Batch Transesterification Process of Palm Kernel Oil with Ethanol in Biodiesel Production and Characterization of the Key Fuel Properties

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Abstract

The transesterification of palm kernel oil with ethanol using sodium hydroxide, a homogenous basic catalyst and the characterization of itsbiodiesel properties was carried out.The results of the biodiesel properties obtained compared well with those reported in literature. The characterization of the produced biodiesel involves keyfuel properties which include the following and their results; kinematic viscosity (45 cSt at 40°C), density (865.02 kg/m^2 at 25°C), pour point (12°C), flash point (125°C), fire point (270°C), moisture content (310ppm), sulfur content (1.25%), iodine value ($63.79 mgI_2/g$), saponification value (209mgNaOH/g) and acid value (0.98mgNaOH/g), respectively.The effects of different operating parameters that were varied were also studied. The best parameters that produced the optimum conversion of palm kernel oil into biodiesel were;catalyst concentration of 2.5wt%, temperature of 80 °C, 1:18 palm kernel oil to ethanol molar ratio, reaction time of 1hr.30minsand a stirring speed of 700rpm. These operating conditions produced an optimum conversion of 95% of palm kernel oil to biodiesel.

Keywords: Transesterification, biodiesel, palm kernel oil, ethanol, catalyst and conversion.

1. Introduction

The global fear and worry about the finite nature and environmental pollution associated with the over dependence on fossil fuel has given rise to the development of alternative energy sources that are efficient and renewable, as substitute for traditional fossil fuels. Biodiesel is recognized as one of the renewable energy fuel sources, that can serve as an alternative to the conventional petroleum diesel (Kombe, et al.,2013). Biodiesel is a biodegradable fuel, non-toxic with fewer emissions, also with the advantage of improved lubrication properties and, can be blended in specific ratio with conventional diesel. Biodiesel is derived from edible and non-edible vegetable oils and animal fats, which is suggested to substitute a substantial proportion of fossil diesel in this century(Alhassan and Eemura, 2016).It is a liquid biofuel that is capable of combustion

in conventional diesel engines either alone or as a blend with petroleum diesel (Vicente, 2001 & Vicente et al., 2004). It is obtained by the chemical processes of transesterification whereby the vegetable oil or animal fat (Triglyc-eride) reacts with alcohol in the presence of catalyst or with-out catalyst, to give the corresponding alkyl esters of the fatty acid mixture that is found in the parent vegetable oil or animal fat (Garpen, 2005 and Meher et al., 2006). Transesterification reaction can be uncatalyzed, base-catalyzed, acid-catalyzed or enzyme-catalyzed.Stoichiometrically,transesterification reaction requires a bench molar ratio of 1:3 of oil to alcohol to produce biodiesel,using either homogeneous or heterogeneous catalyst (Rashid et al., 2009). However, experience has shown that a larger molar ratio of triglycerides to alcohol is essential for obtaining higher yield of alkyl esters (Alhassan and Eemura, 2016).Short-chain alcohols such as methanol, ethanol, and butanol are the most frequently used, and their selection is based on cost and performance consideration (Anastopoulos et al., 2009). The choice catalyst is known to

have a significant effect on the reaction rate. While basic catalysts require short times to complete the reaction even at room temperature, acidic catalysts, e.g. sulfuric acid, require higher temperatures (100°C) and longer reaction times (3 – 4 hrs) (Schwad et al., 1987; Fukuda et al., 2001 and Canakci&Gerpen, 2001). The alkalis that are used generally include sodium and potassium hydroxides, carbonates, and alkoxides such as methoxide, ethoxide, propoxide, and butoxide.

Palm kernel oil is a known edible plant oil, obtained from the kernel of the oil palm *Elaeisguineensis*(Poku, 2002), commonly found in West Africa.It is a vegetable oil, high in saturated fats and way more saturated than palm oiland it is comparable to coconut oil (Chow, 2007).Its high saturation makes it a good candidate for this purpose. Suffice to note that over 14 million tonne of palm kernel oil is produced annually. It is on record that palm kernel oil is commonly used in commercial cooking due to its lower cost than other oils and,is able to maintain stability at high cooking temperatures. It is recognized that the oil can be stored longer than other vegetable oils

and it is used in the manufacture of soaps, washing powders, medicinal and personal care products.Through the process of saponification, it produces fatty acids, with glycerin (glycerol) as a byproduct *(*Faessler et al., 2007).The aim of this study is to derive biodiesel from palm kernel nuts and to characterize its key biodiesel properties.

2.Materials and Methods

2.1. Materials

3 L of palm kernel oil was purchased from Ughelli Market in Delta State.Ethanol,n-hexane, sodium hydroxide, anhydrous sodium sulfate were obtained from Charlec Nig. All the chemicals used were analytical reagent grade.

2.2. Experimental procedure

2.2.1. Biodiesel production via tranesterification reaction

This was carried out according to the method described by Idibie et al., (2020). Using a 500 ml round bottom flask as the reactor attached to a condenser and a magnetic stirrer,the transesterification reactions were carried out, under agitation of 700 rpm.The process involved weighing 200 g of the oil into the reactor and was placed in a fixed heating bath. According to the amounts established for each experiment the sodium hydroxide catalyst was dissolved in the ethanol and the resultant mixture was transferred to the heated oil in the reactor. Upon introduction of the sodiumhydroxide/ethanol mixture into the three-necked round bottom flask at a set temperature, the reaction was allowed to run at various pre-determined times. At the end of each ethanolysis reaction,the mixture of the products separatedunder gravity when allowed to stand for 3 hrs. The elimination of glycerinefollowed the evaporation of ethanol, and theproduced ethyl ester was cleaned with warm distilled water severally. The essence of the cleaning was to removeresidual compounds such as sodium hydroxide, glycerol and ethanol. Finally, the derived ethyl ester was heated (105°C)to eliminate the presence of water by heating.

2.3 Analytical methods

2.3.1 Chemical analysis

The conversion of the palm kernel oil into ethyl ester was analyzedaccording to the procedure described by Meneghetti et al., (2007). Here,a Shimadzu HPLC system equipped with Lab-solutions lite software (version 5.5) having a column of length 150mm and outer diameter of 10 mm was used. The detector being a differential refractive detector (RID-10A) was held at 45°C, while a mixture of ethyl ester in n-hexane (ratio 1:30 of) was used to find the response. The mobile phase was a mixture of n-hexane and ethanol. While the flow rate of the mobile phase was fixed at 1.0 mL/min, 20 μLof the mixture of the mobile phase was injected at each time interval. At the end, the triglycerides conversion was calculated according to the equation (1)(Alhassana and Uemuraa, 2016):

Triglycerides conversion = (1- {x/w}) X 100

$$(1)$$

where: x is the peak area of triglycerides in ester sample and w is peak area of triglycerides in the feedstock.

2.3.2 Physical analysis

The biodiesel properties of the produced ethyl ester were determined according to standard methods. These include; kinematic viscosity at 40°C (ISO 3104),density at 25°C (ISO 3675), pour point (ASTM 2500), flash point (EN 22719), fire point (ASTM D445),moisture content (ASTM D2709), saponification value (mKOH/moil, mg/g) (Anastopoulos et al., 2009 & Zhu et al., 2006), sulfur content (ASTM D5453), and acid value (ASTM D664).

3.Results and Discussion

Theanalysis of the biodiesel produced from the transesterification reaction between ethanol and vegetable oil obtained from palm kernel, under the catalysis of sodium hydroxide, shows the results of its physico-chemical properties as well as the effects of several reaction parameters on the transesterification process. Among the parameters considered which influenced the process are the NaOH concentration, reaction time, palm kernel oil to ethanol molar ratio and the reaction temperature.

3.1 Physico-chemical properties

Produced ethyl ester (biodiesel) was studied in terms of itsphysico-chemical properties to determine its quality. The variousproperties of the produced biodiesel were also compared with that of the palm kernel oil before the transesterification reaction. The results of analysis as presented in Table 1 were within the range reported in literature (Bello et al., 2015 &Anastopoulos et al., 2009).The kinematic viscosity of the oil was 33.67 (cSt, 40°C) while that of the produced ethyl ester was 4.5(cSt, 40°C). The viscosity of liquid fuels is known toaffectthe cold flow properties, sprayatomization, vaporization, and air/fuel mixture formation (Bello et al., 2015). Higher viscosity usually has a serious negative effect on the combustion of vegetable oils in existing diesel engines, fuel pumps and injectors. However the viscosity decreases with temperature. While the density of the palm kernel oil (PKO) was 930 that of the produced ethyl esters was 865.02 (kg/m^3, 25 °C). The determined pour points of both the PKO and biodiesel are both of temperatures 19°C and 12°C, respectively.Pour point generally represents the lowest temperature at which oil can flow under gravity. Although Bello et al.,(2015) had reported the pour points for both PKO and its corresponding methyl ester to be20^{o}C and 10°C, respectively. On the other hand, while the flash point of the PKO was found to be 240°C that of the ethyl ester was 125°C. This of course, is the temperature at which the vapour over the liquid will ignite upon exposure to an ignition source or flame. It is reported that the flash point of vegetable oils is usually very high ($>180^0$ C) and the heating values could range between 36 – 40 MJ/kg, as compared to diesel fuels which is about 42-45 MJ/kg. However, it is noted that the presence of chemically bounded oxygen in vegetable oils lowers their heating values by about 10% (Bello et al., 2015). The fire points and moisture contentsfor the PKO and synthesized biodiesel were determined to be 250°C (PKO) and 270°C (biodiesel) and 0.35 (PKO) and 310 ppm (biodiesel), respectively.

Table 1: Properties of fatty acid and produced ethyl esters

Property	Property of palm kernel oil	Property of biodiesel
Kinematic viscosity (cSt, 40°C)	33.67	4.5
Density (kg/m^3, 25 °C)	930	865.02
Pour point (^{o}C)	19	12
Flash point (^{o}C)	240	125
Fire point (^{o}C)	250	270
Moisture content (ppm)	0.35	310
Sulfur content (%)	12.9	1.25
Iodine value (mgI$_2$/g)	18	63.79
Saponification value (mgNaOH/g)	198.8	209
Acid value (mgNaOH/g)	0.72	0.98

The fire point is regarded as the temperature at which the vapour produced by that given fuel will continue burning forat least 5seconds after ignition by an open flame. The oil contained 12.9% sulphur which reduced to 1.25% after transesterification. Sulphur can be desirable in fuel because it contributes to friction reduction but it is capable of causing acid rain and thus posing a threat to the environment. The iodine value represents the amount of unsaturation in fatty acids. The unsaturation arising in the form of double bonds interacts with iodine compounds, and thusthe higher the iodine number, the more C=C bonds are present in the fat. The iodine value in PKO and the produced biodiesel are 18 and 63.79 mgI2/g, respectively. This indicates the presence of small number of C=C bonds in the oil which is usually associated to the high degree of saturation. However, unsaturationin the fatty acid chain is attributed to the main cause of instability in vegetable oils (Stavinoha, 1999).

Saponification value indicates the number of milligrams of alkali required to saponify 1g of fat, and thus, it is the measure of the average molecular weight (or chain length) of all the fatty acids present. It can be used in checking adulteration of products (Ibeto

et al., 2011). Results obtained showed high saponification values for PKO (198.81mgKOH/g) and ethyl ester (209mgKOH/g), which indicates high presence of fatty acids that could facilitate soap formation. Usually these values are known to be high for vegetable oils hence PKO is widely used for soap production because it lathers very well (Bello et al., 2015). However, soap doesn't encourage the separation ofbiodiesel and glycerin fraction (Meneghetti et al., 2004), hence in this study it was difficult to achieve full conversion of oil (100%) to biodiesel, as result will reveal in later section. But the parodox is that while high amount of soap can result in irregular combustion and thick exhaust smoke, it will however, increase the cleanliness of the fuel internal components and reduce friction between rubbing parts. The acid values for PKO and the produced biodiesel were determined to be 0.72% and 0.98 %, respectively.

3.2 Effect of catalyst concentrationon oil conversion to biodiesel

The effect of catalyst concentration on the conversion of palm kernel oil to an ester at a controlled time of 1hr is presented in Figure 1. Catalyst concentrations ranging from 0.5 – 3.5 wt % were used and, the result clearly shows that catalyst concentration of 2.5 wt % was able to drive the transesterification process to the highest conversion of 62 %. However, at catalyst concentration above 2.5 wt %, the conversion did not improve by increasing the concentration of the catalyst; rather there was reduction in the rate of conversion.
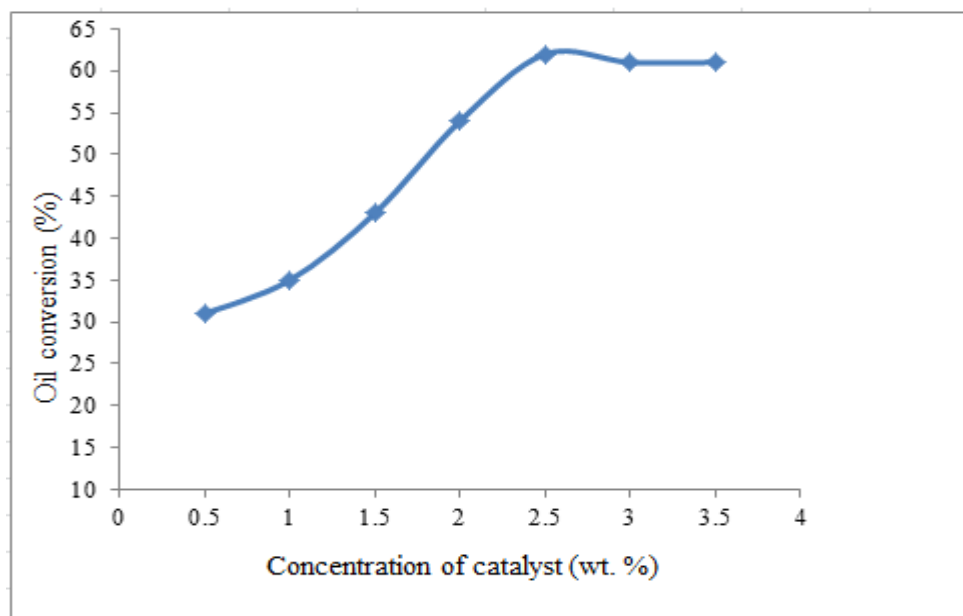
**Figure 1:** Effectof catalyst concentrationon PKO oil conversion at 1hr reaction time.

The decrease in the rate ofconversion can be attributed to the formation of soap and glycerin (Alhassan and Uemura, 2016). Suffice to mention that addition of more sodium hydroxide catalyst beyond 2.5 wt % leads to the formation of suspension, thereby increasing the viscosity of the reaction and thus posing difficulty in glycerol recovery and in overall, complicating the separation process of the biodiesel (Zhang et al., 2003).

3.3 Effect of time on oil conversion to biodiesel

The effect of time on the PKO conversion to biodiesel through the transesterification reaction was investigated to ascertain the actual time that will produce the optimum conversion of oil to
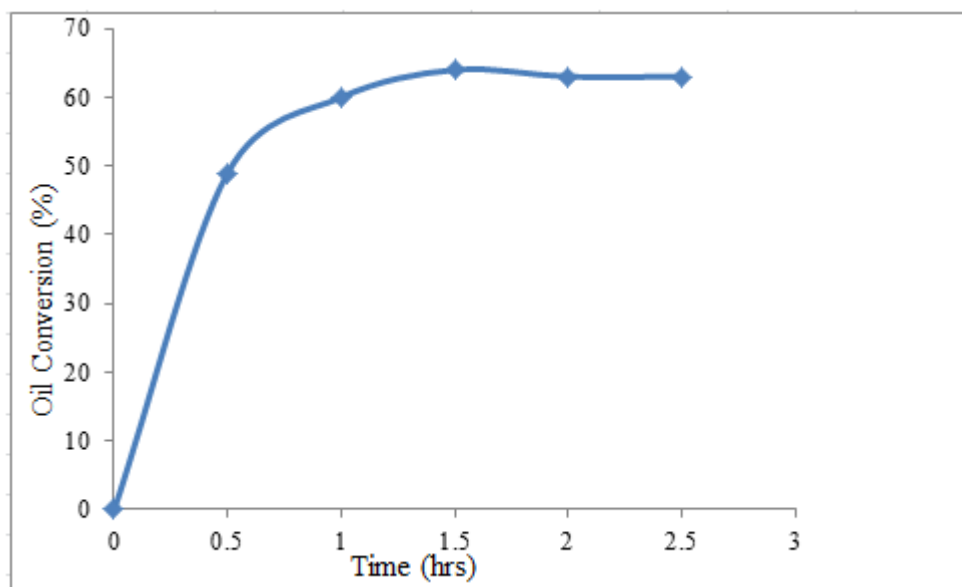
Figure 2: Effect of interaction time on PKO oil conversiontobiodiesel

biodiesel. The reaction was studied at different time intervals between 30 mins – 2hr:30mins. The result as presented in Figure 2 shows that 1hr:30mins of reaction time produced the highest conversion. Increasing the interaction time above this time could not yield any better conversion.As a result, the required time of 1hr:30mins became the time for optimum conversion of the PKO oil to its ethyl ester.

3.4 Effect of ethanol/PKO molar ratio on biodiesel production

Research has shown that the production of biodiesel stoichiometrically through transesterification process requires one mole of oil to react with 3 mole of alcohol (i.e. 1:3) to produce three moles of biodiesel together with one mole of glycerol(Alhassan and Eemura, 2016). Sincetransesterification reaction is an equilibrium process where an additional alcohol is important for effective completion of transesterification, common sense is needed to increase the reaction ratio that will produce the optimum conversion. As a result, in this study the molar ratios of

the PKO to ethanol used ranged between1:3-1:24.
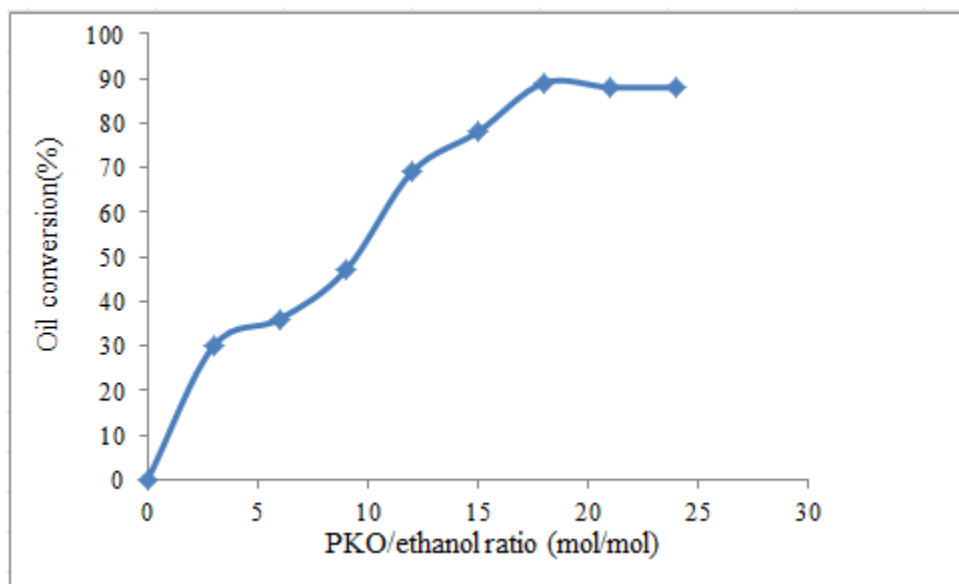
**Figure 3:**Effect of ethanol/PKO molar ratio on biodiesel production

Figure 3 presents the conversion of triglycerides versus molar ratio of ethanol/PKO. The result reveals a rise of PKO/ethanol stoichiometric ratio from 1:3 up to 1:18. This is in line with previous studies (Alhassan et al., 2013, Alhassan and Eemura, 2016 &Alhassan and Eemura, 2016). Above this ratio (i.e.,1:21 and 1:24), there was no positive conversion. Hence, alcohol/PKO ratio of 1:18 became the ideal ratio for optimum (~90%) conversion of PKO to biodiesel.

3.5. Effect of reaction temperature on the PKO oil conversion to biodiesel

Effect of reaction temperature on the PKO oil conversion to biodieselwas also studied using molar ratio of PKO/ethanol (1:18), 2.5% sodium hydroxide catalyst, time of 2hr:30mins and stirring speed of 700rpm. The temperature range investigated was between $30 - 90^{o}C$. The result presented in Figure 4 shows that there was a progressive conversion which resulted in an optimum conversion at $80^{o}C$that was way above 90%,

and thus, the conversion efficiency was enhanced. When the temperature of the reaction was raised above 80°C, the rate of conversion decreased which can be associated with the lost in amount of alcohol (Alhassan and Eemura, 2016).
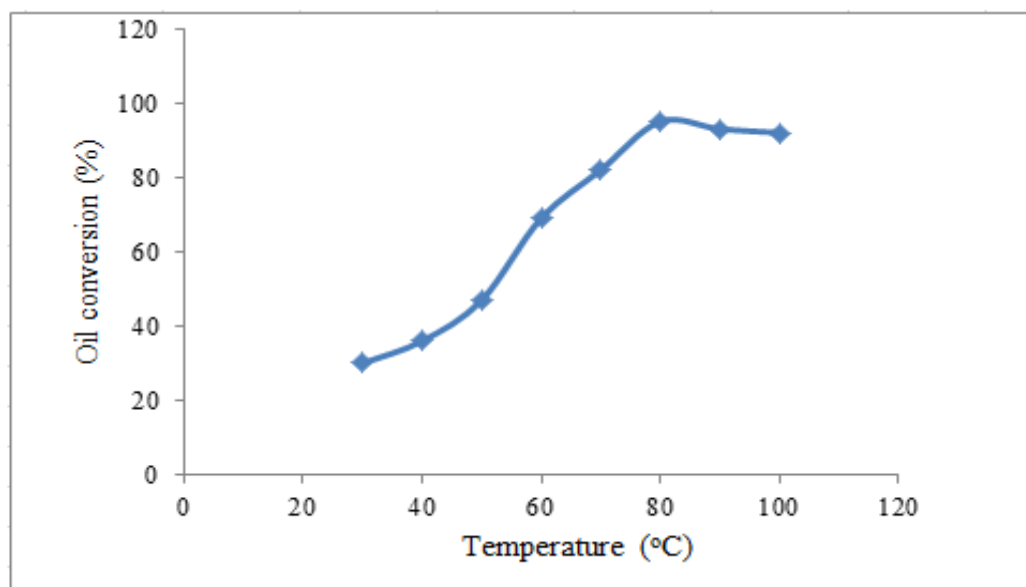
Figure 4: Effect of reaction temperature on PKO oil conversion to biodiesel

Conclusion

The conversion of palm kernel oil to biodiesel has been carried out using ethanol and a homogenous basic catalyst, sodium hydroxide.The biodiesel properties obtained compared well with those reported in literature.The best parameters that produced the optimum conversion of palm kernel oil into biodiesel were catalyst concentration of 2.5%, temperature of 80 °C, 1:18 palm kernel oil to ethanol molar ratio, reaction time of 1hr:30minsand a stirring speed of 700rpm. These operating conditions produced an optimum conversion of 95% of palm kernel oil to biodiesel.

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