

Transesterification of Oil Extract from Locally-Cultivated *Jatropha curcas* using a Heterogeneous Base Catalyst and Determination of its Properties as a Viable Biodiesel

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Solvent extraction using hexane of oil from *Jatropha curcas* nuts yielded 32.17% crude oil. The acid value of 107mgKOH/g sample indicates a high free fatty acid content which explains high yield of saponification products via the homogeneous base-catalyzed transesterification. Heterogeneous hybrid inorganic-organic base catalysts for transesterification were then designed and developed to facilitate a more efficient conversion of *Jatropha curcas* oils to bio-based fuels. Three types of solid catalysts were developed; amino-functionalized Zeolite Y, amino-functionalized MCM-41 and TBD-functionalized MCM-41. Transesterification using 10% by weight of the developed catalysts and a methanol-oil molar ratio of 15:1 at 80°C for two hours resulted in a biodiesel yield of 86.60%, 74.94%, and 81.86%, respectively. Gas chromatogram showed the transesterified triglyceride components of *Jatropha* oil consisting of 14.35% methyl palmitate, 1.14% methyl palmitoleate, 6.89% methyl stearate, 43.67% cis-9-oleic methyl ester, 30.88% methyl linoleate. Density and refractive index of the transesterified *Jatropha* oil were found to be 900 kg m⁻³ and 1.45 respectively and with a 38,589 kJ kg⁻¹ heat of combustion.

Key Words: fatty acid methyl ester, heterogeneous catalyst, MCM-41

INTRODUCTION

The possibility of a future fuel crisis and the increasing awareness of the health and environmental damage wrought by burning fossil fuels have motivated a lot of research on the development of clean and renewable alternative energy sources. Agriculture-based economies are putting their stake on biodiesel production from energy crops. With no competing food uses, this characteristic turns attention to *Jatropha curcas* which grows in tropical and subtropical climates across the developing world (Openshaw 2000). Cultivation of *Jatropha curcas* nut as diesel substitute has been found to be viable due its drought resistance and potential to produce oil from marginal semi-arid lands. The genus *Jatropha* contains

approximately 170 known species. The plant is planted as a hedge (living fence) by farmers all over the world around homesteads, gardens, and fields because it is not browsed by animals. The use of *Jatropha curcas* nut seed oil for biodiesel production has been reported in many literatures.

To be used as biodiesel, triglycerides (the major component of vegetable and animal oil) must be chemically altered into an ester via transesterification (Figure 1). Base-catalyzed transesterification is commonly used for large-scale or commercial productions for its faster rate and is less corrosive as when using the acid-catalyzed process. The first step (Eq. 1) of the base-catalyzed transesterification is the reaction of the base with the alcohol producing an alkoxide and the protonated catalyst. The triglyceride will then undergo a nucleophilic reaction (Eq. 2) as the alkoxide

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attacks the carbonyl group of the triglyceride forming a tetrahedral intermediate which then forms a diglyceride anion and an alkyl ester (Eq. 3). This resulting alkyl ester will deprotonate the catalyst (Eq. 4), regenerating the active species and ready again to start another catalytic cycle with another molecule of the alcohol (Eq. 5).

Base-catalyzed transesterification represents the best alternative to produce biodiesel. However, it still has some disadvantages. The transesterification reaction is sensitive to the presence of water which reacts with the alkyl esters to produce free fatty acids (FFAs). Low free

fatty acid content and anhydrous reagents are therefore required due to the saponification possibility. This soap formation lowers the ester yields and can hinder the stages of separation and purification of ester and glycerol, as well as the washing stage. Furthermore, catalyst recovery process is slow and expensive, increasing the operating costs (Om Tapanes et al. 2008).

For environmental and economic reasons, heterogeneous catalysts are better than homogeneous catalysts because heterogeneous catalysts are more easily recovered and recycled. For this purpose, several inorganic

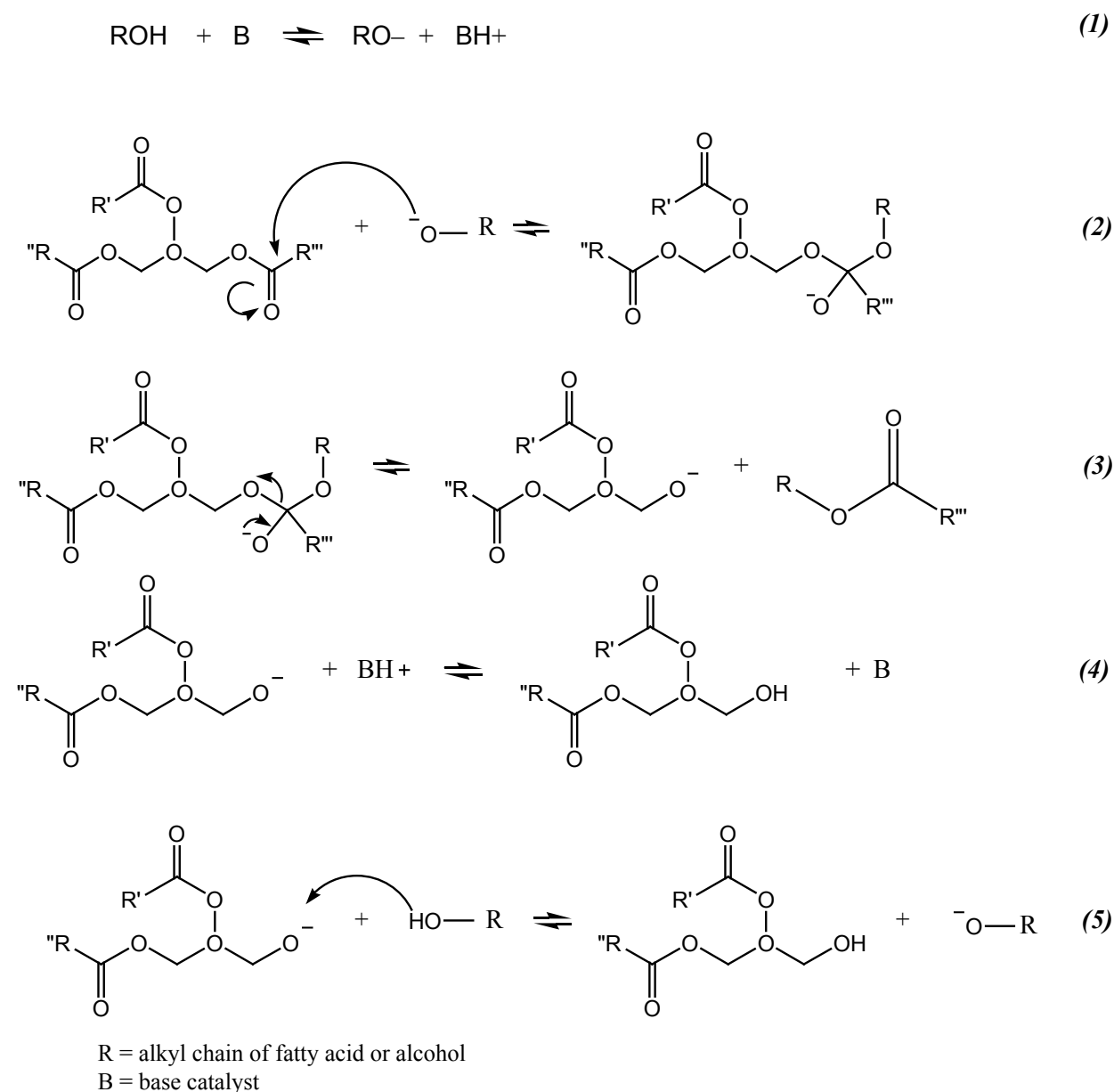


Figure 1. Schematics of base-catalyzed transesterification reaction of triglycerides with methanol.

heterogeneous base catalysts like CaCO_3 , MgCO_3 , Na_2CO_3 , K_2CO_3 , Na_2O , CaO , MgO , ZnO , La_2O_3 , Al_2O_3 , BaO , CeO_2 , ZrO_2 , Co_2O_3 , Mo_2O_5 , SnO_2 , and $\text{Ba}(\text{OH})_2$ have been tried for transesterification reactions. Other approaches involved immobilizing water-soluble organic bases like guanidines and enzymes (lipases) on insoluble substrates like polymers (Schuchardt et al. 1998). The conversions of vegetable oil under optimized conditions in presence of co-solvent (n-hexane) obtained with solid base catalyst $\text{Na}/\text{NaOH}/\gamma\text{-Al}_2\text{O}_3$ is comparable to that obtained with conventional homogeneous NaOH catalyst (Kim et al. 2004). Heterogeneous solid oxide catalysts of the type $(\text{Al}_2\text{O}_3)_4(\text{SnO})$ and $(\text{Al}_2\text{O}_3)_4(\text{ZnO})$ (Xie and Huang 2006) have been examined for transesterification of vegetable oil using different chain length alcohols. The highest yield of 84% was observed with methanol. Om Tapanes et al. (2008) found that calcined Mg–Al hydrotalcite at 400°C was most effective catalyst for the transesterification of jatropha oil, obtaining conversion of *Jatropha* oil of 96%. Theoretical calculations and experimental procedures demonstrated that the reactions of transesterification of jatropha oil using catalyst of hydrotalcite are not affected with use of ethanol or with presence of water in the reaction. The mechanism of a heterogeneous base-catalyzed transesterification of triglycerides differs only slightly from the homogeneous base-catalyzed process. The same with the homogeneous process, the organic base immobilized on the surface of the silica converts the alcohol into an alkoxide, which in turn will react with the triglyceride. The reaction of the immobilized propylamine and TBD are illustrated in Figure 2.

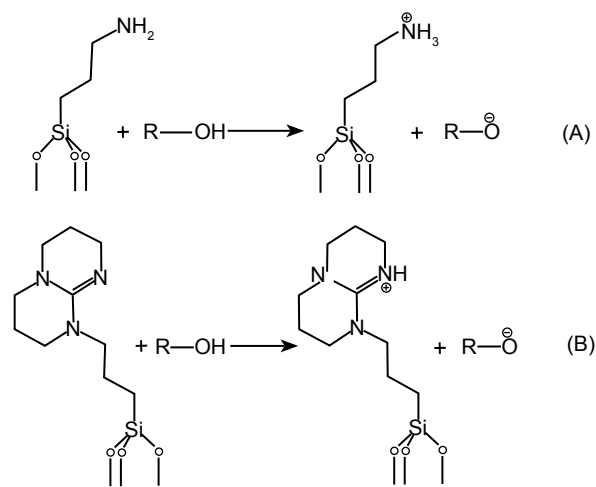


Figure 2. Reaction of (A) MCM-NH₂ and (B) MCM-TBD with an alcohol.

Besides being recyclable, heterogeneous catalysts also prevent the formation of soaps, which delay the separation of the biodiesel layer from the glycerol layer. The ease by which the heterogeneous catalyst is separated from the product mixture similarly offers the benefit of hastening and simplifying the purification of the biodiesel and glycerol products. Other advantages of using heterogeneous catalysts include waste reduction, which not only helps the environment but also lowers the overhead cost of biodiesel production because costly waste treatment procedures will be rendered unnecessary.

Jatropha oil contains about 14% free fatty acid (FFA), which is far beyond the limit of 1% FFA level that can be converted into biodiesel by transesterification using an alkaline catalyst. Hence, an optimized procedure for converting *Jatropha* oil, which contains high FFA% into biodiesel, is very much required (Tiwari et al. 2007). This project involved the extraction and transesterification of *Jatropha curcas* oil extracts and the study of the acid profile to assess its viability as a biodiesel. As the main contribution to new knowledge, heterogeneous catalyst was developed for transesterification to increase efficiency and prevent drawbacks such as difficult removal of glycerine and aqueous base-catalyst from the product mixture and interference of water and free fatty acids with the transesterification reaction. The solid support has to have a high surface area so that a large amount of organic bases can be attached to its surfaces. Silicas like the microporous Zeolite Y (3D channel structure, 7A pore diameter, 12A cavity diameter) (Knothe 2001) and the mesoporous MCM-41 are suitable solid supports because of their very large surface areas and their large pore diameters, which allow reactant molecules to enter their cavities and interact with the organic bases inside.

MATERIALS AND METHODS

Materials

MCM-41 (Sigma-Aldrich) and Zeolite Y (Sigma-Aldrich) were dried in a vacuum oven at 110°C for eight hours before use. Toluene (JT Baker) and methanol (JT Baker) were dried by adding activated molecular sieves (Sigma-Aldrich) prior to utilization. KBr (Merck), 3-aminopropyl-triethoxysilane or 3-APTES (Sigma-Aldrich), hexamethyldisilazane or HMDS (Sigma-Aldrich), 1,5,7-triazabicyclo[4.4.0]dec-5-ene or TBD (Fluka), HCl (Mallinckrodt), acetone (JT Baker), HNO_3 (Univar), H_2SO_4 (JT Baker), KSCN (JT Baker), AgNO_3 (Merck), $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (Univar), anhydrous ethanol (JT Baker), isopropanol (JT Baker) and hexane (JT Baker) were used as received. The dried *Jatropha curcas* seeds used in this study were obtained from

Tarlac Agricultural College. Technical grade hexane used in the solvent extraction of the oil was vacuum distilled prior to utilization. Standard fatty acid methyl ester (FAME) mix of from Supelco was refrigerated and sealed until use.

Thin layer chromatography using silica gel 60 F₂₅₄ (Merck, pre-coated TLC plastic sheets) was used to monitor the progress of the reaction. Dipping the plates in the eluent with 90:10:1 proportions of hexane:ethyl acetate:acetic acid and then placing them in an iodine chamber visualized the TLC plates. Experiments were conducted in a laboratory scale set-up.

Equipment

Products were characterized by the usual techniques. FTIR and TGA were used to confirm and measure the success of grafting. FTIR spectra were recorded using Shimadzu IR-Prestige 21 Fourier Transform Infrared Spectrometer with a DRS-800 diffuse reflectance attachment using KBr as reference. Thermal gravimetric analyses were carried out in a Shimadzu TGA-50 Thermal Gravimetric Analyzer. The heterogeneous base catalyst samples were vacuum-dried for four hours before being hermetically sealed in aluminum pans (Shimadzu). After the weights of the samples at room temperature were taken, each was heated at a rate of 10°C per minute up to 520°C under a 30-mL per minute nitrogen flow. *Jatropha* FAME components were determined by gas chromatography using SHIMADZU-14B GC-FID with the following parameters: column: J&W Scientific 122-7032 DB-WAX, 30 m, 0.25 mm; carrier gas: N₂; injector temperature: 250°C; detector temperature: 250°C; column temperature: 180°C; flow rate: 5mL/min with a split ratio of 1:15. High Performance Liquid Chromatography (HPLC) using Shimadzu LC10 with Shimadzu SPD10AV UV detector set at 205nm and Waters Microbondpak C18 column was used to determine the FAME yield. The mobile phase gradient used for the gradient elution reversed-phase HPLC was from 100% methanol to 50% methanol in equilibrium with the corresponding amount of isopropanol-hexane with a 5:4 volume ratio. Total run time was 15 minutes at a flow rate of 1-mL per minute. Parr 1341 Calorimeter was used to find out the energy of combustion. The index of refraction was determined using Abbe refractometer while the density was calculated through constant weighing.

Experimental Procedure

Crude Extraction of *Jatropha* Oil

Dried *jatropha* seeds were ground and sieved using screen sieve with wire mesh number 5. Five hundred grams of the dried and ground *Jatropha curcas* nut were soaked in 1 L distilled hexane in a tightly sealed glass jar for at least

24 hours before collecting the extract through filtration. A second extraction of oil from the sample was done by adding another 500 mL of the hexane to each glass container to soak for 24 hours. Hexane was evaporated using rotary evaporator and the crude oil extracts from two extractions were combined. The crude oil yield was determined for every one kilogram sample.

Determination of Acid Value

A published method by the American Oil Chemists Society (AOCS 1980) was used to determine the acid value taken to be mg KOH/g sample. A 5g sample was dissolved in 100mL 95% ethanol with 0.5mL phenolphthalein indicator (heated until a homogeneous solution was achieved) was titrated with 0.5N KOH until the first pink color persisted for 30 seconds. Acid value determined as 107mg KOH/g sample was very high indicating large amount of FFA in the sample.

Purification of *Jatropha* Oil

Refining of *jatropha* oil consists of three steps: (1) degumming, (2) alkali treatment, and (3) bleaching. Degumming removes the phospholipids and other water soluble impurities from crude oil. (Loterio et al. 2006) Distilled water (1-2% by weight) was added to the crude oil and was heated to 80-90°C. The mixture was stirred vigorously for 30 minutes. The hydrated phospholipids and other hydrophilic impurities were then separated from the oil through centrifugation. Alkali treatment is done to neutralize the oil by removing the FFA. This is accomplished by adding NaOH to the degummed oil, at 70-80°C under vigorous stirring until pH reaches 8 then removing the precipitates through centrifuge. In this case however, the FFA content is so high that saponification occurs. This step is skipped and the degummed oil is bleached without the alkali treatment. The bleaching step was done by allowing the degummed oil to stand in contact with activated clay for 24 h, and then centrifuged to remove the clay. Under these conditions adsorption of color bodies, trace metals, and oxidation products, as well as residual soaps and phospholipids remaining after washing neutralized oils, takes place. Oil yield after the purification process was determined to be 28.15/kg sample.

Preparation and Characterization of Heterogeneous Catalysts

A. Preparation of Amino-functionalized MCM-41. (MCM-NH₂)

Ten grams of MCM-41 was dried for 2 h at 120°C then refluxed in a three-necked flask containing 200mL of boiling anhydrous toluene under nitrogen with constant stirring. After one hour, 4.82g of

3-aminopropyltriethoxysilane (APTES) was added. The mixture was stirred and refluxed at 110°C for another 5 h. Half gram of hexamethyldisilazane (HMDS) was then added and the mixture stirred for another 5 h. The white amino-functionalized MCM-41 was filtered off from the mixture and after thoroughly washing with toluene, dried in a vacuum oven at 50°C for 12 h. The dried solid was stored in airtight vials. This solid catalyst will be referred to as MCM-NH₂. (Blanc et al. 2000; Bourlinos et al. 2001; Zhang et al. 2005).

The IR spectra of organo-functionalized silicate had a stretching vibration band (2900cm⁻¹), a bending vibration band (1400cm⁻¹), and a rocking vibration band (750cm⁻¹) from the -CH₂- of the propyl-chain and the methyl groups

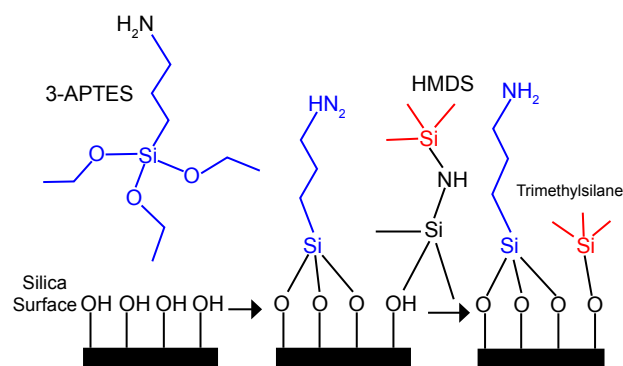


Figure 3. Surface modification of MCM-41 or Zeolite-Y through the grafting of 3-aminopropyl-triethoxysilane (3-APTES) followed by hexamethyldisilazane (HMDS).

of the trimethylsilylamine moieties. These bands appear on all the IR spectra of the developed heterogeneous catalysts since the base sites were all tethered to the silicate substrates by propyl-chains. The infrared spectrum of the aminopropyl-functionalized MCM-41 (MCM-NH₂) has bands corresponding to the N-H bending vibration at around 1600cm⁻¹, as well as, the C-N bond-stretching signal from the primary amine at around 1100cm⁻¹. The C-N band, however, overlaps with the broad Si-O-Si band making it hard to distinguish.

B. Grafting Preparation of TBD-functionalized MCM-41. (MCM-TBD)

An attempt to immobilize TBD molecules on the surfaces of MCM-41 through the formation of covalent bonds between the propyl chains and TBD molecules was based on a procedure adapted from Blanc (2000) and Sayari and Hamondi (2001). To a stirred suspension of dry MCM-NH₂ (10-grams) in toluene under reflux in nitrogen atmosphere, 4-grams of TBD were added. The mixture was then stirred and refluxed (under nitrogen)

for five hours at 110°C. The precipitate centrifuged, washed, dried and stored in the same way as described in the preparation of MCM-NH₂. This solid product was referred to as MCM-TBD.

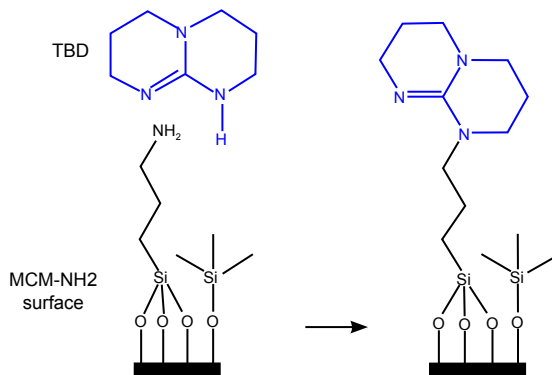


Figure 4. Preparation of MCM-TBD from MCM-NH₂.

Confirmation of the success of grafting of TBD on the surfaces of MCM-41 would be indicated by the disappearance of -NH₂ bands (around 1600cm⁻¹) and the appearance of the C=N band (about 1650cm⁻¹) due to the substitution of the primary amine groups in MCM-NH₂ with TBD. The absence of secondary-amine bands (3300-3400cm⁻¹) in the MCM-TBD spectrum would also signify that the TBD present are all covalently attached to the propyl-chains and are not just adsorbed or trapped inside the pores of MCM-NH₂. Since MCM-TBD was synthesized from MCM-NH₂, the MCM-TBD IR spectrum exhibited some peaks similar to that found in the MCM-NH₂ IR-spectrum, such as the peaks for the methylene groups in the propyl-chain and for the methyl groups in the trimethylsilylamine. In view of the fact that the amine groups in MCM-NH₂ are not very good leaving groups, no nucleophilic substitution reaction was observed to occur between the TBD molecules and the amine groups in MCM-NH₂. The retention of the IR bands of the primary amine despite the large excess of TBD in the synthesis reaction indicates that the amine groups in MCM-NH₂ were retained. The presence of the C=N band (around 1650cm⁻¹), however, shows that the TBD molecules are entangled between the aminopropyl chains and held strongly in place by H-bonds, instead of being covalently tethered to MCM-41.

C. Preparation of Amino-functionalized Zeolite Y. (ZY-NH₂)

Ten grams of dried Zeolite Y was refluxed in a three-necked flask containing 200mL of boiling anhydrous toluene under nitrogen with constant stirring. After one hour, 4.82g of 3-aminopropyltriethoxysilane (APTES)

was added and the mixture stirred and refluxed for another five hours at 110°C. Half gram of hexamethyldisilazane (HMDS) was then added and the mixture stirred for another five hours. The resulting solid catalyst was then filtered off from the mixture and after thoroughly washing with toluene, dried in a vacuum oven at 50°C for 12 hours. The dried solid was stored in airtight vials. This solid catalyst will be referred to as ZY-NH₂.

Due to the similarity of the functional groups grafted on ZY-NH₂ with that on MCM-NH₂, the same bands present in the infrared spectrum of MCM-NH₂ were observed in the IR spectrum of ZY-NH₂. These bands are: the methylene band at 2900cm⁻¹ and the bands at 1600 and 1500cm⁻¹ for the primary amine group. The broad Si-O-H band came from the silanol groups found in the inner surfaces of the porechannels in microporous zeolite Y (pore diameter = 7-angstrom).

The amount of adsorbed substances as well as the thermal stability and amount of organic material grafted on silica were determined using thermal gravimetric analysis for the three heterogeneous base catalysts. Density of the catalytic base sites in the three synthesized heterogeneous catalysts was determined using the Volhard titration method.

Transesterification of *Jatropha* Oil

Base catalyzed transesterification was carried out using 1:3 *Jatropha* oil-to-methanol mole ratio (with excess 30% methanol) and 1.3% KOH or NaOH, base catalyst,

refluxed with constant stirring at 70°C in a 250 mL three-necked round-bottom flask for at least one hour. Reaction progress was monitored using thin layer chromatography. Heterogeneous catalyzed transesterification was also carried out using 10% by weight of the developed catalysts and a methanol-oil molar ratio of 15:1 under reflux with constant vigorous stirring at 80°C for two hours. Inorganic bases are soluble in methanol, while both the alcohol and the inorganic base are insoluble in oil. Also, both FAME and glycerol were found to be soluble in methanol, but the oil reactant was not. For the reaction to occur, therefore, the reactants have to be thoroughly mixed. Increasing the mass fraction of FAME, the solubility of methanol in the oil + FAME phase was found to increase. The transesterification reaction was carried out in the methanol phase, and so when FAME content increases to 70%, the oil + methanol + FAME mixture became a homogeneous phase (Zhou et al. 2006). Initially, the reaction is slow due to mass transfer limitations. But as more methyl esters are formed, the reaction proceeds faster because the products act as surfactants, which increases the solubility of the reactants in each other. Glycerol has a low solubility in both oil and FAME; hence, it is easily separated from the final product of biodiesel. The solubility was found to be temperature independent. The heterogeneous catalyst was recovered by centrifugation. The samples were then cooled to room temperature and were allowed to stand for phase separation. The organic layer was extracted using hexane which was removed by evaporation.

Table 1. Summary of the details from the TGA of the three heterogeneous base catalysts.

	ZY-NH ₂		MCM-NH ₂		MCM-TBD	
	Weight loss (%)	Temperature Range [°C]	Weight loss (%)	Temperature Range [°C]	Weight loss (%)	Temperature Range [°C]
Adsorbed substances	7.3	24.34 - 230.21	3.76	23.97 - 132.24	0.72	27.95 - 69.8
Organosilanes	3.43	255.4 - 505.15	8.40	233.11 - 519.81	7.91	267.27 - 519.86

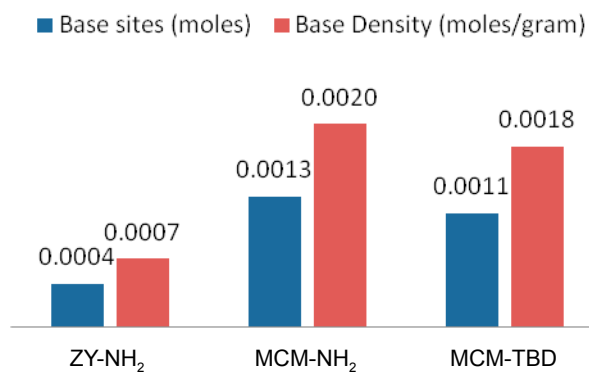


Figure 5. Density of catalytic base sites in the three synthesized heterogeneous catalysts.

Table 2. Fatty acid composition of crude *Jatropha curcas* oil based on literature (Gubitz et al. 1999).

Fatty acid	Structure	Wt%
Myristic	14:0	0-0.1
Palmitic	16:0	14.1-15.3
Palmitoleic	16:1	0-1.3
Stearic	18:0	3.7-9.8
Oleic	18:1	34.3-45.8
Linoleic	18:2	29.0-44.2
Linolenic	18:3	0-0.3
Arachidic	20:0	0-0.3
Behenic	22:0	0-0.2

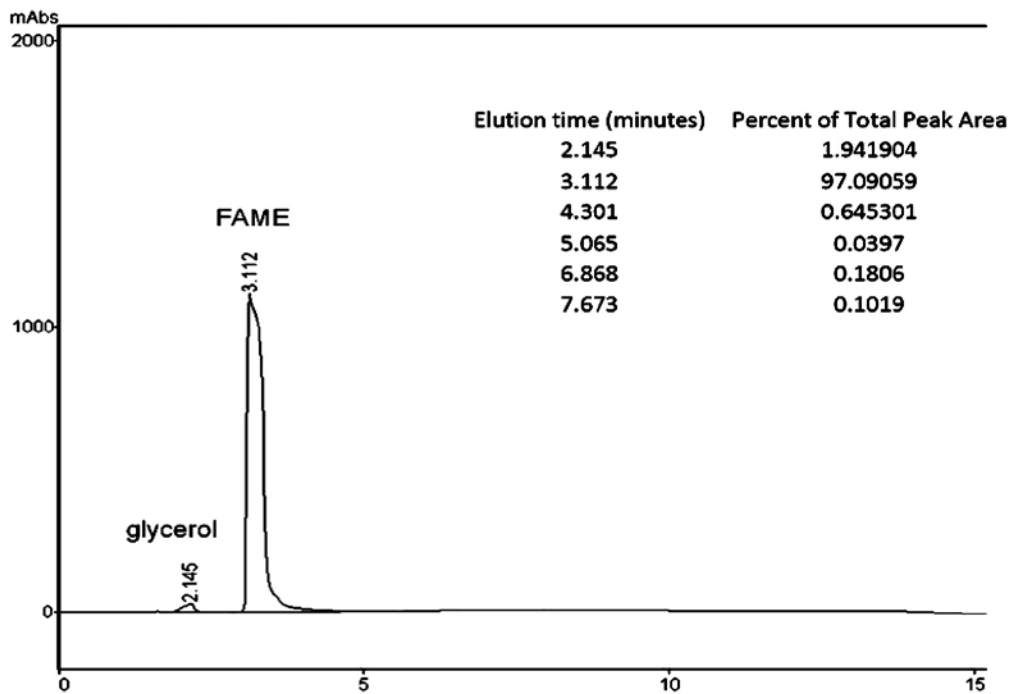


Figure 6. HPLC of *Jatropha curcas* FAME.

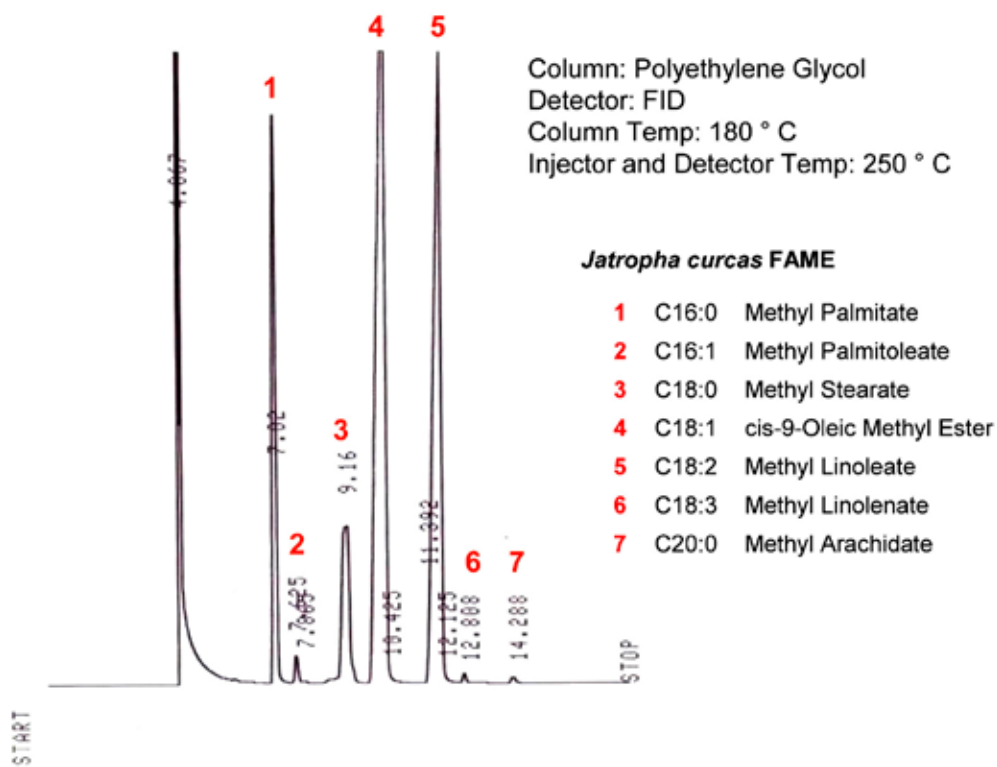


Figure 7. GC of *Jatropha curcas* FAME

RESULTS AND DISCUSSION

Crude extraction of jatropha oil using hexane yielded 32.17% oil with an acid value of 107mg KOH/ g sample. The high acid value indicates very large amount of free fatty acids (FFA) in the sample as confirmed by the large spots corresponding to FFA in the TLC profile of the jatropha oil extract. The crude oil was refined to remove phospholipids, free fatty acids and other organic substances which were extracted together with the oil. However, no substantial difference was observed in the TLC profile before and after the process.

Alkali based transesterification used potassium hydroxide (KOH) and sodium hydroxide (NaOH) as base catalysts as they are the most commonly used due to their low cost and availability. Base-catalyzed transesterification of the unrefined oil however was not successful even with a large excess of alcohol and at higher amounts of catalysts. The large amount of free fatty acids in the unrefined *Jatropha* oil hindered the transesterification process. Free fatty acids compete for the catalyst in the reaction as it undergoes saponification process producing soaps and thereby decreasing the desired yield. Transesterification of the refined *Jatropha* oil following the methanolic KOH catalyzed procedure has yielded methyl esters. It is however hard to extract pure methyl esters as there is a remaining large amount of free fatty acids which cannot be separated from the desired product. In fact, use of NaOH as the catalyst resulted into soap formation even with the large excess of alcohol. This undesirable saponification reaction reduces the ester yields and presents a considerable problem in the recovery of the glycerol due to the formation of emulsions. In this case, the simple homogeneous base-catalyzed transesterification of the jatropha extract is not an efficient route for methyl esters production. Moreover, the high FFA content makes the refining process ineffective and impracticable. Furthermore, storage of *Jatropha curcas* seed oil extract prior to utilization could result to changes in its physical and chemical properties (Berchmans and Hirata 2008). Various chemical reactions such as hydrolysis, polymerization, and oxidation could occur. As jatropha oil contains higher concentration of unsaturated fatty acids (i.e. linoleic acid (18:2) and oleic acid (18:1)), auto oxidation of these unsaturated fatty acids component due to the presence of double bonds in the chains can easily occur leading to degradation of the oil (Canacki 2007). Degradation of the oil could result to an increase in FFA concentration and so is the presence of moisture as it could lead to hydrolysis of triglycerides (Monyem and Van Gerpen 2001; Leung et al. 2006; Oversen et al. 1998).

In order for the shift to biodiesel to be feasible and to be commercially competitive with other existing energy

sources, heterogeneous catalysts were selected to replace the homogeneous catalysts currently commonly employed. Solid catalysts are less sensitive to the presence of FFAs and allow the use of cheaper less refined oils.

Transesterification reactions catalyzed by MCM-NH₂, MCM-TBD or ZY-NH₂ were conducted to determine which of the three catalysts produced the highest FAME yield. The catalyst with the highest yield was then employed in the optimization of the reaction parameters with the greatest impact on the FAME yield. Figure 8 shows the different FAME concentrations resulting from the transesterification of the refined jatropha oil using the different heterogeneous base catalysts. The yields were compared with the results using the homogeneous base catalyst and the unmodified MCM-41 and Zeolite Y. FAME concentration was reported as the total area percent of the FAME peak areas in the HPLC chromatogram. The FAME peaks were identified from the HPLC chromatogram of the standard FAME mix.

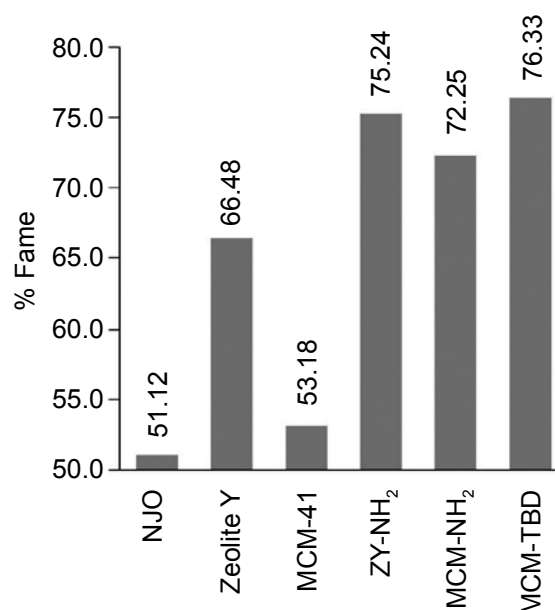


Figure 8. FAME concentrations of refined *Jatropha* oil from homogeneous base-catalyzed transesterification (NJO) and from the heterogeneous base-catalyzed transesterification reactions.

Use of heterogeneous catalyst resulted in a significant increase in the FAME yield of the transesterification reaction. The characterization of the MCM-NH₂, MCM-TBD and ZY-NH₂ heterogeneous base catalysts indicated that only a small amount of basic organosilanes were grafted onto the surfaces of Zeolite Y compared with MCM-41. The presence of sodium ions in the crystalline matrix of Zeolite Y, however, gives ZY-NH₂ a strong basic

nature even without the grafted organic bases. Likewise, ZY-NH₂ exhibited a high conversion rate compared with MCM-NH₂ despite the comparatively low density of active base sites (0.7-mmol base/gram) because of the presence of highly basic sodium ions in its lattice. It is more active than MCM-NH₂ (2.0-mmol base/gram) and approaches the same level of activity as MCM-TBD (1.8-mmol base/gram), which produced the highest FAME yield of the three modified silica. Because MCM-TBD exhibited the highest activity among the three base-functionalized porous silica and being the most thermally stable, it was chosen for the optimization of the transesterification of *Jatropha curcas* oil.

As the transesterification reaction is reversible, increasing the concentration of the alcohol beyond the stoichiometric ratio favors the formation of the products. The optimum molar ratio of alcohol to oil was found to be 15:1 as illustrated in Figure 9. At higher molar ratios, the increase in the FAME yield was not as high due to the dilution of the reactive species, which in this case is the methoxide anion.

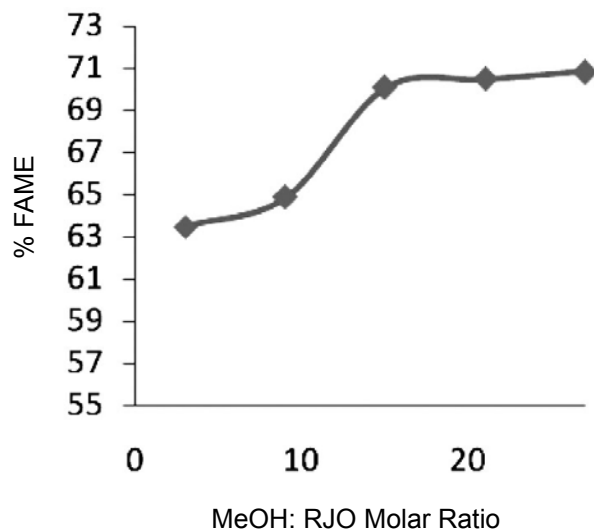


Figure 9. The effect of different alcohol-to-oil molar-ratio on the heterogeneous-base-catalyzed transesterification yield.

Increasing the amount of the catalyst generally increases the rate of the reaction and, consequently, the yield. At concentrations higher than 10% MCM-TBD (of the weight of the oil), there is a decrease in the FAME yield as can be observed in Figure 10.

Higher temperatures above the boiling points were used to increase the rate of reaction as solubility of the reactants is increased and there is lower mass transfer resistance. The FAME concentration generally increased as the reaction temperature was raised until 80°C, which

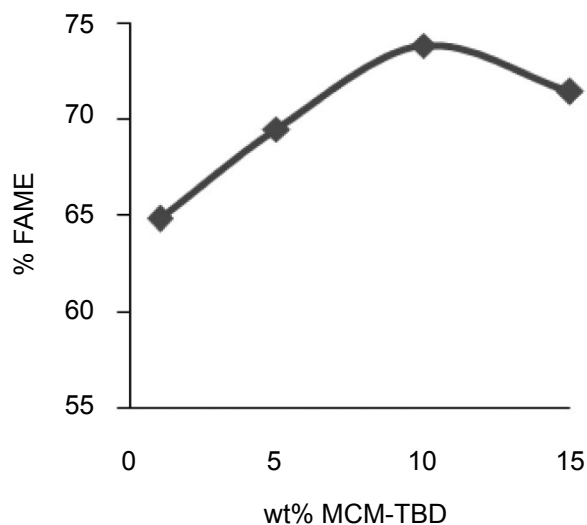


Figure 10. The effect of different catalyst concentrations on the heterogeneous-base-catalyzed transesterification yield.

is the optimum temperature. At 80°C, highest yield of FAME was achieved without having to operate at higher pressure. However, at temperatures above 80°C, a drastic reduction in the FAME yield was observed as shown in Figure 11. This can be due to the drastic loss of methanol (B.P. = 64.7°C) that has escaped the condenser. A Parr reactor, a metal vessel which can withstand high pressures necessary for a much higher temperature reactions, can be used for a more accurate determination of the optimum temperature. Figure 12 shows the optimum reaction time to be at two hours. Reaction times longer than 2.5 h are too long for future applications of this technology and so were not tested.

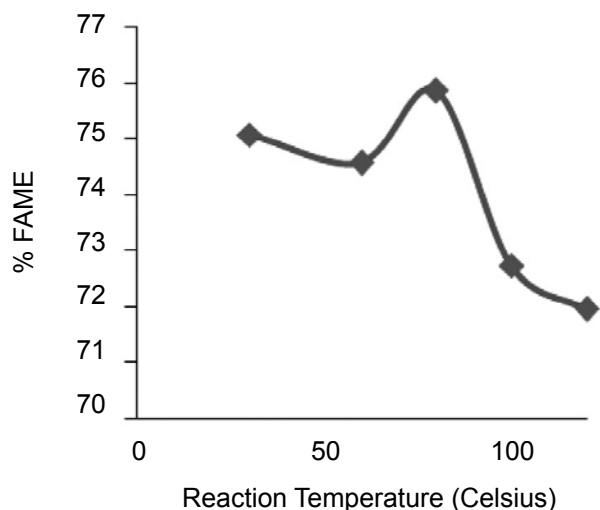


Figure 11. The effect of different temperatures on the heterogeneous-base-catalyzed transesterification yield.

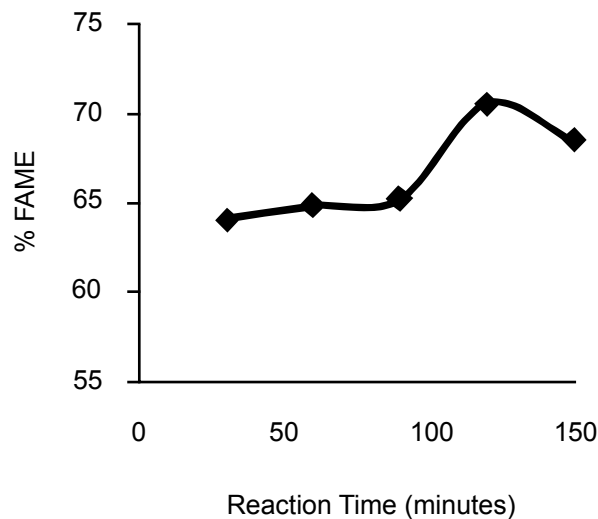


Figure 12. The effect of different reaction-times on the heterogeneous-base-catalyzed transesterification yield.

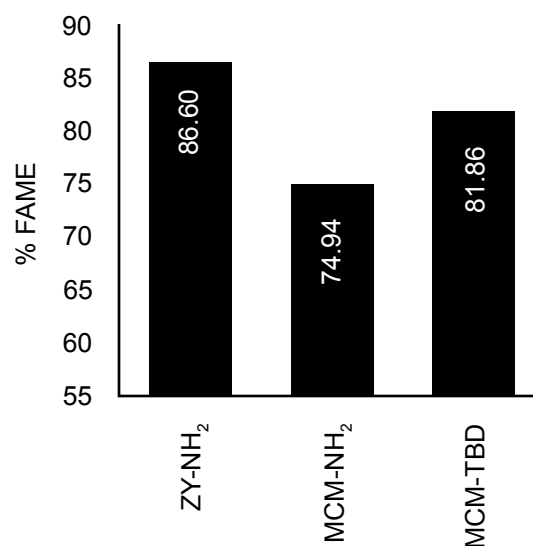


Figure 13. FAME yields of the three heterogeneous base catalysts at the optimized conditions.

Table 3. Summary of % composition of transesterified *Jatropha* oil.

	Methyl Compound	% Composition
Methyl Palmitate		14.35
Methyl Palmitoleate		1.14
Methyl Stearate		6.89
cis-9-Oleic Methyl Ester (Methyl Oleate)		43.67
Methyl Linoleate		30.88

At the optimum conditions using 10% by weight of the developed catalysts and a methanol-oil molar ratio of 15:1 at 80°C for two hours, MCM-NH₂ and ZY-NH₂ both produced higher yields. The yields of each catalyst using these reaction conditions are charted on Figure 13.

The yield from the MCM-NH₂-catalyzed reaction increased from 72% to 75%, and still remains the least active among the three developed heterogeneous catalysts. The catalyst with the highest yield among the three catalysts developed in this study was ZY-NH₂, which

increased from 75% to 87%. The presence of strongly basic sodium ions in the lattice of Zeolite-Y may have contributed greatly to the high FAME yield of ZY-NH₂. There is a possibility, however, of sodium ions leaching out of the solid catalyst and promoting a homogeneous catalysis of the transesterification reaction. This will give the catalyst some disadvantages, such as significantly reducing the recyclability of the catalyst and contaminating the product with sodium ions, which complicate the purification of the FAME product. The deactivation of catalysts due to these phenomena is well documented for homogeneous catalysts that are immobilized on solids or in porous materials only through adsorption. (Albuquerque et al. 2008; Cubillos and Hölderich 2007; De Vos et al. 2002; Di Serio et al. 2006; Lotero et al. 2006; Weitcamp et al. 2001) A base-functionalized mesoporous silicate that could have a better performance as a catalyst may be developed through co-condensation instead of grafting. This way, the bases will be evenly distributed throughout the entire external and internal surfaces of the mesoporous silicate. The co-condensation method may also allow higher loadings of the organic base. However, a better method other than calcination for removing the surfactant template during the synthesis of the porous silicate remains to be developed. Otherwise, the organic base moieties in the silicate will be vaporized along with the surfactant and template during calcination. (Weitcamp et al. 2001; Wight and Davis 2002; Zhang et al. 2008) All three catalysts did not yield a complete reaction like that found using a homogeneous base catalyst, such as KOH. This is commonly due to mass transfer limitations between the oil and alcohol, and particularly when using heterogeneous catalysts.

Comparison of the gas chromatographs of the transesterified *Jatropha* oil with that of the FAME standards indicate that the oil components are mainly 43.67% cis-9-oleic methyl ester and 30.88% methyl linoleate. Other fatty acid components of the *Jatropha* oil are 14.35% methyl palmitate, 1.14% methyl palmitoleate, 6.89% methyl stearate. These values are in agreement with previous works. Density and refractive index of the transesterified *Jatropha* oil were found to be 900 kg m⁻³ and 1.45 respectively. The heat of combustion is determined to be 38,589 kJ/kg.

CONCLUSION

Physical and chemical properties of *Jatropha* oil extract were investigated to determine its viability as a biodiesel. One of the main concerns is the high FFA content which significantly reduces the methyl esters yield in base-catalyzed transesterification process. To

facilitate conversion, three heterogeneous catalysts were developed by amino functionalization of Zeolite Y and MCM-41 and by TBD grafting on MCM-41. Significant increase of FAME yield was observed with the use of the solid catalysts. Comparison of the results showed amino-functionalized Zeolite Y had the highest methyl ester yield of 87%. Kinetic studies may be performed to further understand the reaction mechanism and have a better control of the transesterification reaction.

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