

Catalytic Conversion of RBD Palm Oil to Gasoline: The Effect of Silica-Alumina Ratio in HZSM-5

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Abstract

The RBD palm oil was converted to gasoline by passing its vapor through HZSM-catalyst. Three samples of HZSM-5 with different silica-alumina ratio ($\text{SiO}_2/\text{Al}_2\text{O}_3$) of 30, 50 and 70 were prepared and used to investigate the effect of silica-alumina ratio of HZSM-5 to the process. XRD was employed to confirm that the catalyst prepared were HZSM-5. FT-IR analysis for middle range spectra and near range spectra both were engaged to give structural characteristic of the catalyst and to analyze the hydroxyl (OH) groups of the catalyst respectively. The effect of silica-alumina ratio can be seen clearly from the result as HZSM-5 with 30 silica-alumina ratio produced the highest gasoline selectivity compare with the other two catalysts.

Keywords: RBD Palm Oil; Gasoline; HZSM-5; Silica-Alumina Ratio

1.0 Introduction

Strong needs to find the alternative sources of petroleum now become a priority since the rise of petroleum price in the world market. Several alternatives were proposed, but almost all of the suggestions are still in the research and development process. Natural gas for example looks like the best alternative, but the problem of transportation and safe handling of the gas makes it difficult to distribute the gas to rural areas. Coal investment in liquid fuel production had almost ceased after exploration of the petroleum around a half- century ago. Bio-fuel appears as a promising alternative for petroleum. The advantages of bio-fuel hydrocarbons are; it comes from renewable sources, is environmental friendly due to low sulfur and nitrogen content and easy on handling and transportation, as it appears in liquid form. The vegetable oils have relatively long chain $-\text{CH}_2-$ units of fatty acids, which incorporate oxygen atoms and thus have higher heat of combustion. For example, castor oil ($\text{C}_{57}\text{H}_{104}\text{O}_9$) contains high-energy value of 37 MJ/ kg compared with starch ($\text{C}_6\text{H}_{10}\text{O}_5$), a carbohydrate which has 7.5 MJ/ kg [1]. A type of vegetable oil that is abundantly grown in Malaysia, palm oil, has a potential to be a raw material for bio-fuel production. Statistic by Asia Features Services [2] stated that Malaysia for four consecutive years produced the largest volume of palm oil. In 1999/2000, Malaysia produced about 10.55 million tonnes palm oil, compared with Indonesia's 6.06 million tonnes. Many researchers have studied the applicability of converting plant material to liquid gasoline [3, 4, 5, 6, 7, 8] but results of their research can still be improved. Because the viscosity of palm oil is very high, a suitable method to crack the triglycerides is essential. Low in selectivity of gasoline is the main problem in this research and it seems that it is not commercially viable. The research of vegetable oil catalytic cracking, especially palm oil catalytic cracking has a bright prospect in the future.

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More studies have to be done to make sure this process is economically viable. The ultimate challenge still lies in catalyst development. A stable, shape selective and high acidic catalyst is needed in order to achieve high conversion and selectivity in this process. The researchers in this field also agree that the process of converting vegetable oils to gasoline depends on the acidity of the catalysts, especially Brönsted acid sites. Therefore, this research will try to find the suitable catalyst for the catalytic cracking of palm oil to gasoline, by modifying the HZSM-5 properties.

2.0 Materials & Method

2.1 Raw material

The raw material was a refined, bleached and deodorized (RBD) commercial grade palm oil 'Vesawit' that was purchased from the local market. Some of the properties of Vesawit were listed in Table 1.

Table 1 Some of the properties of Vesawit brand palm oil.

Fatty acid contents	Less than 0.1% (as palmatic acid)
Saponification value	194-202 mg KOH
Iodine value	Not less than 56
Melting point	Not more than 24 °C
Density	0.907 g/cm ³
Data from Yee Lee Edible Oils Pvt. Ltd	

Chemicals used in synthesis of HZSM-5 were aluminium sulfate hexadecahydrate (Fluka), tetrapropylammonium bromide (TPABr, Fluka), sulphuric acid (Baker), sodium silicate solution (Merck), sodium chloride and ammonium nitrate (Fluka).

2.2 HZSM-5 Preparation

HZSM-5 was prepared via direct synthesis method following the procedure by Plank et al. [9] with slight modification by Sharif [10]. NaZSM-5 was prepared by mixing SiO₂ into tetrapropyl ammonium bromide (TPABr) solution. The dissolved SiO₂ then was mixed with aluminium sulfate, Al₂(SO₄)₃.16H₂O solution. The mixing was placed in autoclave non-stirred pressure vessel. Three solutions, namely solution A (contained Al₂(SO₄)₃.16H₂O, TPABr, H₂SO₄ and distilled water) solution B (contained NaSiO₃, H₂SO₄ and distilled water) and solution C (contained NaCl and distilled water) were prepared. Solution C was put in the pressure vessel and then was stirred by Heidolph RZR-2000 stirrer. Then solution A and solution B were slowly poured into solution C at the same time. The white slurry product then was stirred for 15 hours. The autoclave was sealed and put into the oven at 170°C. After that, the zeolite was washed and filtered. The zeolite then was dried in the oven for 15 hours at 100°C. After the drying process, the zeolite was calcined in the furnace at 550°C for 5 hours. NaZSM-5 then underwent ion-exchange process to change from Na form of ZSM-5 to NH₄ form of ZSM-5. Then the mixture was refluxed for 6 hours at 80°C. Finally the zeolite was filtered, washed and dried at 100°C before it was again calcined at 550°C. NH₄ ion then was disposed because of the effect of the heat and the resulting white soft solid was HZSM-5 zeolite. The chemicals were prepared with certain weight in order to synthesize HZSM-5 with 30, 50 and 70 SiO₂/ Al₂O₃.

2.3 X-ray Diffraction (XRD)

X-ray powder diffraction was employed to determine the value of relative crystallinity (RC). The commercial zeolite, HZSM-5 was assumed to have 100% crystallinity. The determination of the value was based on the area of the characteristic peaks in the 2θ range of 22.5° - 25° [11]. Diffractometer D5000 Siemens Kristalloflex was employed to carry out the test with Cu-K α radiation ($\lambda = 1.540560\text{\AA}$). 2θ angular regions from 5° to 60° were scanned. Samples were saturated over concentrated NH_4Cl solution in desiccators to ensure complete dehydration before recording the pattern as that could affect the lattice parameter. The powder was grinded before it was mounted on the glass slide.

2.4 Fourier Transform Infra Red (FTIR)

For framework studies, Fourier transform infrared (FTIR) was performed using Perkin Elmer 1600 spectrophotometer with 4 cm^{-1} resolutions. Spectrum was recorded in 400 cm^{-1} – 1500 cm^{-1} regions. The KBr wafer technique was used in this study. For sample preparation, the samples were mixed with KBr. About 1-3g mixture of samples and KBr were placed in the die and pressed with 10 ton pressure. For hydroxyl group studies, the analysis was performed using Shimadzu 8000. The equipment was set to 2 cm^{-1} resolution and 10 runs per sample. The spectrum in 3400 cm^{-1} to 3900 cm^{-1} region was recorded. For the analysis of hydroxyl groups, about 1-3g sample was grind and pressed with 5 ton pressure about 15 second. The disc-like sample then was placed in the sample holder. The sample holder then was put into the quartz cell with CaF_2 window. Cell was placed in tube furnace and connected to vacuum system. The sample was heated to 100°C , 300°C and 400°C under vacuum condition ($P = 1 \times 10^{-8}$ mbar). For each temperature, the heating process was done for five hours. Infrared spectrum was recorded after the sample was cooled to room temperature.

2.5 Determination of Brönsted Acid Sites Number

Number of Bronsted acid sites is determined with the equation below:

$$\text{No. of Bronsted acid sites (mmol/g)} = \frac{B (\text{cm}^{-1}) \times L (\text{cm}^2)}{\epsilon (\text{cm } \mu\text{mol}^{-1}) \times g (\text{g})} \times 1000 \quad (\text{Eq. 1})$$

which B = Peak area, obtained from FTIR computer software (cm^{-1})
L = Sample surface area (0.7857 cm^2)

* ϵ = extinction coefficients for bridging OH groups at 3604 cm^{-1} ($4.05\text{ cm } \mu\text{mol}^{-1}$)
g = Gram sample ($5.92 \times 10^{-3}\text{ g}$)

* $\epsilon (\text{cm } \mu\text{mol}^{-1})$ value was given by literature [12]

2.6 Catalytic Activity Testing

The testing of the catalytic activity was carried out in a fixed-bed reactor. The catalyst was placed in a stainless-steel tube reactor and supported with glass wool. The experiment was carried out at atmospheric pressure and the operating temperature fixed at 450°C . The reactor was loaded with 1g of the catalyst and heated to the operating temperature in a stream of nitrogen (1L/h). After 2 hours of preheating, the N_2 flow was shut off and syringe pump injected palm oil continuously in order to supply the palm oil into the system. The palm oil

vapor than went through the axial stainless-steel reactor, which was heated by a programmable furnace. The liquid product, known as Organic Liquid Products (OLP), was collected in a glass trap cooled with ice. The gas however was released to the atmosphere because the gas chromatography was unable to do the analysis for gas. The run period was about 4 hours. After the pump was shut off, the reactor was flushed with N₂ at low flowrate for an hour. Because the OLP still contained impurities, which cannot be analyzed by gas chromatography, the OLP then was distilled at 100°C. The distilled products then were injected into the gas chromatography to identify the components of the products. The products from gas chromatography were lump into 3 categories. The peaks existed before C₅ retention time was known as Other Organic Products (OOP), which could not be identified by our standards. The other categories were Gasoline (C₅-C₁₁) and C₁₂-C₁₅. n- Paraffin mix supplied by Supelco was used as a standard.

The conversion and selectivity was defined based on work by Twaiq et al [8]:

$$\text{Conversion (\%)} = \frac{P - R}{P} \times 100\% \quad (\text{Eq. 2})$$

$$\text{Selectivity of gasoline (\%)} = \frac{\text{Peaks in Gasoline Range}}{\text{Overall Peaks}} \times 100\% \quad (\text{Eq. 3})$$

where P is the palm oil feed weight (g) and R is the residue oil weight (g).

3.0 Results and Discussion

3.1 X-ray Diffraction

Figure 1 shows the diffractograms for 30, 50 and 70 SiO₂/ Al₂O₃ zeolite, as well as commercial HZSM-5. The synthesis HZSM-5 shows similar pattern of diffractogram as commercial HZSM-5. Three characteristic peaks around 2θ = 8, 23 and 45° in commercial HZSM-5 diffractogram also exist in the others zeolite diffractograms. Works by Szostak[13] and Ballmoos [14] also observed the same pattern of diffractogram for HZSM-5. The fact that the pattern did not change very much indicates that the synthesis zeolite can be categorized as a member of HZSM-5 family. All the synthesis HZSM-5s are found to be crystalline and pure, due to the peaks exist [15]. However, the relative crystallinity (RC) of the synthesis HZSM-5s are increased compared with the commercial HZSM-5. Table 2 shows the relative crystallinity of the samples, with respect to commercial HZSM-5 as 100% crystalline. Among synthesis zeolites, the sample with 50 SiO₂/ Al₂O₃ had the highest crystallinity value. The lowest crystallinity value was obtained with 70 SiO₂/ Al₂O₃. Literature [16] indicates that, the increase in crystallinity value is proportional with the increase in SiO₂/ Al₂O₃ ratio. However, 70 SiO₂/ Al₂O₃ did not follow the pattern. There are several reasons why changes in relative peak intensity occurred. Changes in peak intensity can occur due to the removal of an organic additive from the pores and also from the changing of counter-ions.

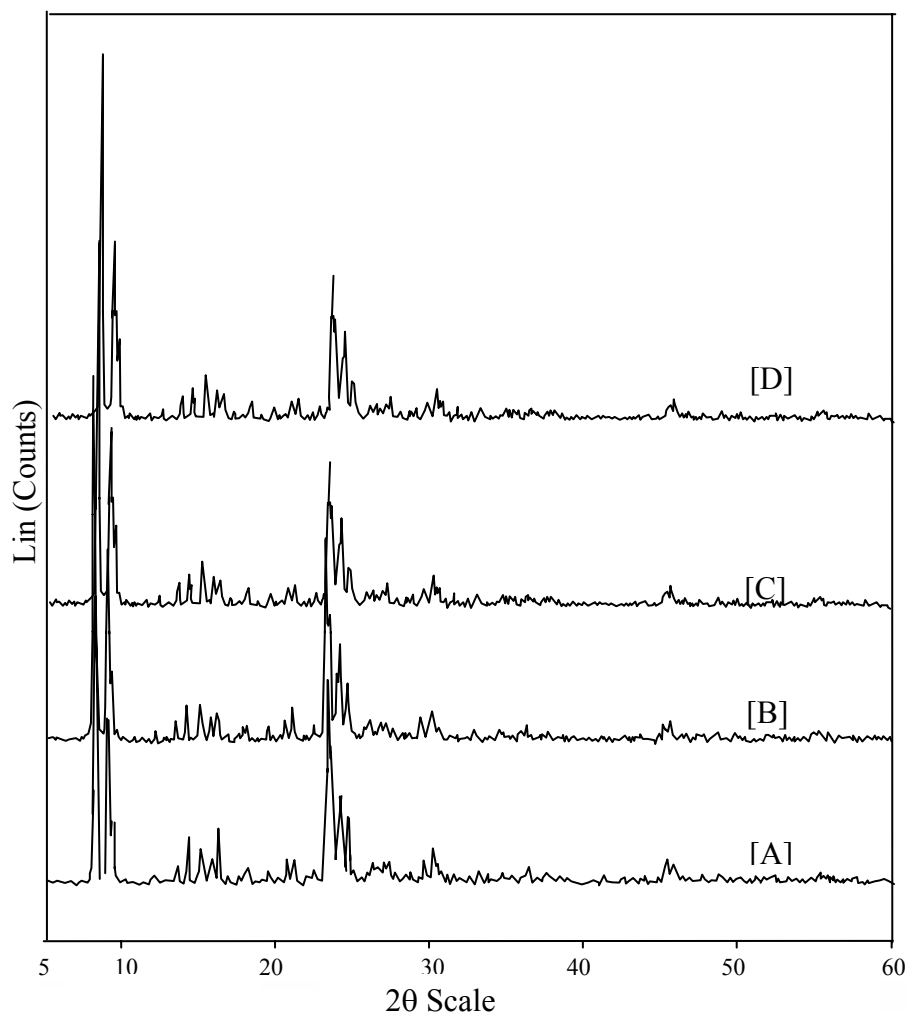


Figure 1 XRD patterns of the zeolites:[A] 30 SiO₂/ Al₂O₃, [B] 50 SiO₂/ Al₂O₃, [C] 70 SiO₂/ Al₂O₃, [D] commercial HZSM-5

The changes can also happen when large crystals have a preferred orientation in the X-ray sample holder and when other ions are substituted into the framework structure [17]. However, in this case, the catalysts were prepared by the same procedure. Furthermore, no other ions were substituted into the framework structure. The possible reason why there were changes in peak intensities is maybe due to a change in crystal size. The increase of crystallinity value of 50 SiO₂/ Al₂O₃ compared to 30 SiO₂/Al₂O₃ maybe due to the fact that specific peak of XRD tends to become sharp and large with the size of crystallite. In the case of 70 SiO₂/ Al₂O₃ the crystallinity value decreased maybe because the sample contains small crystallite. Small crystallite will provide more amorphous ZSM-5, which are too small to detect in XRD [16].

Table 2 Relative crystallinity value for the commercial and synthesis catalysts..

SiO ₂ / Al ₂ O ₃	Relative Crystallinity (RC)
Commercial HZSM-5	100
30	109
50	123
70	102

3.2 Fourier Transform Infrared (Mid-range Spectra)

Infrared spectra of the zeolites taken in the middle range region ($400 - 1400\text{cm}^{-1}$) gave clue to the structural characteristics of the zeolites. The IR spectra of commercial HZSM-5 and synthesis HZSM-5 with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios are given in Figure 2. The characteristic bands at 450 cm^{-1} (T-O band), 550 cm^{-1} (double ring), 795 cm^{-1} (symmetric stretching), 1000 cm^{-1} and 1220 cm^{-1} (both are T-O-T band) are all exist in the samples confirming the presence of structural features of ZSM-5. This is in agree with work done by Narayanan et al.[15]. Table 3 tabulates the wavenumber of the samples obtained from IR analysis. The main asymmetric stretching, at band at 1100 cm^{-1} are varies in frequency. This is due to the number of Al atoms in the framework structure. Breck [18] stated that the frequency of main asymmetric stretch of the tetrahedra, which is a peak at 1100 cm^{-1} , varies with the number of Al atoms in the framework structure. Among the synthesis zeolites, the sample with 30 $\text{SiO}_2/\text{Al}_2\text{O}_3$ zeolite gave the lowest frequency number, followed by 50 and then 70 $\text{SiO}_2/\text{Al}_2\text{O}_3$. This was because the 30 $\text{SiO}_2/\text{Al}_2\text{O}_3$ sample, with the lowest silica to alumina ratio contained more Al in its framework compared to the 50 and 70 $\text{SiO}_2/\text{Al}_2\text{O}_3$ samples.

3.3 Fourier Transform Infrared (Near-range Spectra)

To analyze the hydroxyl (OH) groups of the catalysts, the IR analysis for the near range frequency was performed. Figure 3 shows the near range spectra for the synthesis catalyst. Two peaks can be observed in each spectra. The first peak, around 3609.5 cm^{-1} was assigned for aluminum framework hydroxyl bridge [Si-(OH)-Al] bond while the second peak, around 3743 cm^{-1} was assigned for silanol [Si-(OH)] bond. The absorbance of Si-(OH)-Al increased significantly with the decrease of $\text{SiO}_2/\text{Al}_2\text{O}_3$. Sample 30 $\text{SiO}_2/\text{Al}_2\text{O}_3$ gave strong signal at 3743 cm^{-1} , followed by 50 $\text{SiO}_2/\text{Al}_2\text{O}_3$ and 70 $\text{SiO}_2/\text{Al}_2\text{O}_3$. This indicated that the sample with 30 $\text{SiO}_2/\text{Al}_2\text{O}_3$ contained more hydroxyl groups compared to other samples. The presence of hydroxyl groups in the catalysts is important as it will affect the acidity of the catalysts. Peak at 3609 cm^{-1} closely related to Bronsted acid sites. Method proposed by Wichterlova et al. [12] was used to determine the number of Bronsted acid sites. Bronsted acid sites plays an important roles in cracking activity [19]. Figure 4 shows the number of Bronsted acid sites in the synthesis catalysts. HZSM-5 with 30 $\text{SiO}_2/\text{Al}_2\text{O}_3$ produced the highest number of Bronsted acid sites, 0.61 mmol/g . This was because the sample contained more hydroxyl group than other sample. The 50 $\text{SiO}_2/\text{Al}_2\text{O}_3$ sample produced the second highest number of Bronsted acid sites, 0.58 mmol/g while the 70 $\text{SiO}_2/\text{Al}_2\text{O}_3$ produced the lowest number of Bronsted acid sites, 0.30 mmol/g . The result indicated that the modification of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in HZSM-5 can affect the acidity of the catalysts. The same results was also obtained by Segawa et al., [20] and Ivanov et al.[21] in their works. The results also proved that the decrease in acid sites is proportional to the increase of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, as proposed by Costa, [22]. Szostak [17] also stated that varying the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in the series of zeolites can alter acid strength. Furthermore, Chu [23] and Topsoe [24] indicated that the acidity is associated with the aluminum atom in the crystalline framework. Acidity decreases as aluminum is removed from the crystal and increases as aluminum is inserted into the framework.

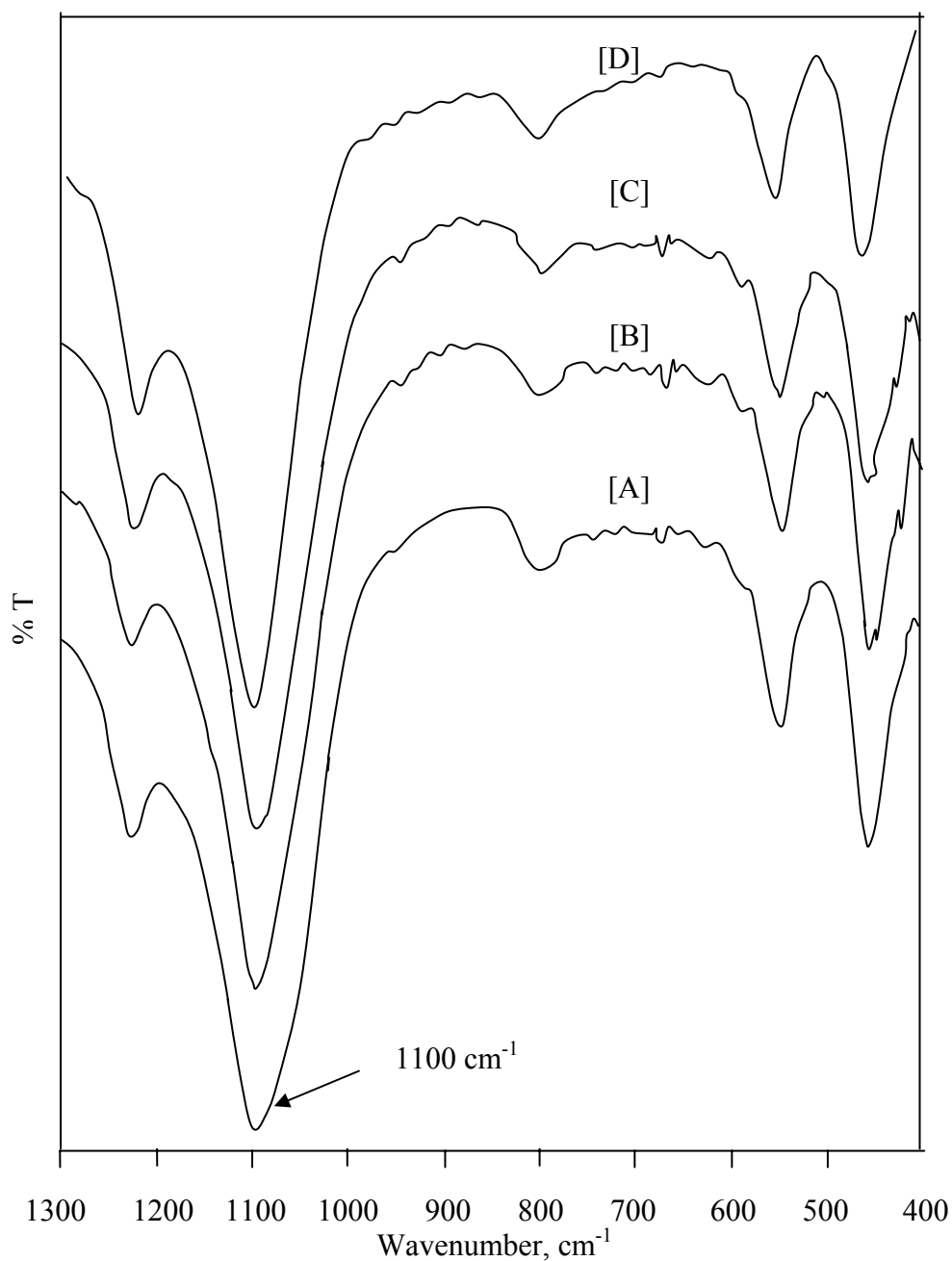


Figure 2 IR spectra for synthesis zeolites: [A] 30 SiO₂/ Al₂O₃, [B] 30 SiO₂/ Al₂O₃, [C] 70 SiO₂/ Al₂O₃, [D] commercial HZSM-5.

Table 3 Wavenumbers of IR analysis for commercial and synthesis zeolite.

Samples	Wavenumbers (cm-1)				
Commercial	1225.2	1100.3	794.5	547.7	455.8
30 SiO ₂ / Al ₂ O ₃	1223.7	1095.5	795.6	545.8	454.2
50 SiO ₂ / Al ₂ O ₃	1225.7	1096.5	795.6	547.7	451.3
70 SiO ₂ / Al ₂ O ₃	1226.6	1098.4	798.5	547.7	455.2

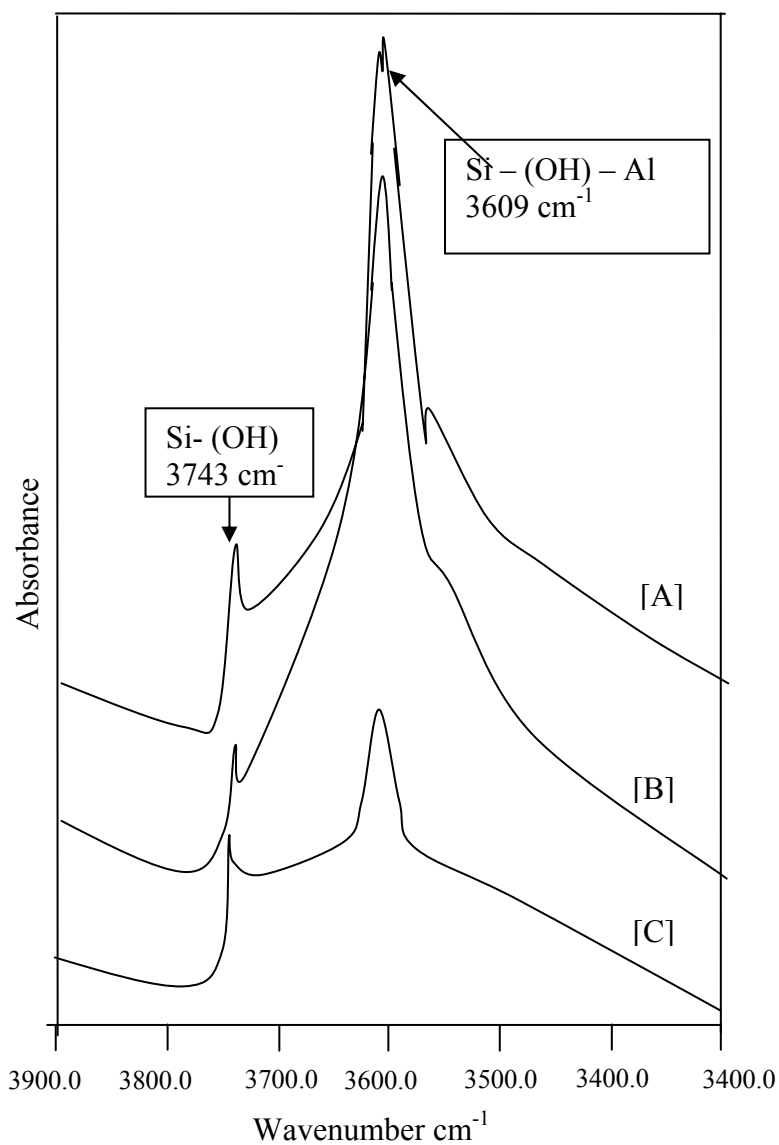


Figure 3 Near range IR spectra for synthesis zeolites: [A] 30 SiO₂/ Al₂O₃, [B] 50 SiO₂/ Al₂O₃, [C] 70 SiO₂/ Al₂O₃

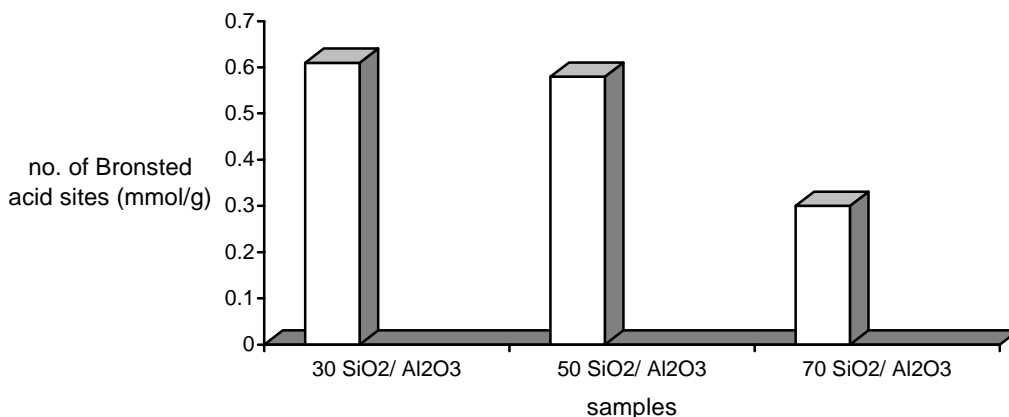


Figure 4 Number of Bronsted acid sites for 30, 50 and 70 SiO₂/ Al₂O₃ synthesis zeolites.

3.4 Effect of SiO₂/ Al₂O₃ to the Catalytic Cracking of Palm Oil to Gasoline Process

It appears that the difference in SiO₂/ Al₂O₃ ratio does effect the OLP obtained from the catalytic conversion of palm oil to fuels. Two assumptions were made prior to calculate selectivity. The first assumption was the conversion for the process was 100%. The second assumption was that the area percent obtained from gas chromatography was equal to weight percent of the product.. After the distillation process, OLP produced gasoline range hydrocarbons, C₁₂-C₁₅ range hydrocarbons and unknown products, also known as other organic products (OOP). Figure 5 shows the weight percent of products obtained in the experiments with 30, 50 and 70 SiO₂/ Al₂O₃ HZSM-5.

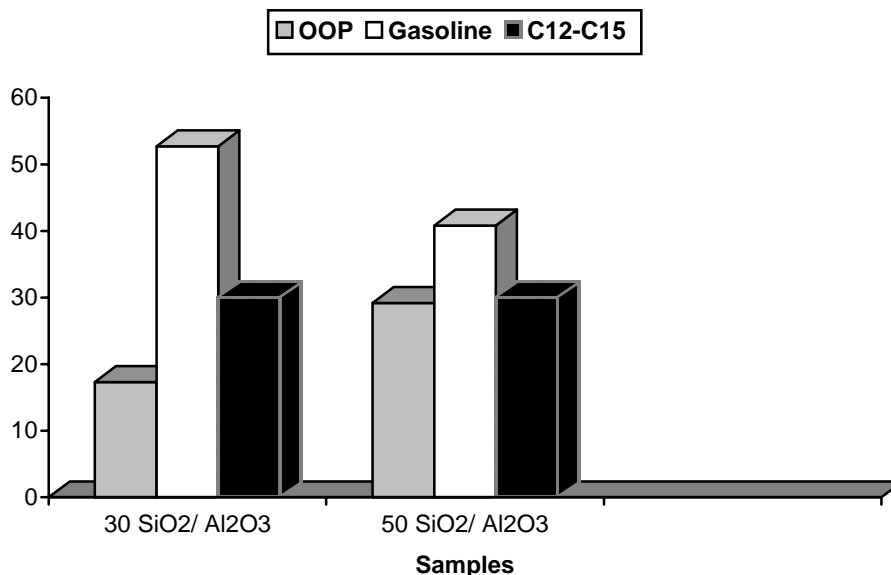


Figure 5 Selectivity of Gasoline, C₁₂ – C₁₅ and OOP Obtained.

The 30 SiO₂/Al₂O₃ sample produced 52.7% gasoline range hydrocarbons, 30% C₁₂-C₁₅ range hydrocarbons and 17.3 % OOP products. 40.8% of gasoline range hydrocarbon was obtained with 50 SiO₂/ Al₂O₃. 30% is in C₁₂-C₁₅ range hydrocarbons and the rest 29.2% was OOP products. 70 SiO₂/ Al₂O₃ catalysts however did not produced any liquid products at all. The

acidity of the catalysts played pivotal roles in the process. Figure 6 shows the relations between acidity of the synthesis catalysts and the products obtained. From the figure it shows that the percent of gasoline obtained increased with the increase of number of Bronsted acid sites. This was because acidity, especially Bronsted acid sites are very important in cracking process [25, 26]. Vitolo et al, [27] reported that Bronsted acid sites play dominant roles in catalytic upgrading of pyrolytic oils over HZSM-5 zeolite. The importance of catalysts acidity in the cracking of vegetable oils is published elsewhere by numerous researchers. Idem et al. [6] for example ran experiments to test the role of catalysts acidity in catalytic conversion of canola oil to fuels. They observed that the canola oil conversion, yields of various products and composition of OLP fractions obtained increased when acidic catalysts such as HZSM-5 and γ – alumina were used. Furthermore, works by Prasad and Bakhshi [3] and Prasad et al. [2] found that the acid site of HZSM-5 was very important in the catalytic conversion of canola oil and mustard oil respectively. This is probably because secondary reactions such as isomerization and aromatization take place on the strong acid sites. As shown in Figure 6, 30 SiO₂/ Al₂O₃ catalyst with the highest numbers of Bronsted acid sites, 0.61 mmol/g produced 52.7 % gasoline range hydrocarbons. 50 SiO₂/ Al₂O₃ catalysts with 0.58 mmol/g Bronsted acid sites just managed to obtain 40.8% of gasoline range hydrocarbons. The numbers of Bronsted acid sites for 70 SiO₂/ Al₂O₃ catalyst dropped significantly to 0.3 mmol/g. Because the acidic properties in this sample was very low, it enable to convert the palm oil to organic liquid product to liquid hydrocarbons.

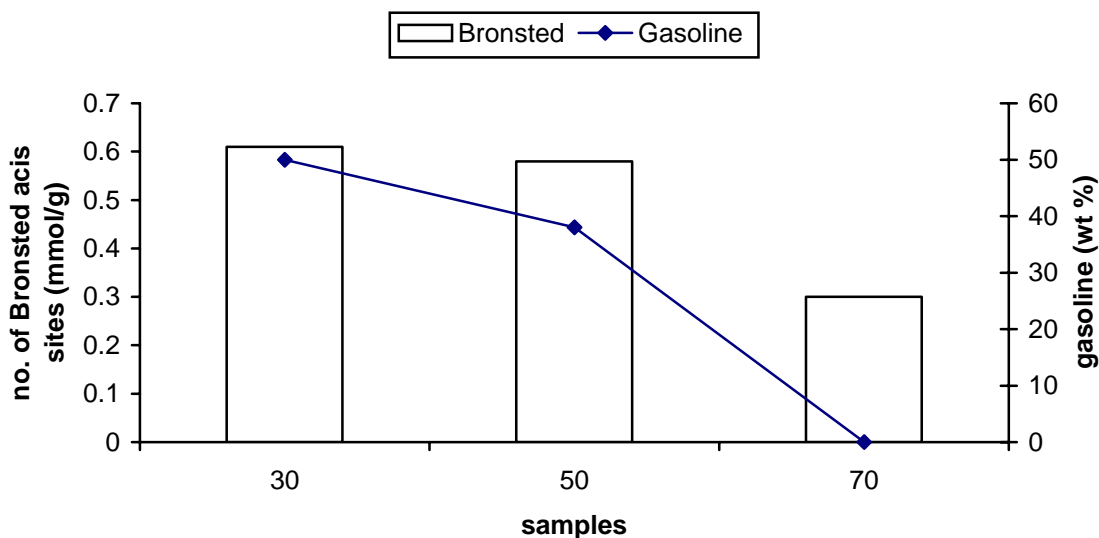


Figure 6 The Relations between numbers of Brönsted acid sites of the catalysts and gasoline obtained.

The formation of hydrocarbon in the range of C₁₂-C₁₅ showed that because of less acidic, 50 SiO₂/ Al₂O₃ catalyst produced more products. This is because the cracking process did not continue until the smaller chain was formed. Even if the smaller chain was formed, most of them would have formed OOP, and this phenomenon would made the OOP products of 50 SiO₂/ Al₂O₃ higher than the OOP products of 30 SiO₂/ Al₂O₃.

4.0 Conclusion

From the experiments above, it can be conclude that firstly, synthesis zeolites are definitely have different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios. This was proved by the FTIR analysis. It is also clear that the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio does effect the product distribution. The lowest $\text{SiO}_2/\text{Al}_2\text{O}_3$, in this case 30, gave the highest number of Bronsted acid sites and also the highest percentage of products in gasoline range. However, the highest $\text{SiO}_2/\text{Al}_2\text{O}_3$ (70), which failed to produce any liquid products, gave the lowest numbers of Bronsted acid sites.

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