



EVALUATION OF PHYSICOCHEMICAL PROPERTIES OF BIODIESEL PRODUCED FROM SOME VEGETABLE OILS OF NIGERIA ORIGIN

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ABSTRACT

The non-edible vegetable oils of Jatropha curcas, neem, castor, rubber and edible oils of soyabean and cotton were investigated for their use as biodiesel feedstock. The analysis of different oil properties, fuel properties of non-edible and edible vegetable oils were investigated in detail. A two-step and transesterification process was used to produce biodiesel from high free fatty acid (FFA) non-edible oils and edible vegetable oils respectively. This process gives yields of 96.1 – 98.5 % of biodiesel using potassium hydroxide (KOH) as a catalyst. The fuel properties of biodiesel produced were compared with diesel. The properties of the oils analysed showed that biodiesel from non-edible and edible vegetable oil are comparable with ASTM biodiesel standards and is quiet suitable as an alternative to diesel.

Keywords: Biodiesel, Edible oil, Non Edible oil, Transesterification.

INTRODUCTION

Energy is the main driver of socio-economic growth of any nation. It plays a vital role in the overall frame work of development worldwide. Energy is an indispensable commodity and all aspect of human activities is hinged to it. The operations of our Technological Society depend upon the production and use of large amount of energy. Nations are fast developing industrially and in social status, as a result, more individuals own cars, trucks, heavy duty machines, power generating plants and other forms of mechanical devices which operate from one form of fuel or the other, this brings about an exponential increase in the use and demand for fuel in terms of transportation, mechanized agriculture and power generation. The sources of fuel to run these engines have so far been extracted from our stock of fossil fuel such as crude oil and to a lesser extent coal and natural gas, all of which are finite and environmentally intolerable (OPEC Bulletin 1994).

There is already growing concern worldwide about global warming due to the emission of greenhouse gas and other environmental hazards associated with the production and consumption of fossil fuels. Thus there is the need to move away from any activities and processes that may endanger global climate stability. On this note, renewable energy source becomes the alternative energy candidate for the world energy need and utilization without hazardous effect (Akinbami 2001).

Vegetable oil is one of the renewable fuels that have become more attractive recently because of its environmental benefits and the fact that it is made from renewable resources (Ma and Hanna, 1999; Ramadhas *et al.*, 2004). Vegetable oils are a renewable and potentially inexhaustible source of

energy with energy content close to diesel fuel. The fuels were not acceptable because they were more expensive than petroleum fuels. However, with recent increases in petroleum prices and uncertainties concerning petroleum availability, there is renewed interest in vegetable oil fuels for diesel engines (Demirbas, 2003). According to Jeong *et al.* (2009), there are two principal considerations in the cost of biodiesel production: the cost of raw materials (oil and alcohol) and the process operation. The cost of raw materials represented approximately 60 -75% of the total cost of biodiesel production (Ma and Hanna, 1999). In this study the feedstocks employed were four non edible oils (Jatropha carcus, Castor, Neem and Rubber seed oils) and two edible (Soya bean and Cotton seed oils) which are relatively cheap, thereby keeping the total cost of production economically attractive.

Exploring new energy resources, such as biodiesel fuel, is of growing importance in recent years. Biodiesel is recommended for use as a substitute for petroleum diesel mainly because it is a renewable, domestic resource with an environmentally friendly emission profile and is readily available and biodegradable (Zhang *et al.*, 2003). Hence, this paper evaluates the properties of biodiesel produced from vegetable oils of selected plants seeds.

MATERIALS AND METHODS

Sources of the sample seeds

The studied plant seeds were collected from different places within the Northern part of Nigeria. Castor seed (*Ricinus communis*), neem seeds (*Azadirachta indica*), and Soya bean (*Glycin max*) were collected dry from Kontagora, Niger state.

Cotton seed (*Gossypium hirsutum*) from Zaria (Jos Road), while *Jatropha* seed (*Jatropha curcas*) and Rubber seeds (*Hevea brasiliensis*) were obtained from National Research Institute for Chemical Technology Zaria.

Sample preparation and oil extraction

The seeds collected were cleaned by removing foreign materials such as ticks, stains, leaves, other seeds, sand and dirt. After cleaning, the seeds were dried in the oven at 50°C for 72 hours until constant masses were obtained. The dried seeds were then mechanically dehauled to remove the seed coat. Removal of the seed coat is imperative because the seed coat contains little or no oil and more importantly inclusion would make extraction less efficient. The dehauled seeds were further dried at 50°C for another 48 hours and ground to powder using mortar and pestle.

The oil was extracted separately from each type of seeds using Soxhlet extractor with n-hexane as a solvent. The percentage oil yield and free fatty acid level were determined.

Transesterification of oils

In the transesterification of the oils two step processes was adopted as follows:

First step: Acid esterification

Acid esterification method using Paratoluene sulphonic acid (PTSA) and methanol was adopted to reduce the high free fatty acids (FFA) level to less than 2% prior to alkaline transesterification. In the esterification set-up, 1000cm³ capacity conical flask was used as a laboratory scale reactor for the purpose of this experiment. A hot plate with magnetic stirrer arrangement was used for heating and stirring the mixture in the flask. The mixture was stirred at the speed of 300rpm for all tests runs. The temperature was maintained at 60°C and 1 hour reaction time.

650g of the pretreated oil was measured into 1000cm³ conical flask (that serves as laboratory scale reactor), 10% paratoluene sulphonic acid (PTSA) was added to 20% methanol and stirred until it is completely dissolved. The homogeneous mixture of methanol and PTSA was then poured into preheated oil in the reactor. Heating and stirring was allowed to continue for 1 hour reaction time. On completion of the reaction, the product was poured into a separating funnel for the separation of excess methanol, PTSA, water and other impurities which move to the upper surface of the separating funnel, and the lower layer comprising esterified oil was separated as feedstock for alkaline transesterification in the second step.

Second step: Alkali transesterification

After removing the impurities of the product of first step (esterification), the oil was transesterified to mono-esters of fatty acids using potassium hydroxide as catalyst. Bench scale transesterification reaction to produce clean biodiesel was carried out in 1-litre capacity conical flask (reactor).

500g of esterified oil sample was poured into the reactor and gently heated to about 40°C to improve the miscibility of oil with the mixture of methanol and catalyst. 5g of KOH (catalyst) was dissolved in 126.6cm³ of methanol and shaken for five minutes to form potassium methoxide, the potassium methoxide was then gently introduced into the heated oil in the reactor and the heating of the mixture was continued for one hour, and the temperature was maintained at 60°C and at stirring speed of 300rpm to ensure uniform agitation. The reacting mixture was then transferred into separatory funnel for phase separation to occur. The bottom layer having a brownish red colour and containing the impurities and crude glycerol was drawn off. The biodiesel formed at the upper layer was collected and washed 2-3 times with clean water to remove the unreacted methanol and traces of catalyst in the biodiesel phase.

The physico-chemical analysis of oils was carried out according to AOAC (1990), AOCs (1997) Standard methods, ASTM (1999 and 2001), and EN (2003) Standard methods were used for the evaluation of biodiesel fuel properties.

RESULTS

The percentage oil yield extracted from the sample seeds using n-hexane and their respective free fatty acid levels were presented in table 1. The yield was generally high with the highest value obtained from Castor seed, implying that all the sample seeds have great potential to be used as feedstock for biodiesel production. From the same table, the high free fatty acid values recorded require that all the sample oils need to be esterified before transesterification. The physico-chemical properties of the sample oil are presented in Table 2. These properties were determined using standard methods to ascertain the quality and suitability of the oil for biodiesel production in terms of moisture content, ash content, kinematic viscosity, iodine value, saponification value and specific gravity. The low values of these properties show that it is possible to have efficient conversion of oil to biodiesel during transesterification. The properties of oils blended with *Jatropha* oil are presented in table 3. *Jatropha* oil is considered as the mainstream alternatives for biofuel development, because it is a multipurpose species with many attributes and a considerable potential for biodiesel. Since the properties of biodiesel from *Jatropha* oil is reported to be comparable to that of the diesel (Reddy and Ramesh 2005), these oils are blended with *Jatropha* oil in ratio of 1:1 to assess the effect of *Jatropha* oil in improving the quality of other oils for maximum conversion and yield of biodiesel. Table 4 shows the properties of biodiesel produced from *Jatropha curcas* oil, Soya beans oil, Castor seed oil, Rubber seed oil, Cotton seed oil and neem seed oil. These properties determine the quality of biodiesel and is very important for the performance and emission characteristics of fuels. The values of the properties evaluated from this study conform to that of ASTM and EN standard.

Table 1: percentage oil yield and free fatty acid level of the samples

Samples	Percentage yield (%)	Acid value mg KOH/g	FFA mg KOH/g
Castor seed oil	48	12.48	6.24
Neem seed oil	47	17.40	8.70
Soya beans oil	45	10.80	5.40
Cotton seed oil	46	12.34	6.17
Rubber seed oil	45	34.4	17.2
Jatropha seed oil	46	8.43	4.22

Note: Free fatty acids (FFA) value is half of the acid value

Table 2 Properties of Feedstocks from Nigerian Edible and Non-Edible Oils

Parameters	Soya beans oil	Jatropha seed oils	Cotton seed oil	Rubber seed oil	Castor seed oil	Neem seed oil
Moisture content (%)	2.34	2.41	2.75	2.82	3.51	2.65
Ash content (%)	10.50	12.5	13.25	12.25	15	11.10
Saponification value mgKOH/g	166.3	210.4	181.0	194.6	164.1	186.4
Iodine value (meq/g)	62.40	62.12	39.60	76.80	45.26	58.20
Peroxide value (meq/g)	42.2	40	83	160.3	10	78.40
S. G. at 15/4 ⁰ C	0.9112	0.9156	0.9659	0.9064	0.9178	0.9327
Kinematic viscosity (MPa)	87.40	88.15	86.67	87.20	81.95	88.40

Table 3 Properties of Feedstocks Blends from Nigerian Edible and Non-Edible Oils

Parameters	Jatropha / Castor	Jatropha / Cotton oil	Jatropha / Soya oil	Jatropha / Rubber	Jatropha / Neem oil
Acid value (KOH/mg)	5.6	3.4	24.8	11.78	4.8
Saponification value (KOH/g)	32.257	40.06	48.323	46.283	40.20
Iodine value (meq/g)	57.12	20.26	30.62	63.40	40.80
Peroxide value (meq/g)	86.0	66.80	58.53	20.0	26.20
S. G. at 15/4 ⁰ C	0.932	0.900	0.911	0.913	0.912
Kinematic viscosity (MPa)	158.60	83.20	89.90	91.60	80.1

Table 4 Properties of Biodiesel from Nigeria Edible and Non-Edible Oils

Parameters	BIODIESEL						
	SME	JME	COME	RME	CME	NME	DISESEL
S. G. at 15/4 ⁰ C	0.8827	0.8780	0.8800	0.8837	0.9235	0.8774	0.8329
Ester content	96.1	98.5	96.1	92.4	90.1	96.7	
Carbon Residue (%)	0.01	0.01	0.01	0.01	0.01	0.01	0.05
Acid Value (mg KOH/gm)	0.11	0.10	0.15	0.12	0.17	0.15	0.21
Sulphur % wt	0.0181	0.0166	0.0173	0.0635	0.1186	0.0335	0.05
Flash Point ⁰ C	182	186	160	197	177	183	65
Pour Point ⁰ F	25	20	25	20	50	50	
Cloud Point ⁰ F	30	50	35	35	-22	55	
ASTM Colour	1.0	0.5	3.0	3.5	<4.0	2.0	
Viscosity at 40 ⁰ C (cSt)	4.465	5.218	4.107	4.572	7.363	4.551	2.957
Diesel Index	26.79	27.88	26.95	27.19	19.98	27.39	
Aniline Point ⁰ F	93	94	92	95	92	92	
Calorific Value (MJ/kg)	39.76	40.43	41.67	39.	39.50	40.178	45.821
Distillation							
IBP ⁰ C	245	221	243	266	220	270	159
5%	325	310	310	321	300	324	
10%	328	320	317	327	320	327	222
30%	330	321	323	330	321	328	
50%	332	322	327	332	333	331	241
70%	334	326	328	337	331	332	
90%	-	-	-	341	-	336	309
95%	-	-	-	-	-	340	
EBP	336	328	329	349	331	343	336
T/R	84	82	85	93	81	96	

DISCUSSION

The oil yields of all the samples (Soya bean 45%, *Jatropha curcas* 46%, Cotton 46%, Rubber 45%, Castor 48% and Neem seed 47%) are shown in Table 1. These results fall within the range of the percentage oil content (30-55%) reported by Azam *et al.*, (2005). The results indicate that all the sample seed contains appreciable quantity of oil enough to be extracted for commercial scale production of biodiesel. The quantity is enough feedstock that can sustain large scale oleochemical industries not only for biodiesel production but also for the production of soap, nitrogenous derivatives, surfactants and detergents (Azam *et al.*, 2005).

The data collected on the free fatty acid level of the samples are presented on Table 1. The acid value is a measure of the amount of carboxylic acid groups present per gramme of the feedstock and the higher value significantly affect efficiency of transesterification and consequently result in low yield, (Canackci and Gerpen 2001). The result on Table 1 shows that all the sample oils contains high acid value, as such the oil cannot be directly transesterified, transesterification can only be achieved when the acid value is 2% or 1% FFA. There is therefore the need to carry out acid esterification of the oil as to reduce high acid value to 2% or less prior to alkaline transesterification, and this could probably lead to optimal biodiesel yield.

The quality of oils and oil blends expressed in terms of the physico-chemical properties such as moisture content, ash content, saponification value, iodine value, peroxide value, specific gravity and kinematic viscosity are shown in Table 2 and Table 3. The moisture content of the samples shown in table 2 are Soyabean 2.34%, *Jatropha* 2.41%, Cotton seed 2.75%, Rubber seeds 2.82%, Castor seed 3.51% and Neem seed 2.65%. These values are low signifying that the sample seeds can dry well and can be stored for a long time. However, high moisture content, along with high value of free fatty acid shown in Table 1, can have significant effects on the transesterification of glycerides with alcohol using KOH catalyst (Goodrum, 2002). The effect could manifest in form of soap formation that can cause difficulty in the separation of the product, this can result into low yield of biodiesel during transesterification.

The ash contents are fairly low indicating that mineral contents are low. It is also an indication that the oil content may contain less contaminant.

The values for specific gravity of oils samples shown in table 2 were found to be within the range of 0.717 - 0.921 as reported by Danguguwa (1983) except values for cotton and the neem seed oil that were insignificantly above the range. Vaughan (1990) in his work mentioned that the specific gravity of oils is inversely related to the molecular weight. The saponification values were low when compared with the value of 190 – 194 reported by Eteshola (1990); this signifies that these oils are of good quality for use as feedstock for biodiesel production. High saponification values of oils indicate normal triglycerides best use as raw material for the production of liquid soap and Shampoo.

In Table 3, Iodine values decreases for all the blends with exception of *Jatropha*/Castor oil blend. Higher iodine value suggests their use in the production of alkyl resin shoe polish varnishes (Akintayo, 2004). For peroxide value, there was a general decrease for blends with exception of *Jatropha*/ Castor oil and *Jatropha*/Soya oil blends. Similar trend as peroxide value were observed for specific gravity (S.G) and kinematic viscosity for the oil blends. The low level of peroxide value is a proof of oxidative stabilities of the oils relatively (Gunstone, 2004). Peroxide value is a function of unsaturated fats/oils, length of storage and storage environment, high peroxide value leads to high rancidity which is a tendency by oxidation. A general decrease in the level of some properties such as acid value, saponification value and iodine value as oils are blended with *Jatropha* oil used in this experiment as control, indicate not

only an improvement in oil properties but also a proof of suitability of *Jatropha* oil as feedstock for biodiesel production world over.

The fuel properties of Soyabean methyl ester (SME), *Jatropha* methyl ester (JME), cotton oil methyl ester (COME), rubber methyl ester (RME), castor methyl ester (CME) and neem methyl ester (NME) in comparison with that of diesel are shown in Table 4. The results obtained in this study show that, the transesterification process improved the fuel properties of the oil with respect to specific gravity (SG), ester content, carbon residue, acid value, sulphur content, flash point, pour point, cloud point, colour, viscosity, diesel index, aniline point, calorific value and distillation. The comparison of these properties with diesel shows that density, carbon residue, acid value, sulphur content and calorific value of biodiesel are lower than diesel fuel. For biodiesel, acid value is an indicator of the presence of any unreacted fatty acids still in the fuel; it also indicates the condition of stability of the fuels as the fuel ages. The propensity the fuel will form carbon deposit in the engine was also determine by the carbon residue (%). These properties compare relatively closer fuel property values to that of conventional diesel.

The calorific values of all the biodiesel in this study are similar to what is obtained in literature, that calorific value are lower than that of diesel because of their oxygen content (Sahoo and Das, 2009). The presence of oxygen in the biodiesel helps for complete combustion of fuel in the engine. The flash point of all the biodiesel is lowered by transesterification but it is still higher than that of diesel. A small percentage addition of biodiesel with diesel increases flash point of diesel. Hence, it is safer to store biodiesel-diesel blends as compared to diesel alone.

Kinematic viscosity is an important fuel property that represents the flow characteristics of fuel. One of the reasons why biodiesel is used as an alternative fuel instead of pure vegetable oils is as a result of its reduced viscosity which enhances fuel flow characteristics. In addition, kinematic viscosity is an important parameter regarding fuel atomization and combustion as well as fuel distribution (Solomon *et al.*, 2010). As shown in Table 4, the kinematic viscosity of castor oil biodiesel (CME) is higher than JME, NME, COME, RME and SME. This is in line with Ramos *et al.* (2009) that reported kinematic viscosities of 4.0Cst and above for biodiesel. According to Knothe *et al.* (2003), kinematic viscosity increases with fatty acid chain length and with increasing degree of saturation of either the fatty acid or alcohol moiety in a fatty ester.

The flash point of a fuel is the temperature at which it will ignite when exposed to a flame, and it is used to assess the flammability hazard of fuels. All the test samples have flash point well above 130min specified in ASTM standard. This high value of flash points indicates that biodiesels obtained are less likely to inflame accidentally. A small percentage addition of these biodiesels with fossil diesel increases flash point of fossil diesel and that makes it safer not only for transportation purposes but also for storage as compared to diesel alone. Higher flash points obtained in this study correspond to that reported by Sarin *et al.*, 2007.

Cloud point is the temperature at which wax first becomes visible to the naked eye when the fuel is cooled. At temperatures below the cloud point, larger crystals fuse together and agglomerations that eventually become extensive enough to prevent pouring of the fluid and consequently affecting the performance of fuel lines, fuel pumps and injectors. The low-temperature behavior of biodiesel is significantly influenced by molecular structure. Low-temperature properties depend mostly on the saturated ester and the effect of unsaturated ester composition can be negligible (Sarin *et al.*, 2007).

The ester content of JME (98.5%) and NME (96.7%) is slightly higher than minimum limit of 96.5% specified by EN 14214 standards and consequently meets the biodiesel specification. This result shows the purity of JME and NME and completeness of the alkaline transesterification reaction. The ester content of SME (96.1%), COME (96.1), and fall within the range of 96-98% reported by Ramos *et al.* (2009), however, the ester content of RME (92.4%) and CME (90.1%) are lower but the difference is not significant enough to have attributed it to the quality of oil or the method used.

The ASTM Colour describes the visual evaluation of biodiesel products based on ASTM colour scale, the result on Table 4 shows that the colour values of all test samples were low and fall within the standard range of 0.5 - 8.0 on ASTM colour scale. (SME 1.0, JME 0.5, COME 3, RME 3.5, CME

>4.0, NME 2.0). These values indicate that the biodiesel produced are of high grade, possess light colour and have not undergo auto-oxidation that may suggest possible contamination and the formation of insoluble sediment.

CONCLUSION

The edible and non-edible vegetable oils, and fuel-quality of biodiesel produced there from were investigated in this study. All the evaluated properties of both the seed oils and the biodiesel produced complied with the limits prescribed by AOAC, AOCS, EN and ASTM standards. The study has also enabled us to confirm that all the sampled seed oils can be used as raw materials to obtain biodiesel fuel of high quality and could be suitable alternative to fossil diesel.

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