Full Length Research Paper

The effects of transesterification on selected fuel properties of three vegetable oils

Emmanuel I. Bello*, Taye S. Mogaji and Makanju Agge

Department of Mechanical Engineering, Federal University of Technology, Akure, Ondo State, Nigeria.

Vegetable oils have fuel properties that are not compatible with the requirements for use as diesel engine fuel, the common method of properties modification is by transesterification which involves stripping glycerines from the triglycerides. To determine the effects of transesterification, 5 properties were selected and their values were measured before and after transesterification. The fatty acid profile of the vegetable oils was also measured by a chromatography analyzer to determine the impact of fatty acids composition. The results obtained shows that for example, density reduces by 7 to 9% while cetane number increased by 60 to 78%. Transesterification tends to make the properties of vegetable oils close to those of diesel.

Key words: Transesterification, fatty acids, fuel properties, castor oil, pumpkin oil, groundnut oil.

INTRODUCTION

Plants make vegetable oils from about six to seven different fatty acids and glycerol, which is a form of alcohol. Vegetable oil is thus a mixture of a number of different glycerides esters of fatty acids called triglycerides which are structurally one molecule of glycerol esterified to three molecules of long chain monocarboxylic (fatty) acids. The chemical formula for vegetable oil is in the form $C_{19}H_{34}O_2$ with O_2 constituting about 10% by weight and that of diesel fuel is in the form $C_{16}H_{34}$. The presence of O_2 in vegetable oil lowers the heating value by 5 to 8% of that of diesel fuel because O_2 has lower heating value, than the carbon and hydrogen present and occupies the space that would otherwise have been occupied by them which reduces the energy per unit mass (Probstein and Hicks, 1982). In recent years, there has been an upsurge in the testing of vegetable oils as alternative fuel for diesel engine because of its renewable source, similarity of its physical structure and properties to diesel fuel and the fact that it is available in every part of the world. The oxygen content also helps combustion, which allows for more complete combustion and hence reduced exhaust emissions. Many reports have concluded that vegetable oil hold promise as alternative fuel for diesel engines (Scholl and Sorenson, 1993; Wagner and Peterson, 1982; Bagby and Freedman, 1988; Bagby and Freedman, 1987; Barsic and Humke, 1981; Bartholomew, 1981; Blumberg et al., 1982)

The major hindrance to the use of vegetable oil as diesel engine fuel is the very high viscosity which affects atomization of the fuel, cold flow properties and causes unacceptable increase in carbon deposits on the engine internal components. The heating value and cetane number are also lower than that required for efficient operation of diesel engines (Ma and Hanna, 1999; Dorado et al., 2002; Mittelbach and Remschmidt, 2004). The most viable process for transforming the properties toward the requirement for diesel fuel is by transesterification and is the process of converting vegetable oil to esters. The transesterification process uses alcohol in the presence of a catalyst to chemically breakdown the molecules of the vegetable oil, during which the glycerol from the triglycerides are removed and replaced with radicals from the alcohol used. This transforms the branched molecular structure of vegetable oil into smaller straight chain molecular structure, identical to but much longer than that of diesel fuel (Meher et al., 2006). The process results into the formation of mono-alkyl esters (biodiesel) and glycerol as shown in Figure 1.

Transesterification is the process of reacting vegetable oils with alkali in the presence of a catalyst to produce an ester of the vegetable oil, which is generally called

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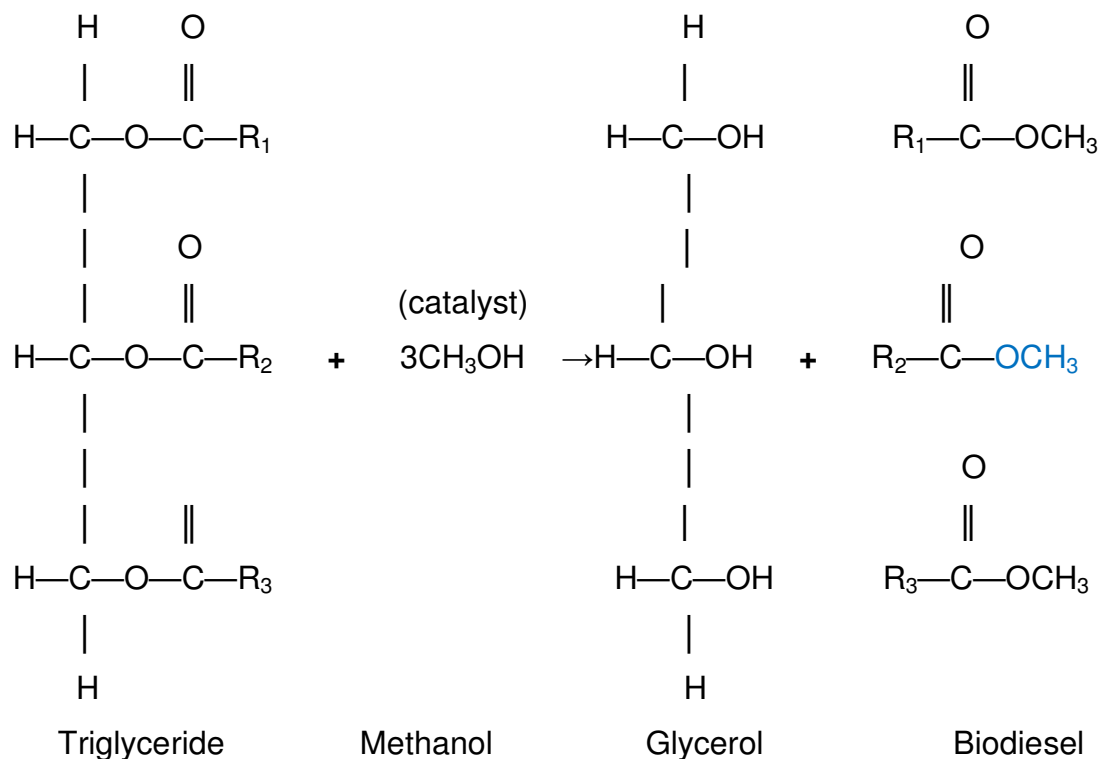*Corresponding author. E-mail: eibello2005@yahoo.com

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\begin{array}{ccccccc}
\text{H} & \text{O} & & & \text{H} & & \text{O} \\
| & \| & & & | & & \| \\
\text{H—C—O—C—R}_1 & & & & \text{H—C—OH} & & \text{R}_1\text{—C—OCH}_3 \\
| & & & & | & & \\
| & \text{O} & & & | & & \text{O} \\
| & \| & \text{(catalyst)} & & | & & \| \\
\text{H—C—O—C—R}_2 & + & 3\text{CH}_3\text{OH} & \rightarrow & \text{H—C—OH} & + & \text{R}_2\text{—C—OCH}_3 \\
| & & & & | & & \\
| & & & & | & & \text{O} \\
| & \| & & & | & & \| \\
\text{H—C—O—C—R}_3 & & & & \text{H—C—OH} & & \text{R}_3\text{—C—OCH}_3 \\
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Triglyceride   Methanol   Glycerol   Biodiesel

Figure 1. Esterification process.

biodiesel. It has also been defined as the displacement of ester by another ester (Otera, 1993). Biodiesel is the mono alkyl ester of vegetable oil or animal fats (Knothe, 2005). Biodiesel is chemically simple, consisting of no more than six or seven fatty acid esters in the mixture. Transesterification reduces the molecular weight and viscosity while also increasing the volatility but maintains the cetane number and heating value (Lague et al., 1987; Canakci and Van Gerpen, 1999). Additional advantages include reduction in most exhaust emissions, improved biodegradability, inherent lubricity, higher flash point and domestic source of feedstock (Knothe, 2006). Since different vegetable oils and animal fats may contain different types of fatty acids, the fuel related biodiesel properties are generally affected by the choice of raw materials (Graboski, 1997). The length and degree of saturation of the fatty acid alkyl chains affect properties such as cetane number, oxidation, cloud point and NO_x emissions.

Thus, the final physical properties of biodiesel will depend on the properties of the component free fatty acids present and this allows biodiesel can be formulated and selected to have a specific property. The saturated acids exhibit higher freezing points than the unsaturated acids. The boiling points of the acids are however, dependent on the length of the carbon chain but nearly independent of the degree of unsaturation. The effect of transesterification on vegetable oil is well known but only very little quantitative investigation have been conducted.

The aim of this study is to quantify the effect of transesterification on the fuel properties of three selected vegetable oils.

MATERIALS AND METHODS

Castor, pumpkin and groundnut oils were extracted by soxhlet extraction method and pretreated with sulphuric acid to neutralize the high free fatty acids level. 3 g/L of sodium hydroxide was added to methanol in a mixer and stirred at 350 rpm until it is completely dissolved. It was then mixed with each of the vegetable oils a 250 ml reactor equipped with a heater/magnetic stirred at a molar ratio of 6 to 1. It was next stirred at 1000 rpm for 3 h at 60°C for the reaction to take place. The mixture was allowed to settle for 8 h to drive the reaction to completion and for the mixture to separate into two layers of biodiesel and glycerol, which is denser at the bottom. The mixture was separated using a separating funnel. The biodiesel was washed by mixing with 20 vol.% distilled water and stirred gently for 10 min. It was allowed to settle and it separated into two layers of pure biodiesel and hydrated methanol with the lighter biodiesel at the top which was separated using a separatory funnel. The purpose of washing was to remove impurities such as diglycerine and monoglycerine, catalyst, soap and excess methanol which can affect combustion and exhaust emission. The procedure was repeated three times (Dorado et al., 2002) before being heated to 120°C to remove any water vapour still present.

Chromatography analysis

The fatty acids profile was determined using the modified AOAC

Table 1. Fatty acid compositions of the selected vegetable oils.

Fatty acid	Class	Castor oil	Pumpkin oil biodiesel	Groundnut oil
Dihydroxystearic acid	-	0.7	-	-
Eicosanoic acid	C20:0	0.3	-	-
Linolenic acid	C18:3	0.3	4.4	0.49
Linoleic acid	C18:2	4.2	45.3	23.7
Myristic	C14:0	-	-	0.46
Oleic acid	C18:1	3.0	29.6	42.9
Palmtic acid	C16:0	1.0	11	12.4
Stearic acid	C18:0	1.0	9.7	5.8
Lauric acid	C12:0			0.41
Ricinoleic acid	C18:1	89.5	-	-
Arachidic	C20:0	-	-	4
Behenic	C22:0	-	-	5.1
Erucic	C22:1	-	-	2.3
Lignoceric	C24:0	-	-	2.3
Total unsaturated	-	2.00	20.7	-
Total unsaturated	-	98.00	79.3	-

965.49 and AOAC 996.06 official methods; 50 mg of the extracted fat content of each of the fuel sample was esterified for 5 min at 95°C with 3.4 ml of 0.5 M KOH in dry methanol. The mixture was neutralized by using 0.7 M HCl and 3 ml of 14% boron triflouride in methanol was added. The mixture was heated for 5 min at a temperature of 90°C to achieve complete methylation process. The fatty acid methyl ester was thrice extracted from the mixture with redistilled n-hexzane. The content was concentrated to 1 ml for gas chromatography analysis and 1 µl was injected into the injection port of the Gas Chromatography (GC). The fatty acid methyl esters were separated using HP 6890 Gas Chromatography analyzer powered by HP ChemStation Rev A 09.11 [1206] software and equipped with a flame Ionization Detector (FID) and HP INNOwax column (30 m × 0.25 cm × 0.20 µm film thickness) The carrier gas was nitrogen and the oven initial temperature was at 60°C. The first ramping was at 10°C/min for 20 min and maintained for 4 min. The second ramping was at 15°C/min for 4 min and maintained for 10 min. The detector temperature was 320°C while hydrogen and compressed air pressures were 22 and 35 psi respectively.

Measurement of fuel properties

The properties of the fuels were determined following the American Society for Testing and Materials. The density was determined at 15°C using a density meter following the ASTM. The pour and cloud points were determined using the Cloud point apparatus following the ASTM. The flash point measurements were done according to method D93(ASTM D6751). A closed cup Pensky-menrtens apparatus was used. Cetane numbers were measured by a cetane method Diesel Fuel rating single cylinder engine according to ASTM D613.

RESULTS AND DISCUSSION

The fatty acid composition of the three selected oil are shown in Table 1. Castor oil contains 89% ricinoleic acid and is the only source of an 18-carbon hydroxylated fatty acid with one double bond in each of the fatty acid chains

(Conceicao et al., 2005; Conceicao et al., 2007). The presence of a hydroxyl group at C12 of the ricinoleic acid, the ester linkages, double bonds and hydroxyl groups provide reaction sites that makes it unusually polar which provides sites for the production of a wide range of natural and synthetic resins, waxes, polymers and elastomers.

It also has excellent emollient and lubricating properties, a marked ability to wet and disperse dyes, pigments and fillers (Azumbuja and Dias, 2006; Ogunniyi, 2006) as well as several medicinal values (Brown, 1995). Castor oil has excellent solubility in methanol and hence theoretically an ideal oil for transesterification to biodiesel, requiring a minimum amount of catalyst and heating which can reduce costs of production (Kulkarni and Sawant, 2003). Pumpkin oil biodiesel contains 45% linoleic and 36% oleic acids; 20.7 total saturation and 79.3% total unsaturation, which are unsaturated thus making the methyl ester unsaturated (Schinas, 2009). Groundnut oil biodiesel contains 23.7% linoleic, 42.9% oleic acid, 30.4% total saturation and 67% total unsaturation. It is mostly used as cooking oil because of its very high protein value.

Density

Density is the weight of a unit volume of fluid. It affects the performance of pumps and fuel spray atomization. Fuel injection equipment for example, operates on a volume metering system, hence a higher density would result in the delivery of a slightly greater mass of fuel and hence more power per unit mass flow. Diesel has higher density than biodiesel hence would develop more power for equal mass flow rate. As shown in Figure 2, the
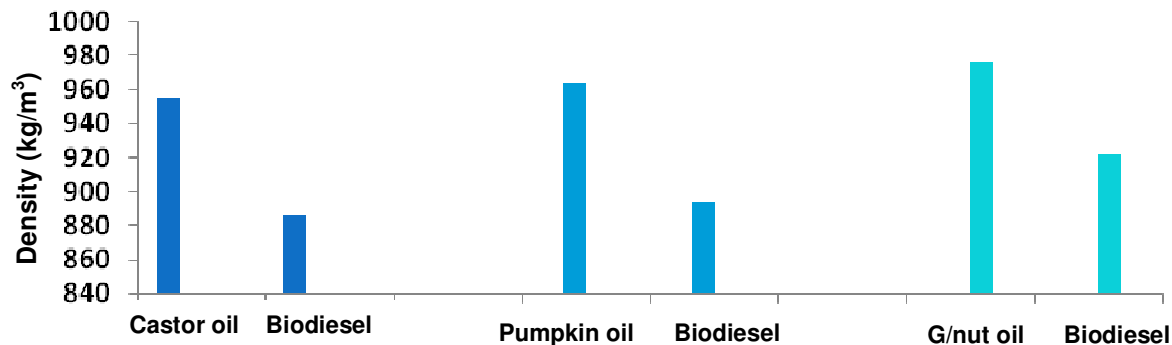
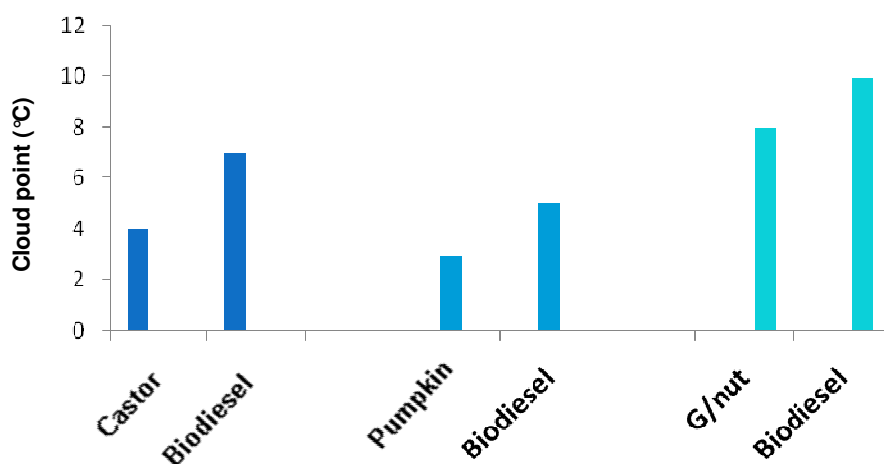**Figure 2.** Change in density after transesterification.

Figure 3. Cloud point after transesterification.

density after transesterification reduced by 9% for castor oil, 7.2% for pumpkin oil and 9% for groundnut oil.

Cloud point and pour point

The cloud point is the temperature at which wax first becomes visible when the fuel is cooled. Cloud point can be modified by using additives that retard the formation of solid crystals in the biodiesel or by blending feed stocks that are relatively high in saturated fatty acid with feed stocks that have lower saturated fatty acid content. The Pour Point is the temperature at which the amount of wax out of solution is sufficient to gel the fuel, thus it is the lowest temperature at which the fuel can flow. Biodiesel has higher cloud and pour points compared to conventional diesel fuel and the value depends on the feed stock used. All biodiesel fuels exhibit poor and different cold flow properties with cloud and pour points 10 to 15°C higher than those of diesel fuel. The data on blends of soya beans methyl ester and tallow methyl ester with diesel fuel fuels indicate that cloud and pour points increased with the increasing ester content

(Midwest Biofuels, 1993). As can be seen in Figure 3, after transesterification the cloud point of castor oil decreased by 75% from 4°C while the pour point decreased from -15 to -26°C a whopping 73%. For pumpkin oil, the cloud point increased by 66% while the pour point decreased by 50% from 3°C. The cloud point of groundnut oil increased from 8 by 2.2% while the pour point decreased from -3 to -6°C representing 100% increase Figure 4. These are substantial improvements in the cold flow properties and castor oil can be used in extremely cold regions.

Flash point

This is the lowest temperature to a barometric pressure of 101.3 kPa (760 mmHg) at which a liquid sample produces sufficient vapour for the air-vapour mixture above the surface to flash momentarily on exposure to a standard source of ignition. Flash point is a measure of volatility and residual alcohol in the fuel, and a determinant of flammability classification of materials. It provides an indication of fire risk in storage under
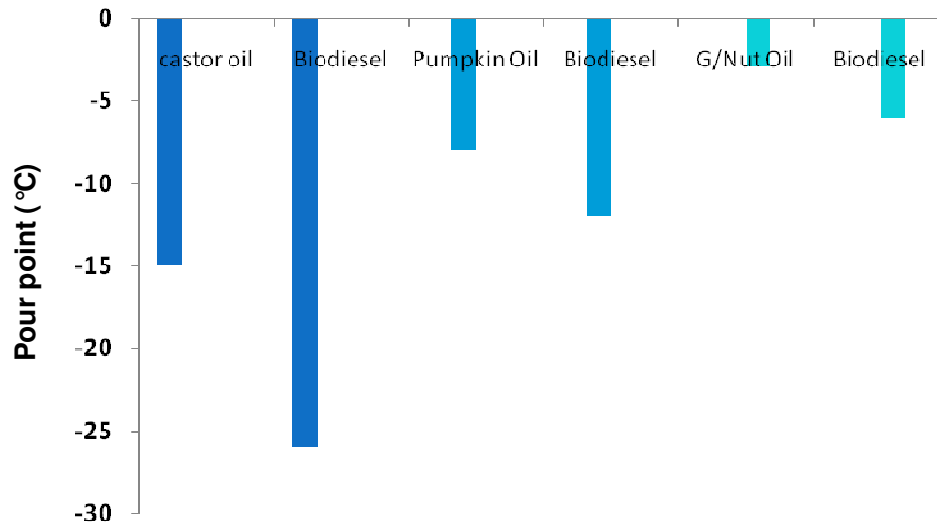
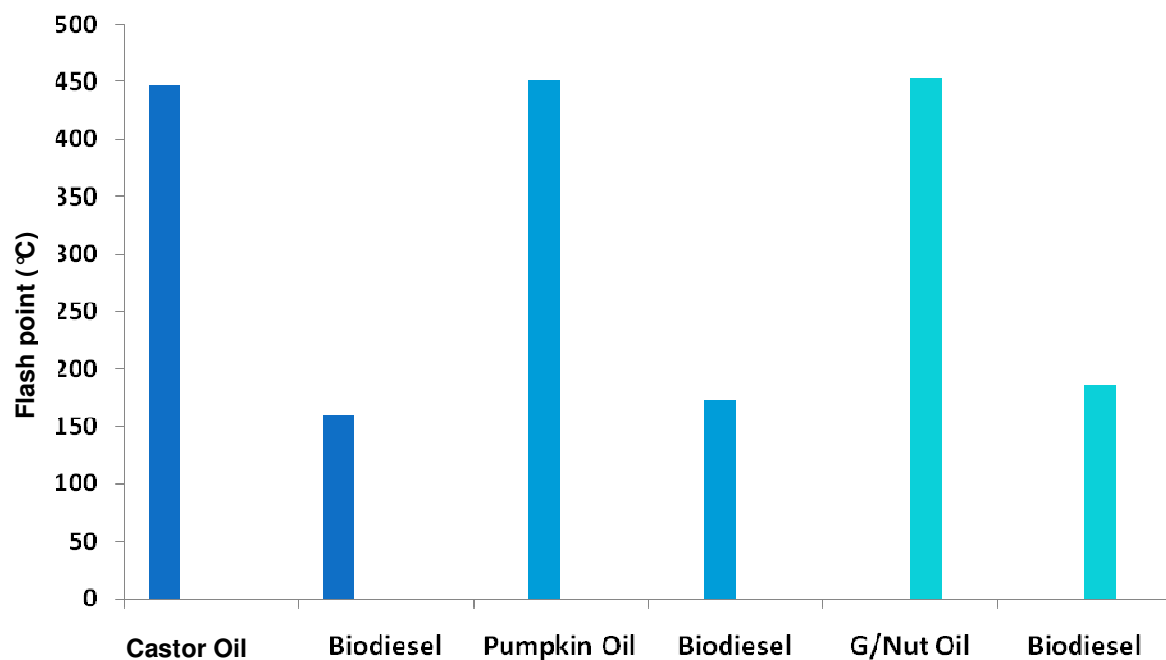**Figure 4.** Change in pour point after transesterification.

Figure 5. Change in flash point after transesterification.

ambient conditions. A fuel becomes difficult to handle if the flash point falls below 130°C limit set by ASTM standards. As shown in Figure 5, after transesterification the flash point of castor oil decreased from 447 to 160°C representing 64% while that of pumpkin decreased from 451 to 172°C while that of groundnut oil decreased from 458 to 180°C which is 56%. Even though the flash point had decreased on the average by 60%, it is still well above the 120°C mark, after which a fuel can be classified as unsafe.

Cetane number

Cetane number is a measure of the ignition quality of diesel fuels and one of the prime indicators of the quality of diesel fuel. It relates to the ignition delay time of a fuel upon injection into the combustion chamber, it influences
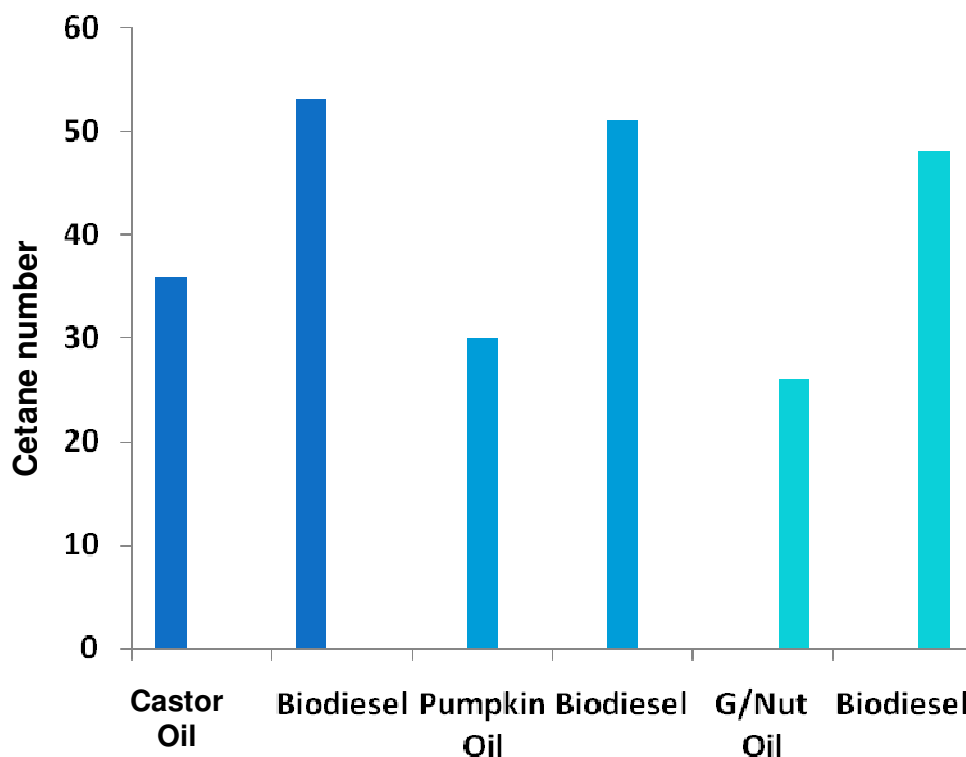
Figure 6. Change in cetane number after transesterification.

ease of starting, duration of white smoke after start up, drivability before warm up and intensity of diesel knock at idle. The shorter the ignition delay time, the higher the cetane number and vice versa. High cetane rating suggests easy cold start and low idle noise and lower emissions and white smoke because of more complete combustion. Biodiesel has a higher cetane number than diesel fuel because of its oxygen content (Ladommatos and Goacher, 1995). Van Gerpen (2005) has shown that the cetane number of biodiesel depends essentially on the distribution of fatty acids in the feedstock. The longer the fatty acid carbon chains and the more saturated the molecules, the higher the cetane number. The unsaponifiable matter in biodiesel does not appear to have an impact on the cetane number.

Diesel engines vary widely in their cetane requirements. In general, the lower an engine speed, the lower is the cetane number it can use. Hence, large marine engines can tolerate fuels with cetane number as low as 20 while high speed engines can require a cetane number of as high as 50. Biodiesel has higher cetane number than diesel because the chemical constituents present in the fuel have very high octane number. In some cases as high as 100, thus it would be possible to formulate biodiesel to have cetane number of 100, but the fact that long chain fatty acids have saturated molecules, they are solid at room temperature and have high crystallization temperature, they cannot be used as fuel for diesel engines. The changes in cetane number is shown in Figure 6. After transesterification, the cetane number for castor increased from 36 to 53 that is 53%, that of pumpkin increased from 30 to 51, 70% while groundnut increased from 26 to 49 which is 186.6%.

Sulfated ash and phosphorus

Sulfated ash is the alkaline catalyst residue remaining after a fuel sample has been carbonized, and the residue subsequently treated with sulfuric acid and heated to a constant weight. It is a measure of the mineral ash residue when a fuel is burned. It is an important test for biodiesel, because it is an indicator of the quantity of residue metals in the fuel that came from the catalyst used in the transesterification process. Especially for base catalyzed transesterification in which the sodium hydroxide and potassium hydroxide commonly used have low melting points and may cause engine damage in combustion chamber.

Thus standards are aimed at the prevention of injector deposits, after transesterification, the sulfated ash of castor oil reduced from 0.02 to 0.008 while phosphorus increased from 1.85 to 3.02. For pumpkin, the sulfated ash decreased from 0.01 to 0.006 while phosphorus increased from 1.68 to 2.93. The sulfated ash of groundnut increased from 2.13 to 4.17 a 95.7% increase and higher than 0.02 ASTM D874 limit as shown in Figure 7. However, phosphorus increased from 2.13 to
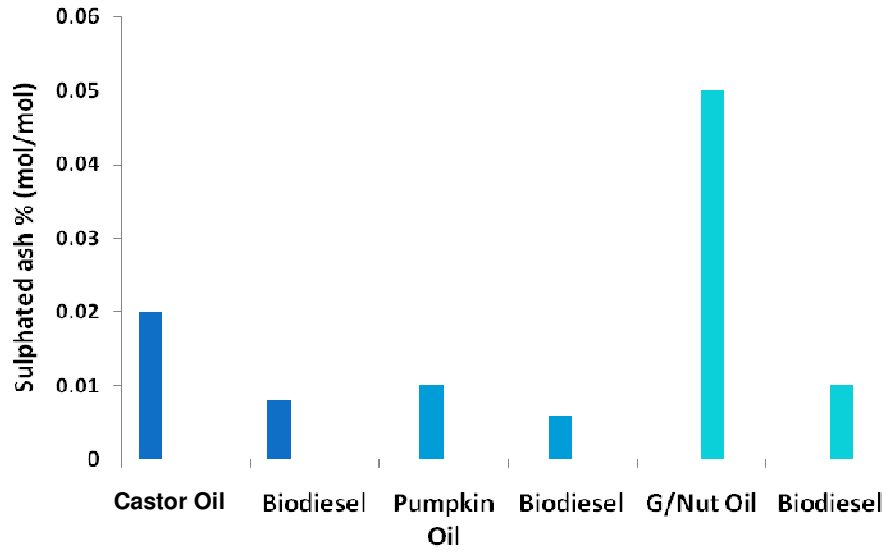
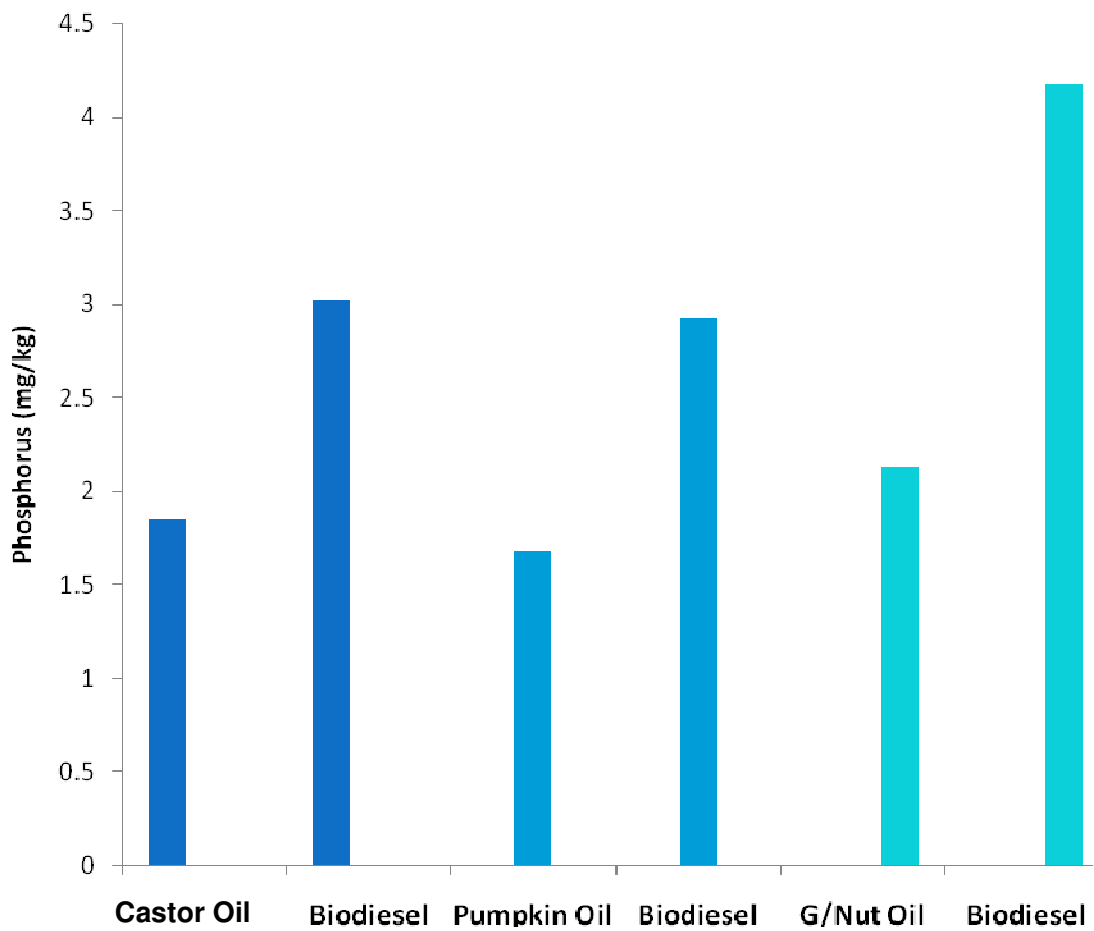**Figure 7.** Change in sulphated ash after transesterification.

Figure 8. Change in phosphorus after transesterification.

4.17 as shown in Figure 8. Phosphorous tends to increase with transesterification, which is detrimental to the use of exhaust catalytic systems the values are however still below the 10.0 mg/kg EN 13107 limit.

Conclusions

It is possible to predict the post transesterification properties of vegetable oils to a reasonable degree of accuracy. Transesterification has positive effects on the properties of vegetable oils which make them compatible with the requirements for diesel engines.

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