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Comparative Study of Physico-Chemical Properties from Roosted and Refined Palm Kernel Methylester

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Abstract

Biodiesel was prepared using refined Palm kernel oil (PKO) and Roosted Palm Kernel Oil (RPKO) via transesterification. The transesterified oil samples with methanol and potassium hydroxide gave their corresponding methyl esters (Biodiesel) which were washed and dried at 55°C. The physico-chemical analysis of the refined palm kernel methyl ester (PKOM) and it's blend with the convensional diesel fuel (PKOM B20) gave the following result; Viscosity (centipoises), Carbon residue (mg/cm^3) Rate of open combustion (cm^3/min), Specific gravity (g/cm^3), Heat of combustion (MJ/Kg), Acid value (mgKOH/g), Flash point (°C), Peroxide Value (mg/g), Moisture content (%) and colour to be: 6.27 and 4.11, 0.19 and 0.20, 5.02 and 3.15, 0.89 and 0.87, 41.20 and 41.30, 133.00 and 130.00, 4.30 and 8.30, 0.23 and 0.22, 0.04 and 0.08, pale yellow and deep yellow respectively. The analysis of the roosted palm kernel methyl ester (RPKM) and its blend with the conventional diesel fuel (RPKOM B20) gave these corresponding values under the same reaction conditions; 3.75 and 2.45, 0.19 and 0.18, 2.21 and 1.72, 0.88 and 0.87, 39.90 and 40.10, 0.20 and 0.21, 130 and 128, 4.70 and 14.90, 0.23 and 0.21, 0.05 and 1.00, light brown and dark brown respectively. The two biodiesel samples and their blends with the petroleum based diesel all gave good fuel characteristics and can be used effectively in place of petroleum diesel.

Keywords: *Methyl ester, Transesterification, Triglyceride, Physico-chemical properties.*

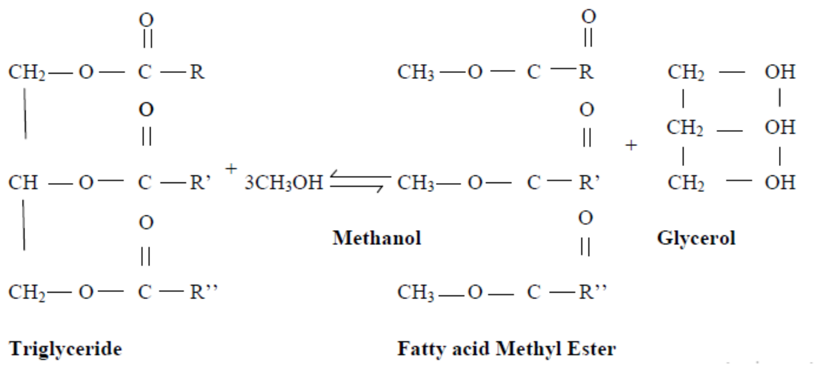
1. Introduction

The process of biodiesel production from fat/oil is not a new process as it was discovered as early as 1853 when scientists Duffy and Patrick conducted the first transesterification of vegetable oil (Meng*et al.*, 2008). The heating of vegetable oil is similar to that of diesel fuel. It's use in the direct engine injection is however restricted by some unfavourable physical properties particularly the viscosity of vegetable oil which is approximately ten times higher than that of diesel fuel. Therefore, the use of vegetable oil in direct engine creates carbon deposition on the injection and fuel built in the lubricating of engine fouling (Encinar *et al.*, 2002).

The techniques applied to overcome the difficulties encountered is using vegetable and animal oil in engine include pyrolysis (thermal cracking) process has been investigated for years, especially without petroleum deposits. Pyrolysis is strictly defined as the conversion of one substance into another mean by heat or by heat with the aid of catalyst (Surma *et al.*, 2020) Pyrolysis can also be defined the heating of biomass in the absence of air at a temperature of 300 to 500 ^oC with the aid of a catalyst. (Surma *et al.*, 2020). Under these conditions, the components which remain are charcoal (solids), and volatiles. The volatiles can after treatment be used as biodiesel fuel (Scragy, 2003) The pyrolysed material can be vegetable oil, animal fats, fatty acids and methyl esters of fatty acids. Micro-emulsification is one of the potential solutions for solving the problem of vegetable oil viscosity. Micro-emulsifications are defined as transparent, thermodynamically stable colloidal dispersion. The droplet diameters in micro-emulsions range from 100 ^oA-1000 ^oA, formed spontaneously from two normally immiscible liquids and or non amphiphiles (Parawa, 2010). Micro-emulsification can be made from vegetable oil with an ester and dispersant (co-solvent) or of vegetables, and alcohol and a surfactant and a cetane improver with or without diesel fuels. All micro-emulsifications with butanol, hexanol, and octanol met the maximum viscosity requirement for diesel fuels. Micro-emulsions are formed by the dispersion of a mixture of oil, water, surfactants and short chain alcohol such as methanol, ethanol, and butanol (Scragy, 2003). This fine dispertion of organic medium is stabilized by amphiphilic molecules, present in an interface through which the hydrochloric molecules results in reduction of viscosity, increase in cetane number and good quality characters in biodiesel (Fukuda *et al.*, 2010).

Another technique applied to overcome the difficulties of using vegetable oil directly in the engine is transesterification of oils to biodiesel (Ong *et al.*, 2014). This method seems to be the most promising as the high viscosities of the vegetable oils are reduced through this process (Ong *et al.*, 2014). Transesterification is a catalyzed chemical reaction involving triglyceride molecule (Vegetable oil/fats) with excess of alcohol (methanol, ethanol, Isopropanol or butanol) in the presence of a catalyst (KOH, NaOH, H_2SO_4 etc.) to produce glycerine (glycerol) and fatty esters,(Mahlia *et al*., 2020; Ong *et al*., 2009). The excess alcohol is used to shift the equilibrium to the product side considering that it is a reversible reaction. To complete a transeterification reaction stoichiometrically, 3:1 molar ratio of alcohol to triglyceride is necessary. In practice, the ratio needs to be higher to drive the equilibrium to a maximum ester yield (Saribayik *et al*., 2012; Raja *et al*., 2011)

This process is presented as follows;



The Chemistry of transesterification is therefore mainly centered on triglycerides because oil/fats contain 98% triglycerides giving a stoichiometric relationship of 3 moles of alcohol per mol of triglyceride to form one molecule of glycerol and three of the respective fatty acid methylesters,(Demibras, 2009)

Biodiesel can be used in it is pure form known as neat biodiesel or B100. This is the approach that provides the most reduction in exhaust particles, unburned hydrocarbons and carbon monoxide. It is the best way to use biodiesel when its non-toxicity and biodegradability are important. Biodiesel can also be used as a blend. The world mostly use a system known as “B” factor to state the amount of biodiesel in any fuel mix, for example 20% biodiesel, 80% petro diesel blend is labeled B20, 5% biodiesel, 95% petrodiesel is labeled B5 and 100% biodiesel is labeled B100,(Alamu *et al*, 2008).

A lot of research on biodiesel production has been carried out using oil-like materials such as vegetable oils and animal fats as well as used frying oil. The feed stock for biodiesel production is however according to the climate and availability. Generally, the most abundant commodity oils or fats in a particular region are the most common feed stock, (Demibras *et al.*, 2007). Mixed feedstock biodiesel production may be employed to provide biodiesel with improved physical properties in comparison to the individual fuels on their own. It may be economically advantageous to extend the lifetime of a comparatively more expensive feedstock through blending with a less expensive feedstock. The recent of the influence of blending various feed-stocks of biodiesel fuel properties include blends of canola, palm, soybean, and sunflower oil methyl esters (Moser, 2008).

This work was designed to compare the properties of biodiesel made from locally available Refined Palm Kernel Oil (PKO) and Roosted Palm Kernel Oil (RPKO) giving room for more viable options for biodiesel production, then blending with the petroleum based diesel was to reduce the cost impact of biodiesel while retaining some of the emission reduction.

2. Materials And Methods

2.1. Collection of Materials

The PKO and locally made RPKO were purchased from Wurukum market while the petroleum based diesel was bought from A.A Shafa Filling Station North Bank, all from Makurdi Benue State, Nigeria.

The samples were collected in Polyethylene containers and stored in a cool cupboard under room temperature. The reagents used for the biodiesel production and in the chemical characterization were all analytical grade reagents, so were used without further purification.

2.2. Methods

Transesterification of the PKO and RPKO was done by separately mixing 1.5g of 85% KOH and 50ml of methanol and stirring for about 45mins in a 500ml beaker. The methoxide solution was added separately into preheated PKO and RPKO (55°C) in each case and details of this process was followed by the method presented by Nwadinigwe *et al*, 2009 with slight modifications. The biodiesel samples obtained from both oils were washed using the bulk washing method and dried at 55 °C for about 1hr,(Tyagi *et al*., 2010; Alamu *et al.*, 2007). The remaining water was removed by heating the biodiesel sample separately in a beaker to allow for sizzling sounds to end the process. The water free biodiesel samples in each case were filtered under vacuum to recover the suspended compounds that solidify at cooler temperature. The diesel samples in each case were mixed with petroleum based diesel in the ratio of 20% for biodiesel and 80% petrol diesel formulations of PKO and RPKO methylesters known as B20. The biodiesel samples as well as their blends (B20) unit the petroleum diesel were then characterized.

2.3. Physico-Chemical Characteristics

The fuel (physical) properties of the PKOM and RPKOM as well as their blends with the petroleum based diesel were determined according to standard methods. Viscosity was determined with a Rotational Viscometer at 30°C, the specific gravity of all the samples was determined the density bottle method. The flash point was determined by using the open cup standard method described by Odega *et al*., 2021, the heat of combustion was determined by an oxygen bomb calorimeter. The following chemical properties of PKOM and RPKOMas well as their blends with the petroleum diesels were determined; acid value and peroxide value were determined by the method of Association of Analytical Chemists as presented by Tor et al, 2017. The moisture contents and carbon residue of the samples were also determined.

3. Results And Discussion

3.1. Results

Table 1. *Characteristics of biodiesel produced with PKO and Its Blend with Petroleum Diesel*

Property	Unit	Biodiesel from PKO	Blend Of Biodiesel With Petroleum Diesel (PKO 20)
Viscosity	Centipoises	6.27	4.11
Carbon Residue	Mg/cm^3	0.19	0.20
Rate of Open Combustion	cm^3/mins	5.02	3.15
Specific Gravity	g/ cm^3	0.89	0.87
Heat Combustion	Mj/kg	41.20	41.30
Flash Point	^0C	133.00	60.00
Peroxide Value	Mg/g	4.30	8.30
Acid Value	mgKOH/g	0.23	0.22
Moisture Content	%	0.04	0.08
Colour		Pale yellow	Dark yellow

Table 2. *Characteristics of biodiesel Produced with RPKO and Its Blend with Petroleum Diesel*

Property	Unit	Biodiesel from RPKO	Blend Of Biodiesel With Petroleum Diesel (RPKO 20)
Viscosity	Centipoises	3.75	2.45
Carbon Residue	Mg/cm^3	0.19	0.18
Rate of Open Combustion	cm^3/mins	2.21	1.72
Specific Gravity	g/ cm^3	0.88	0.87
Heat Combustion	Mj/kg	39.90	40.10
Flash Point	^0C	130.00	58.00
Peroxide Value	Mg/g	4.70	14.90
Acid Value	mgKOH/g	0.23	0.21
Moisture Content	%	0.04	0.08
Colour		Pale yellow	Dark yellow

3.2. Viscosity

The viscosities of the PKOM and RPKOM samples were determined using a Rotational Viscometer at 30^0C. The values obtained in centipoises were 6.27 and 3.75 respectively. The corresponding values obtained were when the viscosity was repeated for the blend with petro-diesel which yielded PKOM B20 and RPKOM B20 samples under the same conditions. The following values in centipoises were obtained respectively: 3.75 and 2.45. These values are in agreement with the values specified by ASTM 7467 for biodiesel blend with petro diesel (B20) which is in the range of 1.9 – 4.2 mm^2/s at 40 $^\circ$C. The value obtained from the result of PKOM was however slightly higher than the range specified by ASTM D443 for biodiesel. Viscosity influences the ease of starting an engine. The fuel with very low viscosity provides a very fine spray in an engine, this gives good optimization and complete combustion of the biodiesel inside the engine which allows room for a healthier engine, (Alptekon, 2009).The performance of the samples as obtained from the results is in increasing order: RPKOM B20, RPKOM, PKOM B20 and PKOM.

The result obtained from the analysis also indicates that the removal of glycerine during the transesterification process is to make the resulting biodiesel less viscous and this has been achieved in this study making the RPKOM B20 and RPKOM even more viscous. This result is in agreement with results presented by Nwadinigwe *et al.,* 2009.

3.3. Specific Gravity

The specific gravity of biodiesel is lower than that of water as result of the fatty acid content which usually always determines the specific gravity. It is known that the biodiesel density depends on its ester content and remaining quantity to alcohol, in essence this choice of the vegetable oil, the denser the vegetable oil, the denser the biodiesel, (Encinar *et al*, 2010, Alnuami *et al.,* 2014). The results of the specific gravity in g/cm^3 obtained from the PKOM and its blend with the petro-diesel PKOM gave the following values; 0.89 and 0.87 respectively. The corresponding values obtained when the RPKOM and its blend with the petro diesel RPKOM B20 were determined under the same conditions gave the following values; 0.88 and 0.87 respectively. All the samples gave values within the acceptable value specified the European for standardization EN 14214 biodiesel fuel which is within the limit of 0.86 – 9.00 g/cm^3 indicating that substantial amount of heat of combustion will be generated when using these fuels (Kirk and Otham, 2005).

3.4. Carbon Residue

Carbon residue of a sample is indicative of carbon depositing tendencies of the fuel. Carbon residue show high correlation with the presence of free fatty acid, glycerin, soaps, polymers and other impurities. The values of carbon residue obtained from the result of the biodiesel samples; PKOM and RPKOM as well as their blends with the petroleum diesel, PKOM B20 and RPKOM B20 gave the following results in mg/cm^3: 0.19, 0.19, 0.20, 0.18 respectively. The values obtained from RPKOM B20 and PKOM B20 were much lower. However all the values were within European Committee for Standardization EN14214 biodiesel fuel which is 0.30 max.

3.5. Rate of Open Combustion

Open combustion of a system allows both energy and mass in and out of a system. In this system, there is continuous interaction between energy and mass transfer thereby leading to rapid oxidation of fuel. In this reaction a huge amount of energy is released. The rate of open combustion values obtained from the analysis yielded the following results for the PKOM and RPKOM: 5.02 and 2.21. The corresponding values of 3.15 and 1.72 were obtained for the analysis of the blend with petro based diesel RPKOM B20 and CPKOM B20 when the analysis was done under the same conditions.

3.6. Heat of Combustion

The heat of combustion of the biodiesel samples of PKOM and RPKOM was determined with an oxygen bomb calorimeter. The values which were obtained in Kj/g were 41.20 and 39.90. The following values were obtained when the analysis of PKOM B20 and RPKOM B20 was done under the same conditions; 41.30 and 40.10 respectively. These values are in agreement with the specification for biodiesel standard which is 33 – 40 MJL^{-1}. This indicates that the PKOM and RPKOM as well as their blend with the petroleum based diesel PKOM B20 and RPKOM B20 Samples will give out substantial heat on combustion in a diesel engine.

3.7. Flash Point

Flash point is the minimum temperature at which the fuel will give off enough vapours to produce an inflammable mixture above the fuel surface when the fuel is heated under standard conditions (Chuepeng *et al.,* 2010). The results of the flash point determination of the biodiesel samples PKOM and RPKOM as well as their blends with the petroleum diesel gave the following values in degree celsius; 133, 130, 70, and 68 respectively. From the results, the value of blends with fossil based fuel RPKOM B20 and PKO B20 was only slightly higher than the acceptable limit given by ASTM D7467 which is 52^0C. This is owing to the fact that biodiesel with lower viscosity tend to have lower flash point which is in agreement with results presented by Odega *et al*, 2021. The values of the biodiesel samples were all within the permissible limit given by ASTM D93 which is 130 °C min and 150 ˚C max. This indicates that all the samples pose no risk of fire outbreaks allowing easy handling and storage of the fuel samples, (Belewa *et al.,* 2010).

3.8. Peroxide Value

The peroxide value determination of the PKOM and RPKOM gave the following results; 4.30 and 4.70 mg/g respectively. Analysis of the fossil based diesel PKOM B20 and RPKOM B20 were also determined under the same reaction conditions and the following values were obtained; 8.30 and 14.90 mg/g respectively. The PKOM and RPKOM gave lower values indicating that the fuel samples are less susceptible to oxidation so can be stored for a longer period of time. The fossil/biodiesel blend PKOM B20 and RPKOM B20 gave higher values indicating that they are more susceptible oxidation forming peroxides, a condition known as rancidity. Therefore, a lot of care should be taken during storage, (Encinar *et al.,* 2002).

3.9. Acid Value

The acid value determination is used to quantify the presence of acid molecules in a biodiesel sample, (Asoquo, *et al*., 2010). The acid values of all the samples of PKOM, RPKOM and their blends with the petroleum based diesel PKOM B20 and RPKOM B20 yielded the following results in mgKOH/g: 0.23, 0.23, 0.22 and 0.21 respectively. These values are within the permissible value given by ASTM D664 which is 0.5 max and ASTM D7467 which is 0.3 max for the blend with petro diesel. The presence of free fatty acid in fuels more than this value can lead to corrosion of engine waves, (Nwadinigwe *et al.,* 2009). This also indicates that, there was minimal moisture retained in the biodiesel.

3.10. Moisture Content

Biodiesel water content is an important parameter because it affects biodiesel oxidation and stability therefore influencing the storage life of the fuel. Dias *et al*, 2008. The moisture content of the PKOM and RPKOM was determined and the values obtained were 0.04 and 0.05% respectively. These values are within the acceptable limit given by ASTM for biodiesel D2709 which is 0.05% max. The values obtained when the moisture contents of the petro-diesel blend PKOM B20 and RPKOM B20 were determined under the same conditions yielded the following results; 0.06 and 0.08 % respectively. These values were slightly higher than the specification given by ASTM. This could have been as a result of dissolved water molecules in the petroleum diesel that was used for this work. This agrees with results presented by Nwadinigwe *et al*., 2009 since the moisture content in their petroleum diesel was reported to be 1.00% values much higher than this value can contribute to microbial growth in the fuel, a problem that can occur in both biodiesel and petroleum diesel fuel and can result in acidic fuel and sludges that plug fuel filters, (Nwadinigwe *et al.,* 2009).

4. Conclusion

The transesterification of PKO and RPKO yielded their methyl esters PKOM/RPKOM which when blended with the petroleum based diesel gave PKOM B20 and RPKOM B20 respectively. Physico-chemical analysis of the biodiesel from the two samples showed that they are very important sources of fuel for the diesel engine. The biodiesel from PKO amazingly gave very low viscosity giving the biodiesel more excellent performance in the engine. The other critical parameters of specific gravity, flash point and acid value of all the biodiesel samples compared well with the specification given by ASTM.

The biodiesel from PKO and RPKO samples showed minimal amount of moisture indicating that it can be stored effectively and will not support microbial growth. The blends of the biodiesel with the petroleum based diesel however should be stored properly and used on a short term base as its moisture content was higher in the samples.

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