Nigerian Journal of Technology (NIJOTECH)
Vol. 34 No. 1, January 2015, pp. **119 – 126**
Copyright© Faculty of Engineering,
University of Nigeria, Nsukka, ISSN: 1115-8443
www.nijotech.com
http://dx.doi.org/10.4314/njt.v34i1.15

TRANSESTERIFICATION OF CRUDE JATROPHA CURCAS *LINNAEUS* OIL CATALYZED BY WASTE MARBLE DERIVED SOLID CATALYST

M. A. Olutoye*
DEPARTMENT OF CHEMICAL ENGINEERING, FEDERAL UNIVERSITY OF TECHNOLOGY, MINNA, NIGER STATE, NIGERIA
E-mail Address: *m.olutoye@futminna.edu.ng*

ABSTRACT

Transesterification of crude jatropha oil with methanol was investigated using a heterogeneous catalyst derived from waste marble. The barium enhanced waste marble catalyst was prepared via precipitation/impregnation methods and showed high performance to methyl ester conversion when calcined at 830 °C for 4 h. The high activity of the solid oxide catalyst resulted from the basic-sites generated from the synergetic composite formed with high dispersion of the active species as indicated from characterization data with Brunauer-Emmett-Teller (BET) surface area, 56.01 m^2/g, average pore size, 123.63Å, and pore volume, 0.17 cm^3/g. The methyl ester content of 70.36% was achieved over the catalyst within 4 h under the optimal transesterification conditions of methanol/oil molar ratio of 15:1, catalyst amount of 5 wt % and reaction temperature of 65 °C. The research provides insight into application of waste marble enhanced with barium as potential catalyst in the heterogeneously catalyzed transesterification of crude jatropha oil in mild conditions.

Keywords: *Waste marble; Crude jatropha oil; Heterogeneous catalyst; Transesterification*

1. INTRODUCTION

Worldwide oil consumption continues to climb consequent of energy wasting habits, increasing population and industrialization [1]. The demand for oil as sole sustaining economy for energy is rising continuously. Thus, the rummage for alternative fuel (biodiesel derived from renewable source) for energy requirements has persisted in many countries of the world. The technology chiefly employed in biodiesel production depended on the transesterification of vegetable oils using homogeneous catalysts. In this process, associated problems (mainly in product purification and residues generation) have induced further research for solid catalyst with high activity at profitable operating conditions [2]. The development of an environmentally friendly solid catalyst for the process seems to be promising route. In addition, biodiesel is renewable, provides complete combustion and emits less pollution-causing gases [3].

Many types of heterogeneous catalysts for biodiesel synthesis have been reported ranging from strong acid catalysts to strong base catalysts [4-9]. Zeolites, heteropoly acids and sulphated zirconia, alkaline earth oxide based catalysts, alkali metal supported alumina are few examples [5, 10-12]. All these materials reveal interesting results but only in respect with surface functions (acidic or basic) catalytic aspect. Also, in order to achieve good catalytic performance, some of the catalysts can used only at elevated conditions, such as high temperature, high methanol content or in presence of extracting co-solvent, and in some cases, starting from high quality triglycerides feedstock. However, most feedstock used in transesterification such as waste cooking oil, poultry fat and other non-edible oils such as crude jatropha oil, pongamiapinnata (karanj) oil and rubber seed oil contain higher amounts of fatty acid, thus limiting the application of heterogeneous solid catalysts. Heterogeneous catalysts offer some advantages because they are environmentally friendly and present minimal disposal problems. They are also much easier to separate from liquid products and can be designed to give higher activity and longer catalyst lifetimes [13]. So, the need for a cheap and recyclable catalyst for biodiesel synthesis from non-food source (crude jatropha oil) is essential. In most of the experimentation using heterogeneous catalysts, transesterification of oils proceeds at a somewhat

*** Tel: +234-803-405-9454**

sluggish rate compared to those conducted with homogeneous catalysts. The slowness of reaction rates are due to diffusion problems ensuing from the activities of heterogeneous media such as a three-phase system [14].

Waste marble (WM) materials are found dumped indiscriminately at many construction sites and in some instances used as landfill. Huge amounts of waste marble from repositories and marble cutting industries are being produced and to reduce cost of disposal as well asof the consequent environmental hazards, its full utilization as catalyst in transesterification is significant. The potential of this low cost material (WM) as a source of CaO and its enhancement with barium metal to produce biodiesel from crude jatropha oil has not been explored and pose a riveting challenge.

In this work, it is reported that waste marble embellished with barium as a solid catalyst can be used in transesterification of high FFA crude jatropha oil in one stage at the reflux temperature of methanol into biodiesel. The efficiency of barium/waste marble solid catalyst under mild reaction conditions was explored and investigated. Effects of parameters on the content of fatty acid methyl esters (FAME) such as: reaction time, molar ratio of oilto methanol, catalyst concentration and reaction temperature were studied. Furthermore, the possibility of catalyst reuse was evaluated.

2. MATERIALS AND METHODS

2.1 Materials

Crude Jatrophacurcas L. oil (CJO) was purchased from Telegamadu Bdh. Sdn., Butterworths, Penang, Malaysia. The fatty acid profile of the oil contains variable amounts of palmitic (14.3%), stearic (7.0%), oleic (44.7%), and linoleic (33.0%) fatty acids. Waste marble (CaO source) were collected from various retail tiles shop, Penang. Barium nitrate ($Ba(NO_3)_2 \approx$ 99%) obtained from Merck was used to meliorate the waste marble. Analytical reagent grade 99.9% methanol (High Performance Liquid Chromatography grade) purchased from Merck (Malaysia) was used for the transesterification reactions. Other chemicals used in the experiment such as analytical grade NH_4OH ($\approx$ 85%) and n-hexane (96%) used as solvent for gas chromatography (GC) analysis was obtained from Merck, Malaysia. Methyl heptadecanoate $\approx$ 99.5% used as internal standard for GC analysis was purchased from Fluka, Malaysia. These reagents were used without further purification for catalyst synthesis and the transesterification of crude jatropha oil.

2.2 Catalyst preparation

The waste marble, collected from various retail tile shops were washed to remove debris. The cleaned marble was crushed to fine powder using mortar and pestle and sieved to obtain size range of 125-250 microns. Based on 100 g of catalyst preparation, 95 g of fine waste marble powder was oven dried at 120 °C for 2 h to remove adhered moisture and volatiles. The dried powder was transferred into precipitated barium hydroxide from its nitrate solution using 5 M NH_4OH. Prior to this, 5% $BaNO_3$ dissolved in 50 mL distilled water was stirred on a magnetic plate until completely dissolved. The mixture was stirred continuously for 6 h until homogenized slurry paste was formed. The wet slurry was allowed to dry in a crucible and calcined at 830 °C for 4 h to obtain an active oxide material, except otherwise stated, designated as Ba/WM catalyst and was employed immediately for transesterification reaction.

2.3 Catalyst characterization

Ba/WM was characterized to understand its physical and chemical properties. The BET surface area was calculated using the ASAP Micromeritics 2020 using Brunauer-Emmett-Teller (BET) at approximately 77 K nitrogen dosed on the catalyst surface in a bath of liquid nitrogen, relative pressure of 0.99 bar and the total pore volume was evaluated. Energy dispersive X-ray spectrophotometer (EDX) was measured for the sample mounted on the microscope using Philips XL30S model SEM. The sample was placed on the carbon tape on the aluminum stub and coated with gold. The sample was then vacuumed for 20 minutes before an analysis. SEM analysis was carried out to identify the surface morphology of the catalyst. Fourier Transform Infrared Spectrophotometer (FTIR) was used to identify the functional group of the catalyst. FTIR Spectroscope (Perkin Elmer FTIR-2000, US) was used to measure absorption of various infrared light wavelengths emitted by the sample. Sample was ground and diluted with 0.1 wt% potassium bromide (KBr) prior to analysis.

2.4 The catalyzed transesterification reaction procedure

The transesterification reaction was carried out using the crude jatropha oil (CJO) as purchased. The oil and methanol were measured according to the desired ratio and were then charged into the glass reactor containing 3.99 g catalyst (equivalent to 5.0 wt % catalyst loading weight of oil and methanol/CJO ratio of 15:1). The temperature of the reaction was controlled at 65 °C using PID (Proportional Integral Derivative) controllerand was stirred at 1000 rpm for 4 h. Three of the important parameters (reaction time, catalyst loading and methanol to oil ratio) were varied during transesterification reaction at constant temperature. At the end of the experiment, the reactor was allowed to cool and its content was poured into a glass bottle. Two distinct layers were formed after allowing the content of the bottle to settle. The top and bottom layers represent fatty acid methyl ester (FAME) and glycerol, respectively. The product in the glass bottle was allowed to settle overnight. The top layer was further centrifuged at 3000 Xg for 15 minutes after which the top layer was analyzed using the gas chromatography.

2.5 Product analysis

The centrifuged sample was then analyzed using Shimadzu GC-2010 plus with Flame Ionization Detector (FID), equipped with Nukol capillary column of 15 m x 0.5 mm x 0.5 µm. The carrier gas that was used was Helium. Each sample was carried out by dissolving 20 µl of FAME into 250 µl of methyl hepadecanoate which was used as the internal standard. 1µl of the prepared sample was then injected into the GC and FAME yield was calculated. The yield is defined as the ratio of the weight of methyl esters determined by GC, to the weight of vegetable oil used as shown in Eq. 1.

$$\text{Yield} = (\text{Weight of methyl ester, } W_1) / (\text{Weight of oil used, } W_2) \times 100\% \qquad (1)$$

2.6 Catalyst reusability

The reusability of the Ba/WM solid catalayst, which represents its capacity to perform the same catalytic activity was evaluated by conducting several experimental runs after the first batch at the conditions obtained for highest FAME yield. The solid catalyst after the first reaction was recovered and washed with n-hexane to remove any residue adhered to the surface of the catalyst. The washed catalyst was then dried and filtered for 12 h. The catalyst was then used for second and third consecutive runs to obtain FAME using CJO. All experiments were conducted in one stage process. The prolonged use of the catalyst to evaluate the significance and the feasibility of the catalyst for industrial application was studied.

3. RESULTS AND DISCUSSION

3.1 Characterization of the catalyst

The performance of the catalyst was characterized to gain insights into its performance in transesterification. Table 1 shows the specific surface areas measured by the BET method. The BET surface areas for WM and Ba/WM catalysts are 40.19 m^2g^{-1} and 56.01 m^2g^{-1}, respectively. Although the surface areas obtained for the catalysts are low, the surface area for Ba/WMexceeds that of WM and lies in the range of mesoporous structure believed to have contributed to its performance.

Table 1: BET surface area, pore size and average pore volume of the synthesized catalyst

Structural Properties	WM	Ba/WM
BET surface area (m^2g^{-1})	40.19	56.01
Pore volume (cm^3g^{-1})	0.13	0.17
Average pore size (Å)	127.40	123.63

EDX was used to verify the composition of the WM and Ba/WM catalyst and the results are given in Table 2. It shows the different elemental composition of the two catalysts, with and without addition of Ba. From the observation, calcium and oxygen are present insignificant percentages. Ba is present in the enhanced waste marble only with 5 wt% of barium nitrate.

Table 2: Elemental composition of the waste marble derived catalyst

Elements	Weight (%)	
	WM	Ba/WM
Oxygen (O)	30.93	30.37
Copper (Cu)	00.40	-
Silver (Ag)	1.12	-
Calcium (Ca)	67.55	65.20
Barium (Ba)	-	4.43

The potential ofCaO as a solid catalyst in transesterification of vegetable oils to methyl esters was reported by [15]. The addition of Ba in the present work was to increase the stability of WM. Initial experiment revealed high amount of active sites leaching due to impurities in the WM samples. In previous studies, high leaching was reported when pure CaO or supported CaO was used although high

FAME content was obtained [16, 17]. The reason is attributed to the homogeneous contribution of the CaO catalyst during transesterification due to leaching of active phase in the medium. The modification with barium helped to stabilize the activity of CaO using high free fatty acid (FFA) CJO. The morphology and composition of Ba/WM were investigated by SEM and SEM-EDX analyses. Fig.1shows the SEM micrograph after the enhancement process indicating that there exists only crystals of CaO and BaO, and there is no bulk metal formed in observable size outside the catalyst composite crystals.

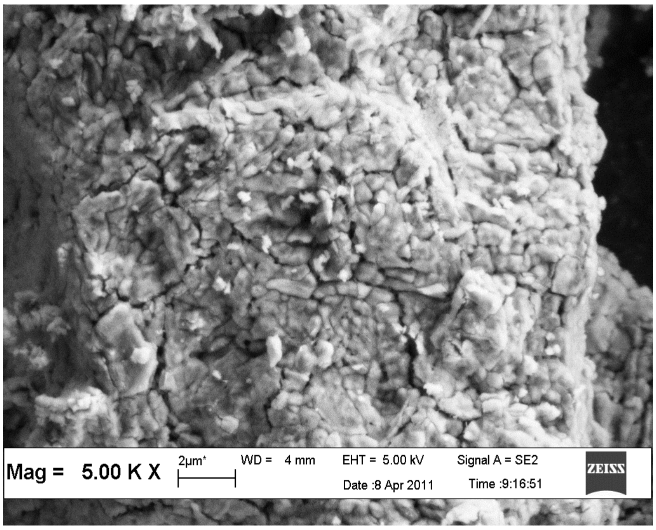


Figure 1: Scanning electron micrograph (SEM) image of the calcined waste marble
(magnification = 5000x) after treatment with barium (Ba/WM) at 830 °C for 4 h

The method used for the preparation of catalyst (incipient wetness impregnation) does not cause any observable defects in its structure as supported by XRD results. There are few clusters observed in the catalyst which consist of Ba particles. The particles of the Ba compound are hardly observed due to the small amount used during preparation to spice the WM which indicates that the small particles of the Ba-compound are homogeneously dispersed.

Fig. 2 shows the XRD patterns of the WM and Ba/WMcatalyst samples. The XRD patterns of the WM catalyst revealed the formation of mostly monoclinic type single phase as obtained from the diffractogram with peaks corresponding to $Ca(OH)_2$, CaO and Ca_2SiO_4 crystalline phase and is characteristic of orthorhombic symmetry.

The X-ray patterns of the Ba/WM show the same lines as WM with shift to higher 2θ angle values (2θ =53.96°, 64.22° and 67.43°) when barium was added.

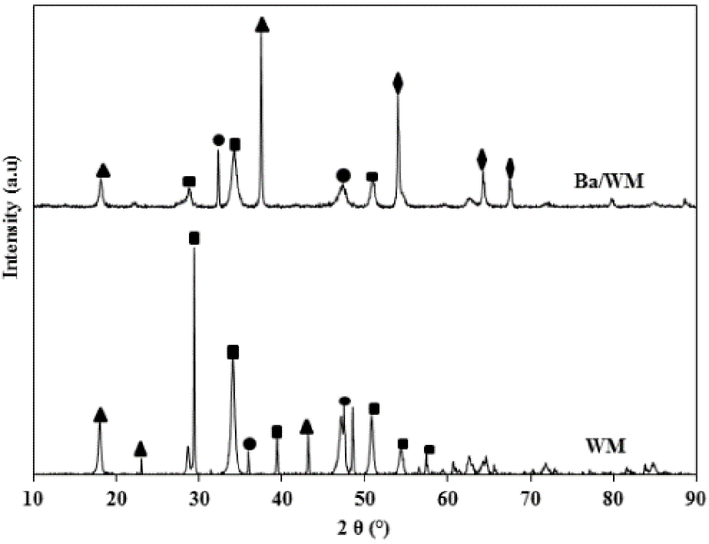


Fig. 2: XRD patterns of WM and Ba/WM catalysts (■ $Ca(OH)_2$, ● CaO, ▲ Ca_2SiO_4 and ♦ $CaBaSiO_4$)

A reduction in the peak intensity corresponding to $Ca(OH)_2$ at 2θ = 29.40° and 34.05° crystal phases were observed in the enhanced Ba/WM resulting in appearance of $CaBaSiO_4$ at 2θ =64.22° and 67.43° crystalline phases which is believed to be more active and contributed to the catalyst stability during transesterification.

The FTIR spectroscopy was used to further elucidate the characteristic and reactivity of the synthesized catalyst. The functional groups detected on both WM and Ba/WMwere at bandwidth O-H stretching vibration of hydroxyl functional group around 3580-3680 cm^{-1} and 2500-3300 cm^{-1}. The weak band observed at 1230 cm^{-1} can be assigned to a monodentate nitrite species on BaO. The bands observed at 2512, 2504, 1799, 1424, 875 and 712 cm^{-1} can be assigned to bands associated with surface carbonate species and nitrate species. It is worth noting the spectra of Ba/WM, the band corresponding to 1799 cm^{-1} corresponding to carbonate species disappeared when barium was added. The appearance of BaO species was consistent with the results obtained although the intensity of the amount of surface nitrate species was slightly lower.The shoulder of the bands of 1278 and 1052 cm^{-1} could be assigned to the symmetric stretching vibration of C-O bonds. The bands in the low-wavenumbers region (556, 875, 712 and 875 cm^{-1}) correspond to the deformational modes of the orthorhombic structure. Additional peaks were also observed for surface nitrite species at 1277 and 1278 cm^{-1}, but were not clearly resolved in the Ba/WM spectrum due to low intensity.

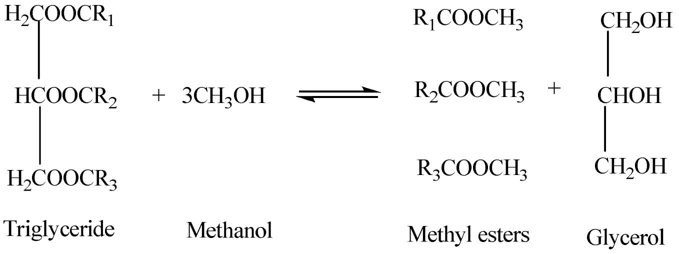
3.2. Transesterification of crude jatropha oil with methanol

3.2.1. Influence of reaction temperature on CJO conversion to FAME during transesterification

One of the variables affecting the triglyceride conversion to ester during transesterification is the reaction temperature. The temperature for the present study was set at constant value of 65 °C. A higher reaction temperature can decrease the viscosities of oils and results in an increased reaction rate at relatively short time [18]. A decrease in product yield could occur at high reaction temperature because saponification reaction of triglycerides is speeded at high reaction temperatures. Usually, methanolysis of vegetable oil is investigated close to the boiling point of methanol in order to ensure that the alcohol will not leak out through vaporization. The reaction carried out at methanol reflux temperature could be very interesting for industrial scale production because of the energy savings that it would imply [19]. In this present work, the methanolysis of CJO was studied with waste marble spiced with barium as solid catalyst at temperature of 65 °C. The methanol to oil molar ratio in the range of 5:1 to 20:1 was used for all experiment. The ester formed reached 70.36% at 4 h reaction time showing the effect of temperature on ester formation. At such a low temperature for high FFA feedstock from the economical point of view will allow the reduction of process costs. The low conversion observed is attributed to waste marble consisting mainly of$CaO$and other impurities after enhancement with barium and thermal treatment at 830 °C for 4 h. Calcium oxide exhibits strong basicity because of the presence of surface oxygen ions that attract protons readily and it also exhibits weak Lewis basicity, which is ascribed to Ca^{2+} ions [20].

3.2.2. Effect of methanol/crude jatropha oil molar ratio on transesterification

The methanol to oil molar ratio is one of the main factors affecting the yield of FAME. Theoretically, the reaction requires 3 mol of alcohol for 1 mol of triglyceride to produce 3 mol of fatty acid ester and 1 mol of glycerolaccording to equation (1). However, an excess of alcohol is used to ensure complete conversion and to drive the reaction forward at faster rate. This is because the excess will enable the reacting phases to overcome mass transfer barriers. In the present investigation, Ba/WMcatalyst was used at molar ratio range 5:1 to 20:1 and reaction temperature of 65 °C using CJO. Fig. 3 shows the FAME content obtained at constant reaction time of 4 h for all the experiments carried out. It was observed the ester yield increased as the methanol to oil molar ratio is raised beyond 5 and reaches a maximum.



$$\begin{array}{ccccccc} H_2COOCR_1 & & & & R_1COOCH_3 & & CH_2OH \\ | & & & & & & | \\ HCOOCR_2 & + & 3CH_3OH & \rightleftharpoons & R_2COOCH_3 & + & CHOH \\ | & & & & & & | \\ H_2COOCR_3 & & & & R_3COOCH_3 & & CH_2OH \\ \text{Triglyceride} & & \text{Methanol} & & \text{Methyl esters} & & \text{Glycerol} \end{array}$$

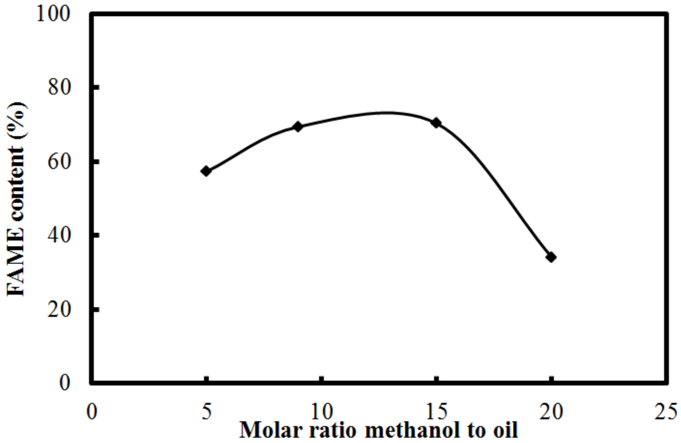


Fig.3: % FAME yield at different methanol/CJO molar ratio at constant reaction temperature 65°C, 5 wt% catalyst loading and reaction time of 4 h

A decrease in ester yield was observed with further increase in the amount of alcohol beyond 15. Thus, all other experiments were performed with a molar ratio 15:1 to avoid adding to the cost of separation. At this condition a methyl ester conversion of 70.36% was obtained. This result is similar to those found in the literature [12]. Although at higher molar ratio, more triglyceride will be reacted, however, an excess of methanol will interfere with the glycerin separation because of increase in solubility and part of glycerin remained in the methyl ester phase. Therefore the molar ratio of 15:1 seems to be the most appropriate.

3.2.3. Effect of catalyst loading

The catalyst concentration was investigated during the transesterification of crude jatropha oil. Fig. 4 shows the yield of FAME content obtained at different catalyst loading range 2.0-8.0 wt %. The triglyceride conversion increased with increasing the catalyst concentration. As can be observed, at Ba/WM catalyst loading of 5 wt% the ester yield achieved was 70.36% during 4 h of reaction.

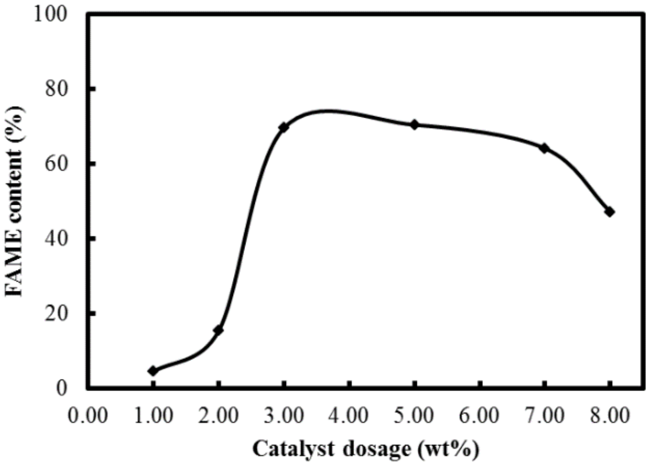


Fig. 4: % FAME yield at different catalyst dosage with methanol/CJO molar ratio of 15:1, constant reaction temperature 65°C and time 4 h

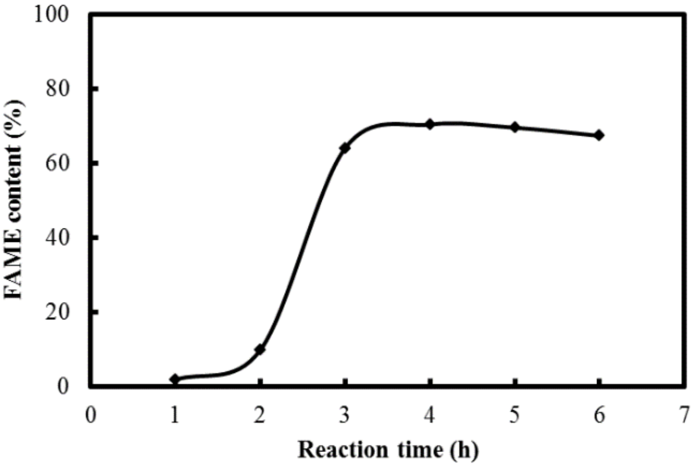


Fig.5: Dependency of FAME yields on reaction time at catalyst loading of 5.0 wt %, methanol/CJOmolar ratio of 15:1 and temperature of 65 ºC

The addition of excess amount of catalyst beyond this value gives rise to the formation of an emulsion and leads to the formation of gel. Also, this effect will hinder the glycerin separation, facilitate dilution of methyl ester and consequently a decrease of ester yield was observed. The observed trend is due to the high acidity of the oil with FFA value of 7.24%. The fact is in accordance with the Encinar et al., (2007) when there is a large free fatty acid content, the addition of more alkaline catalyst compensates the acidity in the oil and avoids catalyst deactivation [21]. However, addition of an excessive amount of catalyst gives rise to the formation of an emulsion, which increases the viscosity and leads to the formation of gels [22]. The more catalyst used during the process will increase the complexity of separation of product and cost of production. Thus, this study revealed that transesterification reaction of high FFA CJO is favoured by low loading of catalyst to avoid emulsion and the optimum catalyst loading obtained for this reaction was 5.0 wt%.

3.2.4. Effect of reaction time

Reaction time is significant operating parameters which determine the energy costs of biodiesel production process. Fig. 5 shows the effect of reaction time on the transesterification

of CJO at a constant catalyst loading of 5 wt %, methanol to oil molar ratio of 15:1, and reactiontemperature of 65 ºC. The reaction was studied within a time range of time 1-5 h using CJO and Ba/WM as catalyst.

Transesterification is a reversible reaction and require a longer time to reach its equilibrium state. It was observed that high FAME yield was obtained at 65 ºC when the reaction time increased beyond 3 h. The reaction was observed to increase steadily with increasing time to reach a maximum value above 70% FAME within 4 h. Several researchers reported that the conversion of vegetable oils to FAME was achieved at different reaction times which depend on the composition of the feedstock and the reaction conditions [23]. The initial low conversion obtained in the first 1 h could be attributed to slow mass transfer during heterogeneous reaction.

3.2.5 Effect of water and FFA contents in the feedstock

The water and FFA contents are critical factors during transesterification reaction. It has been reported that transesterification would not occur if FFA content in the oil was above 3 wt% [24]. The presence of water gives greater negative effect than that of FFAs because water can cause soap formation and frothing which can cause increase in viscosity [25]. In addition formation of gels and foams hinders the separation of glycerol from product ester [26]. The quality of oil is expressed in terms of the physicochemical properties such as acid value and saponification value. The saponification value of CJO was reported as 193.6 mg KOH/g. The acid value of CJO employed was found to be 14.47 mg KOH/g oil corresponding to a free fatty acid (FFA) level of 7.24%. The moisture content of CJO used in this work is high with a value of 3.28%.This may lead to degradation of the fatty materials by hydrolysis during transesterification reaction rendering the product material poor in stability. Acid catalysts are generally considered to be more tolerant of the water and high FFA levels in low-cost feedstock compared to base catalyst due to a lack of saponification. Refaat, (2011) reported that when water concentration in oil was below 0.5 wt% at 80 °C there was almost no effect on the FAME yield [27]. However, when water concentration in oil was above 0.5 wt%, the FAME yield linearly decreased. It was reported that hydrogen ion could bind to water molecules more effectively than to methanol, resulting in a weaker acid. Furthermore, with the increase in water concentration in the reaction system, the water-rich clusters around the hydrogen ion also increased. It could inhibit the catalyst from coming into contact with the hydrophobic oil molecules to a greater extent, which would slow down the reaction rate. The effectiveness of Ba/WM was shown in its ability to overcome the high moisture content and high FFA. Future work intends to improve on the activity of the catalyst to enhance methyl ester yield.

3.2.6 Reusability

The stability and economic potential of Ba/WM catalyst was assessed by the reusability experiments carried using CJO. The catalyst was filtered and it was repeatedly used for FAME synthesis in a new reaction cycle after washing with mixture of hexane and methanol to remove adhered oil and glycerol from the catalyst surface. The conditions at which the highest FAME was obtained were used, that is, 5 wt% catalyst loading, 15:1 methanol to oil ratio and 4 h reaction time. The consistency in the obtained results after three consecutive cycles indicate the stability role of barium in the Ba/WM catalyst with 62.25%, 57.40% and 55.07% of FAME yield.This clearly showed that the reusability of the solid catalyst showed there was a strong interaction between barium and waste marble(source of CaO) that promotes the catalyst stability.

4. CONCLUSIONS

The activity of a derived solid catalyst from waste marble in heterogeneous transesterification of high FFA CJO using one stage process under mild reaction conditions was investigated. The catalyst was able to produce FAME content over 70% at 4 h reaction time using 5 wt % catalyst loading, methanol/oil ratio of 15:1 and at a constant reaction temperature of 65 °C. The performance and stability of the catalyst was attributed to the enhanced waste marble with barium which resulted into a catalytic active crystalline phase ($CaBaSiO_4$) as revealed by characterization results. This has contributed to the catalyst stability during transesterification by preventing distortion to the composite structure and reduced leaching. The catalyst can be reused up to three cycles with consistent FAME yield and seem promising for the methanolysis of crude jatropha oil in one stage process. The catalyst provides effective utilization of waste for conversion of non-edible oil to useful product in an economically and environmentally benign process that will encourage the growth of indigenous industries.

REFERENCES

[1] A. Sarkar, Geo-politics of oil trading: scanning the global business scene, (2009).

[2] O. R. Momoh, H. I. Audu, Z. B. Binta, Investigating the production of biodiesel from Alphonso mango seed oil, *Nigerian Journal of Technology*, 33 (2014) 497-503

[3] G. Knothe, Biodiesel and renewable diesel: A comparison, *Progress in Energy and Combustion* Science, 36 (2010) 364-373.

[4] A. Kawashima, K. Matsubara, K. Honda, Development of heterogeneous base catalysts for biodiesel production, *Bioresource Technology*, 99 (2008) 3439-3443.

[5] A. Macario, G. Giordano, B. Onida, D. Cocina, A. Tagarelli, A.M. Giuffrè, Biodiesel production process by homogeneous/heterogeneous catalytic system using an acid–base catalyst, *Applied Catalysis A: General*, 378 (2010) 160-168.

[6] J.A. Melero, J. Iglesias, G. Morales, Heterogeneous acid catalysts for biodiesel production: current status and future challenges, *Green Chem*., 11 (2009) 1285-1308.

[7] Y.C. Sharma, B. Singh, J. Korstad, Advancements in solid acid catalysts for ecofriendly and economically viable synthesis of biodiesel, *Biofuels, Bioproducts and Biorefining*, 5 (2011) 69-92.

[8] J. Encinar, J. González, A. Pardal, G. Martínez, Rape oil transesterification over heterogeneous catalysts, *Fuel Processing Technology*, 91 (2010) 1530-1536.

[9] M. A. Olutoye, B. H. Hameed, Transesterification of palm oil on $K_yMg_{1-x}Zn_{1+x}O_3$ catalyst: Effect of Mg-Zn interaction, *Fuel Processing Technology*, 91 (2010) 653-659.

[10] M. C. G. Albuquerque, I. Jiménez-Urbistondo, J. Santamaría-González, J.M. Mérida-Robles, R. Moreno-Tost, E. Rodríguez-Castellón, A. Jiménez-López, D. Azevedo, C.L. Cavalcante Jr, P. Maireles-Torres, CaO supported on mesoporous silicas as basic catalysts for transesterification reactions, *Applied Catalysis A: General*, 334 (2008) 35-43.

[11] Z. Wan, B. H. Hameed, Transesterification of palm oil to methyl ester on activated carbon supported calcium oxide catalyst, *Bioresource Technology,* 102 2659-2664.

[12] K. Georgogianni, A. Katsoulidis, P. Pomonis, M. Kontominas, Transesterification of soybean frying oil to biodiesel using heterogeneous catalysts, *Fuel Processing Technology,* 90 (2009) 671-676.

[13] M. A. Olutoye, B. H. Hameed, $K_yMg_{1-x}Zn_{1+x}O_3$ as a heterogeneous catalyst in the transesterification of palm oil to fatty acid methyl esters, *Applied Catalysis A: General*, 371 (2009) 191-198.

[14] B. Yoosuk, P. Udomsap, B. Puttasawat, P. Krasae, Improving transesterification acitvity of CaO with hydration technique, *Bioresource Technology,* 101 (2010) 3784-3786.

[15] P. L. Boey, S. Ganesan, S. X. Lim, S. L. Lim, G. P. Maniam, M. Khairuddean, Utilization of BA (boiler ash) as catalyst for transesterification of palm olein, *Energy*, 36 (2011) 5791-5796.

[16] M. L. Granados, D. M. Alonso, I. Sadaba, R. Mariscal, P. Ocon, Leaching and homogeneous contribution in liquid phase reaction catalysed by solids: The case of triglycerides methanolysis using CaO, *Applied Catalysis B: Environmental,* 89 (2009) 265-272.

[17] M. Kouzu, S. Yamanaka, J. Hidaka, M. Tsunomori, Heterogeneous catalysis of calcium oxide used for transesterification of soybean oil with refluxing methanol, *Applied Catalysis A: General,* 355 (2009) 94-99.

[18] D. Leung, Y. Guo, Transesterification of neat and used frying oil: Optimization for biodiesel production, *Fuel Processing Technology*, 87 (2006) 883-890.

[19] V. Jordan, B. Gutsche, Development of an environmentally benign process for the production of fatty acid methyl esters, *Chemosphere,* 43 (2001) 99-106.

[20] H. Hattori, Solid base catalysts: generation of basic sites and application to organic synthesis, *Applied Catalysis A: General*, 222 (2001) 247-259.

[21] J. Encinar, J. González, A. Rodríguez-Reinares, Ethanolysis of used frying oil. Biodiesel preparation and characterization, *Fuel Processing Technology*, 88 (2007) 513-522.

[22] N. A. A. Rahman, M. A. Olutoye, B. H. Hameed, Synthesis of methyl esters from palm (Elaeis guineensis) oil using cobalt doped MgO as solid oxide catalyst, *Bioresource Technology,* (2011).

[23] S. Baroutian, M. K. Aroua, A. A. A. Raman, N. M. N. Sulaiman, Potassium hydroxide catalyst supported on palm shell activated carbon for transesterification of palm oil, *Fuel Processing Technology,* 91 (2010) 1378-1385.

[24] M. Canakci, J. Van Gerpen, Biodiesel production from oils and fats with high free fatty acids, *Transactions-American Society of Agricultural Engineers,* 44 (2001) 1429-1436.

[25] M. A. Olutoye, B. H. Hameed, Synthesis of fatty acid methyl ester from used vegetable cooking oil by solid $Mg_{1-x}Zn_{1+x}O_2$ catalyst, *Bioresource Technology,* 102 (2011) 3819-3826.

[26] I. Atadashi, M. Aroua, A. Abdul Aziz, N. Sulaiman, The effects of water on biodiesel production and refining technologies: A review, *Renewable and Sustainable Energy Reviews,* 16 (2012) 3456-3470.

[27] A. Refaat, Biodiesel production using solid metal oxide catalysts, *Int. J. Environ. Sci. Tech*, 8 (2011) 203-221.