



Synthesis of Biodiesel from Palm Kernel Oil using Mixed Clay-Eggshell Heterogeneous Catalysts

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P A P E R I N F O

Paper history:

Received 4 April, 2016

Accepted in revised form 27 May 2016

Keywords:

Anthill
Biodiesel
Chicken-eggshell
Palm kernel oil
Transesterification

A B S T R A C T

The synthesis and characterization of clay-eggshell mixed catalysts was carried out for the transesterification of palm kernel oil using methanol as solvent. Clay from anthill and waste chicken eggshells were powdered and mixed via incipient wet impregnation in 50-50, 80-20 and 20-80% proportions of clay to eggshell on mass basis. The resulting mixtures were oven dried at 120 °C and calcined in the furnace at 900 °C for 4 hours. The uncalcined raw clay sample was characterized via the X-ray fluorescence method while the as-synthesized catalyst samples were characterized via the Fourier Transform Infrared Radiation Spectroscopy and Scanning Electron Microscopy. The performance of the as-synthesized catalysts was tested in transesterification of palm kernel oil (PKO) via a 2 level factorial experimental design optimizing four variables including reaction time, reaction temperature, methanol/oil molar ratio and catalyst loading in which case the yield was the required response. The 50-50 catalyst attained a maximum yield of 56.2% at 70 °C, methanol/oil ratio of 12:1, reaction time of 180 min, catalyst loading of 5 wt.% compared to the 65.2% achieved with the 80-20 catalyst at 90 °C, methanol/oil ratio of 12:1, reaction time of 180 min., catalyst loading of 5 wt% and the 70.7% obtained for the 20-80 catalyst at 70 °C, methanol/oil ratio of 12:1, reaction time of 180 min, catalyst loading of 3 wt%, thus, indicating mixed effect of variables as fully discussed. The developed catalysts were found to be good for biodiesel production and have the ability of improved performance.

doi: 10.5829/idosi.ijee.2016.07.03.14

INTRODUCTION

Due to the panic of probable fuel crisis that may result from the predicted near future exhaustion of crude oil, its staggering cost, and environmental worries that arise from fossil fuels burning, the pursuit for an environmental friendly substitute has intensified and in turn gained importance in recent years [1]. Fossil fuels derived from natural gas, coal and crude oil have due existence, the oxidation of these fuels has been singled out as the major wellspring of discharges that are causation agents of air contamination and global warming. These problems have engineered the pursuit for clean burning and stable cost renewable fuels [2]. In this view, triglycerides from plant oils or animal fats are reacted with a simple alcohol (commonly methanol) to obtain a fuel known as biodiesel in form of fatty acid

methyl ester (FAME) but in the presence of a proper catalyst [3].

The triglycerides used for the production of biodiesel spring from numerous types of lipids including edible oils such as coconut oil, non-consumable oils such as neem oil, waste cooking oils such as frying groundnut oil from the canteen, animal fats such as lard and sometimes from micro-organisms [4]. In Nigeria however, biodiesel has a bright future due to the cultivation of different oil plants in several regions of the country based on the weather/climatic conditions. These oil plants include oil palm (*Elaeis guineensis*) and coconut palm (*Cocos nucifera*) in the southern part, while in the northern region there is groundnut (*Arachishypogea*), soyabean (*Glycine max*), shea butter (*Sesomum indicum*) etc. In this present work however, palm kernel oil was used for biodiesel production due to its ready availability as Nigeria is rated next to Malaysia and Indonesia among

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the leading producers of PKO in the world and ahead of a host of others like Zaire, Cote d'ivoire, Colombia, Thailand etc. [5]. PKO in its pure form or recovered from spent bleaching earth (SBE), can be used as biodiesel. Several researchers have produced biodiesel from PKO by transesterification using the conventional homogenous catalysts such as potassium hydroxide or sodium hydroxide [6] but the aftermath of homogeneous processes are not usually desirable as may involve difficulties in the removal of catalysts from the reaction products, subsequently resulting in excess waste water generation and high cost [7]. As a pivotal approach to conquer such worries, heterogeneous catalysts are used as low cost replacements [8].

One of the main solid wastes generated from food manufacturing and processing plants are eggshells [9, 10]. According to Chojnacka [11], the chemical compositions (by weight) of an eggshell were found to be 94% calcium carbonate (CaCO_3), 1% magnesium carbonate (MgCO_3), 1% calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$) and 4% organic matter. It is thus possible to prepare from eggshell an active heterogeneous catalyst due to the high CaCO_3 composition, the intrinsic pore structure, and its availability in abundance. Successful experiments on the use of these waste chicken eggshells as cheap sources of CaO for use as low cost heterogeneous catalysts have been recorded [12-15].

As reported by Manut and Satit [16], raw clay has been employed in some cases as catalyst for esterification and/or transesterification reactions. To mention but a few, Prakash *et al.* [17] reported transesterification of dicarboxylic acid with a variety of alcohols using Mn⁺-montmorillonite clay as catalyst while Dubois *et al.* [18] had made biodegradable polyester through transesterification using clay as catalyst. Recently, Olutoye *et al.* [19] synthesized methyl esters/biodiesel from waste cooking oil using barium-modified montmorillonite K10 catalyst. Thus, in this study, a mixture of anthill (a form of clay) and eggshell was employed as catalyst for transesterification of PKO to produce biodiesel for use as substitute in diesel engines.

MATERIALS AND METHOD

Materials

For this study, the materials for the experiment were liquid methanol, powdered chicken eggshell, fine clay and vegetable oil (PKO). Anhydrous methanol (analytical grade, ~99.5%) was purchased from a chemical laboratory (Minna, Niger state). Refined palm kernel oil was purchased from Kure ultra modern market (Minna, Niger state). Clay was sourced from anthills situated behind the school sports field, Gidan Kwano campus, Federal University of Technology, Minna, Niger state. Waste chicken egg shells were gathered from an eatery in Bosso local government area, Minna, Niger state.

Catalyst preparation

The waste chicken eggshells were rinsed thoroughly with tap water to get rid of left over mucous, inner white membrane and impurities attached to the surfaces and then subsequently with deionized water. The shells were drained of water and sun-dried for considerable period of time. The dried eggshells were ground with a combination of mortar and pestle, and grinding stone till powdered, then passed through a sieve of 125 μm aperture on a mechanical shaker to obtain uniform particle size distribution. Similarly, the obtained clay was ground and reduced with the same method earlier stated as with the eggshell. The prepared eggshell powder and fine clay were weighed and mixed in 50-50, 80-20 and 20-80% proportion of clay to eggshell into a container (beaker). Adequate amount of distilled water was added to the mixtures to form suspensions and stirred for 2 hours on a magnetic stirrer to homogenize at least. The mixtures were then placed in a vacuum oven to dehydrate at a temperature of about 120 °C. The three different proportions of dried mixed clay-eggshell powders were thus calcined in a muffle furnace under static air conditions at a temperature of about 900°C for 4 hours.

Characterization of synthesized catalyst

The composition compounds of the fine clay (raw/uncalcined) was determined through the X-ray fluorescence method (XRF). A High Resolution Scanning Electron Microscope (HRSEM) was used on the as-synthesized catalysts to identify the surface topography or morphology. The Fourier Transform Infrared Radiation Spectrophotometry (FTIR) was used to analyze the catalysts to obtain the infrared spectrum of absorption of the functional groups present in the catalyst.

Experimental design

The optimum reaction conditions were determined via a simple 2^k factorial design. Four variables i.e reaction temperature, catalyst loading, methanol/oil molar ratio, reaction time were studied at two levels (high and low) with the required response being the yield of methyl ester/biodiesel. The low level of temperature was 70 °C and the high level was 90 °C. The high level of catalyst loading was 5% while the low level was 3% (wt% of oil mass used). The low level chosen for methanol/oil ratio was 6:1 and the high level was 12:1. The high level reaction time was 180 min and the low level was 120 min.

Transesterification of PKO with methanol

Palm kernel oil was transformed to its methyl ester via transesterification. The reaction was carried out in a batch reactor (a 250ml two way round bottom flask). For every run, 25ml of the palm kernel oil was measured with a measuring cylinder into the reaction flask. The required amount in volume of the methanol solvent was measured

with a measuring cylinder and poured into a beaker, the required amount in mass of the catalyst was as well measured from a weighing balance and added to the methanol. The beaker was covered with foil paper and the content vigorously mixed. The prepared methanol-catalyst mixture was thus added to the oil in the glass reactor. All reactants were charged into the reaction flask at room temperature. The reactor was fitted with a reflux condenser to return most part of the vaporized methanol as reactions took place at temperatures higher than its boiling point. Stirring was initiated at a reasonable speed, the maximum allowable speed by the design of the magnetic stirrer used (close to 500rpm). Stirring speed was kept constant for all experiments. The mixing of the reactants improves the conversion by promoting the rate of reaction. The aforementioned variables including methanol-oil molar ratio, reaction time, reaction temperature and catalyst loading were thus varied accordingly based on the experimental design.

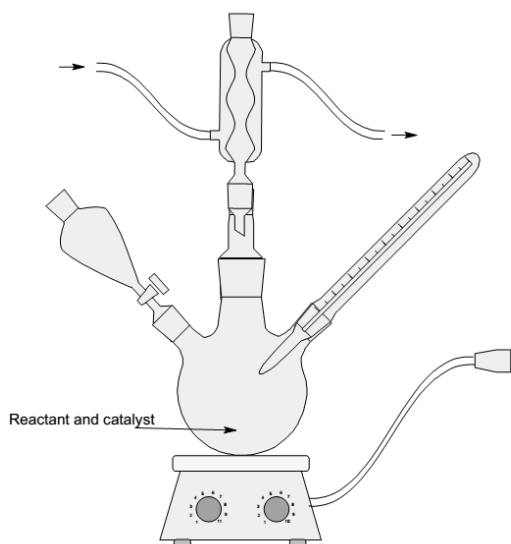


Figure 1. Experimental setup for the transesterification process

Product yield and analysis

After the reaction was stopped, the resulting mixture was cloth filtered to remove the catalyst and then poured into a separating funnel to allow to settle. The catalyst was removed as it will result in clogging at the exit of the separating funnel. After settling, the product mixture was separated into two liquid layers: crude methyl ester (biodiesel) layer above and glycerol layer at the bottom since the biodiesel layer is lighter than the glycerol layer. Unreacted methanol was seen above in cases of incomplete reaction or when in true excess. On separation from the glycerol by-product, the biodiesel was washed by adding an equal amount (to the volume of the biodiesel) of warm distilled water to it in the separating funnel, the separating funnel was swirled severally and

clamped on a retort stand for some minutes till water layer was separated from diesel layer. The water (now impure) was drained off from the bottom of the funnel. After washing, the biodiesel was dried by heating on a hot plate and the yield recorded. The yield was calculated theoretically as thus,

$$\text{Yield \%} = \frac{\text{biodiesel volume(ml)}}{\text{oil volume(ml)}} \times 100$$

RESULTS AND DISCUSSION

Catalyst characterisation

The chemical composition of the anthill (raw clay) sample were checked with the X-ray fluorescence (XRF) method and presented in Table 1 below. The result showed that the main constituents are silicon oxide (SiO_2), aluminium oxide (Al_2O_3) and iron (III)oxide (Fe_2O_3) having a percentage of 54.8, 24.7 and 12.86%, respectively with the silicate and aluminate summing up to a total of 79.5%. This observation as with respect to silicon and aluminium oxide confirms with the chemical analysis of clay and is close to the values obtained by Bhaskar and Parthasarathy [20] for kaolin clay samples.

Table 1. Chemical composition of anthill clay by X-ray fluorescence

Compound	Weight (wt %)
Aluminium oxide (Al_2O_3)	24.7
Silicon oxide (SiO_2)	54.8
Trioxosulphate (SO_3)	0.23
Potassium oxide (K_2O)	1.47
Calcium oxide (CaO)	1.97
Titanium oxide (TiO_2)	1.75
Vanadium oxide (V_2O_5)	0.085
Chromium Oxide (Cr_2O_3)	0.0096
Manganese oxide (MnO)	0.183
Iron (iii) oxide (Fe_2O_3)	12.86
Cuprum oxide (CuO)	0.023
Zinc oxide (ZnO)	0.006
Silver oxide (Ag_2O)	1.58
Europeum oxide (Eu_2O_3)	0.19
Rhenium oxide (Re_2O_7)	0.080
LOI	0.0634
Total	100

Calcium oxide (CaO), Titanium oxide (TiO_2) and Vanadium(iv)oxide (V_2O_5) are present in very small amount by weight (<2%) and have been used as high yield heterogeneous catalysts in biodiesel production as reported in literature [13, 21]. The sample was also found to contain rare metal oxides like Europeum oxide (Eu_2O_3), an inner transition element, and Rhenium oxide (Re_2O_7), a regular transition element, as well as Silver oxide (Ag_2O); these metal oxides are usually scarce and rarely found in clay samples and thus indicates a good discovery. These metal oxides are active in nature for catalysis regardless of their quantity and are suggested to

have aided the functionality of the catalyst mixture for the predefined use.

Scanning Electron Microscopy (SEM)

The surface morphology of the calcined catalysts examined by the scanning electron microscope (SEM) are shown in the Figures 2 to 4. The SEM pictures revealed that the catalysts are rough in surface and contain irregular small and large particles duely formed by the aggregation of clay on eggshell resulting from the impregnation. The roughness indicated could be attributed to the clay particles and unavoidable presence of some sand as powdered eggshell particles would rather exhibit finer texture under the microscope.

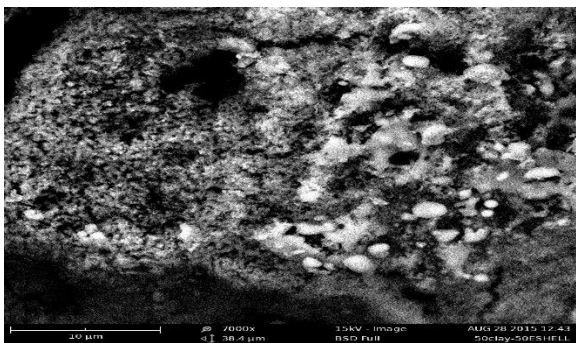


Figure 2. SEM image of calcined 50% clay- 50% eggshell catalyst

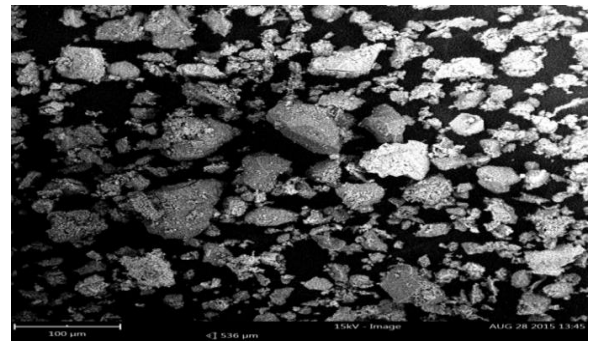


Figure 3. SEM image of calcined 80% clay- 20% eggshell catalyst

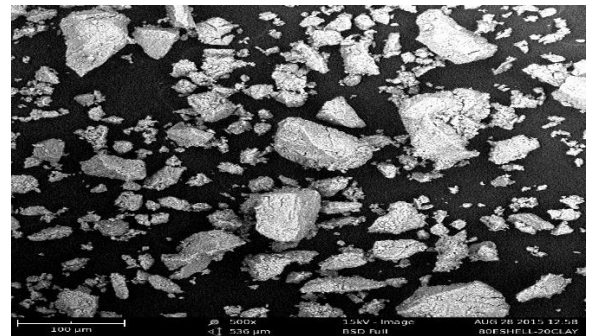


Figure 4. SEM image of calcined 20% clay- 80% eggshell catalyst

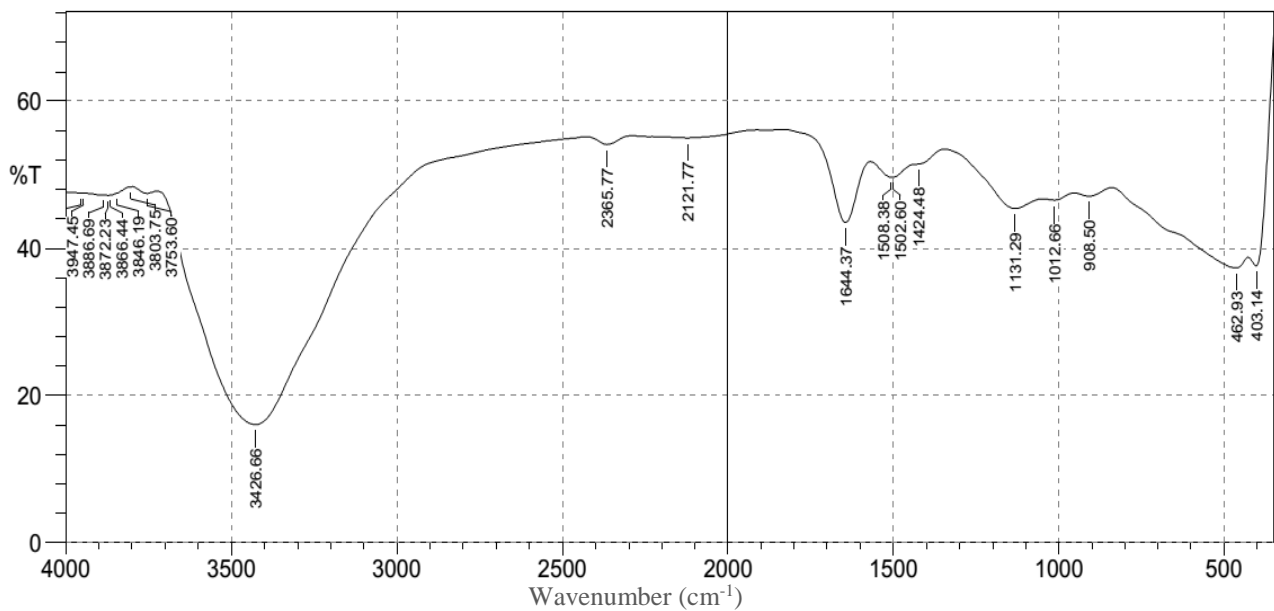


Figure 5. FTIR spectra for the 80% clay - 20% eggshell catalyst (Transmittance vs. Wavenumber)

Fourier Transform Infrared radiationspectroscopy (FT-IR)

The usefulness of quality analysis from the characteristic frequency provides information needed to identify the chemical constituents and functional groups in a substance (compound). Figure 5 shows the infrared radiation spectra (IR) of the calcined 80% clay- 20% eggshell catalyst. The absorption band between approximately 3350 cm^{-1} and 3500 cm^{-1} can be attributed to the O-H stretching from the residual or absorbed water similar to the stretching mode of external and internal hydroxyl group as also observed by Olutoye *et al.* [19]. The appearance of a trough at $2300\text{-}2500\text{ cm}^{-1}$ can be attributed to the asymmetric/symmetric stretching of the C-H bonds in the methylene groups. As well the band between 1800 cm^{-1} and 1600 cm^{-1} can be attributed to the C=O stretching of the aldehydes. The observed band at around 500 cm^{-1} was due to the Al-OH stretching vibration or the sulphate vibrational band width at 450 cm^{-1} . The presence of these functional groups contribute to the good activity of a catalyst [19] and were similar to those observed with the 50% clay-50% eggshell and 20% clay-80% eggshell catalysts (figures not shown).

Table 2. Factorial design for operating variables with biodiesel yield for 80% clay- 20% eggshell

Run	Catalyst (wt %)	Time (min)	MeOH /Oil	Temp. ($^{\circ}\text{C}$)	Biodiesel vol. (ml)	Yield (%)
1	3	120	6:1	70	10.3	41.2
2	5	120	6:1	70	10.4	41.6
3	3	180	6:1	70	12.2	48.8
4	5	180	6:1	70	9.7	38.8
5	3	120	12:1	70	14.5	58
6	5	120	12:1	70	11.3	45.2
7	3	180	12:1	70	12.7	50.8
8	5	180	12:1	70	12.9	51.6
9	3	120	6:1	90	12.5	50
10	5	120	6:1	90	12.4	49.6
11	3	180	6:1	90	12.5	50
12	5	180	6:1	90	15.4	61.6
13	3	120	12:1	90	14.9	59.6
14	5	120	12:1	90	12.1	48.4
15	3	180	12:1	90	12.7	50.8
16	5	180	12:1	90	16.3	65.2

Effect of Reaction Parameters

The result obtained on the influence of the operating parameters on the yield of biodiesel are summarized in Table 2. These effects are discussed in details below;

Effect of Reaction Temperature

From the results, it can be observed that at the maximum reaction temperature ($90\text{ }^{\circ}\text{C}$), the yields obtained were mostly above those attained at the low level of temperature ($70\text{ }^{\circ}\text{C}$). For example, 16.3 ml of the 25 ml of oil reacted was obtained as biodiesel after a run of reaction (run 16) at $90\text{ }^{\circ}\text{C}$, 12:1 methanol/oil ratio, 180 min reaction time and 5 wt% catalyst loading thus having

a theoretical yield of 65.2%. Although, other variables were also at their high levels, it can be deduced that temperature must have played a great part in this yield since a similar run (run 8) that proceeded at $70\text{ }^{\circ}\text{C}$ with other variable being the same as already stated, resulted in a 51.6% yield which is relatively low. Similar trend was observed with the other catalysts (tables not shown).

Thus, the operating temperature for heterogeneous transesterification processes (except enzymatic processes) varies depending on the activation energy and conditions to produce high yield of fatty acid alkyl esters.

Effect of Reaction Time

It was observed that even though, coincidentally, the lowest yield (38.8%) was obtained at the maximum reaction time (run 4), the yield was positively affected by the time extent of reaction in quite a number of other runs. At 5 wt.% catalyst loading, 6:1 methanol/oil ratio, $90\text{ }^{\circ}\text{C}$ reaction temperature and time of 180 min (run 12), the yield observed was 61.6%, this value of yield is the closest to the maximum yield (65.2% at run 16) obtained under the same conditions of temperature and others except the methanol/oil molar ratio. Whereas, at similar conditions to run 12, but during a 120 min (1 hour less) reaction time, the yield obtained was 49.6%, indicating time effect and overall mixed effect of variables.

Effect of Catalyst Loading

Just as is the case with other reaction parameters/variables, catalyst loading also affects biodiesel yield. This can be illustrated from the results of experiment. where unlike in the case between runs 6 and 7 where a high catalyst loading was overshadowed by the effect of time, runs 7 and 8 showed the catalyst effect. These two runs were confidently selected for illustration since all parameters except the catalyst loading were at the same condition. It was thus observed that at run 7 where 3wt% catalyst was used at 180min reaction time, methanol/oil ratio of 12:1 and temperature of $70\text{ }^{\circ}\text{C}$ a yield of 50.8% was achieved. At run 8, a yield of 51.6% was resulted at 5wt% all other conditions as with run 7 being the same, this was attributed to the effect of high catalyst loading. Similar effect was observed between runs 1 and 2 just as above but experimental results don't usually come without any flaws as catalyst loading refused to prevail between some other runs.

Effect of Methanol/Oil Molar Ratio

Molar ratio of alcohol to oil at 6:1 is determined as the standard ratio [22, 23]. Thus, ratios 6:1 and 12:1 were used, the higher ratio was observed to have a positive effect on yield as confirmed in most of the runs like run 5, 6, 7, 8, 13, 14. However, this ratio (12:1) was found to result in excess unreacted methanol after separation of products which will be wasteful unless reused. Ratio 6:1 relatively yields high at high temperature and is

recommended as the optimum for similar works of this nature.

Determination of Fuel Properties of PKO and Biodiesel Characteristics

The physicochemical and/or fuel properties of the palm kernel oil and the biodiesel produced from three catalyst ratios were analyzed and summarized in the table below.

Table 3. Physicochemical and Fuel Properties determined for Palm Kernel Oil and its Biodiesels

Properties	Palm kernel oil	Palm kernel biodiesel
Density at [25]° C (kg/m ³)	933	887 – 899
Kinematic viscosity [40]° C (m ² /s)	1.973 × 10 ⁻⁵	865 × 10 ⁵
Acid value (mg KOH/g oil)	20.68	2.36 – 2.53
Saponification value (mg KOH/g oil)	261.56	231.66 – 253.04
Free fatty acid (mg KOH/g oil)	10.34	1.18 – 1.26
Odour	Burnt smell	Light burnt
Solubility	Soluble in non polar solvents	Soluble in non polar solvents
Flash point (°C)	220	110 – 140
Cloud point (°C)	22	7 – 9
Pour point (°C)	19	11 – 12

The density/specific gravity of the biodiesel samples from the three catalysts ranged from 887-899 kg/m³ in conformance with the ASTM standard (860-900 kg/m³) and significantly lesser than the 933 kg/m³ obtained for the raw PKO sample.

The kinematic viscosities as measured for the biodiesel samples were well reduced from the value obtained for the PKO, the result showed a drop in viscosity by about 56.2% of that of the palm kernel oil, indicating the effect of alcoholysis (transesterification). The biodiesel viscosity on comparison with the ASTM standard does not meet the requirements as it does not fall within the range (3.5-5.5 mm²/s), this behaviour can be attributed to/guessed to be due to possible incomplete reaction which may have resulted from inadequate reaction temperature or low reaction time.

As obtained, the acid value for the palm kernel oil was 20.68 mg KOH/g and that of its biodiesel samples at maximum yields for the three catalysts were between 2.36-2.53 mg KOH/g, this signifies by difference that a minimum 18.15 mg KOH/g of palm fatty acid distillate was converted to biodiesel indicating a 87.77% conversion at that value.

The saponification value obtained for the palm kernel oil was 261.56 mg KOH/g. This value as seen is high indicating the reason why palm kernel oil is widely used in soap making. That of the biodiesels were between 231.66-253.04 mg KOH/g indicating only a slight drop. High soap content in biodiesel can result in abnormal combustion pattern of engines and thick smoke from the exhaust but will on the other hand enhance the sliding of rubbing parts by reducing the friction between them.

The flash point is an important safety factor considered during fuel transportation and storage. The reduction from 220 °C for the PKO to 140 °C for the biodiesel indicates an improvement in oil volatility by the transesterification. These values have met the biodiesel standards (≥120 °C) and are as well higher than that of petrol diesel signifying improved fuel characteristics.

An important criteria in determining the quality of biodiesel are the cold flow temperatures in terms of the cloud point and the pour point. This is due to the fact that at very low temperatures some oil tend to freeze, thus causing blockage of the fuel filter components of the diesel engine, subsequently depriving the engine of fuel. These properties of biodiesel depend on the molecular weight or chain length and the degree of unsaturation. The cloud and pour point of the biodiesel as measured were between 7-9 °C and 11-12 °C respectively. These properties have reduced on transesterification as shown on table 3 and were negligibly above their respective ASTM standards of ≤5 °C and ≤10 °C.

Conclusion

The major achievements in this research work is the synthesis and characterisation of mixed clay-eggshell heterogeneous catalysts and their performance testing in biodiesel production from palm kernel oil. The results of characterization as discussed showed that anthills can serve as little or no cost source of clay for use in heterogeneous catalysis, same can be said of the waste chicken eggshells. The formulated clay-eggshell catalysts showed slow but good activity in transesterification with palm kernel oil. The variation of operating variables affected the response (biodiesel yield), one important consideration is the positive effect of high temperature. Some of the physicochemical and/or fuel properties of the biodiesel produced showed conformance with the ASTM standard while some did not. Thus, the catalyst may require improvement/modifications.

Also, on the accord of the highest yields attained, the 20% clay-80% eggshell catalyst is assumed as the best proportion of the three and thus should be improved and tested/clarified with various/differing oil types.

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Persian Abstract

DOI: 10.5829/idosi.ijee.2016.07.03.14

چکیده

سنتز و شناسایی کاتالیزور مخلوط خاک رس-پوسته تخم مرغ برای تبادل استری روغن هسته خرما با استفاده از متانول به عنوان حلال انجام شد. خشت از خاکریزی که مور هنگام لانه سازی در اطراف لانه خود ایجاد میکند و زباله پوست تخم مرغ و از طریق اشباع مرطوب اولیه در ۵۰-۵۰، ۸۰-۲۰ و ۸۰-۲۰٪ نسبت خاک رس مخلوط به پوسته تخم مرغ بر اساس جرم شد. مخلوط حاصل در ۱۲۰ درجه سلسیوس خشک شده و در کوره در دمای ۹۰۰ درجه سلسیوس به مدت ۴ ساعت کلسینه شدند. نمونه خشت خام uncalcined از طریق روش فلورسانس اشعه X مشخص شد در حالی که نمونه کاتالیزور به عنوان سنتز از طریق FT-IR و SEM مشخص شد. عملکرد کاتالیزور به عنوان سنتز در تبادل استری روغن هسته خرما (PKO) از طریق یک سطح آزمایشی فاکتوریل بهینه سازی چهار متغیر از جمله زمان واکنش، دمای واکنش، متانول / نسبت مولی روغن و بارگذاری کاتالیست که در این صورت عملکرد بود مورد آزمایش قرار گرفت پاسخ مورد نیاز. زمان واکنش ۱۸۰ دقیقه، بارگذاری کاتالیست از ۵ درصد وزنی نسبت به ۶۵٫۲ درصد به دست با ۸۰-۲۰ کاتالیزور: این کاتالیزور ۵۰-۵۰ حداکثر عملکرد ۵۶٫۲٪ در ۷۰ C، نسبت متانول به روغن ۱۲٪ به دست آمد. در ۹۰ درجه سلسیوس، نسبت متانول به روغن ۱۲: ۱، زمان واکنش ۱۸۰ دقیقه، بدست آمد. کاتالیست از ۵ درصد وزنی و ۷۰٪ به دست آمده برای ۲۰-۸۰ کاتالیزور در ۷۰ C، نسبت متانول / نفت ۱۲: ۱، زمان واکنش ۱۸۰ دقیقه، بارگذاری کاتالیست از ۳ درصد وزنی، در نتیجه، نشان می دهد اثر مخلوط از متغیرهای عنوان شده به طور کامل بحث شده است.