

## SOLVENT, TEMPERATURE AND TIME EFFECT ON THE YIELD AND PROPERTIES OF BIODIESEL PRODUCED FROM TWO TYPES OF VEGETABLE OILS

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### Abstract

*The growing concerns about energy security and sustainability, environmental effects and over-reliance on Fossil fuel that emits enormous amount of greenhouse gases (GHGs) which leads to climate change makes for the need for an alternative renewable, green, eco-acceptable and friendly fuel like Biodiesel. The effects of Methanol and Ethanol at different time and temperature using potassium hydroxide as a base trans-esterification catalyst on the yield and properties of crude Palm kernel and Soybean oils and biodiesels were investigated using standard analytical procedures. The crude Palm kernel and Soybean oils has appearance, colour, odour/taste, volatile matter, slip melting point and acid value were within but, net volume is a bit high while free fatty acid and iodine values are above permissible NIS 290: 2000 limit. The Biodiesel yield ranged from 71.2 to 98.2% and it increased with the time and temperatures of reaction for both solvents but methanol were generally higher than ethanol. The average density ranged from 0.84 to 0.90 g/cm<sup>3</sup>, viscosity at 40°C from 4.38 to 4.98 Cst and flash point from 134 to 148°C. Densities, viscosity, flash point except pour point of the Biodiesels were found to conform to ASTM standards making Soybean oil and Palm kernel oil suitable feedstock for high quality biodiesel.*

**Keywords:** Methanol, ethanol, biodiesel (B100), crude palm kernel and soya bean oils

### Introduction

Most of the world's energy is provided by fossil fuels and it has prospered with cheap and abundant energy allowing for widespread industrialization in the last century providing high standards of living and economic prosperity. However, there are growing concerns about their sustainability and environmental impacts. Over-reliance on fossil based fuel for energy purposes result into emission of enormous amount of greenhouse gases (GHGs) which can lead to climate change [1]. Also, the supply of these fossil resources is inherently finite and instability in oil producing areas has impacted on the prices of oil in the last few years with a barrel of oil costing \$70 in July, 2007 rising to over \$100.24 in February, 2011 [2], and \$54 in August 2015 [3].

The Energy Commission of Nigeria (ECN) recently reported that Nigeria's fossil-led economy is under severe pressure, with Nigeria currently importing about 80% of its petroleum requirements and has been hit hard by rapidly increasing cost and uncertainty. In the Niger Delta region, unfortunately as the

centre for oil extraction, severe environmental impacts have been ignored in the country's haste to develop the oil industry. Prospecting is a nearly impossible task for the multinational companies in Nigeria and as a result, the production of reserves will go on increasing in Nigeria [4].

These situations have led researchers to develop alternative sources for energy generation [5] and among these alternative sources are solar, geothermal, wind, hydropower and biomass. This trend is expected to change with intensive research being carried out to minimize our dependence on fossil based fuels. In this respect, plant biomass has been identified as the only sustainable renewable carbon source for liquid fuel. Biomass is an inexpensive, renewable and abundant source of carbon [6]. Its utilization generates less greenhouse gas emissions and can even be greenhouse gas neutral if efficient methods for biofuels production are developed [7].

Among the biofuels that are being developed, biodiesel has generated a lot of interest because of its compatibility with the existing

fuel distribution infrastructure. Currently legislative and regulatory incentives are easing the path of biodiesel into the market [8].

Biodiesel fuel is a natural, clean, sustainable and renewable domestic fuel to substitute fossil fuels made from vegetable oil and does not contribute to global warming due to its closed carbon cycle. Biodiesel acceptance as a substitute for fossil derived diesel has grown the world over.

However, the food-fuel debate over conventional vegetable oils has rekindled research interest in exploring lesser known and minor oil crops, owing to their availability, various oils have been in use in different countries as feed stocks for biodiesel.

Biodiesel production from conventional vegetable oils (soybean, sunflower, safflower, palm, rapeseed etc.) has progressively stressed food uses, price, production and availability of these oils [9]. In addition, the chemistry of trans-esterification, a process of converting vegetable oil into biodiesel, is well known.

This process is basically a reaction between fats/oils and alcohol in the presence of a suitable catalyst (KOH, NaOH or  $H_2SO_4$ , HCl) to produce fatty acid alkyl ester (biodiesel) and glycerol [10]. Common feedstock for biodiesel includes animal fat, edible and non-edible vegetable oils waste vegetable oils, algae.

This study is aimed at comparing the yield of biodiesel produced from crude Palm kernel oil and Crude Soybean oil using KOH catalyzed trans-esterification process, the effect of methanol and ethanol on the yield and compare the properties of the biodiesel obtained to petroleum diesel.

## Materials and Methods

### Materials

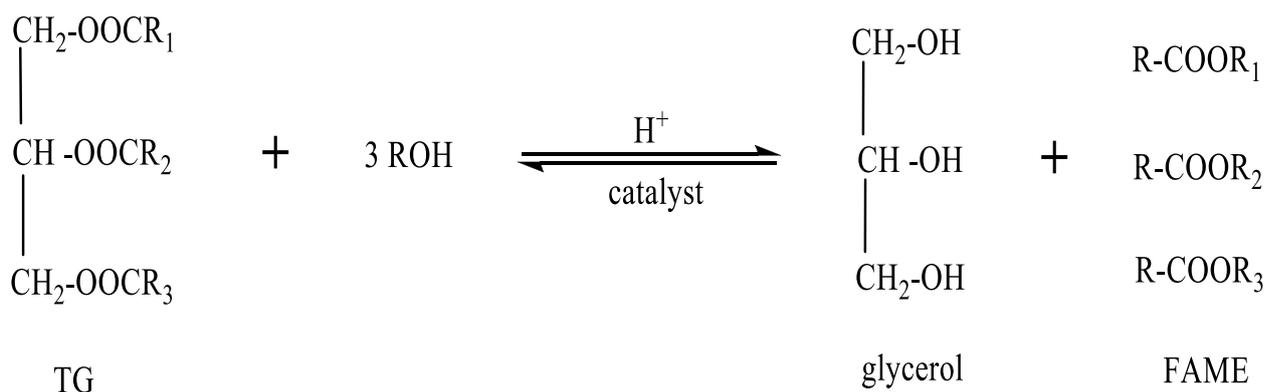
The crude oil samples of Palm kernel and Soybean oils were obtained from an indigenous vegetable oil refinery (AR-Rachid Ventures Limited) in Owode-Yewa, Ogun State, Nigeria. **Experimental set-up**

The 2000 cm<sup>3</sup> flat bottom flask (reactor) was set-up with the top (neck) opening with the support of the cork, reflux condensation unit and a fixed thermometer. The set-up was refluxed on a hot plate magnetic stirrer. The condenser was in-turn connected to tap water for in-and-out flow of cold water to prevent loss of alcohol (solvent) during the transesterification reactions.

### Method

#### Transesterification of Crude Palm kernel oil and Crude soybean oil using Methanol and Ethanol.

Transfer of the oil using analar methanol, ethanol at varied concentrations was used. 32.4 g ethanol and 50.0 g of oil were first measured in two separate beakers that have been previously washed and dried. 0.5 g (0.5 % by weight) of the analar potassium hydroxide catalyst was weighed and dissolved in the ethanol and the resultant solutions was then charged into the 2000 cm<sup>3</sup> flat bottom flask (reactor) and pre-warmed. The magnetic stirrer was set to 500 revolution per-minute and the pre-warmed oil in a separate beaker was carefully added to the potassium methoxide in the reactor and then subjected to heating at varied time of between 1 to 3 h and temperature of 55 °C to 70 °C. Also 45 g of methanol and 50.0 g of the oil were measured into separate clean beakers. After which 0.5 g of the potassium hydroxide was weighed and dissolved in the ethanol and pre-warmed in the reactor, placed on the magnetic stirrer set at 500 rpm and the pre-warmed oil in a separate beaker was carefully added to potassium ethoxide in the reactor and then heating at varied time between 1 to 3 and temperature of 55 °C to 70 °C of trans-esterification reactions and after the reaction, the mixture was poured into a separating funnel and was allow to stand for approximately 24 h to allow for distinct biodiesel and glycerol separation. The above procedure was repeated using Methanol-Ethanol mixtures. The phases were then separated to recover the biodiesel for further purification and drying.



**Scheme 1.0: Trans-esterification reaction between triglyceride (oil) and alcohol to produce fatty acid methyl esters (FAME) (B100) and glycerol as by-product.**

Triglyceride (TG)

Fatty acid methyl ester (FAME)

R: alkyl group of alcohol

R1, R2, R3: long alkyl chain of fatty acid

### Physico-chemical analysis of Oils and Biodiesel

#### Appearance:

A physical eye check was carried on the oil sample.

#### Odour/Taste:

The odour of the oil was determined by smelling the oil and imploring sensory check

**Slip melting point:** It was determined by casting a 10 mm column of the oil in a glass tube with an internal diameter of about 1 mm and a length of about 80 mm, and then immersing it in a temperature-controlled water bath. The slip point is the temperature at which the column of the solid begins to rise in the tube due to buoyancy.

#### Colour Test:

This was carried out using a colour comparator made up of two curvets, (a reference and test sample). Samples for analysis was introduced into the test curvet and compared with the reference sample [11].

#### Moisture content at 105 °C.

20 g of the sample weighed in a previously empty dish and kept in the oven for 2 h after which the sample was cooled in the desiccator and re-weighed. The process was repeated until a constant weight is attained.

$$\% \text{ Moisture content} = \frac{\text{Weight of volatile}}{\text{Weight of sample}} \times 100$$

#### Acid value and %Free fatty acid (FFA).

The result and method of the analysis is as documented and compared with the NIS 290: 2000; ASTM, 2002 Standards. To 25 cm<sup>3</sup> of the ethanol was added to 1 cm<sup>3</sup> of 1% phenolphthalein indicator and titrated with 0.1 N NaOH solution. 5 g of the oil added to the solvent mixture and titrated with the 0.1 N NaOH solution. The end point was indicated by permanent pink coloration [14].

$$\text{Acid value} = \frac{56.1 \times V \times N}{w}$$

#### % Free fatty acid (FFA)

$$\% \text{ FFA (as Lauric acid)} = \frac{20.0 \times N \times V}{w}$$

$$\% \text{ FFA (as Oleic acid)} = \frac{28.2 \times N \times M / \text{of alkali}}{\text{Weight of Sample}}$$

Where V - Volume in cm<sup>3</sup> of NaOH solution

N - Normality of the NaOH

W - Weight (mg) of the sample taken for the analysis.

#### Peroxide value

5 g of the oil was weighed in a conical flask and 30 cm<sup>3</sup> solvent in ratio 20:10 of acetic-chloroform mixture was added. The flask was swirled and 5 cm<sup>3</sup> of saturated potassium-iodide was added. This was allowed to stay in the dark for one to two minutes. Then 30 cm<sup>3</sup> of distilled water was added, swirled and

titrated with 0.01 N sodium thiosulphate, using starch solution as indicator [14].

$$\text{Peroxide value} = \frac{(S - B)N \times 1000}{W}$$

Where S - volume of thiosulphate used on titration with sample

B - volume of thiosulphate used on titration with Blank

W - Weight (g) of sample used.

#### Iodine value

8 g of iodine trichloride was dissolved in 200 cm<sup>3</sup> of glacial acetic acid, 9 g iodine in 300 cm<sup>3</sup> carbon tetrachloride. The two solutions were mixed and diluted to 1 litre of glacial acetic acid known as Wij's solution. About 0.5 g of oil was weighed into a glass stoppered

bottle of about 250 cm<sup>3</sup> capacities. 10 cm<sup>3</sup> of carbon tetrachloride was added and then 20 cm<sup>3</sup> Wij's solution. This was allowed to stand in the dark for 30 mins. 0.5 cm<sup>3</sup> potassium iodine solution was added and 100 cm<sup>3</sup> of distilled water. The mixture was titrated with 0.1N sodium thiosulphates solution using starch as indicator, just before end point, a blank Titration was carried out simultaneously [14].

$$\text{Iodine value} = \frac{(B - S) \times 1.26}{\text{Weight of sample}}$$

Where B - volume of thiosulphate used on titration

S - sample of oil

W - weight of sample

## RESULT AND DISCUSSION

**Table 1.0: Physico-chemical properties of the Crude oils**

Parameter/Unit	Crude palm kernel oil	Crude soy bean oil	Limit NIS 290:2000
Appearance	Golden viscous liquid	Golden viscous liquid	Conform
Colour (Hz)	5.1	5.3	3-6
Odour/Taste	Product characteristics	Product characteristics	Conform
Net Volume (L)	25.2	25.4	25.0
Moisture content (%)	0.08	0.09	0.1 maximum
Slip Melting point (°C)	19.6	19.9	22.4
Acid value (mgKOH/g)	6.16	6.32	10
Free fatty acid (as palmitic Acid) %	3.08	3.16	0.1max.
Iodine value (g/100g)	57.2	58.1	56 min.

**Table 2: Biodiesel properties of PKO and Soybean oils with Methanol and Ethanol in KOH at 55°C for 1, 2 and 3 hrs**

Sample	PKO oil Biodiesel with Methanol					Soybean oil Biodiesel with Methanol				
	BD Yield (%)	Density 15°C (g/cm <sup>3</sup> )	Viscosity at 40°C (Cst)	Flash Point (°C)	Pour Point (°C)	BD Yield (%)	Density 15°C (g/cm <sup>3</sup> )	Viscosity at 40°C (Cst)	Flash Point (°C)	Pour Point (°C)
<b>1</b>	80.0	0.86	4.62	139.0	-3.0	89.0	0.87	4.60	143.0	-3.0
<b>2</b>	71.2	0.86	4.61	142.0	-3.0	89.4	0.88	4.65	145.0	-6.0
<b>3</b>	88.8	0.85	4.50	146.0	-3.0	89.2	0.88	4.65	143.0	-6.0
	PKO oil Biodiesel with Ethanol					Soybean oil Biodiesel with Ethanol				
<b>4</b>	64.0	0.91	4.45	138.0	-3.0	86.4	0.88	4.63	140.0	-6.0
<b>5</b>	75.2	0.89	4.38	140.0	-6.0	87.2	0.89	4.64	139.0	-3.0
<b>6</b>	86.6	0.91	4.46	142.0	-6.0	88.4	0.89	4.66	140.0	-6.0

**Table 3: Biodiesel properties of PKO and Soybean oils with Methanol and Ethanol in KOH at 60°C for 1, 2 and 3 hrs**

Sample	PKO oil Biodiesel with Methanol					Soybean oil Biodiesel with Methanol				
	BD Yield (%)	Density 15°C (g/cm <sup>3</sup> )	Viscosity at 40°C (Cst)	Flash Point (°C)	Pour Point (°C)	BD Yield (%)	Density 15°C (g/cm <sup>3</sup> )	Viscosity at 40°C (Cst)	Flash Point (°C)	Pour Point (°C)
<b>7</b>	88.6	0.88	4.64	146.0	-3.0	93.5	0.87	4.62	143.0	-6.0
<b>8</b>	87.2	0.87	4.60	143.0	-5.0	93.2	0.87	4.65	146.0	0.0
<b>9</b>	90.2	0.89	4.67	134.0	-3.0	93.9	0.88	4.67	143.0	-3.0
	PKO oil Biodiesel with Ethanol					Soybean oil Biodiesel with Ethanol				
<b>10</b>	87.2	0.89	4.72	142.0	-3.0	90.6	0.88	4.63	141.0	-3.0
<b>11</b>	85.8	0.88	4.65	143.0	-6.0	91.0	0.88	4.66	140.0	-3.0
<b>12</b>	89.6	0.90	4.98	146.0	0.0	92.0	0.89	4.68	139.0	0.0

**Table 4: Biodiesel properties of PKO and Soybean oils with Ethanol and Methanol in KOH at 70°C for 1, 2 and 3 hrs**

Sample	PKO oil Biodiesel with Methanol					Soybean oil Biodiesel with Methanol				
	BD Yield (%)	Density 15°C (g/cm <sup>3</sup> )	Viscosity at 40°C (Cst)	Flash Point (°C)	Pour Point (°C)	BD Yield (%)	Density 15°C (g/cm <sup>3</sup> )	Viscosity at 40°C (Cst)	Flash Point (°C)	Pour Point (°C)
13	97.2	0.87	4.46	146.0	-3.0	93.6	0.84	4.64	148.0	-3.0
14	98.0	0.87	4.43	143.0	-6.0	94.8	0.87	4.68	146.0	0.0
15	98.2	0.88	4.48	142.0	-3.0	95.2	0.86	4.65	148.0	-3.0
	PKO oil Biodiesel with Ethanol					Soybean oil Biodiesel with Ethanol				
16	91.6	0.90	4.65	142.0	-6.0	89.2	0.87	4.60	141.0	-3.0
17	93.2	0.89	4.60	138.0	-3.0	89.8	0.89	4.61	143.0	-3.0
18	94.9	0.89	4.60	140.0	-3.0	94.0	0.88	4.54	145.0	0.0

## DISCUSSION

The Palm kernel and Soybean oils has appearance, colour, odour/taste, volatile matter, slip melting point and acid value within permissible limit but, the net volume is a bit higher while the free fatty acid and iodine values are above permissible NIS 290: 2000 limit.

Trans-esterification reactions of Palm kernel and Soybean oils were studied at varying temperatures of 55°C, 60°C, 70°C and time of 1 hr, 2 hrs, and 3 hrs'' respectively using Ethanol, Methanol in KOH. The yield in all the biodiesel production process ranged from 71.2% to 98.2% and it increases with increase in temperature and time for both Methanol and Ethanol but higher in methanol which is due to its lower molecular mass and chemical composition, which has similar trend to the values of Soybean and Palm kernel oils biodiesel produced by Hossain and Al-salf, 2010; Alamu *et al.*, 2007. Also the Soybean oil biodiesel yield is higher than PKO oil biodiesel in both Methanol and Ethanol at 55°C and 60 °C but lower in 70 °C but it varies with time.

Density is the mass of a substance occupying a unit volume at 15°C, evaluated using ASTM D4052. When density is higher, slightly large mass of fuel is injected, hence more power and emissions. Biodiesel viscosity is slightly higher than petrol diesel and the viscosity increase in biodiesel leads to density increase [17]. The density ranged from 0.84 to 0.90

g/cm<sup>3</sup> which is fairly within ASTM D6751 Standard of 0.86 to 0.90 g/cm<sup>3</sup> and also close to 0.88g/cm<sup>3</sup> reported for PKO biodiesel produced by Alamu *et al.*, 2007.

Kinematic viscosity is the measure of the resistance to flow of a fluid due to gravity based on time and is inversely proportional to temperature. It has influence on fuel droplet size and spray characteristic, increases with chain length and saturation degree. Higher viscosity needs higher pumping that leads to poor atomization, incomplete combustion, increased carbon deposits. Fuels with lower viscosity may not provide sufficient lubrication for precision fit of fuel injector pumps or injector plungers and may lead to leaks through the clearance between plunger and barrel during fuel compression. Biodiesel viscosity is slightly higher than petrol diesel [18]. The viscosity ranged from 4.38 to 4.98 Cst which was within ASTM Standard of 1.90 to 6.00 Cst but close to 4.3 Cst reported for Soybean soapstock biodiesel which is similar to Soyabeen oil biodiesel produced by Haas *et al.*, 2001.

Flash point is the lowest temperature at which application of ignition causes the vapours of a substance to ignite under specified conditions and is evaluated using ASTM D93. Minimum flash point of fuels is required to meet fire safety specifications by restricting alcohol content, because it may affect engine seals,

elastomers and corrode metal components. Higher flash point decreases the flammability of the fuel and makes combustion quality slow in engine. Higher viscosity increases flash point, it however affects burning quality and atomization [18]. The flash point ranged from 134 to 148°C which was within ASTM Standard of 60 to >130°C but lower than 167°C reported for PKO biodiesel produced by Alamu *et al.*, 2007 and also lower than 169°C reported for Soyabean soapstock biodiesel produced by Haas *et al.*, 2001.

Pour point is important in low temperature fuel applications and is the temperature at which the amount of wax out of solution and the fuel can still flow; therefore higher saturated fatty acids indicate higher pour point of biodiesel [20]. The pour point ranged from -6 to 0.0 °C which was below the ASTM Standard of 15 to 16°C and lower than 2°C reported for PKO biodiesel produced by Alamu *et al.*, 2007.

## CONCLUSION

The use of crude Soybean oil and crude Palm kernel oil as biodiesel feed stock should be greatly encourage because of their yield. The rate of trans-esterification of crude Soyabean oil increased with reaction time and temperature and higher yields were obtained from crude Soybean oil with Methanol than Ethanol. The pour point, flash point, density at 15°C and viscosity at 40°C of the biodiesel produced were within the allowable limit set by the American society for Testing and Materials (ASTM).

These properties make the use of Soybean oil and Palm kernel oil suitable feedstock for high quality biodiesel. Also the use of these biodiesel as fuel will provide useful solutions to various environmental problems because it's renewable nature, bio-gradable ability and reduction in emission of greenhouse gases that goes a long way in solving impending energy availability and security crisis.

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