**CHEMICAL ENGINEERING TRANSACTIONS** Volume 25, 2011
Editors Jiří Jaromír Klemeš, Petar Sabev Varbanov, Hon Loong Lam
 ISBN 978-88-95608-16-7 ISSN 1974-9791
DOI: 10.3303/CET1125142



# Investigation of Biofuels Properties

Nívea De Lima Da Silva*, César Benedito Batistella, Rubens Maciel Filho, Maria Regina Wolf Maciel

Laboratory of Separation process development, School of Chemical Engineering, State University of Campinas, Zip Code 13081-970, Campinas, SP, Brazil
niveals@feq.unicamp.br.

Biodiesel is an alternative diesel fuel derived from a renewable feedstock such as vegetable oil or animal fat. The physicochemical properties of biodiesel such as density, viscosity, heat capacity and enthalpy may influence the combustion and exhaustive emission. This work presents a comparative study of heat capacities, enthalpy, density, viscosity, and iodine value of biodiesel from six raw materials. The biodiesel were made using bioethanol and sodium hydroxide as catalyst in laboratory scale. The raw materials used were crude soybean oil, castor oil, palm oil, animal fat, waste frying oil, and coconut oil. The results show an increase of the viscosity with the density. It is in agreement with Dermirbas (2008) and it is influenced by the original crude oil. The determination of iodine value is important because the unsaturation can lead to deposit formation and storage stability problems with fuel. In this study, only the frying oil biodiesel had an iodine value larger than the Europe specifications.

## 1. Introduction

A complete understanding of the physical properties of biodiesel raw material is necessary to the development of fuel or fuel extenders using this feedstock. The properties of the various individual fatty esters that comprise biodiesel determine the overall fuel properties. Structural features that influence the physical and fuel properties of a fatty ester molecule are chain length, degree of unsaturation, and branching of the chain. These properties are cetane number and ultimately exhaust emissions, heat of combustion, cold flow, oxidative stability, viscosity, and lubricity (Anand et al., 2011; Garnica et al, 2009; Knothe, 2005). Density is one of the most important properties of fuels, because injection systems, pumps and injectors must deliver the amount of fuel precisely adjusted to provide proper combustion. The spray characteristics upon injection have been closely related to NOx content in the exhausts, it depends on the exhausts temperature and on the heat capacity of fuel. According to Dermirbas (2008), an increase in density from 848 to 885 g/L from methyl esters increase the viscosity from 2.83 to 5.12 $mm^2/s$ and the increase are highly regular.
The viscosity of many petroleum fuels is important for the estimation of optimum storage, handling, and operational conditions. Thus, the accurate determination of

Please cite this article as: Da Silva N.L., Batistella C.B., Maciel Filho R. and Wolf Maciel M.R., 2011, Investigation of biofuels properties, Chemical Engineering Transactions, 25, 851-856
DOI: 10.3303/CET1125142

viscosity is essential to many product specifications. The dynamic viscosity is a measure of the resistance to flow or to deformation of liquid under external shear forces (Forson et al., 2004). Enthalpy is the heat energy necessary to bring a system from a reference state to a given state. Enthalpy is a function only of the end states and it is the integral of the specific heats with respect to temperature between the limit state, plus any latent heat of transition that occurs within the interval. The usual reference temperature is 0 °C (32 °F). Enthalpy data is easily obtained from specific heat data by graphic integration. Generally, only differences in enthalpy are required in engineering design, that is, the quantity of heat necessary to heat (or cool) a unit amount of material from one temperature to another (Speight, 1998).

Many publications show the vegetable oils and biofuel properties. Demirbas (2008) describes a method for estimating the physical properties of soybean oil based methyl ester on their chemical composition and structure over a wide temperature range, up to the critical temperature. Other studies confirm the castor oil properties, this oil fatty structure contains about 90 %wt of ricinoleic acid. This acid has a hydroxyl group, and then it is the unique vegetable oil totally soluble in alcohol. Same biofuel properties such as viscosity, heat value, cetane number, flash point, oxidation stability, and lubrification of castor oil biodiesel are different (Da Silva et al. 2010; Cvengros, 2006).

This work shows the influence of raw material composition in the biodiesel properties. The heat capacities, enthalpies, densities and viscosities were measured at atmospheric pressure. The biodiesel raw materials were coconut oil, palm oil, castor oil, crude soybean oil, frying oil and animal fat. Comparative results of these properties for ethyl esters are not present in the open literature for these six raw materials; then this work aims to describe the effect of fatty acids structure on the heat capacities, enthalpies, viscosities and densities.

## 2. Materials and Methods

### 2.1 Raw materials

The castor oil, crude soybean and palm oil were obtained from Aboissa (São Paulo, Brazil), the frying vegetable oil was collected from local Brazilian restaurant, the coconut oil was donated by Copra (Brazil) and the waste animal fat was donated from a Brazilian butcher's.

### 2.2 Raw materials characterization

The raw materials free fatty acids content was determined according to the AOCS official method Ca 5a-40 as oleic acid. Gas chromatography equipped with a flame ionization detector and with a DB 23 column was used for the raw material composition determination. The fatty acid compositions of the fats were determined by gas-liquid chromatography (GLC). The coconut, palm, soybean, frying oil and animal fat were converted into fatty acid ethyl esters (FAEE) according to Hartman (1973). The castor oil composition was obtained according to Da Silva et al. (2010).

Ethyl esters (biodiesel) conversions were determined by high-performance size-exclusion chromatography (Waters, USA) equipped with two columns Styragel HR 0.5

and HR 2 (Waters) were connected in series and with a differential refractometer detector model 2410 (Waters).

**2.3 Biodiesel production**

The reactions were performed in a batch reactor of 1 L. The system was maintained at atmospheric pressure and the experiments were carried out at constant temperature. The agitation was kept constant at 400 rpm. The reaction time was of 30 minutes. The experiments were carried out using sodium hydroxide concentration and ethanol quantity enough to cause a biodiesel conversion above 90 wt.%.

**2.4 Determination of enthalpies and heat capacities**

Biodiesel samples were analyzed in a differential scanning calorimetric (DSC), model DSC-823e and mark Mettler Toledo. Firstly, the samples were weighed and placed in a pan (Aluminum of 40 μL) into the furnace. Samples analyzed for separated with a heating rate of 20 °C/min, using as inert gas nitrogen with flow rate of 50 ml/min, according to ASTM designation E1269-01. The samples were analyzed from 50 to 150 °C.

**2.5 Determination of viscosity and density**

The density and viscosity were determined by Stabinger Viscometer SVM 3000 (Anton Paar). These properties were measurement at 40 °C (313 K) according to the ASTM D-445.

**2.7 Determination of iodine index**

The iodine index (IV) was determined according to the AOCS Cd 1c-85. The method determines the iodine value for edible oils directly from fatty acid composition. This determination is applicable to triacylglicerols, free fatty acids, and their hydrogenated products. After the determination of the raw materials fatty acid compositions by CG the triacylglicerol iodine value is determined according to Equation (1). The iodine values were expressed as grams of iodine absorbed / 100 g of sample.

$$\begin{aligned} IV = &(\% C16:1 x 0.950) + (\% C18:1 x 0.860) + (\% C18:2 x 1.723) + \\ &(\% C18:3 x 2.616) + (\% C20:1 x 0.785) + (\% C22:1 x 0.723) \end{aligned} \quad (1)$$

## 3. Results and discussions

The free fatty acid content of raw materials were 2.87% to animal fat, 1.20% to castor oil, 0.32 to coconut oil, 2.12 to frying oil, 0.19 to palm oil, 0.60 to soybean oil. Table 1 depicts the raw materials fatty acid profile determined by CG. The biodiesel properties were determined for the purified biodiesel samples because trace of impurities such as raw materials, catalysts or glycerol cause wrong determinations of the properties.

*Table 1 – Fatty acid composition*

| Raw Material | 8:0 | 10:0 | 12:0 | 14:0 | 16:0 | 18:0 | 18:1 | 18:1[a] | 18:2 | 18:3 | 20:0 | 22:0 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Animal fat | | | | 2.1 | 24.0 | 23.5 | 45.8 | | | 2.6 | | |
| Castor oil | | | | | 1.6 | 0.9 | 3.0 | 89.5 | 3.7 | | 0.3 | 0.6 |
| Coconut oil | 4.1 | 4.0 | 41.8 | 21.9 | 12.3 | 2.7 | 10.2 | | 3.1 | | | |
| Frying oil | | | | | 12.0 | 5.0 | 25.0 | | 52.0 | 6.0 | | |
| Palm oil | | | 0.3 | 1.5 | 40.0 | 5.0 | 40.0 | | 11.0 | 0.3 | 0.8 | |
| Soybean oil | | | | | 11.0 | 5.1 | 27.0 | | 51.3 | 5.4 | | |

Where: Caprylic (8:0), Capric (10:0), Lauric (12:0), Myristic (14:0), Palmitic (16:0), Stearic (18:0), Oleic (18:1), Ricinoleic acid (18:1[a]), Linoleic (18:2), Linolenic (18:3), Arachinic (20:0), Behenic (22:0).

### 3.2 Iodine value

Table 3 shows the iodine value. This determination is a description of the unsaturation of the vegetable oil. The results show that the frying oil has the highest iodine value, followed by the crude soybean oil, the castor oil, palm oil, animal fat and coconut oil. The greater degree of unsaturated fatty acids such as linoleic acid, linolenic acids in soybean oil and frying oil cause the high iodine value. There is no Brazilian specification for iodine value but according to the EN 14111 (European Committee for Standardization) this value should be lower than 120 mg iodine/100 g sample. Thus, the biodiesel from frying oil and soybean oil are not suitable to be used as an alternative fuel according to Table 2.

*Table 2 – Iodine value*

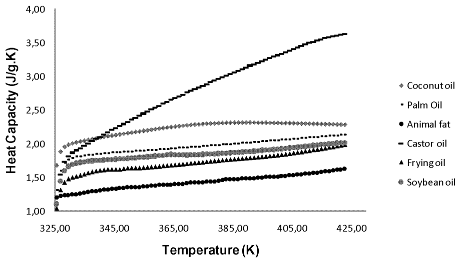
| Raw Material | (IV) |
|---|---|
| Castor oil | 85.96 |
| Palm oil | 54.24 |
| Coconut oil | 14.14 |
| Crude soybean oil | 126.20 |
| Frying oil | 127.26 |
| Animal fats | 46.20 |

### 3.3 Enthalpy and heat capacity

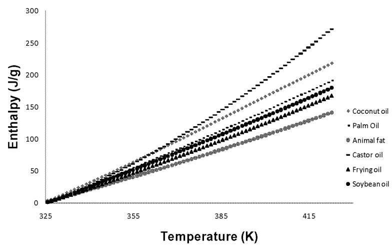
The biodiesel from castor oil presents a faster increase of enthalpy and heat capacity with the temperature and these properties for animal fat biodiesel has opposite effects. The castor oil biodiesel has about 90 % of ethyl ricinoleate and the presence of the hydroxyl group can influence this property. The increase of the heat capacity of biodiesel with the temperature is in agreement with Dzida (2008) for methyl esters of rapeseed oil. The enthalpies increase linearly with the temperature and the heat capacities increase according to four order polynomial equation, Figures 2A and B. Table 3 shows correlations of enthalpies and heat capacities.

*Table 3: Enthalpies and heat capacity correlations*

| Raw material | Correlation | | | |
|---|---|---|---|---|
| | Enthalpy | | Heat capacity | |
| | Equation | $R^2$ | Equation | $R^2$ |
| Animal fat | 1.419T - 382.3 | 0.999 | $-4E\text{-}09T^4 + 6E\text{-}06T^3 - 0.002T^2 + 0.640T - 48.69$ | 0.954 |
| Castor oil | 2.502T - 737.9 | 0.983 | 5.637ln(T) - 30.53 | 0.936 |
| Coconut oil | 2.124T - 616.9 | 0.997 | 1.795ln(T) - 8.438 | 0.846 |
| Frying oil | 1.652T - 469.1 | 0.998 | $1E\text{-}09T^4 - 2E\text{-}06T^3 + 0.001T^2 - 0.447T + 51.63$ | 0.975 |
| Palm oil | 1.876T - 540.5 | 0.998 | 1.267ln(T) - 5.567 | 0.899 |
| Soybean oil | 1.798T - 511.8 | 0.999 | $-2E\text{-}08T^4 + 4E\text{-}05T^3 - 0.019T^2 + 4.679T - 421.3$ | 0.902 |




*(A)*




*(B)*

*Figure 2: (A) Specific heat capacity curves for biodiesel from different raw materials. (B) Enthalpy curves for biodiesel from different raw materials*

### 3.4 Density and viscosity

Table 5 presents the dynamic viscosity and density of biodiesel from different raw materials. The ethyl ester from castor oil presents the highest vicosity and density and the coconut biodiesel has the lowest viscosity and density. The castor oil biodiesel is composed of about 90 wt.% of ethyl esters from ricinoleic acid (C18:1). The molar massa of this ester is 326.5 kg/kgmol, whereas, the coconut biodiesel has 81 % of esters from Caprylic (8:0), Capric (10:0), Lauric (12:0), Myristic (14:0). The coconut biodiesel molar mass is approximately 256 kg/kgmol. Then, these properties increase with the biodiesel molar mass or the ester chain length.

*Table 5: Viscosity and density (40°C)*

| Oil | Raw materials | | Biodiesel | |
|---|---|---|---|---|
| | Viscosity (cSt) | Density (g/cm$^3$) | Viscosity (cSt) | Density (g/cm$^3$) |
| Castor | 245.840±0.302 | 0.9460± 0.0016 | 15.29± 0.014 | 0.9042± 0 |
| Animal fat | 45.250±0.09 | 0.8969±0.0003 | 5.99±0.008 | 0.8565±0 |
| Coconut | 28.749±0.019 | 0.9078±0.0001 | 3.025±0.025 | 0.8492±0 |
| Palm | 41.513±0.1966 | 0.8990±0.0002 | 4.8531±0.0039 | 0.8539±0 |
| Crude soybean | 38.20±0.030 | 0.8908± 0.0001 | 4.3435± 0.013 | 0.8623± 0.0001 |
| Frying | 46.20±0.030 | 0.9048± 0.0002 | 6,41± 0.010 | 0.8664± 0.0002 |

## 4. Conclusions

The determination of enthalpies and heat capacities of several bioesters using DSC equipment as well as evaluation of the behavior of these properties in function of temperature are very important in studies of equipments and systems for industrial plants of biodiesel. Biodiesel from castor oil shows that enthalpy is very susceptible at temperature unlike other biodiesel sources. This fact may be considered due to the hydroxyl group present in the ricinoleic ester. However, the heat capacity behavior is similar to other biofuels.

The ethyl ester from castor oil presents the highest viscosity and density and the coconut biodiesel has the lowest viscosity and density. The results show that the

biodiesel properties are influenced by the original raw materials. The biodiesel viscosity decreases with the increasing in temperature, and according to Goodrum (2002), this happens because the cohesive forces between the liquid molecules decrease with the increase of temperature.
The determination of biodiesel iodine value is important to biodiesel specification because high unsaturations can lead to deposit formation, and storage stability problems. In this study, only the frying oil and soybean oil biodiesel have a iodine value larger than the Europe specifications.

## 5. References

Anand K., Sharma R.P. and Pramod S.M., 2011, A comprehensive approach for estimating thermo-physical properties of biodiesel fuels, Applied Thermal Engineering 31, 235-242.

Cvengros J., Paligová J. and Cvengrosová Z., 2006, Properties of alkyl esters base on castor oil, Eur. J. Lipid Sci. Technol. 108, 629-635.

Da Silva N.L., Batistella C.B., Wolf Maciel M.R. and Maciel Filho R., 2010, Biodiesel Production from Castor Oil: Optimization of Alkaline Ethanolysis, Energy & Fuels 23, 5636-5642.

Dermirbas A., 2008, Relationships derived from physical properties of vegetable oil and biodiesel fuels, Fuel 87, 1743-1748.

Dzida M. and Prusakiewicz P., 2008, The effect of temperature and pressure on the physicochemical properties of petroleum diesel oil and biodiesel fuel, Fuel 87, 1941-1948.

Forson F.K., Oduro E.K. and Hammond-Donkoh E., 2004, Performance of Jatropha oil blends in a diesel engine, Renew Energy 29, 1135-1145.

Garnica J.A.G., Da Silva N.L. and Wolf Maciel M.R., 2009, Production and purification of biodiesel and glycerine, since vegetal oils and kinetic of vegetal oils transesterification reaction for wasted frying oil, Chemical Engineering Transactions 17, 433-438.

Goodrum J.W., Geller D.P. and Adams T.T., 2002, Rheological Characterization of Yellow Grease and Poultry Fat, JAOCS 79, 961-964.

Hartman L. and Lago R.C.A., 1973, Rapid preparation of fatty acid methyl esters from lipidis, Laboratory Practice 22, 475-476.

Knothe G., 2005, Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters, Fuel Processing Tecnology 86, 1059-1070.

Speight J.G., 1998, The Chemistry and Technology of Petroleum, 3th ed., Marcel Dekker, Inc., New York, USA