted and Lewis acidities, respectively [16–17]. The wavenumber of Brønsted acidity for H-ZSM-5 were figured at 1545.8 cm^{-1} and 1635.5 cm^{-1} , while for H-Beta at 1545.8 cm^{-1} and 1637.4 cm^{-1} . The Lewis acidity for H-ZSM-5 were figured at 1453.3 cm^{-1} and 1622.0 cm^{-1} , while for Beta at 1454.2 cm^{-1} and 1621.1 cm^{-1} . The mixed Brønsted and Lewis acid sites were shown at 1489.9 cm^{-1} for H-ZSM-5 and at 1490.9 cm^{-1} for H-Beta. The results indicated that H-ZSM-5 and H-Beta both have Brønsted and Lewis acid sites.

The physicochemical of H-ZSM-5 and H-Beta properties are shown in Table 1. It is shown that the BET surface area and pore size of H-Beta are larger than for

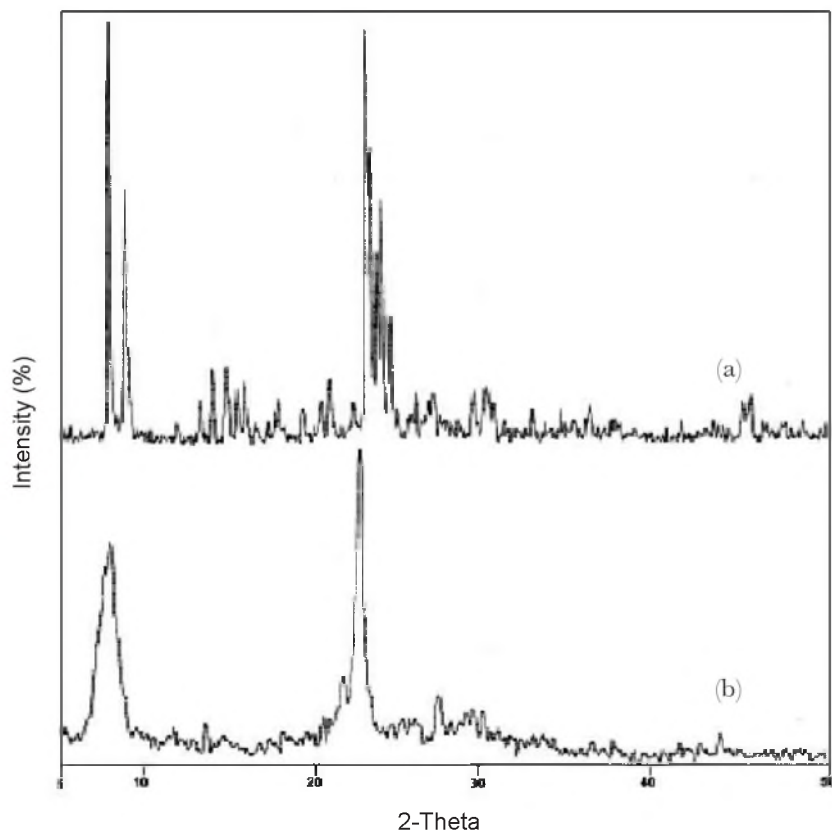


Figure 3 The XRD pattern of the catalysts: (a) H-ZSM-5 and (b) H-Beta

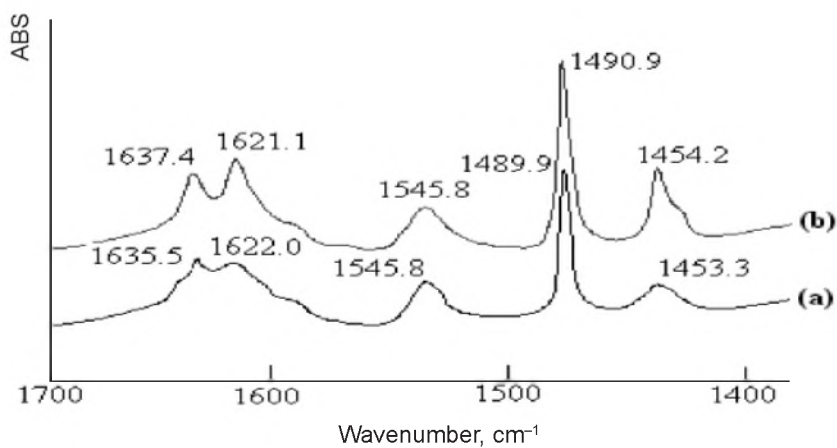


Figure 4 Pyridine absorption infrared (Py-IR) spectrum of (a) H-ZSM-5 and (b) H-Beta

H-ZSM-5. The Brønsted and Lewis acidity of H-Beta are also higher than H-ZSM-5. ZSM-5 is a 10-membered oxygen ring system, known as medium pore zeolites, while Beta is a 12-ring membered oxygen ring system, known as large pore zeolites [18–19]. Both the ZSM-5 and Beta structures exhibit multidirectional channel systems. Zeolite Beta is a disordered intergrowth of several hypothetical polymorphs, whereas ZSM-5 presents ordered elliptical channel system. Accordingly, the channel dimensions in Beta (0.66×0.67 nm and 0.56×0.57 nm) are larger than those in ZSM-5 (0.53×0.56 nm and 0.51×0.55 nm) [20]. Consequently, H-Beta has larger surface area and pore size than H-ZSM-5. The Brønsted and Lewis acidity of H-Beta are also higher than H-ZSM-5. As an aluminosilicate compound, both of ZSM-5 and Beta has Brønsted and Lewis acid sites. The Brønsted acid site is a positive ion hydrogen charge that is connected with tetrahedral AlO_4 in frame work of zeolite, while the Lewis acid site is produced from aluminium species in extra frame work of zeolite [16]. The ZSM-5 has Si/Al of 30 and Beta has Si/Al of 25. Based on the silicon aluminium ratio of both the zeolites, consequently aluminium content of Beta much more than aluminium content of ZSM-5, consequently the Brønsted and Lewis acidity of H-Beta are higher than H-ZSM-5.

Table 1 The physicochemical properties of H-ZSM-5 and H-Beta

Zeolite	BET Surface Area (m^2/g)	BET Pore Size (Å)	Brønsted Acidity ($\mu\text{mol}/\text{g}$)	Lewis Acidity ($\mu\text{mol}/\text{g}$)
H-ZSM-5	333.3	25.1	134	61
H-Beta	539.7	49.4	201	149

3.2 Catalytic Activity

The performance of H-ZSM-5 and H-Beta catalysts having the same particle size (about 35 mesh) was determined according to the gasoline selectivity. The conversion, gasoline selectivity and yield are defined as follows:

$$\text{Conversion (wt\%)} = \frac{F-R}{F} \times 100\% \quad (1)$$

$$\text{Selectivity (wt\%)} = \frac{P}{F-R} \times 100\% \quad (2)$$

$$\text{Yield (wt\%)} = \frac{P}{F} \times 100\% \quad (3)$$

where F is the palm oil feed weight (g), R is residual oil weight (g) and P is the product weight (gasoline, heavy products, residue, gas and coke) (g).

The obtained conversion, yield and selectivity of product at 500°C and WHSV of 2.5 h⁻¹ are shown in Tables 2 and 3. Tables 2 and 3 compile the conversion, yield and selectivity of various products obtained from palm oil cracking using H-ZSM-5 and H-Beta catalysts. The operation conditions were 500°C and a WHSV of 2.5 h⁻¹. The performance of these catalysts was compared in terms of their pore size, surface area and acidity

Table 2 Conversion and product yield of palm oil cracking over H-ZSM-5 and H-Beta at 500°C and WHSV of 2.5 h⁻¹

Zeolite	Conversion (wt%)	Yield of OLP (wt%)	Yield of gas (wt%)	Yield of coke (wt%)
H-ZSM-5	95.81	39.65	47.05	0.8
H-Beta	90.21	36.57	48.36	4.34

Table 3 Product selectivity of palm oil cracking over H-ZSM-5 and H-Beta at 500°C and WHSV of 2.5 h⁻¹

Zeolite	Selectivity of gasoline (wt%)	Selectivity of heavy products (wt%)	Selectivity of residue (wt%)
H-ZSM-5	27.21	9.78	4.39
H-Beta	19.87	11.97	12.02

H-ZSM-5, which has a pore size of 25.11 Å with bidirectional 10 membered ring interconnecting channel, gave higher conversion (about 95.1 wt%) than H-Beta (about 81.8 wt%), which has a pore size of 49.37 Å with unidirectional and tridirectional 12 membered ring channel [18–20]. The gasoline selectivity using H-ZSM-5 was much higher than H-Beta, which was 27.21 wt% and 19.87 wt%, respectively but the yield of OLP was almost the same for both the catalysts. Although surface area and Brønsted acidity of H-Beta were higher than H-ZSM-5, the conversion and gasoline selectivity of palm oil cracking over H-ZSM-5 were better than H-Beta. H-ZSM-5

was more shape selective than H-Beta and this factor plays an important role in secondary cracking, resulting in high gasoline selectivity [21, 22]. Based on gasoline selectivity and selectivity of residue, it could be concluded that using H-ZSM-5 on palm oil cracking is better than using H-Beta.

The effect of temperature on conversion of palm oil over H-ZSM-5 and H-Beta is shown in Figure 5. Conversion of palm oil for both the catalysts increased with increasing reaction temperature and followed a nearly identical curve until 500°C but for H-Beta, it starts to decrease after 500°C. However, the conversion over H-ZSM-5 was higher than H-Beta at all temperatures. It can be clearly seen that an increase in the temperature has strong effect on the conversion, especially for H-ZSM-5, but for H-Beta is shown sharp declined at 525°C. This decreasing might be due to over crack the palm oil.

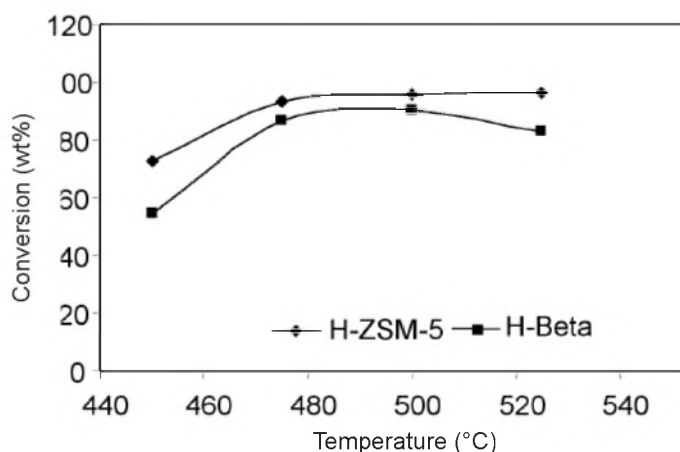


Figure 5 Temperature effect of H-ZSM-5 and H-Beta on conversion of palm oil

Selectivity of products for palm oil cracking at various temperatures are demonstrated in Figures 6. Gasoline selectivity increased with increasing temperature until 525° for H-ZSM-5 only. H-ZSM-5 showed a higher selectivity towards gasoline at temperature 475°C and above, with the maximum selectivity at 525°C. With H-Beta, the gasoline selectivity initially increased with temperature until 500°C and then it begins to decrease with further increasing of temperature. The decreasing trend profile at temperature above 500°C might be related to the sensitive acid site of H-Beta which can be easily deactivated at high temperatures [23]. The heavy products' selectivity with H-ZSM-5 and H-Beta almost linearly decreased with increasing temperature

(Figure 6b). The highest selectivity was obtained at 450°C for both H-ZSM-5 and H-Beta. The heavy products' selectivity using H-ZSM-5 and H-Beta from 475°C until 525°C was sharply decreased, especially for H-Beta. The heavy products' selectivity using H-ZSM-5 was lower than using H-Beta. It might be due to shape selective property of H-ZSM-5 in palm oil cracking to produce gasoline; otherwise gasoline selectivity using H-ZSM-5 was higher than gasoline selectivity using H-Beta, where the liquid product mainly consisted of gasoline and heavy product [10, 23]. The selectivity towards residue also decreased with increasing temperature (Figure 6c).

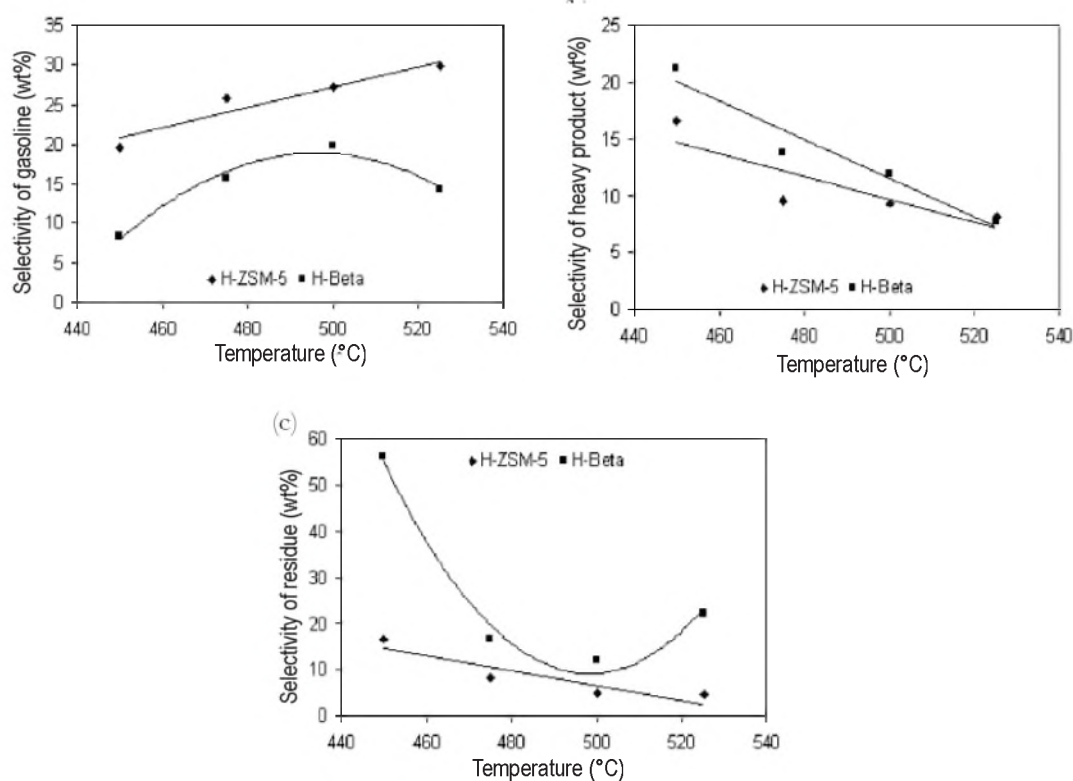


Figure 6 H-ZSM-5 and H-Beta temperature effect (a) gasoline selectivity, (b) heavy product selectivity and (c) residual oil selectivity of palm oil cracking

Figure 7 shows the effect of temperature on OLP, gas and coke yield. The results illustrated that the OLP yield using H-Beta decreased slightly with increasing temperature. However, the trend was almost constant with H-ZSM-5. The cracking

of palm oil produced a high amount of gas. The same trend was observed in the gas yield that the gas product increased with increasing temperature (Figure 7c). The yield of gas using H-Beta was slightly higher than H-ZSM-5, which was 48.36 wt% and 47.05 wt%, respectively. Heavy products consisted of middle distillate fuel, kerosene and diesel. The obtained heavy products' selectivity for H-ZSM-5 and H-Beta were 9.78 wt% and 11.97 wt% respectively. The big difference was on the selectivity of residue. Three times more residue was obtained with H-Beta than with H-ZSM-5. The performance of each catalyst in terms of coke formation from 450°C to 525°C is shown in Figure 7c. The coke produced by both the catalysts decreased with increasing temperature. H-Beta produced more coke than H-ZSM-5. Different zeolite catalysts gave different weight percent of coke, due to their shape selectivity in the coke formation.

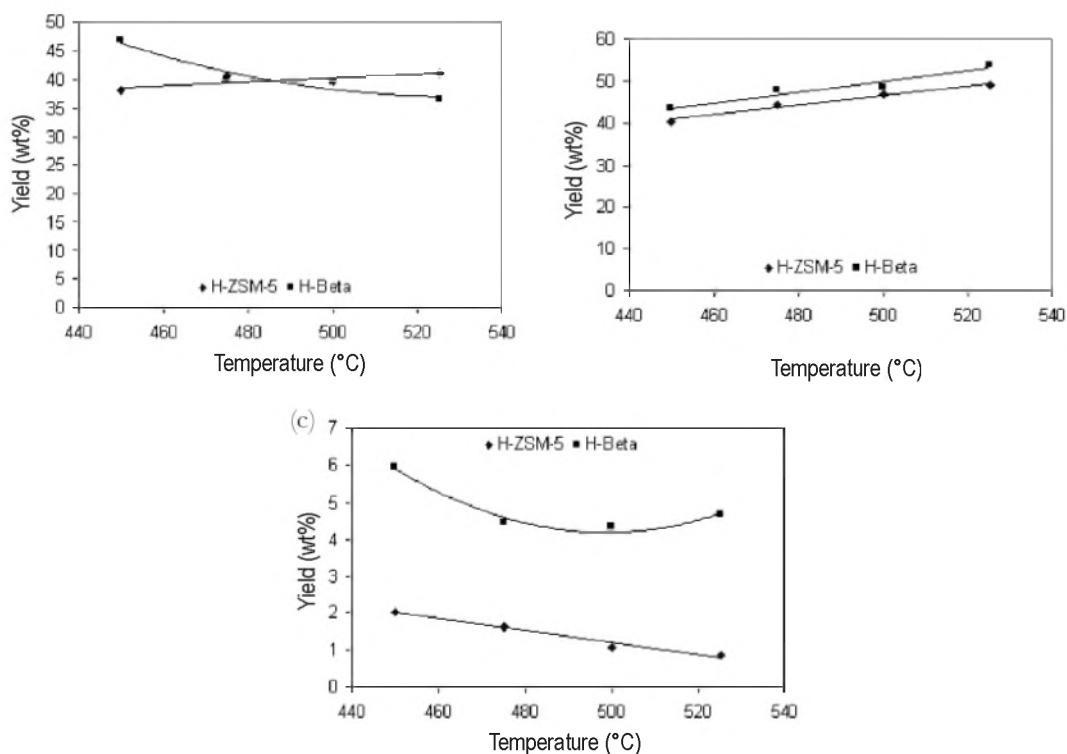


Figure 7 H-ZSM-5 and H-Beta temperature effect (a) OLP product yield, (b) gas product and (c) coke product of palm oil cracking

The distribution of gasoline composition with H-ZSM-5 and H-Beta at various temperatures is tabulated in Table 4. Palm oil cracking over H-ZSM-5 produced gasoline that consisted of a lot of naphthenes, isoparaffins and a small amount of olefins. The best gasoline composition consisted of paraffins, olefins and isoparaffins with less naphthenes and aromatics as indicative of environmental friendly fuel. Generally, this gasoline composition was obtained by using H-Beta.

Table 4 Effect of temperature on gasoline composition over H-ZSM-5 and H-Beta catalyst

Temperature (°C)	H-ZSM-5				H-Beta			
	450	475	500	525	450	475	500	525
<i>Gasoline Composition (wt% of Gasoline Fraction)</i>								
Paraffins	0.17	0.12	0.00	0.00	13.63	9.48	7.87	9.35
Olefins	4.21	2.37	0.59	0.25	39.88	46.39	38.79	42.55
Naphthenes	82.35	80.66	92.34	91.77	24.68	20.78	26.62	30.74
Aromatics	3.15	2.66	1.57	2.15	5.10	5.35	8.70	5.14
Isoparaffins	10.11	14.19	5.49	5.83	16.72	18.00	18.02	12.22

Although the Brønsted acidity of H-Beta was higher than H-ZSM-5, but more gasoline fraction was produced with H-ZSM-5. The high selectivity on gasoline product for H-ZSM-5 was due to its shape selective property of H-ZSM-5 catalyst [10, 23]. Although the pore size of H-Beta was bigger than H-ZSM-5, the conversion of palm oil and selectivity of gasoline using H-Beta were less compared to H-ZSM-5. On the other hand, the selectivity for non-aromatic compounds such as paraffins and olefins increased with the pore size of catalyst. It would appear from these observations that the process of cracking and deoxygenation, which are the initial reaction steps are more enhanced with medium pore size catalyst [9]. Haag and co-worker [2] converted corn oil and castor oil to fuels over H-ZSM-5 at 500°C with a WHSV of 2.5 h⁻¹. Corn oil and castor oil are unsaturated triglyceride, but castor oil has one alcohol group in each of ester chains. They were completely converted to hydrocarbons, water and carbon oxides. Corn oil produced 58.39 wt% of gasoline and castor oil produced 74.14 wt% of gasoline in hydrocarbon product. The gasoline consisted of mostly aromatic compounds of C₇ to C₈ with about 90 wt% of xylene as C₈. Castor oil produced more coke than corn oil; which were 2.18 wt% and 1.51 wt% respectively. The gas products were enriched with propane, 18.49 wt% from corn oil and 11.3 wt% from castor oil. Haag and co-workers concluded that the product distribution depended on the effective hydrogen to carbon ratio, molecular weight and structure of vegetable oils.

Palm oil consists of 50.56 wt% saturated triglyceride and 49.74 wt% unsaturated triglyceride. In this study, palm oil conversion over H-ZSM-5 at 500°C with a WHSV of 2.5 h⁻¹ was 95.81 wt%. The gasoline yield was 26.07 wt%. Gasoline consisted mostly of naphthenes compounds, which was 92.34 wt%. The coke yield was 1.07 wt% and the gas yield was 47.05 wt%.

The differences in this result is due to the difference of fatty acid composition than the fatty acid composition of Twaiq's research that incoming feed before entering the reactor. Furthermore, this difference in fatty acid composition is caused by the second preheating palm oil temperature in evaporator (Figure 2). The unsaturated palm oil, such as palmitoleic (16:1), linoleic (18:2) and linolenic (18:3) have temperature less than 250°C and most of saturated palm oil, such as palmitic (16:0) and stearic (18:0) have higher boiling temperature than 250°C [24]. The fatty acid composition of palm oil that has boiling temperature less than 250°C will be evaporated and then the olefins and gas product as the result thermal cracking of this vaporated palm oil that through oligomerization and cyclization produce naphthenes. It is the reason why in this reasearch produce more naphthenes than aromatics [25]. Furthermore, the fatty acid composition of palm oil that has boiling temperature more than 250°C will be evaporated gradually before entering the reactor and then is cracked catalytically to liquid fuels.

The catalytic cracking of palm oil to liquid fuels was also studied by Twaiq and co-workers [10] using H-ZSM-5, H-Beta and H-USY at various temperatures, ranging from 350°C to 450°C. At 450°C and WHSV of 2.5 h⁻¹, the conversion, the yield of OLP, gasoline, coke and gas were 91.6 wt%, 40.5 wt%, 22.9 wt%, 1.0 wt%, and 44.4 wt% over H-ZSM-5% respectively. The OLP consisted of 22.2. wt% benzene-toluene-xylene, BTX aromatic compounds. The gas product composed mostly of C₃ and C₄ components. With H-Beta, the OLP yield obtained was 53 wt%, gasoline yield (26.3 wt%), coke yield (6.2 wt%) and gas yield (26.5 wt%) with a conversion of 88.2 wt%. The OLP consisted of 6.7 wt% BTX aromatic compounds. The gaseous products composed of mostly C₃. The H-ZSM-5 showed better performance than H-Beta in terms of palm oil conversion, and gasoline, gas, and coke yield.

Particle size of catalyst plays an important role in heterogeneous catalysis. They used zeolite powders with a particle size less than 32 µm. The particle size of zeolites in this work was bigger, which was 0.5 mm. The injected palm oil was not preheated before being fed to reactor and without carrier gas during the reaction process [10]. In this research the palm oil was preheated at 120°C and with a WHSV of 2.5 h⁻¹, before being evaporated at 250°C prior entering the reactor. The function of preheating was to decrease the viscosity of palm oil and through evaporation the liquid palm

oil was expected to vaporize. At low temperature about 450°C, using H-ZSM-5 and H-Beta produced a high amount of wax. Wax is a solid material, a unique type of fatty acid ester [26]. The conversion over H-ZSM-5 was 72 wt% and the gasoline selectivity was 19.64 wt%. The gasoline composition was mostly naphthenes beside isoparaffins, olefins, aromatics and a less amount of paraffins. The gasoline yield was 14.19 wt%. Yield of the OLP, gas and coke were 38.4 wt%, 40.5 wt% and 2.26 wt% respectively. The yield of wax was 16.95 wt%. The gas product was enriched of C₃ and C₄ components. The big difference was in the aromatics' yield. The aromatics yield from this work was 3.15 wt% compared to 17.2 wt% [10]. The aromatics in this work consisted of alkylbenzene without BTX as opposed to BTX only from Twaiq and co-workers [10]. This research produced gasoline enriched with naphthenes. The naphthenes was consisted mostly of 1t,2c,3-trimethylcyclopentane.

With H-Beta in this research, the conversion and gasoline selectivity were 54.67 wt% and 8.25 wt%. The yield of the OLP, gas and coke were 54.67 wt%, 46.73 wt% and 5.95 wt%. The yield of wax was 18.24 wt%. The gasoline composition was distributed to olefins, naphthenes, isoparaffins, paraffins and less of aromatics. The aromatics also consisted of alkylbenzene without BTX. The gas product was enriched with C₃ and C₄ components. The difference in the results might be due to different particle size and procedures.

The best result from this work was at the highest temperature of 525°C and a WHSV of 2.5 h⁻¹ with H-ZSM-5. The conversion was 96.12 wt% and the gasoline selectivity was 29.92 wt%. The gasoline yield was 26.76 wt %. Yield of the OLP, gas and coke were 41.10 wt%, 49.04 wt% and 0.84 wt%, respectively. The gasoline was enriched with naphthenes (91.77 wt%).

Alencar *et al.* (1983) carried out the pyrolysis of crude palm oil from 300°C to 500°C in a Pyrex apparatus. This resulted into 95.55 wt% of a mixer of n-alkanens and 1-alkenes as the major product. Dehydrogenation of paraffins produces olefins. Then through oligomerization and cyclization produces naphthenes [27]. In this research, palm oil was evaporated at 250°C before entering the reactor, which was set at a temperature range of 450°C to 525°C. Therefore, it is assumed that palm oil pyrolysis may have occurred to produce paraffins and olefins. This explains the high naphthenes in gasoline composition gained in this study.

4.0 CONCLUSIONS

H-ZSM-5 gave better performance than H-Beta in terms of palm oil conversion, gasoline selectivity and low coke formation at all temperatures between 450°C and

525°C. The highest gasoline selectivity was obtained at 525°C with 96.12 wt% of conversion and 29.92 wt% of gasoline selectivity. It contained high amount of naphthenes and isoparaffins. The more environmental friendly fuel was obtained by using H-Beta catalyst. It produced high amount of olefins, naphthenes, paraffins and isoparaffins and small amount of aromatics in the gasoline composition. The high selectivity on gasoline products for H-ZSM-5 was due to its shape selective property. Although the surface area, pore size and acidity of H-Beta was bigger than H-ZSM-5, the conversion of palm oil, gasoline selectivity and aromatics compound in the gasoline product were less compared to H-ZSM-5. The gas as side product of palm oil cracking, had a high distribution of C₃-C₄ compound.

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