International Journal of Applied
And Natural Sciences (IJANS)
ISSN(P): 2319-4014; ISSN(E): 2319-4022
Vol. 5, Issue 3, Apr - May 2016; 1-8

International Academy of Science, Engineering and Technology
Connecting Researchers; Nurturing Innovations

COMPARISON OF THE PROPERTIES OF PALM OIL AND PALM KERNELOIL BIODIESEL IN RELATION TO THE DEGREE OF UNSATURATION OF THEIR OIL FEEDSTOCKS

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ABSTRACT

The correlation between biodiesel properties and their degree of unsaturation was investigated. The feed stocks considered were crude palm kernel oil and Palm oil. Crude PKO was extracted from palm kernel seeds using traditional method of extraction. Biodiesel was produced from the crude PKO using base-catalyzed trans-esterification process. Two factors were varied during the production process: methanol-oil ratio and reaction time (minutes). Thirteen experimental runs were carried out and a maximum yield of 87% was obtained at a reaction time of 65 minutes and a methanol-oil ratio of 6.0. The process was optimized using the response optimizer of MINITAB 16 and an optimum yield of 88% was obtained at a reaction time of 58 minutes and a methanol-oil ratio of 7.8. The properties of the biodiesel obtained from crude PKO were also compared with the properties of palm oil biodiesel obtained from literature. The degree of unsaturation of palm kernel oil and palm oil were calculated from the fatty acid composition of both oils. The biodiesel properties were correlated with the degree of unsaturation. Biodiesel produced meets standard specifications (ASTM, EN).

KEYWORDS: Biodiesel, Fatty Acid, Palm Kernel Oil, Palm Oil, Trans-Esterification

INTRODUCTION

The high demand for energy in the industrializedworld as well as in the domestic sector and the pollution problems caused by continuous use of fossil fuels make it very neccessary to develop renewable energy sources of limitless duration and smaller environmental impact than the traditional one (Ojolo*et. al.,* 2012; Sharma *et. al.,* 2008).Biodiesel have been recognized world-wide as a renewable fuel which can be used as an alternative to petroleum-based diesel fuel due to its advantages; it is biodegradable, renewable, non-toxic and have excellent lubricity (Bowman et. al., 2006; Chowdhury et. al., 2007; Viele*et. al.,* 2013). Bio diesel is very similar to the petroleum diesel fuel in terms of physical properties and functionality and therefore can beused as 100% replacement or used at any proportion with petroleum diesel in existing diesel compression-ignition engines with little or no engine modifications (Adebayo *et. al.,* 2011; Fukuda *et. al.,* 2001, Giakoumis, 2013).

Biodiesel is defined as mono-alkyl esters of long chain fatty acids derived from the trans-esterification reaction between plant oil and animal in the presence of a suitable catalyst (Albuquegue *et. al.,* 2008; Akintayo, 2004). The catalyst can either be an acid, a base or an enzyme to improve the reaction rate and yield. The use of enzyme catalyst intransesterification reaction makes the process too expensive while acid catalysed transesterification is a very slow process requiring a minimum duration of 6 hours for the completion of reaction. Base-catalysed trans esterification process is preferred to any of the two other forms of trans esterification due to its economical reasons(Ojolo*et. al.,* 2012)

In most production, methanol or ethanol is the alcohol used (methanol produces methyl esters, ethanol produces ethyl esters) and a base catalyst (KOH or NaOH). Potassium hydroxide has been found to be more suitable for the ethyl ester biodiesel production, either base can be used for the methyl ester.

Palm oil and palm kernel oil are the two feed stocks considered for biodiesel production in this research work. Palm oil is one of the highest yielding oilseed biofuel crops. Being a perennial crop, it has a much higher land productivity than the common annuals such as rapeseed, sunflower and soya(Ojolo *et. al.,* 2012; Viele *et al.,* 2013) Studying the palm kernel oil as an alternative feedstock for biodiesel production to palm oil would be very good for Nigeria as the oil palm tree which grows excellently on the Nigerian soil would still be useful for the production of biodiesel without leading to fuel versus food crisis (Ojolo *et. al.,* 2012)

In comparison to other alternative fuels, there are a number of unique qualities and properties of biodiesel fuel that determine the performance of biodiesel as energy source. Some of these properties include flashpoint, pour point, iodine value, cetane number, density, viscosity and heating value (Ranganathan *et. al.,* 2008; Sharma *et. al.,* 2008).

A very influencing parameter of a biodiesel feedstock properties is its degree of unsaturation. An unsaturated fat is a fat or fatty acid in which there is at least one double bond within the fatty acid chain (Moll, 2015; Giakoumis, 2013). A fatty acid chain is saturated if its C–C bonds contain no double bond, it is monounsaturated if it contains one double bond, and polyunsaturated if it contains more than one double bond (Giakoumis, 2013). The aim of this research work is to produce crude palm kernel oil biodiesel and palm oil biodiesel, and to investigate the correlation of some of their physical properties with the degree of unsaturation of their feed stocks.

METHODOLOGY

Extraction of Palm Kernel Oil

Palm kernel seeds were purchased from local palm processors in Effurun, Delta State. Palm kernel oil was extracted from the palm kernel seeds using the traditional method of heating.

Gas Chromatographic Analysis of Oil

The chemical composition of the fatty acids in the crude PKO and palm oil were determined using a gas chromatograph. The oil samples were sent to Chemistry department laboratory, University of Lagos for the determination of fatty acids composition using GC MS. The result fatty acid composition obtained was used to calculate the molecular weight of triglycerides of the oils.

Determination of Percentage Free Fatty Acid of Oils

The percentage free fatty acid of the feedstocks were determined before and after the pre-treatment of the feedstock. Oil was filtered inorder to remove particulates present. 20g of absolute ethanol was measured and added to the 10g of each of the oil in a conical flask . The mixture was shaken and slightly heated in the oven for about 10 minuites to dissolve the oil. Three drops of Phenolphthalein indicator was added and titration was done with 0.1M NaOH. The End point at which the oil changed from light brown to deep purple was recorded. The FFA values of the oils obtained (>1%) suggested that the oils should be subjected to FFA removal.

FFA Removal

100 grams of each oil was measured into a conical flask and heated up to 40^0C at a steady rate using a magnetic stirer. 10 ml of 0.125M of NaOH was measured using a conical flask and poured slowly into the heated oil. The mixture maintained at 40^0C was continuously stirred for 20 minutes. The mixture was then poured into a separating funnel for clarification to take place. Soap was formed at the base and oil triglyceride was the top layer. Suspended traces of soap formed were first removed. After separation, the wet oil triglyceride obtained was dried in an oven at 110^0C for 2 hrs.

Determination of Iodine Value of the Oils

0.5g of oil was measured into a conical flask and 10 ml of chloroform was added to dissolve the oil. 25 ml of Hanus solution was added into the conical flask containing oil and mixed thoroughly. The mixture was allowed to stand in the dark for exactly 30 mins with occasional shaking. 10 ml of 15% KI and 100 ml of freshly boiled and cooled water were added washing down the free iodine on the stopper. This mixture was titrated against 0.1M sodium trioxo thiosulphate (VI), until the solution started turning almost colourless. Five drops of starch indicator was added and titrated till the solution was completely colourless. A blank was run without samples of oil.

Trans-Esterification of Palm Oil and Crude PKO

100 grams of oil was the basis used for all experimental runs during trans-esterification. The oil was preheated to a steady temperature of 55^0C using a magnetic stirer on a heating mantle. 0.7 gof KOH pellets was completely dissolved in the required quantity of methanol in a conical flask. The potassium methoxide formed was added to the pre heated oil. The content was continuously stirred using a magnetic stirrer at a steady speed of 250 rpm and the set up was maintain at 55^0C for trans-esterification reaction to take place. The reaction time and methanol/oil mole ratio were varied during the experimental runs. The product was poured into a separating funnel mounted on a retort stand and the mixture was allowed to settle for a 6 hours when top layer of biodiesel and bottom layer of glycerol were obtained. The two layers were separated, biodiesel obtained was rid of impurities by washing with warm water and then dried in an oven at 110^0C for 30 minutes.

RESULTS AND DISCUSSION

The amount of iodine that reacted was used to find the iodine number of the oil and this number indicates the degree of unsaturation in the oil. The greater the mass of Iodine used, the greater the number of carbon-carbon double bonds broken. Hence, the greater the Iodine number, the greater the degree of unsaturation.The result obtained shows that Palm oil has a higher degree of unsaturation than Palm kernel oil.

Biodiesel Production

Figure 1 shows the plot of yield versus methanol-oil ratio and reaction time. At every combination of reaction time and methanol-oil ratio,there is a corresponding response (yield). The maximum biodiesel yield of 87% was obtained at two conditions; one was at a reaction time of 65 minutes and a methanol-oil ratio of 6 while the second condition was at a reaction time of 50 minutes and a methanol-oil ratio of 9.

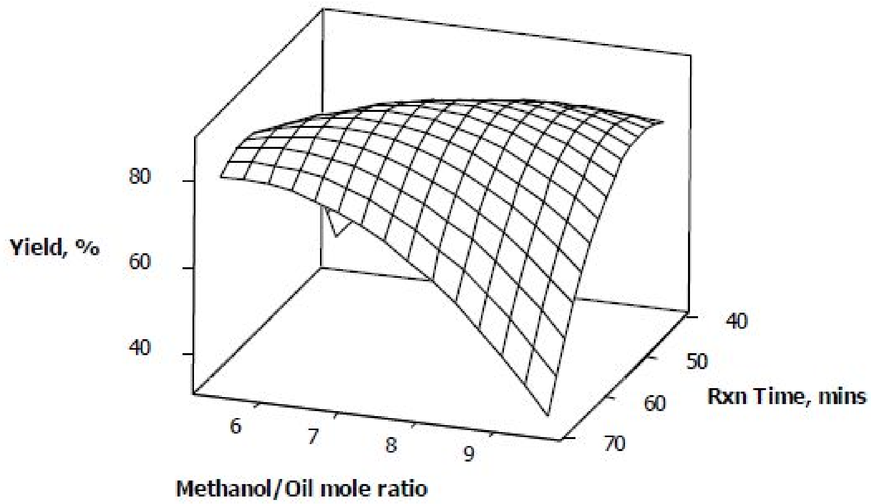

Figure 1: Plot of Biodiesel Yield against Methanol-Oil Mole Ratio and Reaction Time

Using response optimizer, the optimum condition obtained yield of 88 % was obtained at reaction time and methanol-oil ratio of 58 minutes and 7.8 respectively.Table 1shows the properties of crude PKO biodiesel and palm oil biodiesel

Table 1: Properties of Crude PKO Biodiesel and Palm Oil Biodiesel

Property	Unit	Crude PKO	Palm Oil	Standard
Density	(g/ml)	0.8760.884	0.86−0.9	(EN14214)
Pour Point	(^{0}C)	2	**9**	depends on region
Viscosity @ 40^{0}C	(mm^2/s)	5.2 4.8	1.9−6.0	(ASTM D445)
Flash point	(^{0}C)	132	160	>93 (ASTM D93)
Iodine Value	g I/100g	3.8	36	
Higher Heating Value	(Btu/Ib)	19,44217,384		depends on region
Lower Heating Value	(Btu/Ib)	18,31416,121		depends on region

EN = European Biodiesel Standards, ASTM = American Biodiesel Standards

Table 2: Fatty Acid Composition of Palm Oil and Crude Palm Kernel Oil (AOCS, 2015)

Fatty Acid	Crude PKO	Palm Oil
$C_8H_{16}O_2$ (C8, n = 0)	3.25	-
$C_{10}H_{20}O_2$ (C10, n = 0)	4	-
$C_{12}H_{24}O_2$ (C12, n = 0)	45.25	-
$C_{14}H_{28}O_2$ (C14, n = 0)	18.1	3.84
$C_{16}H_{32}O_2$ (C16, n = 0)	9.2	43.5
$C_{18}H_{36}O_2$ (C18, n = 0)	3.03	4.3
$C_{18}H_{34}O_2$ (C18, n = 1)	15.15	38.73
$C_{18}H_{32}O_2$ (C18, n = 2)	2.02	9.63

C = No of Carbon present, n = no of double bonds

Table 3: Distribution of Saturated and Unsaturated Fatty Acids in the Oils

Fatty Acids, %	Crude PKO	Palm Oil
Saturated Fatty Acid (SFA)	82.83	51.64
Mono-Unsaturated Fatty Acid (MUFA)	15.15	38.73
Poly-Unsaturated Fatty Acid (PUFA)	2.02	9.63
Total (%)	**100**	**100**
MUFA + PUFA	17.17	48.36

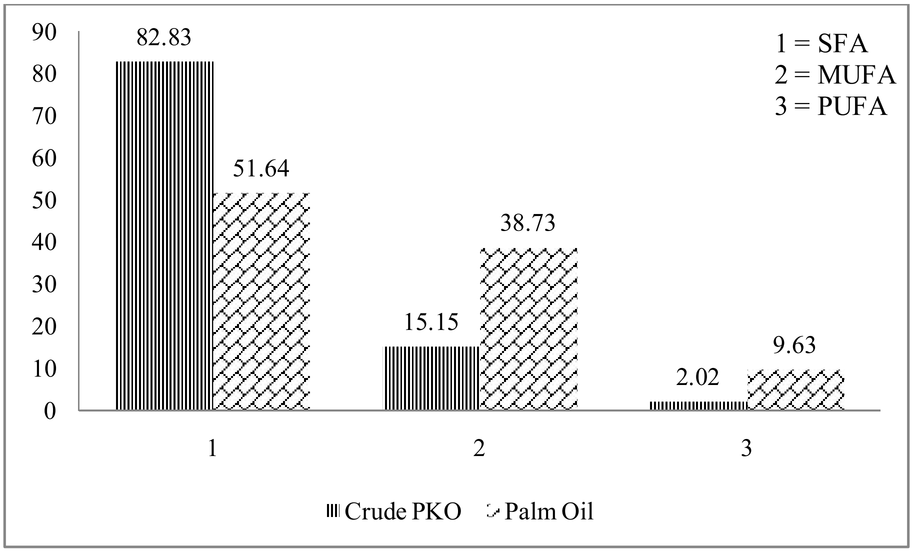

Figure 2: Percentage Composition of Fatty Acids of Crude PKO and Palm Oil

The chemical composition of biodiesel depends upon the length and degree of unsaturation of the fatty acid alkyl chains (Giakoumis, 2013). Tables 2 shows the percentage composition of fatty acids of crude PKO and palm oil. Table 3 and Figure 2 show the percentage composition SFA, MUFA and PUFA of crude PKO and palm oil. The C – C bonds of fatty acids in Crude PKO are majorly saturated (82.83% SFA) while the saturated C – C bonds of fatty acids in palm oil is 51.64%. That is, crude PKO has 17.17% unsaturated C – C bonds (15.15% MUFA, 2.02% PUFA) and palm oil has 48.36% unsaturated C – C bonds (38.73% MUFA, 9.63% PUFA). Crude PKO has higher saturated C – C bonds than its unsaturated C – C bonds; palm oil has almost the same percentage of saturated C – C bonds and unsaturated C – C bonds. Comparing the two oils, both palm oil and crude PKO contain larger amount of saturated fatty acid than unsaturated fatty acid. However, palm contains a higher degree of unsaturation of C – C bonds than crude PKO.

Correlation of Biodiesel Properties to the Degree of Unsaturation of the Oils

A very influencing parameter of biodiesel properties is the degree of unsaturation of its feed stock. Table 3shows the distribution of SFA, MUFA and PUFA incrude PKO and palm oil. Table 1 shows the comparison between the properties crude PKO biodiesel and palm oil biodiesel. The properties of crude PKO biodiesel and Palm oil biodiesel differ due to the difference in the degree of unsaturation of carbon bonds of the two oils.

Density

The density value for crude PKO biodiesel obtained was 0.876g/ml and palm oil biodiesel has a higher density value of 0.884g/ml, both values are within the acceptable EN standard. This shows that the density of Palm oil biodiesel is greater than the density of crude PKO biodiesel. The greater the biodiesel density, the greater the mass of biodiesel the volumetrically-operating fuel pumps will inject. A higher density fuel would lead to a low air-fuel ratio which gives a richer mixture thereby improving the performance of the engine (Giakoumis, 2013; Chowdhury *et. al.,* 2007).It can be concluded that the more unsaturated the feedstock oil, the higher the density of the derived methyl ester (biodiesel), and the greater the fuel mass that will be injected in a diesel engine.

Pour Point

Crude PKO biodiesel has a pour point of 2^0C while palm oil biodiesel has a pour point of 9^0C. From the results obtained, one may conclude that the higher the degree of unsaturation of C – C bonds in the primary oil, the higher the pour point of the biodiesel produced.

Kinematic Viscosity

The lower the viscosity of a fuel, the easier the movement of the fluid in an engine, provided the viscous value is within the standard value range (Giakoumis, 2013). Results show that crude PKO biodiesel has a kinematic visocity of 5.2 mm^2/s while palm oil biodiesel has a viscoity of 4.8mm^2/s. Hence, it can be inferred that the higher the degree of unsaturation of the feedstock, the lower the viscosity of the resulting biodiesel.

Flash Point

From the Table 1, the flash point of crude PKO biodiesel obtained is 132^0C while that of palm oil biodiesel is 160^0C, both meet the ASTM standard specification. Palm oil biodiesel has a higher flash point value than crude PKO, therefore, it can be said that a higher unsaturated feedstock gives rise to methyl ester with higher flash point.

Heating Value

Palm oil biodiesel have a LHV of 16,121 Btu/Ib and a HHV of 17,384 Btu/Ib. Crude PKO has a LHV of 18,314 Btu/Ib and a HHV of 19,442Btu/Ib. The results of heating values obtained in this research are in the favour of the fact that the energy content of fatty acid methyl esters (biodiesel) is directly proportional to chain length. The heating value for crude PKO biodiesel is higher than the heating value of palm oil biodiesel. Therefore, the higher the degree of unsaturation of biodiesel feedstock, the lower the heating value of its methyl ester

Iodine Value

Iodine value measures the degree of unsaturation of oil. The iodine value of palm oil is significantly greater than that of the crude PKO. That is the higher the degree of unsaturation of C – C bonds in oil, the higher the iodine value.

CONCLUSIONS

The physical properties of the biodiesel produced meet the standard specifications. The degree of unsaturation of C – C bonds in the originating oil is directly proprotional to the density, pour point, flash point and iodine value, but inversely proportional to the heating value and viscosity of the resulting biodiesel.

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