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Heat of combustion of biofuels mixed with fossil diesel oil

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Abstract The Brazilian government has presented a biofuel program, which aims the addition of 2% of biofuel in fossil diesel in 2008 and 5% up to 2013. Thus, the knowledge of heat of combustion of biofuel/diesel blends is necessary. The biodiesel was produced by transesterification of soybean oil with a yield of 87%. The diesel-like was obtained by pyrolysis of soybean oil. This biofuel presented all parameters according to ANP. The obtained heats of combustion were 41.36 ± 0.17; 38.70 ± 0.16; and 36.71 ± 0.17 MJ/kg for diesel, diesel-like and biodiesel, respectively. The results show that the heats of combustion of biofuels are approximately 17% smaller than fossil diesel. The obtained data also show that the heats of combustion depend on the methodology used for the biofuel production. Addition of biofuels to traditional diesel fuel results in a linear decreasing of the heat of combustion with the amount of the alternative fuel added to the diesel.

Keywords Blends · Heat of combustion · Biodiesel

Introduction

Fossil petroleum sources have been extensively decreasing day-by-day by because of petroleum uses such as: chemical products, fuel products (gasoline, diesel, kerosene), etc. Moreover, the burning of fossil fuel generates high amounts of toxic by-products, such as SO_x, NO_x, as well as it increases the production of CO_2 contributing to global warming. Thus, the application of renewable fuels represents a great environment and technological importance, which presents some qualities which distinguish them as sustainable fuels, such as: high caloric power, absence of sulfur in chemical composition, its industrial production does not generate harmful substances, and mainly, the decrease of carbon dioxide gases by their consumption during photosynthesis of vegetable cultivation [1–4]. Thus, these alternative fuels can be mixed with diesel, and in this way, it reduces the demand on diesel oil and minimizes the gas emissions that contribute to global warming [1–4].

On the other hand, the direct application of vegetable oils in diesel engines can cause many technological problems such as: carbonization of the injection camera, ejection resistance of the piston segments, dilution of the crankcase oil contamination of the lubricating oil and poor atomization of the fuel, which are mostly assigned to its low volatility and high viscosity [1]. In order to avoid the problems of direct application of vegetable oil in engines, ecofuels can be obtained by transesterification or pyrolysis of vegetable oils. These processes produce new renewable fuels with molecular mass lower than vegetable oil, increasing the volatility and decreasing de viscosity. Therefore, these transformations can produce eco-fuels with physical-chemistry characteristics similar to fossil-diesel [5–7].

Development of environmentally friendly processes to decrease waste and toxic effluents has been increasing by population and governmental authorities pressure on the chemical industry [8]. Besides, the environmental benefits of renewable fuels and the production of these biofuels can also provide economical advantages, because of Brazilian

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Federal Government include the biodiesel program in the frame of ‘Kyoto Agreement’ in the guidelines of the clean development mechanisms. This program demands the addition of 5% (B5) in 2012 [9, 10]. Moreover, this program stimulates the production of biofuels by small Brazilian family farms providing additional profits to simple agricultural bread-winners [10].

The aim of this article is to study the heat of combustion of soybean oil, biodiesel and diesel-like produced from soybean oil and diesel/biofuels blends by using a bomb calorimetry.

Experimental

Chemicals and preparation

Vegetable oil (Soya), gasoline and diesel (ANP), NaOH (Vetec), Methanol (Sigma), H_3PO_4 (Vetec), $MgSO_4$ (Vetec) were used without any purification.

Transesterification

Transesterification reactions were followed by using: 10.0 g of buriti oil, 1.5 g of methanol and 0.1 g of NaOH. Potassium hydroxide was completely dissolved in MeOH under stirring in a glass batch reactor equipped with mechanical stirrer. Then, the vegetable oil was added into the mixture and maintained under stirring for 2 h at 50 °C, as according to Fig. 1. The resulting product was washed with a saturated aqueous NaCl solution. The organic phase was separated by decantation and dried with anhydrous $MgSO_4$. Recovered esters were analyzed by high-performance liquid chromatography (HPLC), using a Shimadzu CTO-20A chromatograph with a UV–Vis detector at $\lambda = 205$ nm, equipped with a Shim-Pack VPODS column (C-18, 250 mm, 4.6 mm i.d.). The solvents were filtered through a 0.45-μm Millipore filter before use. An injection volume of 10 μL and a flow rate of 1 mL) min were used in all experiments. The column temperature was held constant at 40 °C. All samples were dissolved in 2-propanol–hexane (5:4, v/v). A 35-min ternary gradient with two linear gradient steps was using, comprising 30% water and 70% acetonitrile for 0 min, 100% acetonitrile for 10 min, 50% acetonitrile and 50% 2-propanol–hexane (4:5, v:v) for 2 min, and isocratic elution with 50% acetonitrile and 50% 2-propanol–hexane (4:5, v:v) for the last 15 min [11, 12].

Pyrolysis

Pyrolysis experiments were carried out at temperatures ranging from 350 to 400 °C in a 5 L stainless steel batch unit, as described in details before [13]. The vegetable oil (2 L) was introduced into the pyrolysis reactor and then heated by an external electric resistance. The temperature was measured at two sites with calibrated thermocouples. When the temperature inside the reactor achieved 350 °C, the vegetable oil was pyrolyzed, vaporized and a vapor feed left the reaction, by the upper side at temperatures ranging from 200 to 250 °C. Then, the vaporous feed enters into a water cooled heat-exchanger. Two-liquid fractions were obtained in the collector: an aqueous and organic fraction. These fractions were separated by decantation and the organic phase distilled by standard oil laboratory techniques. The distillates were separated into four fractions with distillation temperature ranges: (a) $\_T < 80$ °C; (b) $80\ °C \le \_T < 140$ °C; (c) $140\ °C \le \_T < 200$ °C; (d) $200\ °C \le \_T$ (heavy fraction). The different fractions were weighed and the heaviest one was analyzed according to ASTM standard methods for petroleum fuels, as shown in Fig. 1.

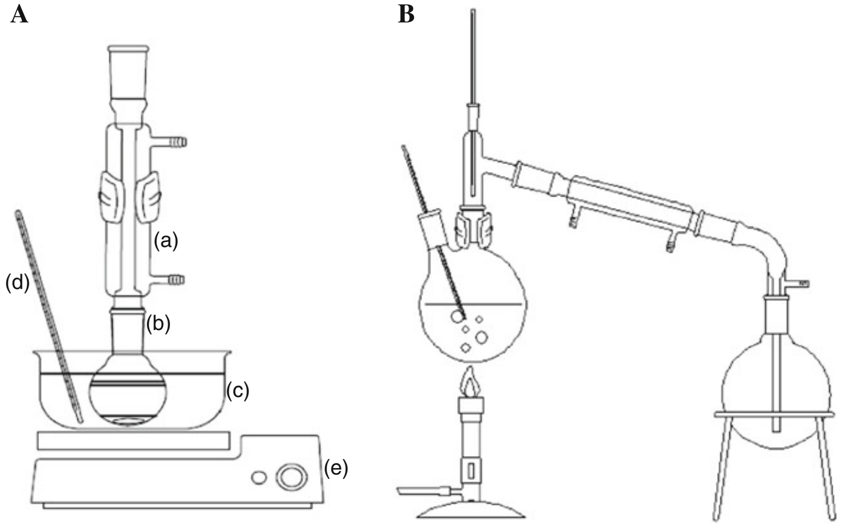


Fig. 1 **a** Transesterification reaction between soybean oil with methanol catalized by NaOH at 50 °C, being condensator (*a*), baloon (*b*), mineral oil bath (*c*), thermometer (*d*), and heating and sttrring system (*e*). **b** Distillation system to cracking soybean oil to produce diesel-like

Diesel-like characterization

Acidity index

Acidity index was determined by using 1.0 g of diesel-like solubilized in 10.0 g of 1:1 toluene:isopropanol solution with 3 drops of an ethanolic solution of phenolphthalein 1.0%, as according to AOCS Cd3d63 standard method.

The mixture was titrated with the ethanolic solution of KOH 0.1 mol/L. Analysis were done in triplicate and the acidity index was calculated by Eq. 1.

$$LA = \frac{V.C.56.1}{m} \tag{1}$$

where V is the volume of titrant, C is the concentration of titrant; 56.1 is the molar mass of KOH, and m is mass of diesel-like.

Density

The density of diesel-like was determined in triplicate by using an electronic densimeter Anton Paar Model DMA 35 N in two distinct temperatures.

Samples were maintained at 15 and 20 °C in a thermostatic bath. Density measures were carried out after temperature equilibrium, as according to ASTM D4052 standard method [14].

Kinematic viscosity

Viscosity was carried out in a Herzog viscosimeter model HVB-438 in triplicate, as according ASTM D 445 standard method [14].

Viscosity was calculated by Eq. 2. Where, η is the viscosity, t is the outflow time, and C is the constant of viscosimeter.

$$\eta = t\,C \tag{2}$$

Cetan index

100 mL of diesel-like were distilled in an automatic distillator (Herzog model HDA 627), as according to ASTM D86 standard method [15].

The temperatures at 10, 50, and 90% of distilled product was anoted and applied in Eq. 3. In order to obtain cetan index.

$$\begin{aligned} CI = \Big\{ & 45.2 + (0.0892\,T_{10\,\mathrm{N}}) + T_{50\,\mathrm{N}}[0.131 + (0.901\,B)] \\ & + T_{90\,\mathrm{N}}[0.0523 - (0.420\,B)] \\ & + 0.00049\left[(T_{10\,\mathrm{N}})^2 - (T_{90\,\mathrm{N}})^2\right] + (107.0\,B) \\ & + \left(60.0\,B^2\right) \Big\} \end{aligned} \tag{3}$$

where, CI is cetan index; T_{10} is temperature of 10% of distilled product; T_{50} is temperature of 50% of distilled product; T_{90} is temperature of 90% of distilled product; $T_{10\ \mathrm{N}}$ is $T_{10}-215$; $T_{50\ \mathrm{N}}$ is $T_{50}-260$; $T_{90\ \mathrm{N}}$ is $T_{90}-310$; D is density at 15 °C, DN is $D-0.85$; B is $[\mathrm{e}^{(-3.5\ \mathrm{DN})}]-1$

Copper corrosion

30 mL of diesel-like and copper blade were added in test tube. The tube was equilibrated at 50.0 ± 1.0 °C during 3 h ± 5 min. Copper blade was separated and the corrosion degree was determined by comparison with reference blade as according ASTM D130 standard method.

Carbon residue

10.0 g of diesel-like were added in a porcelain crucible. The crucible was heated up to smoke formation, the smoke was ignited by a Bunsen flame, as stated by ASTM D189.

Fulgor point

Fulgor point of diesel-like was determined by Pensky-Martens apparatus, as according to ASTM D93 standard method.

Heat of combustion

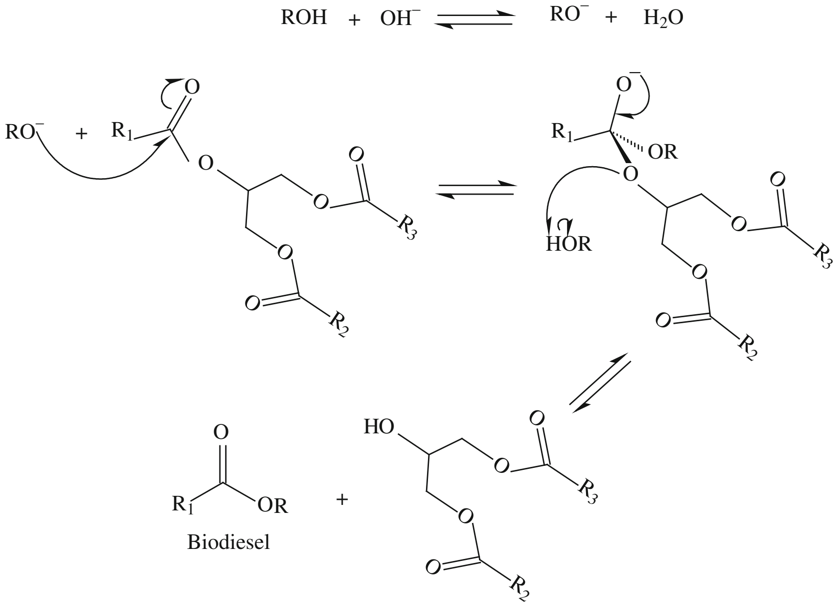
A semi-micro oxygen bomb calorimeter PARR 6272 was used to obtain the heat of combustion of diesel-like and samples of diesel-like adulterated with soybean oil. The semi-micro oxygen bomb calorimeter Parr 6272 is a static calorimeter with temperature resolution of 0.001 °C, capable of oxygen charging pressures up to 40 atm, and can liberate up to a maximum 6680 J per charge. Samples were placed directly in a stainless steel capsule and burned with oxygen at a pressure of 3.0 MPa, as according to ASTM method D240 [10].

Results

Characterization

The reaction of methanolysis of soybean oil catalized by NaOH is based on nucleophylic attack of base on carbonyl of oil produciong methylesters (biodiesel), as according to Fig. 2. Biodiesel obtained by transesterification of soybean oil with methanol was quantified by HPLC analysis (Fig. 3) and Table 1 showed the amounts of free fatty acid, mono-, di-, and triglycerides, as well as their conversion to biodiesel. Chromatogram of Fig. 3 showed that the

Fig. 2 Proposed mechanism of a base-catalyzed transesterification of vegetable oil



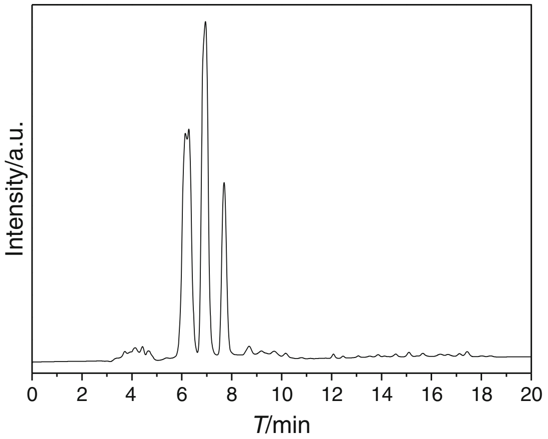


Fig. 3 Chromatogram of biodiesel produced by methanolysis of soybean oil catalyzed by NaOH

Table 1 Products and yields of transesterification of soybean oil

Product	%
Biodiesel	97.08 ± 0.78
Triglyceride	0.67 ± 0.59
Diglyceride	0.98 ± 0.78
Monoglyceride and fatty acids	1.27 ± 0.79

transesterification reaction of soybean oil with methanol catalyzed by NaOH occurred as expected with a yield production of 87% of formed biodiesel.

The production of diesel-like by thermal-pirolysis of soybean oil is based on thermal cracking of vegetable oil forming organic chains such as hydrocarbons with and without insaturations, acrolein, ketenes, and carboxylic acids, as according to Fig. 4. The majority of the properties of diesel-like obtained from cracking of soybean oil according were in accordance with Brazilian oil agency, as presented in Table 2.

Heats of combustion

Samples of biofuel-diesel blends were combusted in a bomb calorimeter at 3.0 MPa. The obtained results represent the estimated burnout of the blends calculated from the individual performance of the cot, assuming that there is an interaction between them.

The values of heat of combustion data gave 41.36 ± 0.17; 38.70 ± 0.16; and 36.71 ± 0.17 MJ/kg for diesel, diesel-like, and biodiesel, respectively. The lowest values of heat of combustion reflect in the increase of automobile fuel consume. The results of the studies of biofuels obtained from pirolysis of soybean oil and their blends with soybean are represented in Figs. 5 and 6, respectively. These data clearly show that the heat of combustion decreases linearly with the addition of the biofuel in fossil diesel. This fact occurred because the organic chain in vegetable oil is longer than in the biofuels. However, according to Brazilian Program, the biofuel must be added up to 5% in mixture with fossil diesel. B5 diesel-like/diesel and biodiesel/diesel blends present heat of combustion of 99.7 and 99.5% of heat of combustion of pure fossil diesel, respectively. Thus, B5 blends presented heat of combustion values very close to fossil diesel. This fact shows that the use B5 blends do not practically affect automobile fuel consume. Moreover, diesel-like presented heat of

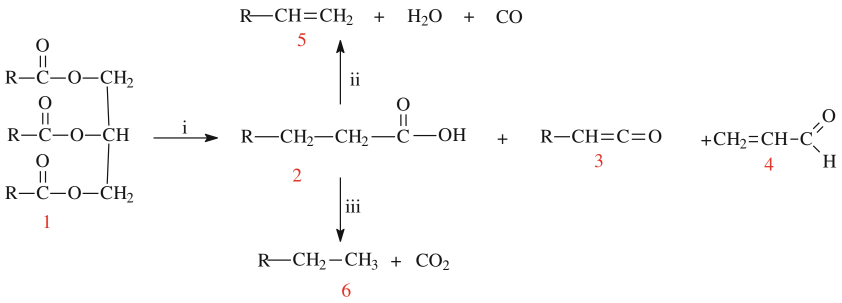


Fig. 4 Pirolysis of vegetable oil (*1*), forming carboxylic acids (*2*), cetenes (*3*), acrolein (*4*), and hidrocarbons with (*5*), and without (*6*) terminal insaturations

Table 2 Characterization of diesel-like and standard values of diesel required by ANP (National Agency of Petroleum, Natural Gas and Biofuels)

		Diesel-like	Diesel
Density 20 °C/Kg/m^3		872.5	820–880
Viscosity 40 °C/mm^2/s		4.93	2.0–5.0
Acidity index/mg KOH/g de óleo		90.15	–
Automatic distillation/°C	10%	147.2	To observe
	50%	293.1	245–310
	85%	318.8	370 (max)
	90%	345.2	370 (max)
Fulgor point/°C		64	38 (min)
Cetan index		36.7	51–54
Copper corrosion		1	1
Carbon residue/%		0.51	0.25

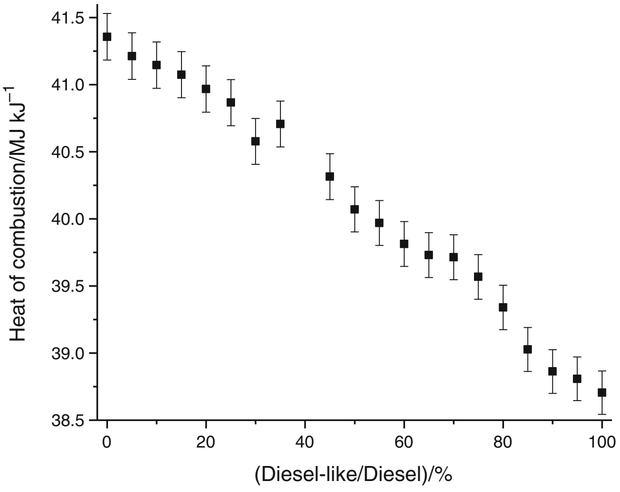


Fig. 5 Heat of combustion of diesel/diesel-like blends obtained by pyrolysis of soybean oil

combustion higher than biodiesel. This fact must have occurred because of the presence of C=C bonds in diesel-like and biodiesel presents more C–C and C=O bonds, which present bond energy lower than C=C bond [10].

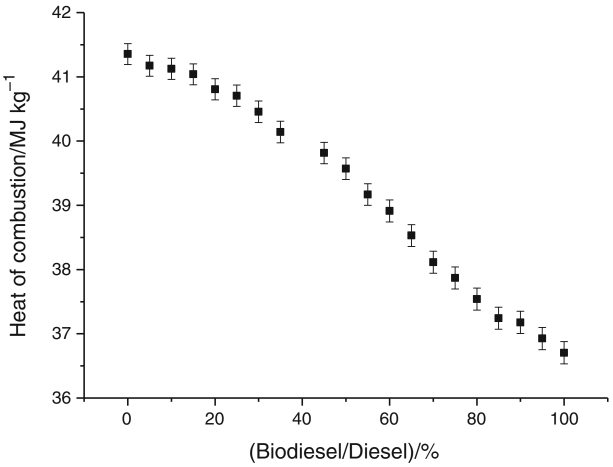


Fig. 6 Heat of combustion of diesel/biodiesel blends obtained by transesterification of soybean oil

Conclusions

The production of biofuels was obtained with success by pyrolysis and by transesterification which are simple and practicable methodologies. The addition of biofuels decreases the heat of combustion of fossil diesel because of the presence of organic chains is lower than fossil diesel. Also, in the specific case of biodiesel, this decrease was caused by the presence of C–O and C–C bonds.

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