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Full Length Research Paper

Cetane number of three vegetable oils, their biodiesels and blends with diesel fuel

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One of the main advantages of biodiesel is the high cetane number that allows for more complete combustion and wider energy release spectrum. To investigate the variation of cetane number with fatty acids profile, transesterification and blending with diesel fuel, the cetane number of cashew nut, egusi melon and rubber seed oils, their biodiesels, 10% (B10) and 20% (B20) blends with diesel fuel were determined analytically by using their distillation characteristics. The fatty acid profile of the three oils, their biodiesels and blends were determined using a chromatography analyzer. The results obtained shows that cetane number increases by an average of 10 to 40% after transesterification and the increase depends on the degree of unsaturation. Egusi melon oil methyl ester the most unsaturated had the lowest cetane number. Blending with diesel decreased cetane number to below that of diesel fuel for all the biodiesels. Highly unsaturated biodiesel tend to have lower cetane number increase after transesterification. They also have higher distillation temperature because they are long chained and have multiple bonds.

Key words: Cashew seed oil, rubber seed oil, melon seed oil, cetane number, fatty acid profile, biodiesel, blends.

INTRODUCTION

Biodiesel is the mono alkyl ester of vegetable oils and animal fats (NBB, 1997; Knothe, 2005) and is gaining worldwide acceptability as alternative fuel for diesel engines because of it agricultural source, high biodegradability, low harmful exhaust emissions, carbon mitigation potentials and high cetane number compared to diesel fuel (Ma and Hanna, 1999; Leung and Guo, 2006; Mittelbach and Remschmidt, 2004; Knothe et al., 2005). Cetane number or index is the principal yardstick for measuring the quality of compression ignition engine fuels. It measures the ignition delay time, it affects ease of starting, duration of white smoke after start up, drivability before warm up and intensity of diesel knock at idle (Laza and Bereczky, 2010). It is generally accepted that a larger cetane number for a diesel fuel results in a shorter ignition delay and duration of the combustion period, less occurrence of knocking, and lower formation of nitrogen oxides (NOx) (Lin and Lin, 2007; Hong et al., 2002; Barabas et al., 2010). Raw vegetable oils commonly have heating and cetane values lower than the minimum set by ASTM for diesel fuel, however, when they are transesterified to methyl esters the heating value increases marginally whereas the cetane number increases between 20 and 40% depending on their fatty acid composition (Bello et al., 2011). Transesterification is the process of reacting vegetable oils with alkaline in the presence of a catalyst to produce an ester of the vegetable oil which is generally called biodiesel along with glycerol. Transesterification reduces the molecular weight and viscosity while also increasing the volatility (Lague et al., 1987; Canakci and Van Gerpen, 1999). Biodiesel is chemically simple, consisting of between six and nine fatty acid esters in the mixture. Biodiesels commonly have a higher cetane number than diesel fuel because of its oxygen content (Laza and Bereczky, 2010) which ensures more complete combustion and also because some of the fatty acids present in the fuel have very high octane numbers. It has also been reported (Knothe, 2005) that the cetane number of biodiesel depends essentially on the distribution of fatty acids in

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the feedstock. The longer the fatty acid carbon chains and the more saturated the molecules, the higher the cetane number. The main properties of the various fatty esters are determined by the structural features of the fatty acid and the alcohol monieties present in the esters. Knothe (2005) reported that the structural features that influences the physical and fuel properties of a fatty ester molecule are chain length, degree of saturation, and branching of the chain and the important fuel properties that are influenced by the fatty acid profile are cetane number, exhaust emissions, heating value, cloud point, pour point, oxidative stability, viscosity and lubricity.

The lower heating value of vegetable oils depends on the composition of the fatty acids, where grown and its vintage among other factors. It increases if the length of the fatty acids increases, and does so to an even greater extent if the content of oxygen in the oil decreases (Laza and Bereczky, 2010). It was reported that methyl esters of saturated acids have a higher cloud point, cetane number and better stability (Ramadhas et al., 2009). Graboski and McCormick (1997) found that the cetane number of biodiesel produced from soybean oil ranges between 45.7 and 56.4. Cherng-Yuan and Rong-Ji (2009) shows that the cetane index of the mixed marine fish-oil biodiesel was 50.9, larger than the cetane index of the commercial biodiesel from waste cooking oil, which was 48.1, because the marine fish-oil biodiesel contained as high as 37.06 wt.% saturated fatty acids, whereas the commercial biodiesel from waste cooking oil contained only 19.77 wt.% saturated fatty acids. Hence, he concluded that cetane index of the biodiesel increased with the proportion of saturated fatty acids. 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 and McCormick, 1997). The length and degree of saturation of the fatty acid alkyl chains also 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 and proportion of the component fatty acids present and this allows biodiesel to be formulated and selected to have a specified 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. Cetane number increases with increasing length of both fatty acid chain and ester groups, while it is inversely related to the number of double bonds.

Many properties of biodiesels vary with chain length, number of bonds and degree of unsaturation (Bagby and Freedman, 1987). It was reported that methyl esters of saturated acids have a higher cloud point, cetane number and better stability (Drown et al., 2001). The effect of blending biodiesel on cetane number is almost linear for mixtures of esters with diesel fuel (Ertan and Canakci, 2009). It has been reported (Knothe et al., 2003) that it is possible to determine the cetane number of esters from their physical properties and equations for predicting the cetane numbers of esters from their properties were developed (Allen et al., 1999; Ladammatos and Goacher, 1995). The effect of transesterification on the cetane number of vegetable oil and its biodiesel 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 cetane number of the three selected vegetable oils

MATERIALS AND METHODS

Three vegetable oils were chosen; cashew nut oil (CNO) which is inedible, cheap and widely available in Nigeria, egusi melon oil (EMO) which is a food item but creates disposal problems when spoilt and rubber seed oil (RSO) which is allowed to waste in rubber plantations. They were transesterified to biodiesel and blended 10% (B10) and 20% (B20) with diesel fuel. The cetane index/number of the biodiesel was calculated using equation 1 (Willard, 1997).

$$CI= -420.34 + 0.016G^2 + 0.192G(\log T_{50}) + 65.01(\log T_{50})^2 - 0.0001809T_{50}^2 \quad (1)$$

where G is the API (American Petroleum Institute) specific gravity and T_{50} is the distillation temperature as 50 vol.% fuel sample distilled and condensed in °F. The vacuum distillation temperatures T_{50} for the samples were determined using the reduced pressure Advanced Distillation Curve (ADC) apparatus and the ASTM D1160 method. The system pressure was set at between 1 and 83 kPa. The uncertainty was less than 1°C for all measurements. The distillation characteristics were determined for the three vegetable oils, their biodiesels (B100), 20% (B20) and 10% (B10) blends with diesel fuel.

The fatty acid profile of the oils were determined by gas chromatography analyzer following the modified AOAC 965.49 and AOAC 996.06 official methods and 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.

Transesterification processes

The rubber seed oil was pretreated with sulphuric acid to reduce fatty acid before transesterification using methanol and sodium hydroxide as catalyst (Ramadhas et al., 2009). 1 litre of methanol and 3.5 g of sodium hydroxide were mixed in a mixing chamber and stirred until it was completely dissolved. The mixture was next mixed with each of the vegetable oils at a molar ratio of 6:1 in a reaction chamber operated at normal pressure and consisting of a heater/mixer set at 60°C. It was stirred at 1000 rpm (Dorado et al.,

Table 1. Fatty acid profile of the vegetable oils, their methyl ester and blends.

Fatty acid	Class	CSO	CSO B100	B20	EMO	EMOME B100	B20	RSO	RSOME 100	B20
Capric	C10:0	1.37	2.23	2.26	-	-	-	-	-	-
Lauric	C12:0	1.83	2.95	3.03	0.66	0.79	0.78	-	-	-
Myristic	C14:0	0.59	0.96	0.97	1.02	0.87	0.87	-	-	0.97
Palmitic	C16:0	28.87	23.13	23.53	12.87	10.24	10.23	19.32	19.64	20.95
Palmitoleic	C16:1	3.16	5.16	5.24	0.74	0.96	0.95	-	-	-
Stearic	C18:0	4.06	5.57	5.67	6.70	11.36	10.32	3.87	5.47	4.83
Oleic	C18:1	34.47	31.65	32.19	13.23	12.84	13.68	23.74	27.82	25.00
Linoleic	C18:2	4.67	7.62	7.75	62.35	62.46	62.22	32.90	35.17	38.48
Linolenic	C18:3	20.97	20.70	19.36	2.42	1.44	0.94	15.16	11.89	10.73
Total unsaturation		67.33			85.44			75.67		

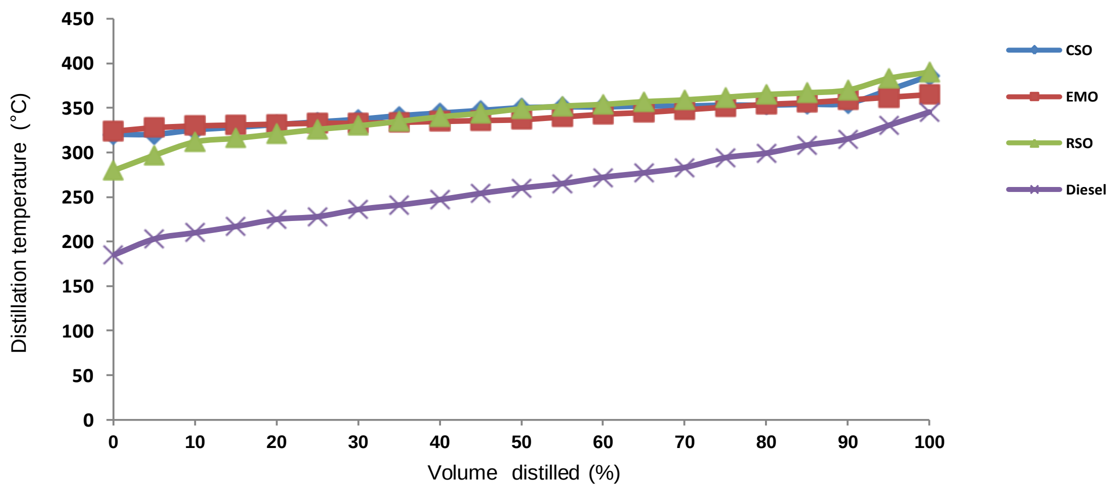

Figure 1. Distillation curves for the oils.

2002] for 4 hours at the set temperature to prevent the escape of the methanol which evaporates at 64.5°C. After stirring, the mixture was allowed to settle overnight for the biodiesel and the glycerol to form different layers and were separated using a separatory funnel. The crude biodiesel was distilled at 70°C to extract the unreacted methanol, which was next first washed by adding 50 wt.% petroleum ether and then washed with 10 wt% distilled water three times to remove other impurities. The washing process resulted into another phase separation made up of emulsified soap plus hydrated methanol at the bottom and biodiesel at the top. This was followed by a distillation process at 105°C to remove the remaining water and unreacted reactant mixture to obtain the biodiesel product for this study.

RESULTS AND DISCUSSION

Table 1 shows the fatty acid profile of the three vegetable oils, their biodiesels and blends. Egusi Melon Oil (EMO) is 85.44%, Rubber Seed Oil (RSO) 75.67% and Cashew Seed Oil (CSO) 67.33% unsaturated. The proportion of the fatty acids changed between 5 to 10% after transesterification and only 1 to 2% after blending. The distillation curves for diesel and the three oils, their biodiesels and blends with diesel fuel are shown in Figures 1 to 4. The initial boiling point for Rubber Seed Oil Methyl Ester (RSOME) is 210°C, for Egusi Melon Oil Methyl Ester (EMOME) is 296°C and Cashew Seed Oil Methyl Ester (CSOME) is 310°C. The distillation temperature corresponding to 50% for diesel is 260°C, those for CSOME, EMOME and RSOME are 335, 345 and 338°C respectively. All are higher than the corresponding temperature for diesel fuel. There is little difference between the distillation characteristics for EMOME and CSOME. The initial temperature for CSO, EMO and RSO are 320, 340 and 280°C respectively and the temperature for 50% distillation for CSO, EMO and RSO are 350, 337 and 349°C respectively. T_{50} region affects the density and viscosity hence biodiesels have higher density and viscosity than diesel fuel. The cetane number of the RSO of 46.3 increased to 51 for the RSOME, reduced to 45.3 and 46.01 for B10 and B20 respectively. That of RSOME is above the minimum limit for biodiesel but reduces with blending because diesel

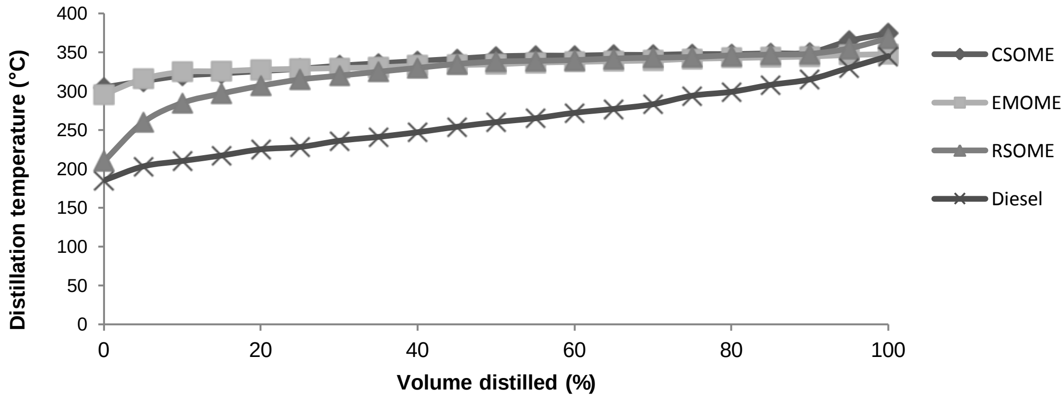

Figure 2. Distillation curves for the esters.

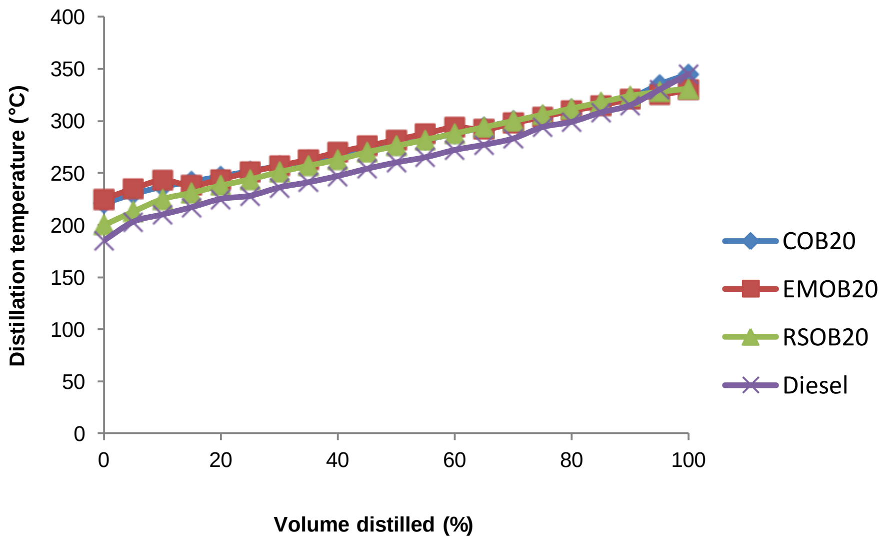

Figure 3. Distillation curves for B20.

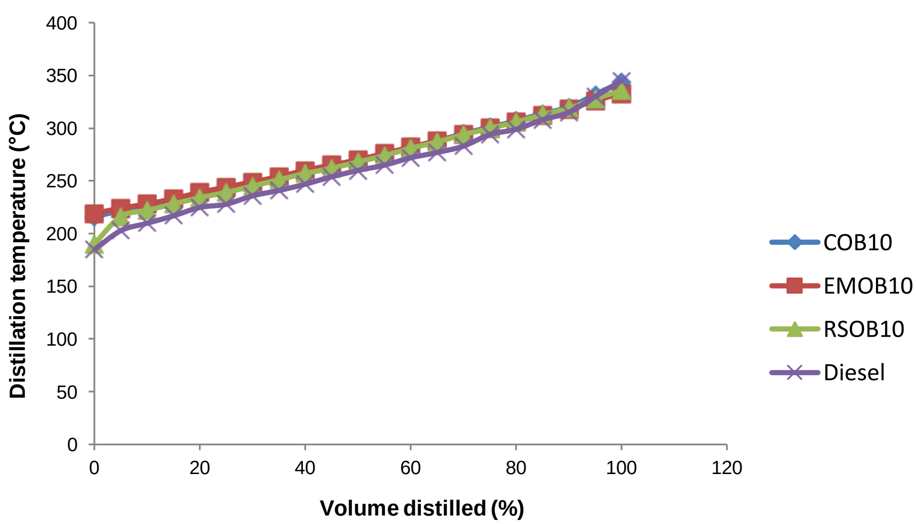

Figure 4. Distillation curves for B10s.

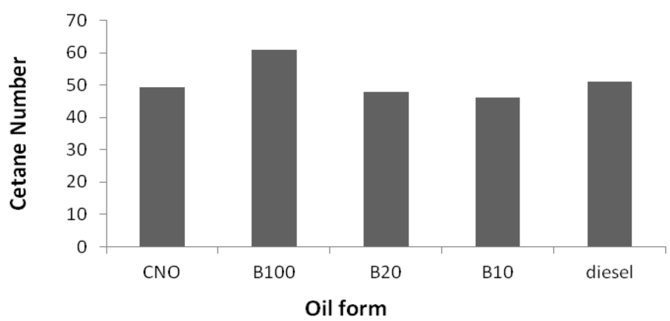

Figure 5. Variation of cetane number of cashew seed oil with form.

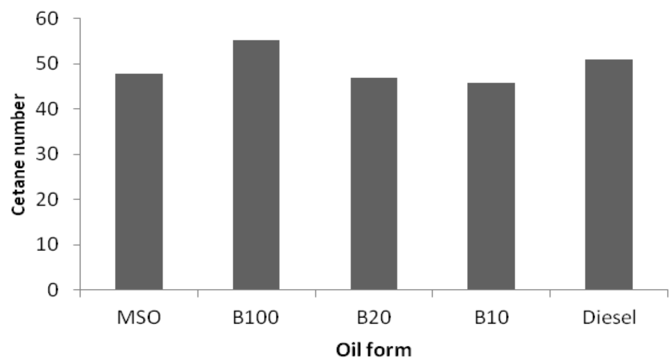

Figure 6. Variation of cetane number of egusi melon seed oil with form.

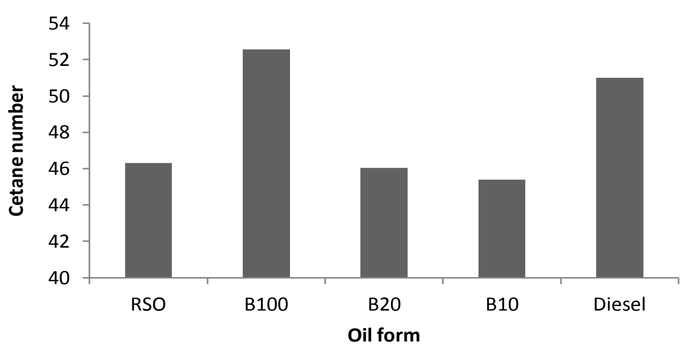

Figure 7. Variation of cetane number of rubber seed oil with form.

has lower cetane number. The calculated cetane numbers for the cashew, egusi melon and rubber seed oils, their methyl ester, B20 and B10 for the oils are shown in Figures 5 to 7 respectively. The cetane number of rubber seed oil increased after transesterification from 46.3 to 52.56. Blending has little effect on the cetane number. The cetane number of cashew seed oil increased after tranesterification from 50 to 63. The cetane number of Egusi melon seed oil increased after transesterification from 48 to 55. Also blending had little

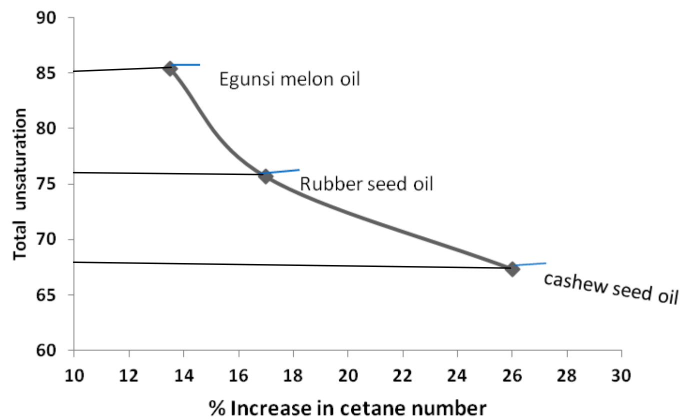

Figure 8. Variation of cetane number with unsaturation.

effect on the cetane number. Cashew seed oil is 67.33% unsaturated, Egusi melon is 75.67% while Rubber seed oil is 85.44% unsaturated. Cetane number tends to decrease with the amount of unsaturation of the oil as shown in Figure 8. The effect of transesterification on the fatty acid profile is not very significant as transesterification is the displacement of alcohol from an ester by another alcohol (Otera, 1993), although the properties may change as a result of the displacement, the net composition remain essentially unchanged. Distillation temperature is a measure of the boiling point of the fuel and affects the combustion characteristics of the fuel. When very high it can shorten the ignition delay thereby making the fuel susceptible to knock.

Conclusions

The cetane numbers of the three selected biodiesels increased after transesterification. Unsaturation decreases the cetane number of biodiesel. Those of the blends decreased with higher diesel content of the blend and have lower values than that of diesel fuel. There is no benefit in using biodiesel blended with diesel fuel as fuel for diesel engines as far as performance index based on cetane number is concern. Highly unsaturated biodiesels have low cetane number and the converse. The temperatures for 50% distillation of all the fuels are higher than that of diesel fuel.

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