OPTIMIZATION OF BIODIESEL PRODUCTION FROM SHEAR BUTTER OIL RESIDUE USING OVAT METHOD

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ABSTRACT
The challenges faced with biodiesel production from oils having high free fatty acid (FFA) content necessitates this research. In this study, biodiesel production from shear butter oil residue (SBOR) was optimized using one variable at a time (OVAT) method. The parameters investigated are catalyst concentration (.0 M – 2.5 M), reaction time (15 min – 75 min) and methanol: oil (SBOR) molar ratio (3:1 – 7:1). The optimum catalyst concentration, reaction time and methanol to SBOR molar ratio were obtained as 1.5M, 45min and 6:1. SBOR conversion as well as biodiesel yield were obtained as: 93.8% and 89.7% at methanol :SBOR of 6:1; 94.0% and 90.6% at catalyst concentration of 1.5M and 93.8% and 89.7% at reaction time of 45 min. This implies that alcohol: oil molar ratio (methanol: SBOR) is the most influential variable on the SBOR conversion as well as biodiesel yield. The essential parameters and the physicochemical properties measured conform to ASTM D6751 standard.

Keywords: *Optimization, OVAT method, SBOR, esterification, transesterification*

INTRODUCTION
Over the years, depletion of natural resources and increased human population as well as environmental pollution are serious challenges confronting the world today due to prolonged use of fossil fuel. Therefore to improve energy security for economic development, it is imperative to search for an alternative fuel that is devoid of the problems faced with fossil-diesel. The emergence of biodiesel as one of the topmost potential renewable energy to adequately replace fossil derived diesel was globally embraced. This is because it is found to be a promising, nontoxic and biodegradable substitute of fossil fuel. (Babajide, 2010)
The consistent use of refined vegetable oils for biodiesel production is commercially impractical due to the high cost of feedstock (which reflects on the final product

biodiesel) and undue competition with food resources. This situation poses a potential threat to the sustainability of the biodiesel industry (Fukuda, 2001)

The maximum global energy with respect to petroleum coupled with the decrease in petroleum reserve and increased interest in saving the environment from pollution has jeered up interest in the search for alternative sources of fuel. Among the identified available alternatives are the biofuels. Nigeria as a country has a great potential for this through varieties of sources. These sources include oil palm, neem, used vegetable oils, biogas, animal fats and tree borne oil seeds such as Shea butter and many others. Among biofuels, biodiesel is gaining worldwide acceptance as a solution to energy problems (Demirba, 2005)

Another alternative fuel for diesel engines is biodiesel which is produced by the chemical reaction of a vegetable oil or animal fat with an alcohol such as methanol. The whole process of biodiesel production is known as transesterification in which the reaction requires the presence of a suitable catalyst, usually a strong base or acid such as potassium or sodium hydroxide as the base catalyst and sulphuric acid as the acidic catalyst, an alcohol such as methanol, ethanol, propanol and butanol. New chemical compounds are called methyl esters are obtained together with other by products mainly glycerol. (Garpen & Canakei, 2000).

Biodiesel, because of its similarity in properties to that of conventional diesel can be blended with any ratio to that of its counterpart or used directly with no modification to existing diesel engines. Among the various vegetable oil sources, non-edible oils are suitable for biodiesel production because of their abundance and relatively cheaper price (Atadashi & Arova, 2012)

The major advantage of biodiesel is that it has excellent lubricating properties thus ensuring longer engine life, it provides a market for excess production of edible vegetable oil and animal fats and eliminates wastage of non-edible ones. Biodiesel is biodegradable and its exhaust emissions are lower compared with petroleum diesel fuel. Biodiesel is derived from domestic resources thus reducing overdependence on imported petroleum and indirectly helps in preserving it (Atabani *et al.*, 2011).

Amidst a host of available oil sources – coconut, citrus, palm kernel, linseed, rapeseed, sunflower, olive, soyabean, etc. – shea butter obtained from shea tree (*Vitellaria paradoxa*) available in the wooded savannah of West Africa (of which Nigeria is inclusive) was used for this research. It is cheap oil, mostly used for skin treatment owing to a great amount of unsaponifiables, with a relatively low FFA value, which are suitable properties for biodiesel production () .

Quite a few researches have been undertaken to investigate biodiesel production from shea butter oil. Galadima and Garba (2009), used sodium hydroxide as catalyst with ethanol to produce FAEE from shea butter oil. With an alcohol to oil ratio of 6:1, reaction of time of 2 hours and temperature of 40°C, FAEE Biodiesel was produced with a yield of 92.8%.

Enweremadu and Alamu (2010), used the two-step acid-alkali catalyzed method to produce biodiesel from shea butter using methanol, sulphuric acid and potassium hydroxide at 55°C for an hour (for each step). Biodiesel produced had a FAME content of 95.21% and conversion of 92.3%. Investigations also showed that ester yield increased with increase in alcohol-oil ratio up to a 6:1. Optimum catalyst concentration was found to be 1.0%wt and optimum temperature at about 62°C.

This study is aimed at synthesizing and characterizing biodiesel from shear butter oil reside which has always been regarded as a waste. This will go a long way towards changing waste to wealth and will also serve as environmental control measure.

MATERIALS AND EQUIPMENT

Reagents and Materials used

All reagents/chemicals used in the course of this study were used as purchased. The SBOR was obtained from Kutigi in Niger state. Sodium hydroxide, hydrochloric acid, methanol, propan-2-ol and phenolphthalein indicator were all obtained from chemical engineering laboratory of Kaduna polytechnic, Kaduna.

Pretreatment

The SBOR was melted and filtered to remove impurities; thereafter, the water content in the oil was removed by heating it to a temperature of 120°C until constant weight was achieved.

Esterification of Shear butter Oil Residue

The reaction was carried out in a three-necked round bottom flask connected with a reflux condenser, a thermometer and a stopper. The pretreated SBOR was reacted with methanol in the ratio 1:2 using H_2SO_4 as catalyst at 50°C and 120 rpm. After 6h, the esterified oil was analyzed for FFA and subsequently collected for the transesterification.

Transesterification of Shear butter Oil Residue

The esterified shear butter oil residue (ESBOR) was transesterified using Methanol (solvent) and NaOH (catalyst) to synthesize shear butter biodiesel at varying reaction time ranging from 15, 30, 45, 60 and 75 min; catalyst concentrations of 0M, 1M, 1.5M, 2.0M and 2.5M and methanol to ESBOR molar ratios of 3:1, 4:1, 5:1, 6:1 and 7:1

respectively. The shear butter biodiesel obtained was cooled and allowed to settle for 24 h in a separating funnel; after which it was separated from the glycerol.

RESULTS AND DISCUSSION

Results

Table 1: Effect of Time

S/N	Quantity of Oil (g)	Molar ratio	Quantity of Catalyst (NaOH)	Time (min)	Percentage (%) Conversion	Percentage (%) Yield
1	5	6:1	1.5	15	78.4	63.2
2	5	6:1	1.5	30	91.4	83.2
3	5	6:1	1.5	45	93.8	89.7
4	5	6:1	1.5	60	83.6	72.1
5	5	6:1	1.5	75	83.1	71.8

Table 2: Effect of Catalyst Concentration

S/N	Quantity of Oil (g)	Molar ratio	Quantity of Catalyst (NaOH)	Time (min)	Percentage (%) Conversion	Percentage (%) Yield
1	5	6:1	0.0 M	30	48.0	33.6
2	5	6:1	1 M	30	61.2	56.4
3	5	6:1	1.5 M	30	94.0	90.6
4	5	6:1	2 M	30	91.3	88.4
5	5	6:1	2.5 M	30	86.2	79.1

Table 3: Effect of Molar ratio

S/N	Quantity of Oil (g)	Molar ratio	Quantity of atalyst (NaOH)	Time (min)	Percentage (%) Conversion	Percentage (%) Yield
1	5	3:1	1.5 M	30	81.0	73.2
2	5	4:1	1.5 M	30	87.4	82.6
3	5	5:1	1.5 M	30	91.2	87.4
4	5	6:1	1.5 M	30	96.0	91.3
5	5	7:1	1.5 M	30	90.7	86.6

Table 4: Properties of Biodiesel produced at optimum conditions and comparison with standards

S/N	Properties	SBOR biodiesel	ASTM Standard
1	Density g/cm^3	886.3	0.85
2	Specific gravity	0.8863	0.82-0.845
3	Kinematic viscosity mm^2/s	4.76	1.9-6.0
4	Flash point (°C)	161.3	100-170
5	Cloud point (°C)	-18	-15 to -30
6	Pour point (°C)	-10.2	-35 to -15
7	Peroxide value	12	
8	Color	Golden yellow	
9	Acid value (mg KOH/g)	0.62	0.59
10	Free fatty acid (mg/g)	0.72	0.67
11	Saponification value (mg/g)	191.55	187.93
12	Iodine value (gI_2/100g)	106.59	112.45
13	Refractive Index	1.621	1.664
14	Cetane number	50.52	40-55

Discussion of Results

In this study, one variable at a time (OVAT) method was used to determine the effect of reaction time, catalyst concentration and methanol: SBOR on the SBOR conversion and biodiesel yield. Prior to the transesterification process, the FFA content of the SBOR was reduced by esterification using sulphuric acid (H_2SO_4) from a high value of 6.76% to 0.93% which is within the acceptable standard limit of <1% (Meher *et al*, 2006).

Reaction time was investigated within the range of 15 min to 75 min. The optimum reaction time was found to be 45 min, where the SBOR conversion as well as shear butter oil residue biodiesel yield was greater. SBOR conversion as well as SBOR biodiesel yield were obtained as 89.7% and 93.8 % respectively. The SBOR biodiesel obtained at this time was also observed to have less glycerol compared to others obtained at the various reaction times investigated. This implies greater selectivity towards SBOR biodiesel formation.

Catalyst concentration was investigated within the range of 0 M (where catalyst was not added) to 2.5 M. The SBOR conversion as well as the biodiesel yield were low without the application of catalyst. However, there was significant increase in both the SBOR conversion as well as the biodiesel yield from 48% to 61.2% and from 33.6% to 56.4% respectively when 1M of the NaOH was added. The optimum catalyst concentration was obtained as 1.5M at which the highest SBOR conversion as well as SBOR biodiesel yield of 94% and 90% were obtained. This implies that the activation energy was lower at 1.5 M and the reaction went into completion earlier and at higher amount. At a higher catalyst concentration above 1.5 M, a decline in SBOR conversion as well as SBOR biodiesel yield was observed. The excessive use of catalyst led to the formation of complexes which resulted into high viscosity of the SBOR biodiesel and more slurries within the product (Canalcci &Van, 2012).

The methanol: SBOR molar ratio was investigated at ratios of 3:1, 4:1, 5:1, 6:1 and 7:1. The methanol: SBOR molar ratio of 6:1 was obtained as the optimum value, giving rise to the highest SBOR conversion as well as SBOR biodiesel yield of 96.0% and 90.3% respectively. The excess methanol tend to shift the equilibrium to the right according to (Le Châtelier, 1884) and more of the oil SBOR is converted until an equilibrium is reached. Further increase of the alcohol: oil molar ratio led to reduction in the conversion and yield respectively. This shows that at higher molar ratios, the methanol rate no longer favour the conversion of the SBOR. It is glaring that the reaction could be limited by the bulk transport of the methanol to the SBOR phase (Dossin *et al.*, 2006).

Comparing the three variables investigated in the transesterification reaction, it was observed that the methanol: SBOR molar ratio displayed a higher influence on the SBOR conversion as well the biodiesel yield. This was followed by catalyst concentration and then reaction time. This order conform to the results obtained by (Birla & Singh, 2012).

The physicochemical properties of the SBOR biodiesel were determined and all conform to or fall within the range of American Society for Testing and Material Standard (ASTM D6751).

The color observed on the product was golden yellow, which is one of the many colors of biodiesel and it has a characteristic sweet smell which is common in biodiesels

CONCLUSION

Based on the study conducted on the production of biodiesel from Shea butter oil residue, it can be concluded that the optimum SBOR conversion as well as biodiesel yield were obtained at methanol: SBOR molar ratio of 6:1, catalyst concentration of 1.5 M and reaction time of 45 min. The methanol: SBOR molar ratio displayed a higher influence on the SBOR conversion as well as the biodiesel yield. The essential parameters as well as the physicochemical properties measured conform to ASTM D6751 standard.

REFERENCE

Atabani, A. E,.Silitonga, A. S., Badruddin, I.A., Maahlia, T.M.I,. Masjuki, H.H. & Makhilef, s. (2012). A Comprehensive Review on Biodiesel as Alternative Energy Source and its Characteristics. Renewable and its Characteristics. Renewable and Sustainable Energy Reviews. 16:2070.2093

Atadashi, I.M. Arova (2011). Refining Technologies for Purification of Crude Biodiesel. Applied Energy, 88: 4239-4251.

Babajide, O.,Petrik, (2010). Use of Coal Fly Ash as a Catalyst in the Production of Biodiesel. Petroleum & Coal, 52(4): 261-272

Birla, A., Singh B. (2012).Kinematics Studies of Synthesis of Biodiesel from Waste Frying Oil Using Heterogeneous Catalyst derived from Snail Shell. Bioresources Technology 106:95 – 100.

Canalcci, M.& Van Garpen, L.(2012). Biodiesel Production from Oils and Fats with High Free Fatty acis, Transaction of the ASAE,44(6): 1429-2849.

Demirba, A. (2005). Biodiesel Production from Vegetable Oils via Catalytic and Catalytic Supercritical Methanol Transesterification Methods. Progress in Energy and Combustion Science, 31: 466-487

Dossin, T. F., Reyniers, M. F., Berger, R. J. and Marin, G. B. (2006). Simulation of heterogeneously MgO catalyzed transesterification for fine-chemical and biodiesel industrial production. *Applied Catalysis B: Environmental*. 67(1), 136-148.

Alamu O.J., Enweremadu C.C., & Alamu O.J., *Development and Characterization of Biodiesel from Shea Nut Butter***,** International Agrophysics, 2010, 24, p. 29-34.

Fukuda, H., .kondo, A. & Noda, H. (2001). Biodiesel fuel Production by Transesterification of Oils Journals of Bioscience and Bioengineering, 92 (5): 405-416.

Galadima A., Garba Z. N., *Catalytic Synthesis of Ethyl Ester from some common oil,* Science World Journal, 2009, 4(4), p. 1-5.

Garpen, J. and Canakei, M. (2000). Biodiesel Production from Oils and Fats with High Free Fatty Acids. *Am. Soc. Of Agricultural Eng*. 44, 1429-1436.

Meher, L.C., Vidyasugar, D. & Naik, S.N. (2006). Technical Aspects of Biodiesel Production by Transesterification. Renewable and Sustainable Energy Review, 10: 248-268.