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Comparative study of calorific value of rapeseed, soybean, jatropha curcas and crambe biodiesel

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Abstract. Biodiesel is a mixture of esters of short chain alcohols, produced as an alternative fuel for mineral diesel substitution. It is originated from renewable sources (fats and oils) and is less pollutants. But for its implementation, it is necessary to analyze some important quality parameters. A very important fuel`s feature is the calorific value, which represents the amount of heat transferred into the chamber during the combustion and indicates the available energy in fuel. The calorific value is obtained experimentally using a calorimetric bomb. The higher the calorific value, the higher is the yield of the fuel. The aim of this study is to determine the calorific value of rapeseed, soybean, jatropha curcas and crambe biodiesel using a calorimetric bomb. The results were associated with the ethyl ester composition of each biodiesel. The crambe biodiesel shows the highest calorific value (ΔH= 40564 J g^{-1}) influenced by the high amount of long chain ethyl ester originated from behenic acid (C22:0) that composes 57.2% of crambe oil. The rapeseed, soybean and jatropha curcas biodiesel that exhibit approximately the same amount of long chain ethyl ester showed calorific values near to ΔH= 39450 J g^{-1}.

Keywords Calorific value, biodFiesel, ethyl ester composition.

1. Introduction

Most of all energy consumed in the world comes from fossil fuels (oil, coal and natural gas). However, these sources are limited and will be exhausted in the near future [1-3]. Biodiesel is a fuel that can replace diesel and it is made from renewable sources such as vegetable oils and animal fats. This fuel is biodegradable and non-toxic and has low profile pollutant emissions compared to petroleum diesel. The use of biodiesel will allow the development of agriculture, economy and environment [4,5].

Biodiesel is produced through a reaction known as transesterification which one mole of triglyceride is reacted with three moles of alcohol (molar ratio of methanol to 3:1 vegetable oil) to form one mole of glycerol and three moles of the respective fatty acid esters [6,7]. Various types of vegetable oils, with a varying composition in fatty acids, can be used for the production of biodiesel. Studies on the influence of the triglyceride composition on the biodiesel properties are scarce [8-11].

The study of the influence of the triglyceride composition on the quality of biodiesel is important. Muniyappa et al. (1996) reported and compared the viscosity, density and cloud point of two biodiesel synthesized by soybean oil and beef tallow. The high cloud point of methyl esters of tallow biodiesel is indicative of a high concentration of saturated fatty acid esters. Cardone et al. (2003) investigated the relationship between the oxidative stability of biodiesel from rapeseed oil and the percentage of linolenic acid raw material. Dmytryshyn et al. (2004) studied four one transesterification of vegetable oils, comparing properties such as density, viscosity, cloud point and pour point and other differences established between them. Currently, the maindisadvantage could be the high costs of some types of raw materials. However, as the petroleum oil reserves become scarce, this behavior could be changed. The main differences between biodiesel and diesel are that the former usually has higher density, viscosity, cloud point and cetane number; and lower volatility, calorific value and sulfur content. Cetane number, viscosity, density and are also important properties of fuels.

Another important parameter of a fuel is the calorific value, which represents the amount of heat transferred to the chamber during combustion and indicates the available energy in a fuel (Demirbas, 2008). The higher the calorific value, the greater the energy contained in the fuel which is obtained experimentally using a bomb calorimeter under defined conditions (ASTM D240). The calorific value of biodiesel is higher (39-41 MJ / kg) compared with other liquid fuels. It is lower than petrol (46 MJ / kg), diesel fuel (43 MJ kg-1) or oil (42 MJ / kg), but higher than coal (32-37 MJ kg-1) [19]. Biodiesel has a calorific value which is about 12% lower than diesel. This property leads to a greater consumer demand for biodiesel to achieve a yield equal to that of diesel [12].

The aim of this study is to determine the calorific value of rapeseed, soybean, jatropha curcas and crambe biodiesel using a calorimetric bomb. The results were associated with the ethyl ester composition of each biodiesel.

2. Material and method

To better understand the results from the calorific values of studied biodiesel, it were study the calorific value of three different ethyl ester since biodiesel is a mixture of different ethyl ester.

To compare with the biodiesel calorific value, it was also determined the calorific value of mineral diesel.

2.1. Samples

For the production of ethyl esters, it was used the reaction of fatty acid with thionyl following the methodology described by Tietze [13]. It was used as reagent the stearic acid (95% purity) and linoleic acid (98% purity), all Vetec brand. The thionyl chloride P.A. and ethyl alcohol with 99.8% purity were purchased from Synth brand.

The purity of the ethyl esters were obtained by thermogravimetric analysis (TGA) and ^{1}H RMN method (Table I).

Table I - Purity of studied ethyl esters.

Ethyl ester	Purity by TGA (%)	Purity by ^{1}H RMN (%)
Palmitate ($C_{18}H_{36}O_2$)	98.34	99.01
Stearate ($C_{20}H_{40}O_2$)	98.33	98.48
Oleate ($C_{20}H_{38}O_2$)	98.18	98.56

The fatty acid composition of the oils used for the synthesis of biodieseis studied is presented in Table II.

Table II - Fatty acid composition of studied vegetable oils.

	soybean	Jatropha	rapeseed	crambe
Octanoic (C8:0)	-	-	-	-
Capric (C10:0)	-	-	-	-
Lauric (C12:0)	0.1	0.02	0.1	0.03
Myristic (C14:0)	0.1	0.07	1.2	0.1
Palmitic (C16:0)	11.3	12.90	2.5	2.0
Stearic (C18:0)	4.1	5.63	2.8	0.9
Oleic (C18:1)	22.7	39.73	63.2	17.2
Linoleic (C18:2)	52.6	40.0	30.0	8.2
Linolenic (C18:3)	7.4	0.22	-	5.0
Araquinidic (C20:0)	0.5	0.18	-	1.1
Gadolenic (C20:1)	0.2	0.07	-	3.7
Behenic (C22:0)	0.5	0.05	-	2.2
Erucic (C22:1)	0.2	-	0.2	57.2
Lignoceric (C24:0)	0.2	0.06	-	0.8
Long chain fatty acid	85.0	85.9	86.6	93.0

The yield of each biodiesel was obtained by nuclear proton ^{1}H RMN: rapeseed (100%), soybean (94%), jatropha curcas (100 %) and crambe biodiesel (97%).

The mineral diesel was kindly donated by Petrobras-REVAP located at the city São José dos Campos-SP.

2.2. Calorific value

The calorific value of the samples was obtained using the calorimetric bomb IKA200 (Figure 1) with the pressure vessel 30 bar with oxygen 97.7%. Results were obtained in triplicate.

Fig. 1. Calorimetric bomb.

3. Results and discussion

The purity of synthesized ethyl esters were analyzed by ^{1}H NMR (Proton Nuclear Magnetic Resonance). Analyses of ethyl palmitate (Figure 2) oleate (Figure 3) and stearate (Figure 4) show no residues of fatty acids after purification since it is not found traces of these fatty acids in the analysis.

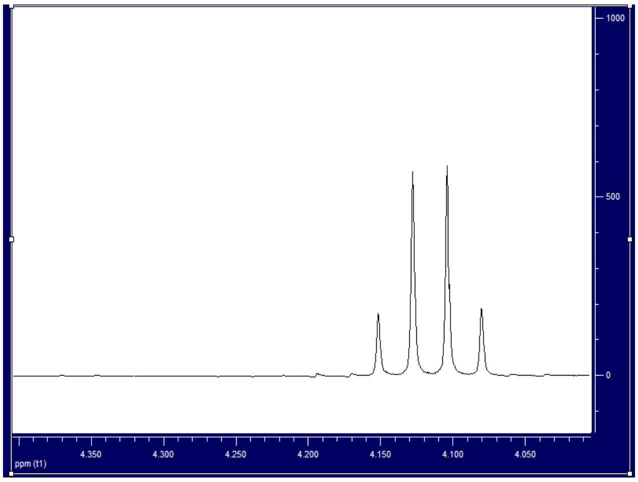

Fig. 2. Quartet characterizing peaks of palmitate.

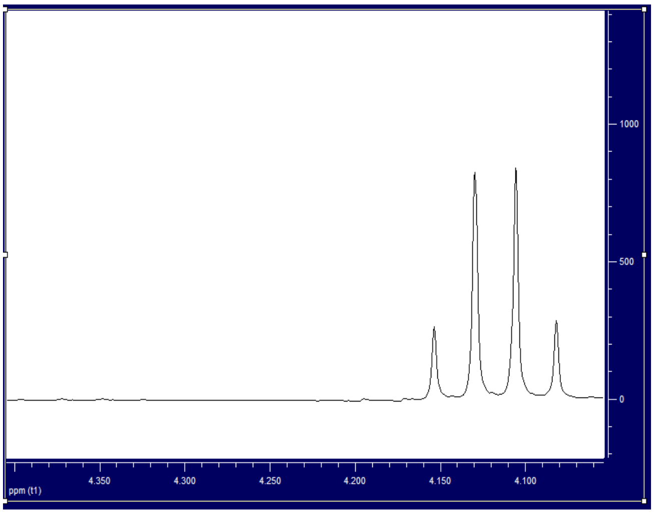

Fig. 3. Quartet characterizing peaks of oleate.

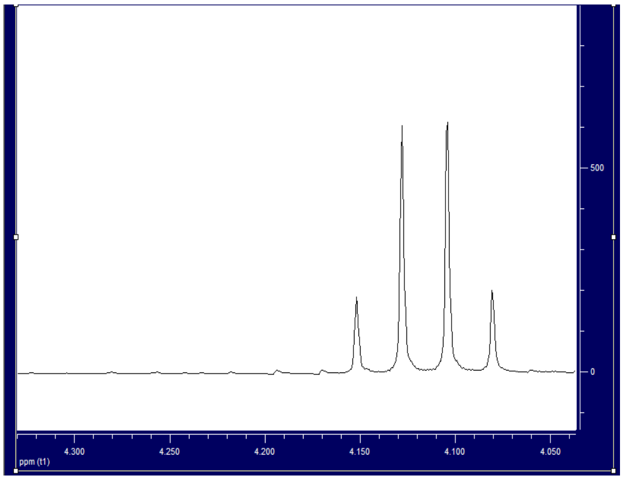

Fig. 3. Quartet characterizing peaks of stearate.

The calorific value of ethyl esters: ethyl palmitate ($C_{18}H_{36}O_2$) has a calorific value $\Delta H=41011$ J g^{-1}, while the ethyl stearate ($C_{20}H_{40}O_2$) $\Delta H=41548$ J g^{-1}. Stearate has a higher calorific value than palmitate, because it has a larger carbon chain size. The ethyl oleate ($C_{20}H_{38}O_2$), has the same size of the molecule of stearate, but has one unsaturation in the carbon chain showing a lower calorific $\Delta H=41450$ J g^{-1} compared to ethyl stearate (Table III).

Table III – Calorific value of ethyl esters.

Ethyl ester	**1º sample (J g^{-1})**	**2º sample (J g^{-1})**	**3º sample (J g^{-1})**	**Average (J g^{-1})**	**S.D. (%)**
Palmitate ($C_{18}H_{36}O_2$)	41034	41022	40977	41011	0,07
Stearate ($C_{20}H_{40}O_2$)	41765	41558	41321	41548	0,53
Oleate ($C_{20}H_{38}O_2$)	41441	41408	41501	41450	0,11

The psycho-chemical properties and the yield of studied synthesised biodiesel are showed in Table III.

Biodiesel	Density (g/cm^3)	Kinematic viscosity (cSt)	Acidity index (mgKOH/g)	Yield (%)
Soybean	0.7071	5.53	0.21	94.18
Jatropha	0.8761	5.08	0.21	100
Rapeseed	0.8879	5.89	0.98	100
Crambe	0.8911	6.64	0.33	97

Among the studied fuels, the mineral diesel, as expected, has the highest calorific value $\Delta H = 45548$ Jg^{-1}. Among the investigated biofuels, the crambe biodiesel has the highest calorific $\Delta H = 40564$ Jg^{-1}, due to the presence of 93.0 % of long chain ethyl ester (mainly the ethyl ester from behenic acid that composes 57.2% of crambe oil). The soybean, rapeseed, and jatropha biodiesel that have almost the same amount of long chain ethyl ester, respectively, 85 %, 86.6 % and 85.9% showed close values for the calorific value, between 39480 J g^{-1} and 39458 J g^{-1} (Table IV).

Table IV – Calorific value of studied fuels.

Fuel	1º sample	2º sample	3º sample	Avarage	S.D. (%)
Soybean	39439	39312	39691	39480	0,48
Jatropha	39808	39300	39257	39455	0,77
Rapeseed	39438	39467	39471	39458	0,18
Crambe	40590	40530	40572	40564	0,47
Diesel	45837	45865	45828	45843	0,41

4. Conclusions

The present study shows that there is a direct relationship between the calorific value and the size of the carbon chain of ethyl esters, since biodiesel is mixture of different ethyl ester. Moreover, the results show that the longer the carbon chain of the ethyl ester the higher is calorific value. This behaviour is reflected on the studied biodiesel. Biodiesel from crambe oil shows larger amounts of ethyl esters with long chain and shows the highest calorific value.

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