Production of Biodiesel Using *Colocynthis Citrullus* L Oil over Green Solid Heterogeneous Catalyst

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Abstract: The production and characterization of biodiesel fuel properties obtained by means of transesterification over green solid heterogeneous catalyst with *Colocynthis citrullus* L oil was investigated. The oil was extracted from the *Colocynthis citrullus* L using normal hexane by means soxhlet extractor. The oil obtained was characterized for specific gravity, viscosity, moisture content, free fatty acid (FFA), acid, iodine, peroxide and saponification values respectively. The biodiesel was synthesized homogeneously using a three-necked round bottom flask at 333 K and the feedstock ratio of catalyst to methanol to oil is 3:10:10. The biodiesel produced was characterized for specific gravity, kinematic viscosity, flash point, American Petroleum Index (API), aniline point and diesel index, respectively. The oil obtained gave a yield of 53% and the values of the various physicochemical properties were: specific gravity (0.91 g/cm^3), viscosity (36.00 mm^2/sec), FFA (1.70 mg KOH/g), acid (3.40 mg KOH/g), iodine (120.00 g/100g), peroxide (8.00 mmol O_2/g) and saponification (191.00 mg KOH/g), respectively. These values were within recommended limits of American Standard for Testing Material (ASTM D6751). The saponification value obtained showed that the oil contained a reasonable proportion of fatty acids. The result revealed that biodiesel produced showed the following properties in the value of viscosity (1.025 mm^2/sec), specific gravity (0.83 g/cm^3), API (40.00^{o}C), flash point (65^{o}C), aniline point (87^{o}C) and diesel index (66.40) respectively. The result showed that the properties of biodiesel produced were relatively close to the ASTM D6751. This study has shown that green solid catalyst (kaolin clay) can be used in the production of quality biodiesel which is an alternative to fossil fuel.

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1. Introduction

Biodiesel as an alternative fuel is becoming increasingly relevant due to diminishing petroleum reserves and adverse environmental consequences of exhaust gases from petroleum composed engines (Guara-Cho et al., 2009). This alternative source of fuel can be obtained from the transesterification of vegetable oils with simple alcohol (Shawn, 2006). The transesterification of plant oils with methanol involves relatively simple processes that yield high conversion with only glycerol as a by-product. Research is being conducted globally to use glycerol as a chemical precursor. The refined glycerol can be utilized directly or converted into other products. This is one the ways of diversifying the economy of any given nation and equally creating employment opportunities for the teaming youths.

Transesterification is also a renewable source of energy that can help reduce green house gas emission. The advantages of the application of biodiesel have been demonstrated by Sheehan et al., (1998). He reported that using pure diesel in urban buses result in substantial reductions in life cycle emissions of total particulate matter, COx and SOx by 32%, 35% and 8% respectively relative to petroleum diesels life cycle.

Currently, diesel engines have become the engine of choice for power, reliability and high fuel economy globally. The diesel engine was developed out of the desire to improve upon inefficient, cumbersome and sometimes dangerous steam engines of the late 18th century (Pahl, 2005). The choice of a particular raw material for the production of biodiesel should be centered on the economics, kinetics and thermodynamic feasibilities (Alumudena, 2007).

Biodiesel can be used in pure form (B100) or can be blended with petro-diesel in the form of B2 (2% biodiesel and 98% petro-diesel), B5 (5% biodiesel and 95% petro-diesel) and B20 (20% biodiesel and 80% petro-diesel). Biodiesel has helped several countries in reducing their dependence on foreign oil reserves as it is domestically produced and can be used in any diesel engine with little or no modification to the engine or the fuel system.

The recovery of biodiesel from the reactor using homogeneous liquid catalysts has proved not to be economically viable. Therefore, biodiesel synthesis using heterogeneous solid catalyst could potentially lead to economical production costs due to possibility of reuse of the catalyst (Suppes et al., 2004; Helwani et al., 2009; Obi, 2016).

The methanol used in most biodiesel production processes is made using fossil fuel inputs. However, there are other sources of renewable methanol made by using CO_2 or biomass as feed stocks, making their production processes free of fossil fuels.

Kaolin used in this study is a clay mineral that makes up the group of industrial materials with the chemical composition $Al_2Si_2O_5$ (OH_4). It is a layered silicate mineral with one tetrahedral sheet of silica (SiO_4) linked through oxygen atoms to one octahedral sheet of alumina (AlO_6). It has wide applications ranging from industrial, domestic, paints, refining, pharmaceutical to cosmetics. It is an environmentally benign alumino-silicate mineral that is insoluble in water. The clay serves as the source of the proton (H^+) which is acidic that functions as catalyst by protonation and deprotonation of surface hydroxyls (Stumm, 1987) as represented in equations 1 and 2 below:

$$AOH_2^+ \rightarrow AOH + H^+ \ldots\ldots\ldots\ldots\ldots\ldots 1$$

$$AOH \rightarrow AO + H^+ \ldots\ldots\ldots\ldots\ldots\ldots 2$$

Where A represents the clay.

Melon seed (*Colocynthis citullus* L.) is a cucurbit crop that belongs to the cucurbitaceous family with fibrous and shallow root system (Ogbonna, 2013). Melon seed popularly known as egusi is widely used among the Igbo people of South Eastern Nigeria, the Ibibio people, the Efik people, the Hausas, the Yorubas, Esan people and Etsako people of the South West of Nigeria. The melon seed is the biological ancestors of the water melon now found all over the world (Lloyd, 1898). The seed is defined as fat and protein rich (Zohary and Hopf, 2000). The oil extracted from the melon seeds can be used for cooking and other applications.

Due to the improper and prolonged non-usage of the oil obtained from *Colocynthis citrullus* L. despite its huge potential and some operational problems encountered using biodiesel have been the focus of this study for utilization and maximization.

Therefore, this study is aimed at utilizing catalytic effects of kaolin clay with *Colocynthis citullus* L. oil in the production of biodiesel.

2. Material and Methods

The melon seeds were bought from Choba daily market in Obio/Akpor Local Government Area of Rivers State, Nigeria. Impurities were removed by winnowing, hand picking and sieving before the seeds were subjected to further processing. The shelled melon was sun-dried for 2-3 days and oven-dried at 120°C until constant weight was obtained. The seeds were further stored in polyethylene bags. The seeds were ground using electric grinder and stored for extraction.

The clay sample used in this study was collected from Ogwuta (Isi Ogo) cave of Unwana new site in Afikpo North Local Government Area of Ebonyi State, Nigeria. The physicochemical properties and the vibrational bands of the functional groups have been characterized by Obi and Agha, (2016) and presented in Tables 2-4.

All the reagents used in this study are of analytical grade.

The oil was extracted from the melon seeds using normal hexane by soxhlet extractor. The percentage yield of the oil obtained was calculated using the expression below:

$$\%\ \text{Yield} = \frac{\text{Weight of oil obtained}}{\text{Weight of sample}} \times 100 \ldots\ldots\ldots 3$$

The oil obtained was characterized to determine the moisture content, acid value, saponification value, peroxide value, iodine value, specific gravity and viscosity (Onwuka, 2005).

The green solid heterogeneous catalyst (15 g) was added to 50 ml of methanol. The mixer was agitated for 4 hrs and then filtered. The residue (catalyst) was washed severally with water and kept for reuse. The filtrate (methoxide) was poured into a 250 ml conical flask (reactor vessel) which was tightly corked throughout the process to limit evaporation of methanol and absorption of moisture by the mixture. The transesterification reaction was carried out in a three-necked 250 ml round bottom flask fitted with a thermometer and was inserted into a hot water bath and the temperature kept at 333 K. At 333 K, 50 ml of the melon seed oil was added to the vessel containing the methoxide and was stirred continuously for 20-25 mins. Then the mixer was transferred into a 20 ml reagent bottle and allowed to stand for 24 hrs. At the end, the biodiesel was separated from the glycerol using a separating funnel for 1-2 hrs. The glycerol being the heavier liquid was collected at the bottom while the lighter liquid (biodiesel) was further washed with warm water. The washing was repeated three (3) times. The biodiesel was later collected in a beaker and the remaining water trapped in the biodiesel was heated off. The biodiesel obtained was further characterized for aniline point, American Petroleum Index (API) gravity, flash point, kinematic viscosity, specific gravity and diesel index.

3. Results

The use of normal hexane in the extraction gave a yield of 53%. The results of other parameters characterized are presented in Table 1.

Table 1. Physicochemical properties of melon seed oil obtained in this study

Parameter	Values obtained	ASTM (D6751)
Color	Yellowish	-
Specific gravity (g/cm^3)	0.91	0.88
Moisture content (% wt)	2.60	0.005 max
Viscosity (mm^2/sec)	36.00	1.90-6.00
Acid value (mg KOH/g)	3.40	0.50 max
Free fatty acid (g/100g)	1.70	-
Peroxide value (mmol O_2/g)	8.00	-
Iodine value (g/100g)	120.00	-
Saponification value (mg KOH/g)	191.00	-
Percentage yield (%)	53	-

Table 2. Physical properties of clay used in this study

Parameters	Values obtained
pH	2.8
Surface Area	133.4m^2/g
Specific gravity	2.16g/cm^3
Pore Volume	0.45m^3/g
CEC	18.8meq/100g

Table 4. Vibrational bands of the clay used in this study

S/N	Band(cm^{-1})	Assignment
1	3695.61	Al-OH: Structural hydroxyl group of Kaolinite.
2	3655.11	Al-OH: Structural hydroxyl group sretching in Montmorillonite.
3	3620.39	Inter octahedral Al-OH stretching for kaolinte.
4	3527.80	H-O-H: Stretching from water molecule in Kaolinite.
5	3392.79	H-O-H: Stretching of water molecule from montmorillonite.
6	1647.21	OH: deformation of water.
7	1618.28	OH deformation in smectite.
8	1124.50	Si-O: stretching in smectite.
9	1006.84	Si-O: in-plane stretching characteristic of kaolinite.
10	904.61	OH: deformation of inner surface hydroxyl group (Al-OH-Al)
11	790.81	Si-O: stretching in quartz.
12	694.37	Al-O-Si: stretching.
13	559.26	Al-O-Si: stretching in hematite.

Table 5. Biodiesel properties obtained in this study

Parameter	Values obtained	ASTM (D6751)
Specific gravity (g/cm^3)	0.83	0.88
Kinematic viscosity (mm^2/sec)	1.03	1.90-6.00
API gravity	40.00	-
Flash point (^oC)	65.00	100.00-170.00
Aniline point (^oC)	87.00	-
Diesel index	66.40	-

Table 3: Metal oxide compositions of the clay used in this study

Element	Concentration (mg/L)	% Oxide composition
Al	159.593	32.601
Si	232.431	47.380
Mg	14.320	2.919
Ca	5.902	1.203
Na	7.952	1.621
K	1.006	0.205
Fe	10.454	2.042
Ti	0.643	0.131
LOI	-	11.409

*LOI – Loss on Ignition

4. Discussions

The percentage yield obtained was in close agreement with other reported data on melon seed oils (Oluba et al., 2008). The oil obtained was observed to be yellowish in color. The moisture content (2.6 % wt) was found to be higher than the American Standard of Testing and Materials (ASTM) acceptable limits. This is an indication that the melon seed was not completely dried and might lead to microbial attack (rancidity). The specific gravity was found to be 0.91 g/cm^3 which implied that the seed oil was less dense than water. The viscosity (36.00 mm^2/sec) was found to be higher than ASTM acceptable limits indicating that the oil was thick. Reports showed that this value was higher than most drying oils (Akintaya et al., 2002). The acid value (3.40 mg KOH/g) was low in relation to the values reported for tropical almond (7.6 mg KOH/g) and close to the value reported for fluted pumpkin (3.5 mg KOH/g) (Christian, 2006). This value equally indicated that the oil obtained is edible (Oluba et al., 2008). The iodine value (120.00 g/100g) obtained was in agreement to those of unsaturated fatty acid-rich oils such as cottonseed oil (100.00-123.00 g/100g), sesame oil (104.00-120.00 g/100g) but lower than that of soya bean oil (124.00-139.00 g/100g) (Aremu et al., 2006). On the other hand, this value obtained in this work was higher than those of saturated fatty acid-rich oils such as cocoa butter (32.00-42.00 g/100g) and palm oil (50.00-55.00 g/100g) (Ige et al., 1984; Aremu et al., 2006). The peroxide value was found to be 8.00 mmol O_2/g of oil. This value was higher than the values reported for bauchiniaracemora (4.900 mmol O_2/g) (Amoo and Moza, 1999). The higher value observed could be due to prolonged exposure of the seeds to drying (either sun-drying or oven-drying) thereby causing lipid oxidation resulting from the absorption of oxygen which increased the formation of peroxides. The saponification value obtained was 191.00 mg KOH/g which is in agreement with values obtained for some vegetable oils (188.00-196.00 mg KOH/g) (Pearson, 1976). The researcher in his work noted that oils with high saponification values contain high proportion of lower fatty acids.

The physical properties, metal oxide compositions and vibrational bands of the clay catalyst used in this study are presented in Tables 2-4.

The characterization of biodiesel obtained from the egusi oil over green solid heterogeneous catalyst is presented in Table 5. It was observed that the properties of the biodiesel are relatively close to ASTM D6751 standard. The results of the characterization showed that fatty acid content will not cause operational problems such as corrosion and pump plugging.

The kinematic viscosity (40.00 mm^2/sec), flash point (65^{o}C) and API (39.66^{o}C) for the biodiesel are all within the ASTM specification. The closeness of the results obtained to ASTM could be because of the structural framework of the kaolin clay used as the green solid heterogeneous catalyst. The viscosity is the most important property of biodiesel since it affects the operation of fuel injection particularly at low temperature where the increase in viscosity affects the fluidity of the fuel. This parameter is also useful for evaluating the methyl and ethyl ester contents of biodiesel samples since there is a correlation between the content of esters and the viscosity. The higher the viscosity, the lower the ester content (Candeia et al., 2009). The viscosity of the biodiesel produced in this study showed higher value than the petrol diesel fuel (Soha and Nour, 2013). In addition, the flash point value of the biodiesel is much lower than those of vegetable oils (Ayhan, 2006). The flash point of biodiesel is the temperature at which the fuel becomes a mixture that will ignite when exposed to flame. This parameter is related to the amount of unconverted triglycerides or a low content of monoalkyl esters. It is known that high flash point ensures more safety in handling, transportation and storage (Candeia et al., 2009). Aniline point obtained was higher than the value obtained by Soha and Nour, (2013) using microalgae Spirulina platensis. However, the diesel index is in close agreement with their work.

Conclusion

This study has shown that green solid heterogeneous catalyst (kaolin) can be a potential environmentally friendly precursor for the production of biodiesel. The oil extracted from the melon seed gives a percentage yield of 53% which is an indication of suitability for biodiesel production. The study indicates that the optimum condition for biodiesel production is in the ratio 3:10:10 of catalyst, methanol and oil at 333 K.

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