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BIODIESEL PRODUCTION BY TRANSMETHYLATION OF NIGERIAN PALM KERNEL OIL

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ABSTRACT

The need for this study arose from the recent energy crisis coupled with the huge potential that Nigeria has for the production of Palm Kernel Oil (PKO). Locally produced PKO was chemically modified (methanolysis) to produce PKO-based biodiesel. The reaction temperature and the catalyst loading were maintained at 60°C and 1.0% weight of oil, respectively. The methanol to oil molar ratio was kept at 6:1. The production of PKO-based biodiesel (at 60°C for 1.5 hours) by transmethylation process in the presence of NaOH as catalyst yielded crude products, Glycerol and biodiesel. Subsequently, PKO (parent oil), automotive gas oil (AGO) and PKO methyl esters transesterified were characterized to determine their properties and suitability as fuels in Compression Ignition Engine (CIE). Results of the transmethylated PKO showed that properties such as viscosity (3.359 cSt), specific gravity (0.8728), water content (nil) and flash point (100°C) conformed to standards (ASTM, BIS). Properties of the PKO biodiesel were comparable with properties of AGO. Emissions assessment showed that CO concentration was reduced by 30% when PKO biodiesel was used in CIE compared with AGO. Hence, PKO-based biodiesel has a promising prospect for partial or total replacement for petro-diesel in CIE.

Keywords: Palm Kernel Oil, transmethylation, alkali catalyst, emissions

1. INTRODUCTION

The ever increasing energy demand around the globe, the depletion of fossil fuels, the fluctuation of crude oil price in the international market as well as greater recognition of the unfavourable environmental consequences of fossil fuels have made renewable biofuels an attractive alternative to conventional petro-fuels. Biodiesel (fatty acid methyl esters; FAMEs and fatty acid ethyl esters; FAEEs) produced from vegetable oils, animal fats and waste oils can substitute petro-diesel. This is because of the properties of biodiesel; especially flash point, cetane number as well as volumetric heating value, which have been shown to be comparable to those of petro-diesel (Ma and Hanna, 1999; Lang et al, 2001; Usta, 2005; Jeong et al, 2006). Biodiesel has some marked advantages over petro-diesel which include non-toxicity, biodegradability CO_2 recycling over short period and environmentally-friendly, that is, it shows a decrease in the emission of CO_2, SO_x and unburned hydrocarbons during the combustion process (Graboski and McCormick, 1998; Antolin et al, 2002).

Previously reported feedstocks employed in the biodiesel production include vegetable oils - edible (soybean), non-edible (Jatropha), animal fats (tallow, lard), and waste oil (canola). Palm kernel oil (PKO) is one of the non edible oils that Nigeria has in abundance (Table 1). Palm fruits; *Elaeis guineensis* contain about 45% PKO which is rich in lauric acid, $C_{12:0}$ (48.3%), myristic, $C_{14:0}$ (15.6%) but also contains other fatty acids like palmitic acid $C_{16:0}$ (7.5%) and oleic acids, $C_{18:1}$ (Rossell, 1985; Goh, 1993; Omar et al, 1998). These fatty acid triglycerides give the fats a solid consistency at ambient temperature that melts below 30°C. World production of PKO was 3236 metric tons in 2003 among which Malaysia produced 1644 metric tons of PKO (MPOB, 2003). Extraction of PKO requires relatively high pressure and temperatures for separation from palm kernel as palm kernel is hard and compact, and has an intricate honeycombed pericarp (Hassan et al, Hassan 2000; Rahman et al, 2001; Zaidul et al, 2006). Separation of PKO from palm kernel using supercritical CO_2 afford development of clean separation process (Bharath et al, 1992) and may require high pressure (>30 MPa).

Table 1: Profile of some vegetable oils in Nigeria

Commodity	Quantity (tons)	% Share
Palm Oil	800,000	50
PKO	270,000	17
Others: peanuts, Cottonseed, Soybean	260,000	16
Imports	270,000	17
National Requirement	1,600,000	100

Source: David (2007)

Methods employed in biodiesel production are hydrotreatment, transesterification, esterification and oleaginous microorganisms. In the transesterification of different types of oils or fat, triglycerides react with an alcohol, generally methanol or ethanol, to produce esters and glycerol. The presence of a catalyst accelerates the conversion. Alkali (NaOH or KOH), acid (H_2SO_4) and enzyme (lipases) are the catalysts that have reported in transesterification. Alkali catalyst is preferred than acid catalyst in the industries. This is because alkali process is more efficient and less corrosive than the acid process. Although, enzyme catalyst has some advantages, however, it also has some disadvantages, among which are: lost of some initial activity due to volume of the oil molecule, number of support enzyme is not uniform and biocatalyst is more expensive that the natural enzyme.

This study investigated Palm Kernel Oil (PKO) as a possible feedstock in transesterification in biodiesel production for use in a diesel engine, to discover its physical and chemical properties and emission characteristics using a Compression Ignition Engine (CIE).

2. MATERIALS AND METHODS

2.1. Reagents and Materials

Chemicals used for the experiment include methanol (CH_3OH), Sodium Hydroxide (NaOH), and Calcium Chloride ($CaCl_2$). They are all of analytical grades. Automotive Gas Oil (AGO) was purchased from Total Service Station at Iyana Ife, Ife-Ibadan Express Way, Ibadan, Nigeria.

2.2. Equipment

The various items of major equipment used include: Magnetic Stirrer and the Hot plates, Water bath, Pensky Marten Closed Cup (PMCC) Tester, Canon Fenske Viscometers, Pour and Cloud Point Tester, Separating Funnel, Seta Lovibond Colour Comparator. Other essential equipment used include: Sensitive Weighing Balance, The Combustion Analyzer, Compression Ignition Engine, Measuring Cylinders, Beakers, Distillation Set Up (including Heating Mantle and Condenser), Oven, Timer, Pump, Pyrex Flasks (flat bottom and conical), Pet Bottles, Thermometers, Safety Wears (Overall, Hand Gloves), Funnel and Sieve.

2.3 Transmethylation Process of PKO-Based Biodiesel

2.3.1 Background to the production of PKO-based biodiesel

Transesterification is an equilibrium reaction in which excess alcohol is required to drive the reaction close to completion. The transesterification reaction (Fig. 2) requires 3-moles of alcohol per one mole of triglyceride to give 3-moles of fatty esters and 1-mloe of glycerol. It is consequential to use excess alcohol or remove one of the products from the reaction mixture to shift the reaction to the right as stated by Le Châtelier's Principle. The latter option is preferred for the reaction to proceed to completion. A reaction temperature near the boiling point of the alcohol (60°C for methanol) and a molar ratio of 6:1 of alcohol to vegetable oil are recommended (Freedman et al, 1984; Noureddini and Zhu, 1997). A catalyst concentration in the range of 0.5 – 1% (w/w) has been found to yield 94 – 99% conversion to vegetable oil esters (Feuge and Gros, 1949; Saka and Dadan, 2001). Additional catalyst will not affect the conversion but only leads to increase in cost because it will be washed away at the end of the reaction (Barnwal and Sharma, 2005).

2.3.2. Production of PKO-biodiesel

It should be noted that the composition of solid or liquid fuel is usually expressed by weight whereas the composition of a gaseous fuel is given by volume. Production trials were done at the Chemical Engineering Department, Obafemi Awolowo University, Ile-Ife, Nigeria. Empirically, 300ml of PKO was measured in a conical flask and it was preheated to 50°C on the Hot Plate with magnetic stirrer. Methanol (100ml) was also measured with the aid of a measuring cylinder and poured into a pet bottle. NaOH (2.8 g) was quickly added and agitated for dissolution of the catalyst. Table 2 showed the synopsis of the measurements taken. The resulting methoxide was turned into the preheated PKO on the Hot Plate.

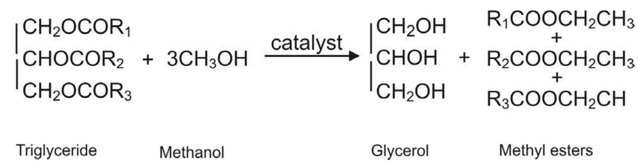

Fig. 2: General equation for transesterification of triglycerides

The Hot Plate temperature Probe was then put back into the oil with the aid of the probe holder, temperature preset to 60°C and lid was secured tightly. Phase separation was noticed, hence, stirring was introduced at 800 rpm, and the reaction was left for 90 min. At the end of the reaction time, the product was poured into a Separating Funnel separation under gravity. The glycerol was tapped off the bottom of the Separating Funnel. The crude biodiesel left in the Separating Funnel was washed with distilled water (preheated to 50°C) to remove the residual catalyst. Settling of the water was performed within 3 min. The water was later tapped off the bottom of the Separating Funnel. This process was repeated until the water was clear. Drying was done with $CaCl_2$ (fused gran) to remove the water content.

Table 2: Transmethylation process parameters

S/N	Production variables	Values for production runs
1	PKO quantity (ml)	300
2	Methanol quantity (ml)	100
3	NaOH catalyst (g)	2.8
4	Reaction temperature (°C)	60 (140°F)

2.4. Characterization of PKO-Based Biodiesel; AGO and PKO

Essentially, the following tests were performed to ascertain the compatibility of PKO-based biodiesel with Internal Combustion Engine (ICE). Specific gravity was measured with the aid of the specific gravity bottle and viscosity was determined with the aid of Canon Fensky Viscometer. Colour was determined with the aid of Seta Lovibond Colour Comparator. Pensky Martens Apparatus was used as recommended by ASTM D-93 to determine the flash point. Pour/Cloud point cabinet was used according to ASTM D-97 to obtain the temperature cloud haze and eventually when it seizes to flow (pour point). Crackle test was also carried out to determine whether there was water content in the oil. Water is not desirable since it will affect its combustion in the CIE and may also cause hydrolytic degradation of the PKO biodiesel most especially when stored over a long period of time.

2.5. Assessment of Emissions

In order to test the suitability of the PKO biodiesel produced in CI engines as well as compare the emissions with that of AGO, 100% AGO and 100% PKO-biodiesel were burnt in a CIE in succession and emissions such CO, NO_2 and NO_x were measured with the aid of the Gas Analyzer.

3. RESULTS AND DISCUSSION

3.1 Prospects of Nigerian PKO and Production of PKO-Based Biodiesel

PKO is in abundance since it took a share of 17% from the significantly available vegetable oils. This percentage can also be increased if resources are channel towards increasing the agricultural output. Transmethylation method used for the PKO Biodiesel production gave excellent results. The glycerol was separated under gravity with the aid of the Separating funnel within few hours (7 – 24 h). Additional time of separation is insignificant. It can be seen that glycerol settles at the bottom, this is an indication that the by-product (Propan-1, 2, 3-triol) is denser than the crude PKO biodiesel. During the washing process to remove the residual catalyst, the water separates out within few minutes (1 – 5). The density of water is higher than that of the biodiesel, hence, it settles at the bottom and the water was tapped off. Clear water was observed after the fifth washing was done. After washing, the biodiesel was heated up to temperature above that of the water by which significant washing-water in the biodiesel was vaporized before it was finally dried with calcium chloride.

3.2 Properties of The PKO-Based Biodiesel Produced

Table 3 showed the characteristics of the biodiesel produced. It also contained the characteristics of the petro-based AGO and the parent PKO used. It can be seen that the specific gravity and viscosity of the parent oil: PKO has been reduced from 0.9208, 32.381 cSt to 0.8728, 3.359cSt, respectively. The kinematic viscosity showed a reduction of about 90% after the PKO has undergone transesterification (alcoholysis) process. Viscosity of vegetable oil (PKO) at 32 cSt may trigger severe problem in the fuel filter and the engine. Knothe (2005) reported that high viscosity of untransesterified oils and fats leads to operational problems in the diesel engine such as deposits on various engine parts. Cold starting may also be very difficult since 'cloud haze' would have been noticed at 23°C (Gautier, 1933). This is evidenced from the results tabulated in Table 3.

Comparison of automotive gas oil (AGO) and PKO methyl esters showed that both of them have very close physical properties like viscosity and specific gravity, hence, both can be blended in ratios. There is also the possibility of using the PKO methyl esters produced 100% since both have similar properties. However, the higher flash point recorded for the PKO methyl esters will be helpful in handling and storage logistics.

Table 3: Properties of AGO; PKO–Biodiesel and PKO

Properties	AGO	PKO-Biodiesel	PKO
Specific Gravity @ 15°C	0.8600	0.8728	0.9208
Viscosity @ 40°C (cSt)	3.073	3.359	32.381
Colour	3.5	0.5	1.0
Flash Point (°C)	71 (159.8°F)	100 (212°F)	190(374°F)
Pour Point (°C)	-16 (3.2°F)	-3 (26.6°F)	18 (64.4°F)
Crackle Test	-ve	-ve	-ve
H_2O Content (% vol)	Nil	Nil	Nil
Cloud point (°C)	-12 (10.4 °F)	3 (37.4 °F)	23 (73.4°F)
Density @ 15°C (kg/m^3)	860	873	921

Essentially, the characteristics of the PKO biodiesel produced conformed to standards. Besides, the pour point (-3°C) is also very good result for the cold starting of the engine. The viscosity (3.359 cSt) is within the standards (ASTM D -445; IS: 1400 – 1974). Crackle test showed no sign of water content. This observation is good for long time storage and the engine performance in general (Knothe, 2005; Gerpen, 2005). Results of emissions assessment are presented in Table 4.

Table 4: Emissions from combustion of biodiesel/diesel in CIE

Fuel Type	CO (ppm)	NO_2 (ppm)	NO_x (ppm)
PKO Biodiesel	278.3	28.3	153.7
AGO	390.0	35.0	159.0

It was observed that CO concentration was reduced by 30% when 100% PKO biodiesel was used in CIE compared with AGO. Both NO_2 and NO_x concentrations were slightly lower when PKO biodiesel was used than in the case of AGO. It has been reported that biodiesel is more environmentally friendly than petro-diesel (Graboski and McCormick, 1998; Antolin et al, 2002).

4. CONCLUSIONS

A number of studies have shown that vegetable oils and animal fats hold great promise as alternative fuels for the Compression Ignition (CI) engines. PKO is not an exception to this. There is colossal potential to be realised from Nigerian PKO since it is also produced in large quantity. The results (viscosity, specific gravity, flash point and density) of the characterisation of PKO-based biodiesel satisfied most international standards. This work will also contribute to appropriating the PKO-based biodiesel as a supplement or total replacement of conventional petroleum based diesel fuel particularly in compression ignition engine.

5. ACKNOWLEDGEMENT

The authors gratefully acknowledged the technical assistance offered by Mr. Akano Adesina of Conoil Nigeria Plc. Equipment donation by World University Service, Germany is acknowledged by E. Betiku.

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