

SYNTHESIS OF HIERARCHICAL ZEOLITE Y CATALYST FOR THE PRODUCTION OF BIODIESEL FROM WASTE VEGETABLE OIL

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ABSTRACT

Hierarchical (mesoporous) zeolites catalysts have received an ever-increasing attention as a result of their improved performance in catalyzed reactions compared to conventional ones. One of the widely applied preparation methods to tailor these modified zeolites is by desilication in alkaline media for optimal combination of efficiency and simplicity. This study synthesized and characterized hierarchical zeolite catalyst to transesterify waste vegetable oil. Y zeolite (FAU topology) was exposed to NaOH treatment, also known as top-down approach, at 60°C for 10min, protonated at 90°C for 2h to produce hierarchical zeolite Y, and calcined at 600°C for 1h to remove organic material within the channel pore of the Y zeolite, leading to the introduction of mesopore with surface area of 331.628 m²/g. This alkaline treatment while it preserved the zeolite's intrinsic properties such as crystallinity and micropore volume, it also brought about an abundance of Al-rich zeolite. The properties of the hierarchical zeolite Y was assessed using FT-IR spectroscopy, N₂ adsorption-desorption isotherm analyzers for BET and XRD. It was observed that the hierarchical Y zeolite possessed superior catalytic properties compared to the conventional ones. Furthermore, the desilication of zeolite Y brought about improvement in the surface area as a result of increase in the total pore volume, thereby providing increase in more active sites which interact with the reactants. Consequently, 89% biodiesel formation was facilitated by the transesterification of the triglycerides in the waste vegetable oil (WVO) carried out under reflux at 60°C, with MeOH/Oil ratio of 7:1, 0.2g hierarchical zeolite Y catalyst mass and optimized time of 2h. The synthesized catalyst has proved to be efficient for biodiesel production from waste vegetable oil.

Keywords: Alumina, Hierarchical, Transesterification, Zeolites, Biodiesel

1 INTRODUCTION

Over the years, acid (H₂SO₄) and base (KOH/NaOH) have been utilized as catalysts for transesterification in the biodiesel production. These are known as homogeneous catalysts. Several problems are on daily basis encountered while using liquid catalysts for producing biodiesel, most especially when it comes to catalyst separation, product purification and catalyst reusability [1]. In addition, soap is formed in the product mixture which causes depletion of triglyceride molecules used in biodiesel formation. All these lead to increase in the cost of production of biodiesel and also make the process very complex [2]. Finding a substitute of fuel resource for diesel is daunting duty for humans [3]. Biodiesel is a tenable fuel option whose production has lately been prioritized by many countries and would play a significant task in diesel industry. There are many advantages offered by biodiesel such as being environmentally friendly, nontoxic and are capable of being broken down with low viscosity. Environmental hazards are due to green house

gases emissions through fossil fuel usage from different sectors which include transportation, heat, and power generation [4]. In addition, the world crude oil reserve is said to be decreasing markedly due to the extent of usage of these traditional fuels [5]. These makes it compulsory to seek for a substitute and better sources of fuel to guarantee energy security that is sustainable. Biodiesel is renewable and can be seen to have high lubrication when compared to the familiar petroleum diesel [6]. Additionally, this fuel can be utilized in blending and very small amount of it is enough in reducing emissions of particulate matter from engines [7]. Lipid sources that can be regenerated like oils from vegetable or animal fats are the avenue through which biodiesel are derived [8]. To assuage these problems encountered while utilizing homogeneous catalyst for the production of biodiesel, the year 2000 remains the originating period of hierarchically structured zeolites. These are zeolites with meso- or macro porosity coupled in the micropores and are referred to as secondary pores. The method usually employed to successfully achieve this is by desilication using a top-down approach. Herein, one of the major components of the zeolites (i.e. silica) is removed by treatment with alkaline (NaOH) solution. Homogeneous catalytic systems constitute a dangerous problem such as production of gigantic amount of waste water and also the challenges of removing and separating the catalysts after the reaction. Heterogeneous catalysts are environmentally friendly because they are easily separated from the reaction medium, reduced corrosion and can be recycled [9]. Notwithstanding, they give reduced yield of biodiesel due to hazards together with leaching and diffusion limitations [10, 11] For high yield in biodiesel production process, efforts are put in place to make the heterogeneous catalyst mesoporous in order to reduce steric obstacle, higher acid energy, and density in addition to thermal and hydrothermal stability to lessen substance that inhibits its activity and cause leaching. The inexpensive nature of zeolites and its environmental palatability makes it possible to be used as hierarchization for high mesoporosity, generous surface area and consequently, greater yield of biodiesel. Therefore, in this study, it is aimed to synthesize and characterize hierarchical zeolite y catalyst for the production of biodiesel from waste vegetable oil by transesterification.

2 MATERIALS AND METHODS

2.1 Materials

The zeolite Y was purchased from Zeoyst International while waste vegetable oil (WVO) was collected from a local restaurant in Minna, This oil was used for the transesterification reaction after undergoing pretreatment and purification. For catalyst synthesis, sodium hydroxide was obtained from Chemical Engineering Laboratory, Federal University of Technology, Minna, and the water used was distilled in WAFT Laboratory of the same institution. Other chemicals used in this study, ammonium chloride and methanol, are reagent grade obtained from Chemical Engineering Laboratory of the aforementioned institution.

2.2 Catalyst preparation

4g of commercial zeolite Y was measured and mixed with prepared 0.3M solution of NaOH in a 250 ml round-bottomed flask. Desilication was executed by applying heat using magnetic stirrer hot plate for a desired time of 10min. at 60°C. Protonation of the desilicated Zeolite Y was performed by dissolving 0.6g NH₄Cl and 1.3 g zeolite Y in 100 ml of distilled water. The mixture which contained in a 250 ml round bottom flask was heated under reflux using a magnetic stirrer for 2 hrs at 90°C. The resulting solution was filtered and dried at 60°C. Afterwards, the protonated zeolite Y was calcined in a hotspot furnace (GallenKamp) at 600°C for 1 hr. The calcined mass obtained was referred as hierarchical catalyst.

2.3 Catalyst characterization

The X-ray diffractions (XRD) patterns of hierarchical zeolite Y powders were recorded on a Bruker D8 Advance diffractometer using Ni-filter Cu Karadiation. Powder samples were scanned in 2θ range varying from 0 to 80 degrees. The commercial zeolite used as the starting material for the post-synthetic treatment composed of a pristine Y with Si/Al ratio 2.4. The functional group of the catalyst was determined with Fourier Transform Infrared (FT-IR) spectroscopy so as to probe the chemical treatment of the zeolites and monitor the reactions taking place in the zeolite Y pores whereas the surface area, total pore volume and pore size distribution of the catalyst were determined

with N₂ adsorption-desorption isotherm analyzers. Surface area was calculated by using BET equation from the adsorption branch of the isotherm in a relative pressure range from 0 to 1.

2.4 Transesterification process

The hierarchical zeolite Y catalyst formed was used to produce biodiesel by the transesterification of waste vegetable oil and methanol. The transesterification was carried out in a 500ml flat bottom flask connecting with a reflux condenser using tap water to condense methanol vapor and a thermocouple probe. The mixture was agitated by using a stainless-steel stirrer. The reactor was placed in a heated water bath. Zeolite Y powder was dissolved in methanol before being poured in the reactor containing 100 g WVO heated up to a desired temperature of 60 C. The reaction was kept at the desired temperature for 1h, 2h and 3h. The molar ratio of methanol to WVO was 7:1 while the amount of zeolite Y catalyst was 0.2 wt% of the WVO. After the transesterifying process, the mixture was poured into a separating funnel. The ester layer was separated by gravity and located in the upper layer. The glycerol, extra methanol and undesired products were in the lower layer and were decanted. The ester layer was washed several times with a small amount of warm water each until the washings were neutral. The ester layer was then dried on a hot plate to achieve the desired product. The yield of biodiesel was determined according to Equation 1.

$$\text{Biodiesel yield (\%)} = \frac{\text{mass of biodiesel (g)}}{\text{mass of oil (g)}} \times 100 \quad (1)$$

2.5 Reusability study

One of the important factors which elucidate the potential of a catalyst for its commercial application is the recovery and use of catalyst. Upon the completion of the transesterification reaction, the used catalyst was recovered by washing with methanol several times so as to remove the adsorbed materials. This recovered catalyst was afterwards calcined at 600°C for 1 h to reactivate it and then reused as the catalyst for the next run. This procedure was followed for the protonated purchased commercial zeolite Y (CZY) used for comparison with the synthesized hierarchical zeolite Y (HZY) catalysts.

2.6 Properties of biodiesel

The characterization of the biodiesel produced was performed by determining the Acid value, free fatty acid, Specific gravity and its conversion after transesterification. The acid value was determined by the acid base titration technique, whereby a mixture of biodiesel sample (1g), ethanol (25ml) and phenolphthalein (2 drops) were titrated with 0.1N potassium hydroxide solution until the appearances of pink color. Then, the acid value, specific gravity and FAME conversion were calculated respectively according to Equations 2, 3 and 4.

$$\text{Acid value, AV} = \frac{\text{ml of KOH} \times \text{N} \times 56.1}{\text{weight of sample}} \quad (2)$$

$$\text{Specific gravity} = \frac{\text{Mass of sample}}{\text{Mass of equal volume of water}} \quad (3)$$

$$\text{FAME Conversion} = \frac{\text{AV}_{t0} - \text{AV}_t}{\text{AV}_{t0}} \quad (4)$$

Where AV_{t0} (acid value of the reaction product at time 0); AV_t (acid value of the reaction product at time t).

3 RESULTS AND DISCUSSION

3.1 Properties of waste vegetable oil (WVO) utilized

The physicochemical properties of the WVO utilized in this study are presented in Table 1. The FFA content of the WVO sample was determined to be 1.98 wt %. The impurities present in the feedstock which is as a result of continuous usage in frying could be accountable to the slightly high amount of FFA. However, the WVO was subjected pretreatment and purification before being used for transesterification with the synthesized zeolite catalyst.

Table 1. Properties of WVO used

Properties	Results
Free fatty acid content (wt %)	1.98
Acid value (mg KOH/g of oil)	3.95
Molecular weight (g/mol)	856
Specific gravity at 25 °C	0.902

3.2 Catalyst characterization

3.2.1 X-Ray Diffraction (XRD) Analysis of Hierarchical Zeolite Y

Figure 1 shows the result of the fingerprint analysis of the synthesized H-Y zeolite via X-ray diffraction before and after desilication with NaOH. The X-ray diffraction (XRD) pattern showed that the parent sample possessed a highly crystalline faujasite in the absence of impurities. The typical diffraction peaks, associated to calcined hierarchical zeolite Y corresponding to highly crystalline zeolite Y were observed at 2θ values of 8.1, 10.3, 16.5, 19.0, 20.3, 24.5, 28.8 and 33.6 [12]. Low intensity peaks which exist at 41.2 and 50.9 indicate the presence of minor amount of Zeolite Y as well as Sodium hydroxide at 2θ of 47.3 [12].

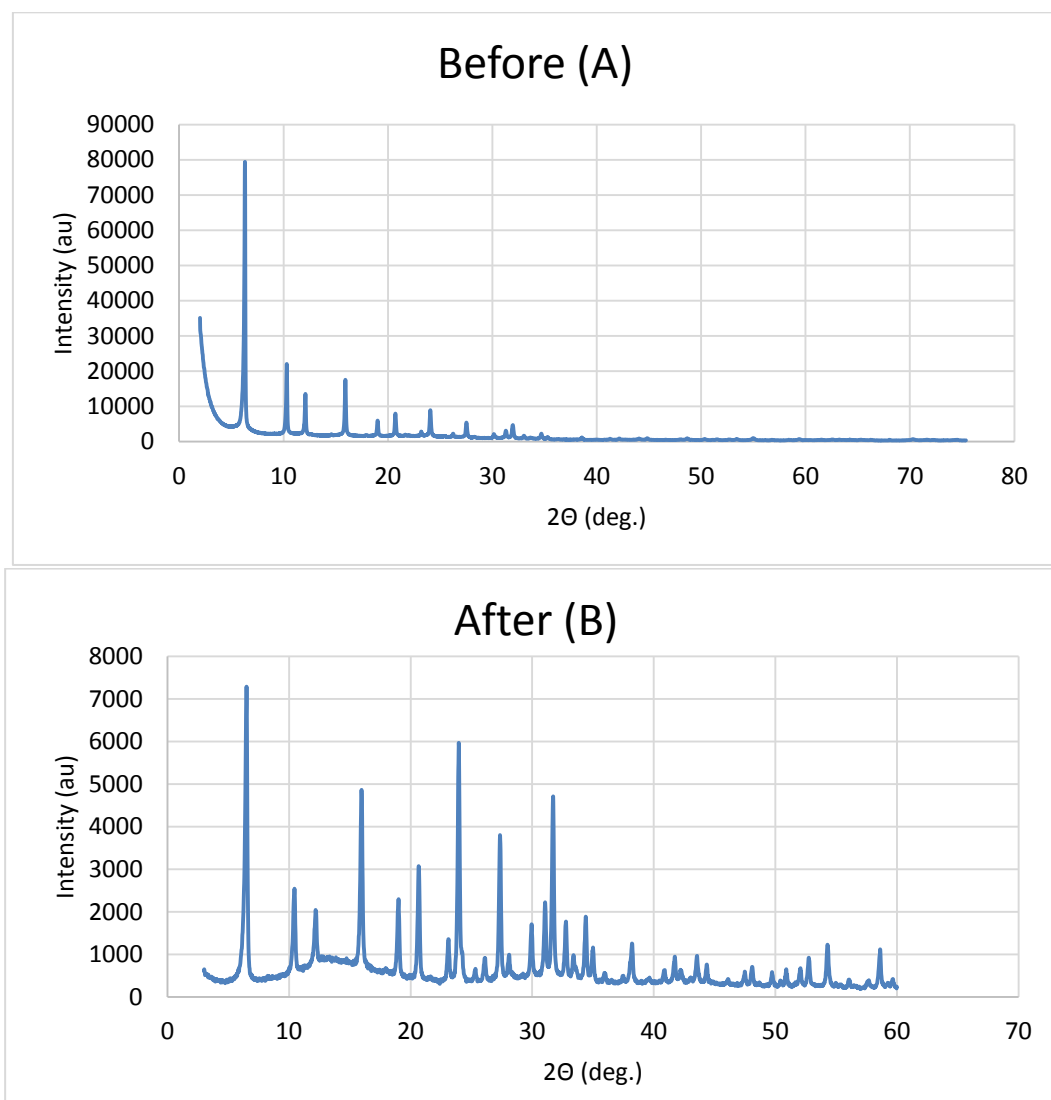


Figure 1. XRD Results of the Synthesized Hierarchical Zeolite Y before treatment (A) and after Desilication by Sodium Hydroxide (NaOH) Treatment (B)

3.2.2 FT-IR Spectroscopy of Zeolite Y

Specifically, functional group information was obtained from the vibrational frequencies of the zeolite lattice which were observed within the range of 500-4000 cm^{-1} (Figure 2). In the spectrum of hierarchical Y zeolite, the most intense and highest frequency band peaks at 3402.64 cm^{-1} , 1643.41 cm^{-1} and 1396.51 cm^{-1} can be assigned to OH group and terminal silanol groups that are on the external surface of the zeolite crystals [13]. Synthesized hierarchical zeolite Y has a much greater external surface area than commercial micrometer-sized zeolite Y sample. Characterization of hierarchical Y zeolite with FT-IR spectroscopy indicates that a greater number of silanol groups are present in hierarchical Y zeolite. The large external surface area and the functional groups (silanol groups) on the external surface are important in the application of hierarchical zeolite Y as catalyst for biodiesel production.

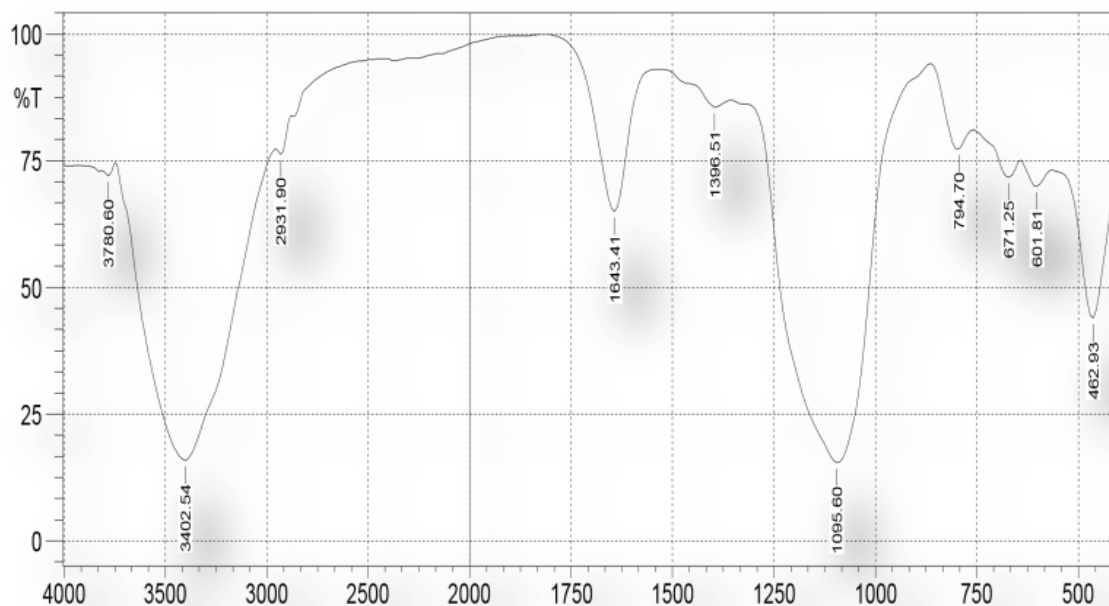


Figure 2. FT-IR spectra of hierarchical Y zeolite.

3.2.3 N₂ adsorption-desorption isotherm analysis of hierarchical zeolite Y

The mesoporous properties of the hierarchical zeolite Y were explored with a porosimeter, in which the N₂ adsorption-desorption isotherms were performed and recorded (Figure 3). Type IV isotherms and H4 hysteresis loops were recognized on the H-Y Zeolite system which is in accordance with BET as well as IUPAC classification. Type IV isotherms are observed on many mesoporous industrial adsorbents, such as zeolites [12, 14]. In brief, the monolayer adsorption of nitrogen on the walls of meso-pores occurred when $P/P_0 < 0.7$, and the capillary condensation happened in mesopores with $P/P_0 = 0.7-0.9$, which was evident with a steep increase and the hysteresis in adsorption isotherm. Multilayer adsorption could be found on the outer surface of the particles at a higher P/P_0 . The H4 hysteresis loop is commonly associated with slit-like pores. The BET surface area and average pore size of the hierarchical zeolite Y were 331.628 m^2/g and 7.5073 nm, respectively. The pore size of the zeolite Y fall within the mesoporous range of 2-50 nm and will allow the passage of the reactants through the pores [14] The Horváth-Kawazoe (HK) method gave a maximum pore volume and BET surface area median pore width of 0.135304 cm^3/g and 0.8071 nm, respectively.

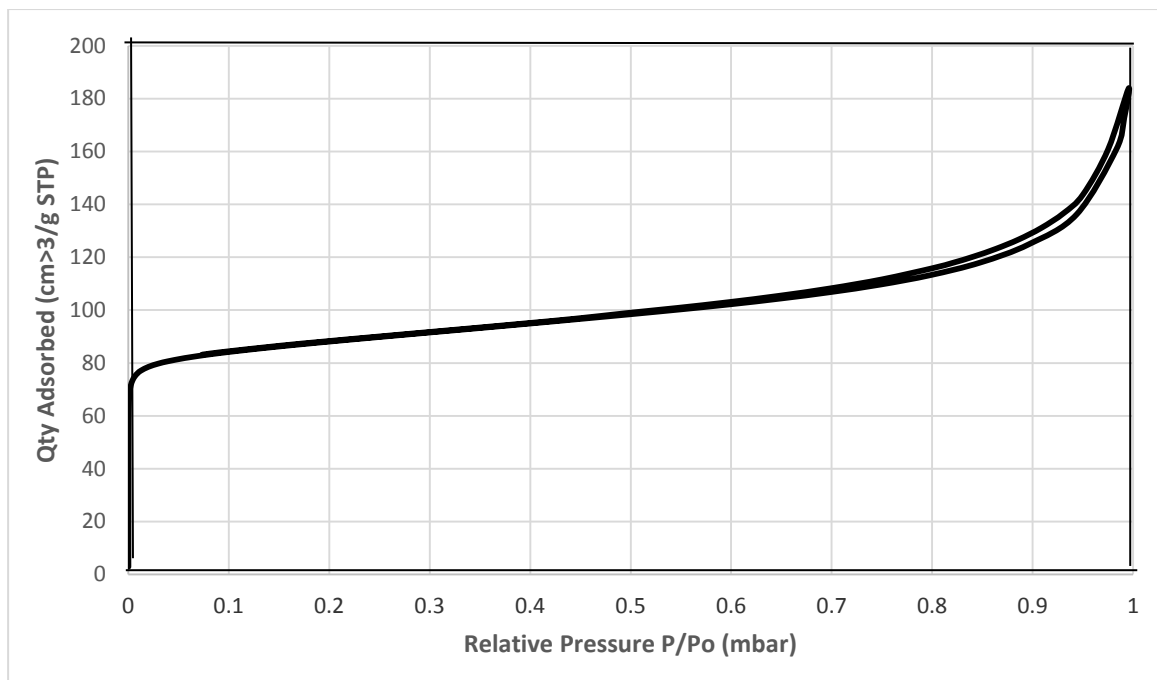


Figure 3. N₂ Adsorption-Desorption Isotherm of Hierarchical Zeolite Y

3.3 Transesterification process

3.3.1 Effect of ratio of methanol to WVO

The methanol/oil ratio is one of the most important factors affecting the yield of biodiesel. Although stoichiometric ratio requires 3:1, the transesterification is commonly carried out with an extra amount of alcohol in order to shift the equilibrium to the proposed product, methyl ester. The methanol/oil ratio is associated with operating parameters such as the type of catalyst used and the quality of oil. In addition, the excess of methanol could also drive the combination of ester product [15] and glycerol into mono-glycerides. The optimum molar ratio of methanol/WVO was 7:1, giving a biodiesel yield of approximately 88–90% after 2h. The optimum ratio chosen in this study was in accordance with that used by other investigators [16]. The increased ratio also enhanced the product settling process. The settling time took hours for the molar ratios below 7:1 while it was only approximately 30 min for the ratio of 7:1. This indicated that there was a certain amount of un-reacted glyceride in the ester phase at the ratios below 7:1.

3.3.2 Effect of temperature

Transesterification can occur at different temperatures, depending on the properties of oils. It could be at ambient temperature; or at a temperature close to the boiling temperature of methanol. However, high reaction temperature speeds up the reaction and shortens the reaction time. Freedman *et al.* [17] found that biodiesel yield depended on temperature in the first 30 min reaction. For example, 94% biodiesel yield was obtained at 60 °C. This temperature has positive effect on the conversion at the methanol/oil ratio of 7:1 in the presence of 0.2 wt% Zeolite Y. However, increasing temperature up to 70 °C, resulted in a slight reduction in the conversion. High temperature enhances transesterification process due to improvement in mass transfer between the mixture. The reduction in the conversion could be due adverse effect of methanol vapourization [18].

3.3.3 Effect of Reaction Time

The conversion rate increases with reaction time. The reaction was very slow during the first minute due to the mixing and dispersion of methanol into vegetable oil. In this work, the effect of reaction time from 1h to 3h on the reaction yield was investigated, keeping catalyst concentration (0.2 wt %), reaction temperature (60°C) and methanol to oil molar ratio (7:1) constant. Reaction time is one of the key parameters during the transesterification reaction for biodiesel production carried out in glass reactor using calcined hierarchical zeolite Y catalyst. The maximum yield of 89% was

obtained in 2h. Increasing time beyond 2h, there was no significant conversion noticed and this can be due to equilibrium reached by reaction in the first 2h which has been observed by other researchers [18, 19].

3.4 Reusability study

The transesterification reaction for the reusability test of the synthesized zeolite catalyst was performed at conditions of 60°C temperature, 0.2 wt% catalyst loads, 7:1 methanol to oil ratio and 2h time. The yield of biodiesel reached 91%, indicating that the hierarchical zeolite Y catalyst was relatively stable and exhibited high catalytic transesterification activity, which provide the opportunity to apply an appropriate recycle stream in continuous process in order to minimize costs in industry. However, there was a slight decrease in the biodiesel yield ranging between 91% and 79% when the catalyst is employed for five reruns. A remarkable reduction in the catalytic activity can be seen at the sixth rerun, whereby the biodiesel yield dropped to 52.5% (Table 2). The reduction in the yield of biodiesel on the sixth reuse of catalyst was possibly due to leaching of active sites compound during the reaction [15]. Also, comparing the performance of the synthesized HZY catalyst and the conventional CZY counterpart in the rerun process, the HZY catalyst prove to be more active in the transesterification reaction.

Table 2. Reusability experiment

Times of repeated run	1	2	3	4	5	6
HZY Biodiesel yield (%)	91	89	85	83	79	52.5
CZY Biodiesel yield (%)	66	61	55	48	41	32

3.5 WVO biodiesel properties assessment

The properties of the waste vegetable oil biodiesel produced from the transesterification reaction with the synthesized hierarchical zeolite Y catalyst and the European standard is shown in Table 3. The Yield of 89 % methyl ester was achieved at conditions of 7:1molar ratio, 60°C temperature, 0.2g catalyst weight and 2h time. Other results of the methyl ester properties namely Acid value which reflects the % FFA in the fuel and specific gravity are in conformity with the EN14214. Acid value of biodiesel should be less than 0.5 mg KOH/g sample in order to handle the fuel properly and safe. If the acid value is too high, the fuel could cause degradation of rubber parts in engines and therefore resulting in filter clogging. Based on the results obtained, it is worth pointing out that the fuel properties examined for the biodiesel synthesized met the EN14214 European standard for biodiesel and a research work performed by Gonzaga et al. [19].

Table 3. Characteristics of WVO Biodiesel produced utilizing Hierarchical Zeolite Y Catalyst

Properties	WVO biodiesel value	Biodiesel standard (EN 14214)
Specific gravity, at 25 °C	0.856	0.862
Acid value (mg KOH/g)	0.45	0.50 max
FFA content (wt %)	0.23	0.25
Yield (%)	89	90

4 CONCLUSIONS

The optimal design of hierarchical zeolites requires the generation of multiple levels of porosity (mesoporosity) being appropriately connected so as to maximize the benefits of hierarchy in catalyzed reactions. In this research work, alkaline treatment of Y zeolite having low Si/Al ratio of 2.4 brought about an abundance of Al-rich zeolite. It was observed that the hierarchical Y zeolite possessed superior sorption and catalytic properties compared to the conventional ones. The FT-IR

spectra of the desilicated hierarchical zeolite Y catalyst revealed silanol groups which was important for higher methyl ester yield. Furthermore, it was observed that the desilication of zeolite Y brought about improvement in the surface area as a result increased the total pore volume, thereby providing the opportunity to increase the number of active sites which interact with the reactants. Consequently, biodiesel formation was facilitated. So far, the improved accessibility has been the main motivation for synthesizing hierarchical Y zeolites. The use of waste vegetable oil in this project bridged the gap between the productions of oils for food and/or for energy and heterogeneous hierarchical zeolite Y catalyst with waste vegetable oil has proven to be potential catalyst and feedstock for use for biodiesel production. Also, the catalyst showed that it can be reused for upto five cycles providing substantial amount of biodiesel making it economical for production.

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