PHYSICAL-CHEMICAL PROPERTIES OF CASTOR OIL AND USED COOKING OIL BIODIESEL

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Abstract. *This work shows the physical-chemical properties of blends of diesel oil with two types of biodiesel, one produced from used cooking oil and the other from castor oil. Both fuels were produced from methanol-based transesterification process. The measured properties were fuel density, kinematic viscosity, cetane index, distillation temperatures, and sulfur content. The measurement methods followed international standards for fuel properties determination. The results were analyzed based on Brazilian legal limits for diesel fuels use in and off metropolitan areas. Maximum biodiesel concentrations in diesel oil are proposed based on the properties investigated to comply with the required characteristics of diesel fuels for internal combustion engine application.*

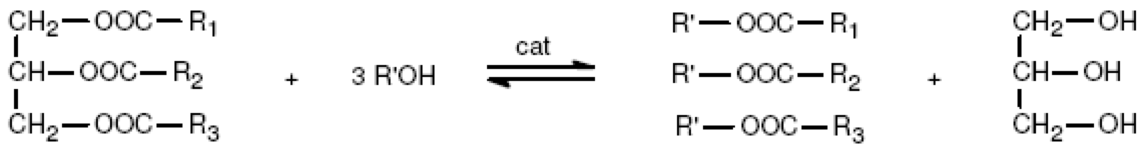
Keywords: *Biodiesel, Properties, Used Cooking Oil, Castor Oil, Biofuels*

1. INTRODUCTION

In a general sense, oils are chemical compounds non miscible with water in liquid state at ambient temperature of 23° C. Oils can be of mineral, vegetable or animal origin. Vegetable oils and fats are substances composed by triglycerides, derived from plants. Vegetable oils are glycerin esters - a blend of soluble fatty acids in organic solvents. Ester is a product of the chemical reaction between an (organic) acid and an alcohol. Use of vegetable oils as diesel engine fuel was first tested in 1895 by Rudolph Diesel, who operated a compression ignition engine fuelled by peanuts oil.

Biodiesel is defined as a fuel composed by mono-alkyl-esters of fatty acids of long chain, derived from vegetable of oils or animal fat. The Brazilian Law n. 11.097, from 13 January 2005, describes biodiesel as "biofuel derived from renewable biomass for compression ignition internal combustion engines application or energy generation, as a partial or total substitute to fossil fuels".

Biodiesel can be obtained from different processes, including cracking and transesterification. Cracking or pyrolysis is a thermal process through which a complex organic molecule of heavy hydrocarbons is modified to light hydrocarbons of simple molecules. Transesterification is a process in which an ester compound is exchanged by an alcohol in the alkyl group (C_nH_{2n+1}), as shown by Fig. 1. These reactions are normally catalyzed by addition of an acid or a base.



Triacilglycerides Alcohol Biodiesel Glycerin

Figure 1: Transesterification process.

The transesterification process is based on the chemical reaction originated from the mixture of a triglyceride with an alcohol under an alkaline or acid catalyst. These alcohols are preferably from the C_1 to C_6 chain, and can be methanol, ethanol, isopropanol or butanol, among others. For obtaining biodiesel in the transesterification process the vegetable oil triglycerides are converted in mono-alkyl esters. In the USA, Canada and Europe methanol is used in the transesterification process for biodiesel production, while Brazil uses both methanol and ethanol.

Biodiesel can be produced from animal fat or vegetable oils. Many oleaginous vegetable species can be used. In Brazil biodiesel has been mainly produced from castor oil, palm tree, sunflower, babassu, peanuts, physic nut, Ethiopian mustard and soybean.

The objective of this work is to present the physical-chemical characteristics of castor oil and used cooking oil biodiesel and discuss it in the light of the required diesel oil characteristics for engine operation. Ideal diesel fuel characteristics include good fluidness in the engine operating temperature range, contamination-free and wax-free, easy ignition, clean and efficient combustion. Typically, petroleum-based diesel fuel viscosity is between 3 and 10 kg/m.s, surface tension is around 3×10^{-2} N/m^2, and density is 800 kg/m^3 (Owen and Coley, 1995). Some physical-chemical characteristics, such as density, viscosity, and metal content, have not yet been defined for Brazilian biodiesel (ANP, 2003). Viscosity is an important fuel characteristic, once it influences pulverization and drop formation in the combustion chamber. Conceição at al. (2005), in a rheological study of castor oil biodiesel, verified its higher viscosity in comparison to mineral diesel oil. Due to its low heating value the engine output power is reduced and fuel consumption is increased with use of pure biodiesel (Cardone at al., 2002), while the thermal efficiency remains constant.

2. PHYSICAL-CHEMICAL PROPERTIES OF DIESEL FUEL

2.1. Density

Fuel density is an essential compression ignition injection system project parameter. The energy amount introduced in the engine is directly dependant on fuel density. For a given engine increased fuel density can result in increased fuel mass consumption, exhaust gas and particulate matter emissions. A reduction in fuel density can simultaneously improve engine efficiency and exhaust emissions. However, it would limit use of diesel oil compounds obtained from oil cracking, which are basically heavy fractions. Furthermore, diesel oil offer would be reduced at increasing demand, thus increasing production costs. Fuel density is a function of temperature.

2.1. Kinematic Viscosity

Adequate fuel viscosity guarantees lubrication of fuel system moving parts and droplet size in the fuel injector exit. As fuel viscosity varies with density and temperature, a variation limit is allowed for diesel fuels. Fuel kinematic viscosity is measured according to ASTM D 445 standard (ASTM, 2006).

2.2. Cetane Number

Diesel ignition quality is measured by the time required to initiate combustion, and depends on engine project, operating conditions and, overall, the cetane number. Cetane number is directly influenced by cetane ($C_{16}H_{34}$, *n-hexadecane*) volumetric concentration present in the fuel. Cetane number is determined through ASTM D 613 standard procedure (ASTM, 2005a) within a scale defined by two pure hydrocarbons. Cetane has the highest ignition quality, scaled 100, while heptamethylnonane ($C_{17}H_{22}$) has the lowest ignition quality, scaled 0. Cetane number strongly influences combustion and, consequently, exhaust gas and noise emissions. Low cetane number can be corrected by addition of organic nitrates, such as amyl nitrate and ethyl-hexyl nitrate.

2.3. Cetane Index

Due to the long time required and the high cost to determine the cetane number, an alternative predicted by ASTM D 976 (ASTM, 2006) or D 4737 standards (ASTM, 2004) is the cetane index, which is a function of the fuel density and evaporation temperature. The cetane index is given by:

$$CI = AP\frac{G_{API}}{100} \tag{1}$$

where AP is the fuel aniline point and G_{API} is the American Petroleum Institute oil classification degree.

Cetane index cannot be used for fuels with additives to correct the cetane number, once such additives do not alter the fuel distillation curve and, thus, do not influence the cetane index. The minimum cetane index recommended for diesel fuel is 45.

Calculation of the cetane index (CI) was first regulated by ASTM D 976 standard (ASTM, 2006), which uses fuel density (ρ) at 15°C and temperature T50 as independent variables (Owen and Coley, 1995):

$$CI = 454.74 - 1641.416\rho + 774.74\rho^2 - 0.554T_{50} + 97.803(\log T_{50})^2 \tag{2}$$

Equation (2) has shown to be inadequate for light oils which final distillation temperature is below 260°C and for fuels with additives to increase the cetane number. Another method to calculate the cetane index is regulated by ASTM D 4737 standard (ASTM, 2004), and uses three points of distillation temperatures (Owen and Coley, 1995):

$$CI = 45.2 + 0.0892(T_{10} - 215) + 0.131(T_{50} - 260) + 0.0523(T_{90} - 310) + 0.901B(T_{50} - 260) - 0.420B(T_{90} - 310) + 0.0049(T_{10} - 215)^2 - 0.0049(T_{90} - 215)^2 + 107B + 60B^2 \quad (3)$$

$$B = e^{[-3.5(\rho - 0.85)]} - 1 \quad (4)$$

2.4. Volatility

Fuel volatility is its ability to turn from liquid into gaseous phase, and is indicated by the temperature at which a fixed volume fraction is vaporized. For instance, the temperature corresponding to 10% of fuel volume evaporated, T_{10}, indicates fuel easiness to evaporate. Fuels of high temperature of 90% fuel volume evaporated, T_{90}, will not be completely burned (Owen e Coley, 1995). Fuel volatility influences diesel engine output power, soot emission and deposit formation in the combustion chamber and in the exhaust system. The more volatile is the fuel, the lower is soot emission and less deposit will be formed.

2.5. Sulfur Content

Sulfur is a natural compound of crude oil and, after combustion, more than 95% is converted into sulfur dioxide (SO_2). The remaining sulfur is aggregated to particulate matter. The presence of sulfur in the fuel wears the engine moving parts, such as cylinder liner and rings. High sulfur concentration in the atmosphere can provoke acid rain. Diesel fuel sulfur content is measured according to ASTM D 4294 standard (ASTM, 2003). In Brazil, fuel sulfur content is presently limited to 500 ppm in metropolitan zones and 2000 ppm in off-metropolitan areas.

3. MEASUREMENT OF BIODIESEL BLEND PROPERTIES

Samples of biodiesel/diesel oil blends were analyzed in the Fuel Testing Laboratory of UFMG. Fuel density was determined using ASTM D 1298 standard (ASTM, 2005b). Fuel kinematic viscosity was measured following ASTM D 445 standard (ASTM, 2006a). The cetane index of the biodiesel blends was determined by the method described in ASTM D 976 standard (ASTM, 2006b). Fuel distillation temperatures were measured according to ASTM D 86 standard (ASTM, 2008). Fuel sulfur content was analyzed following ASTM D 4294 standard (ASTM, 2003). Table 1 shows the biodiesel blends which properties were determined.

Table 1: Biodiesel blends.

NAME	COMPOSITION
B0	Mineral diesel oil
B25M	Blend of 25% castor oil biodiesel and 75% mineral diesel oil
B25U	Blend of 25% used cooking oil biodiesel and 75% mineral diesel oil
B50M	Blend of 50% castor oil biodiesel and 50% mineral diesel oil
B50U	Blend of 50% used cooking oil biodiesel and 50% mineral diesel oil
B75M	Blend of 75% castor oil biodiesel and 25% mineral diesel oil
B75U	Blend of 75% used cooking oil biodiesel and 25% mineral diesel oil
B100M	100% castor oil biodiesel
B100U	100% used cooking oil biodiesel

4. RESULTS

Figure 1 shows that castor oil biodiesel and used cooking oil biodiesel blends have similar densities. Blends of up to approximately 36% castor oil or used cooking oil biodiesel can attend the maximum Brazilian diesel fuel density specification for off-metropolitan areas, of 880 kg/m^3. However, for use in Brazil's metropolitan areas, the maximum diesel fuel density should not be over 865 kg/m^3. In that case, the maximum castor oil or used cooking oil concentration allowed for blending with mineral diesel oil should be about 10%. According to Owen and Coley (1995), higher fuel density can produce more power and soot emissions from diesel engines. For a diesel power generator, as the fuel injection system operates on volumetric displacement basis at a fixed speed, Valente (2008) observed that the higher biodiesel blends density with respect to mineral diesel oil enriched the fuel/air mixture, thus producing increased fuel consumption and emissions of carbon monoxide and hydrocarbons.

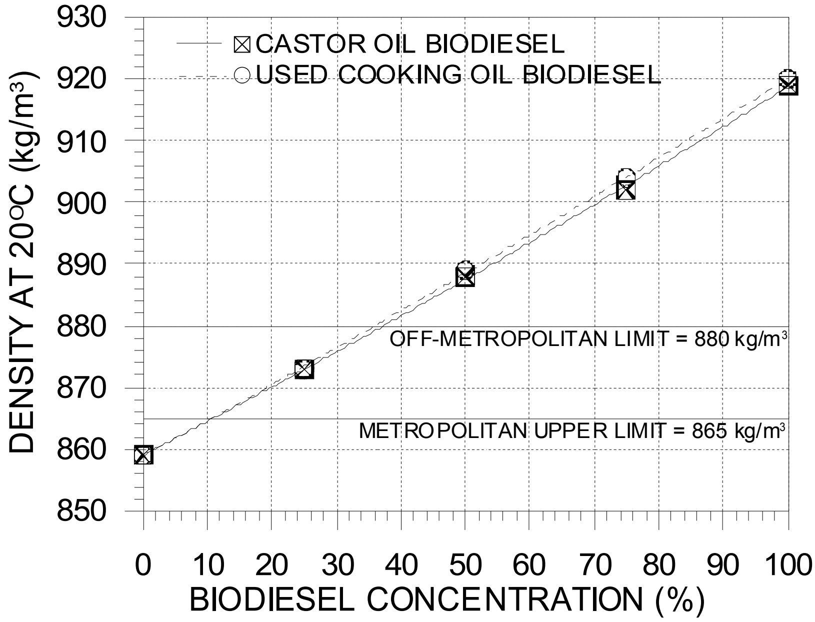


Figure 1: Fuel density variation with biodiesel concentration.

Figure 2 shows that all biodiesel blends present higher viscosity than mineral diesel oil. Castor oil biodiesel blends show viscosity under the maximum recommended limit for diesel fuel, of 5 cm^2/s, up to around 35% concentration in diesel oil. Used cooking oil biodiesel blends attend the maximum recommended viscosity for diesel fuels up to the concentration of 20% in diesel oil. The kinematic viscosity affects injection system lubrication and fuel atomization, being an important parameter to determine fuel injection strategy. High fuel viscosity reduces the fuel amount vaporized prior to combustion (Owen e Coley, 1995).

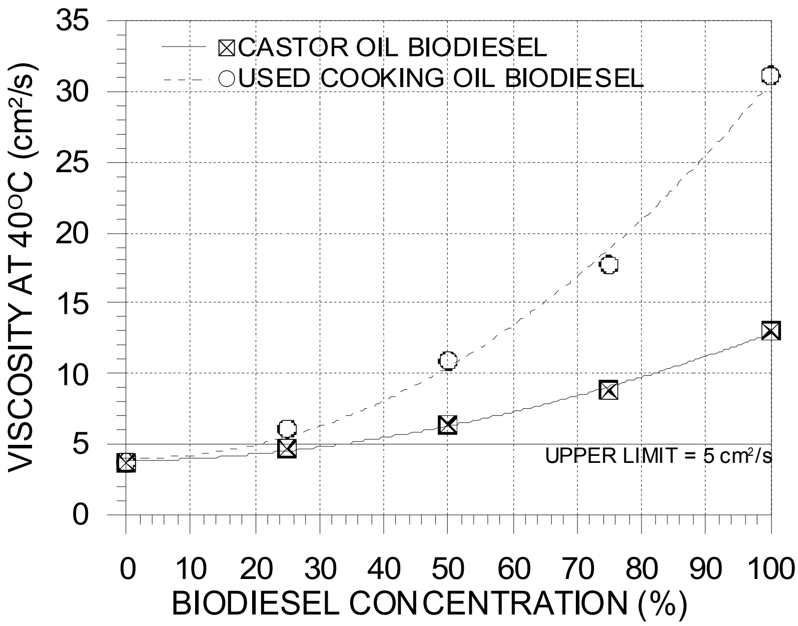


Figure 2: Fuel viscosity variation with biodiesel concentration.

In general, a reduction of fuel volatility is observed with increasing biodiesel concentration, as shown by Figs. 3 and 4. The temperatures corresponding to 10%, 50% and 90% fuel volume evaporated (T_{10}, T_{50} and T_{90}), together with fuel density, are the parameters used to calculate the cetane index. Temperatures T85 (85% fuel volume evaporated) and T90 indicate the fuel tendency to produce soot (Owen and Coley, 1995). Fuel blends with used cooking oil biodiesel concentration over 35% present the temperature T_{50} above the maximum recommended value for diesel fuel, 310 °C

(Fig. 4). For fuel blends with castor oil biodiesel concentration below 50% the T_{50} limit is attended. All biodiesel blends showed temperature T90 below the maximum recommended value for diesel fuels, 360 °C (Figs. 3 and 4), revealing that biodiesel addition to diesel oil reduces the total evaporation temperature.

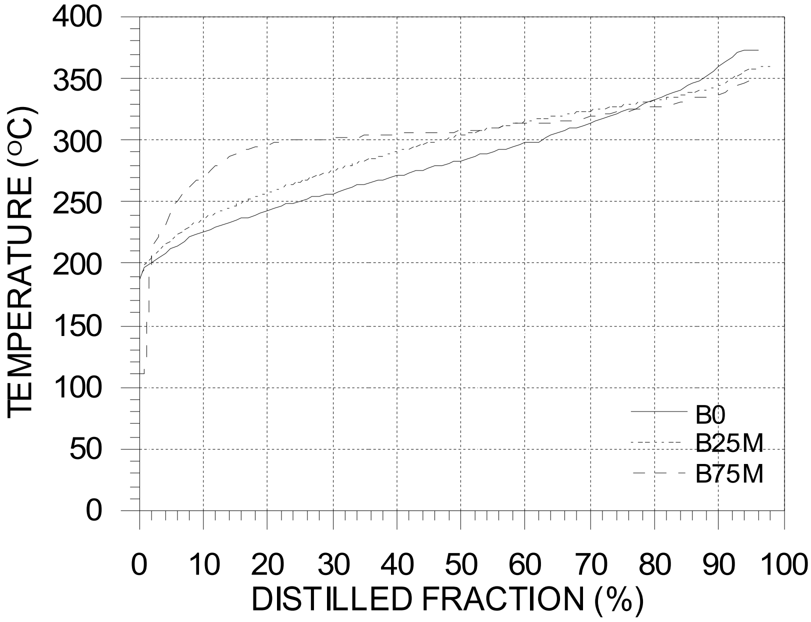


Figure 3: Distillation curve of castor oil biodiesel blends.

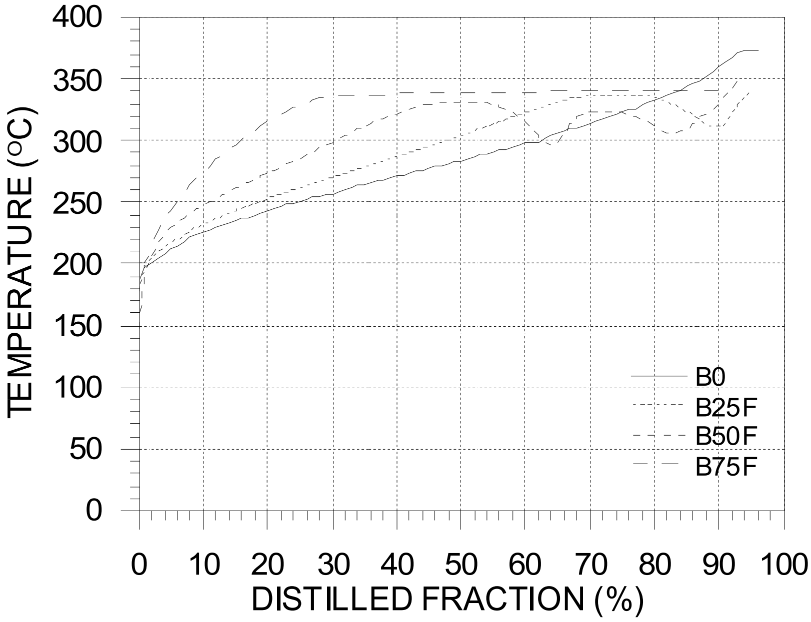


Figure 4: Distillation curve of used cooking oil biodiesel blends.

Figure 5 shows a reduction in the cetane index with increasing castor oil biodiesel concentration in diesel oil. Fuel blends with castor oil biodiesel concentration over 42% fall below the minimum recommended cetane index of 45. For fuel blends with used cooking oil biodiesel an increase in cetane index is observed up to biodiesel concentration of around 30%. With further biodiesel content in the fuel blend the cetane index drops steadily, though staying above the minimum recommended level up to used cooking oil biodiesel concentration of 75%. These results are not in agreement with those found by Sousa Jr. (2009), who found higher cetane number with increasing concentration of soybean biodiesel in diesel oil. Possibly, calculation of cetane index of biodiesel blends through Eq. (2) is not an adequate method, as it was developed for mineral diesel oil. Application of Eq. (3) showed unconvincing results, pointing to even lower cetane index levels with increasing biodiesel concentration.

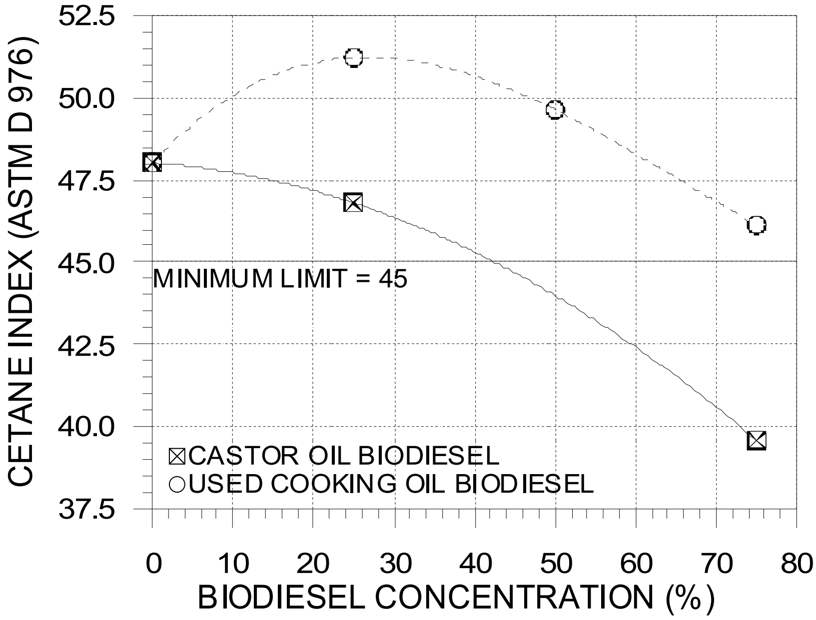


Figure 5: Cetane index variation with biodiesel concentration.

Figure 6 shows fuel sulfur content reducing with increased biodiesel concentration. For 100% biodiesel (B100M and B100F) there is practically no presence of sulfur. All fuel blends presented sulfur concentration below the Brazilian metropolitan limit of 500 mg/kg. Fuel blends with biodiesel concentration over 83% reduce sulfur content below 50 mg/kg, attending present European specification for diesel fuels. Sulfur reduction in mineral diesel oil has been a major task for the Brazilian oil company, due to the high costs involved. Sulfur content limit of 2000 mg/kg specified for off-metropolitan operation is attended by far by all biodiesel blends tested.

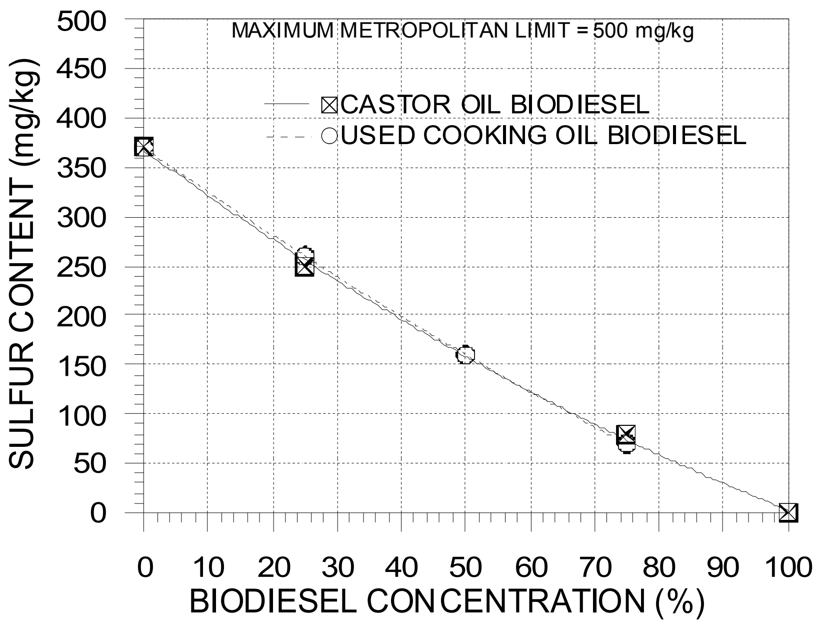


Figure 6: Fuel sulfur content variation with biodiesel concentration.

5. CONCLUSIONS

All castor oil and used cooking oil biodiesel tested presented higher density and kinematic viscosity than mineral diesel oil. The density of fuel blends with castor oil or used cooking oil biodiesel with concentration over 10% was above the recommended metropolitan limit for diesel fuel use, of 865 kg/m^3. Fuel blends with concentrations higher than 35% of castor oil or used cooking oil biodiesel showed density above the recommendation for off-metropolitan diesel fuel use, of 880 kg/m^3. Castor oil biodiesel blends with concentrations under 35% showed viscosity within the maximum recommended limit of 5 cm^2/s at 40 °C, while used cooking oil biodiesel blends exceed that limit with concentrations over 20%.

All biodiesel blends showed higher T_{10} and T_{50} distillation temperatures than mineral diesel oil, meaning that castor oil and used cooking oil biodiesel may introduce difficulties for engine cold start and warm-up operation. With concentrations over 25%, used cooking oil biodiesel blends exceed the maximum T50 temperature recommended limit of 310 °C. On the other hand, lower T_{85} and T_{90} distillation temperatures were found for the biodiesel blends with respect to mineral diesel oil, indicating that castor oil and used cooking oil biodiesel improve diesel fuel capacity to be completely burned, thus reducing exhaust pollutant emissions.

The cetane index decreased steadily with increasing concentration of castor oil biodiesel in the fuel blend, reaching the minimum limit at the biodiesel concentration of 42%. For used cooking oil biodiesel blends the cetane index increased with increasing biodiesel concentration up to 30% then decreased, remaining above the minimum limit throughout the range investigated.

All biodiesel fuel blends showed sulfur content well below the limit of 500 mg/kg for diesel fuel use in metropolitan areas. Castor oil or used cooking oil biodiesel concentrations superior to 85% allow for diesel oil blends reach sulfur content lower than 50 mg/kg, attending present European specifications.

6. ACKNOWLEDGEMENTS

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