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Heats of combustion of biofuels obtained by pyrolysis and by transesterification and of biofuel/diesel blends

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Abstract

The obtained heats of combustion were 46.65 ± 0.20; 38.09 ± 0.31; 39.67 ± 0.22; 41.88 ± 0.31; 37.86 ± 0.46; 39.89 ± 0.09; 41.28 ± 0.31 MJ/kg for diesel, transesterified soybean oil, pyrolysed soybean oil and crude soybean oil, transesterified palm tree oil (*Elaeis* sp.), pyrolysed palm tree oil, crude palm tree oil, respectively. The results show the heats of combustion of biofuels are approximately 17% smaller than traditional diesel. The data also show the heats of combustion depend on the methodology used for the biofuel production. Addition of biofuels to traditional diesel fuel results in a linear decrease of the heat of combustion with the amount of the alternative fuel added to the diesel. However, for blends with 5% biofuels, which is the limit demanded by Brazilian legislation, no significant decrease of the heat of combustion of the commercial diesel was observed.

Keywords: Biofuel/diesel blends; Heat of combustion; Vegetable oils

1. Introduction

Biofuels, especially those derived from vegetable oils, have been highlighted as an alternative for diesel engines due to the similarity of their physical–chemical properties to petroleum diesel and compression ignition engines, and also because they decrease pollutant emissions compared with fossil fuels [1–8]. The main processes for conversion of biomass into diesel engine fuels are alcoholysis and pyrolysis of vegetable oils to produce, respectively, methyl- or ethyl-fatty acid esters and hydrocarbons, as depicted, respectively, in reactions (i) and (ii) of Fig. 1.

Much work has been done in the past two decades on the production and real world market performance of biodiesel [9–13]. Rapeseed, canola, sunflower and soybean oils, beef tallow, and many other oils have been used for the production of biodiesel, usually after methanolysis or ethanolysis catalyzed by alkaline hydroxides or methoxides, mineral acids, oxides and enzymes.

The pyrolysis of vegetable oils had been used for fuel supply during war periods, such as the production of hydrocarbons by the thermo-cracking of Tung oil in China during the Second World War [14]. Since then, numerous studies about thermo [15,16] and catalytic pyrolysis [17–19] have been done. Characterization of gas and liquid products shows that not only the reaction produces the desirable linear and cyclic paraffins and olefins, but also inconvenient oxygenated compounds are produced, such as aldehydes, ketones and carboxylic acids. Recently, we observed that it is possible to isolate a fuel with physical–chemical properties comparable to those specified for petroleum diesel by the pyrolysis of soybean and palm tree oils [3]. A diesel-like fuel was obtained by fractional distillation of the resulting mixture of hydrocarbons and oxygenated compounds, by the adequate choice of temperature intervals.

In 2004, the Brazilian Federal Government launched an ambitious program to partially substitute diesel fuel by biofuels obtained from vegetable oils. Blends containing up to 2% of biofuel (B2) are allowed until January 2008, when it will become mandatory to use B2 and mixtures with up to 5% will be allowed [20]. In the Brazilian biodiesel program there is no preference in the raw-material or production processes. This program stimulates the production of biofuels from vegetable oils by small farms, which could mean an additional profit that could be owned by simple agricultural bread-winners, and as a consequence, improve life for Brazilian agricultural workers [20].

Despite the advantages of this renewable and environmentally friendly fuel, the heat of combustion of biodiesel is lower than that for diesel. The aim of this work is to determine the

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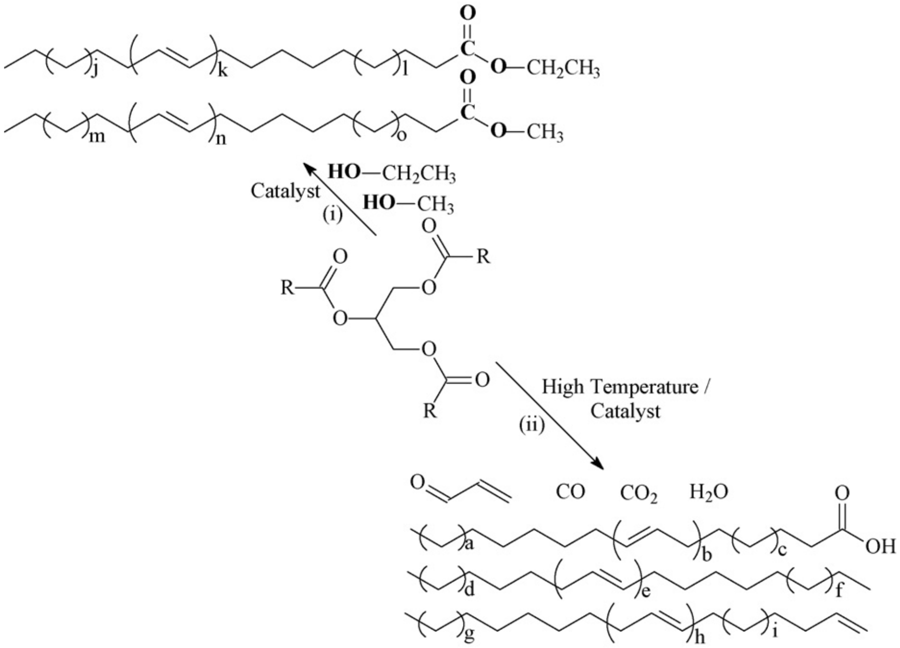

Fig. 1. Transformation of triglycerides into fuels: (i) alcoholysis and (ii) pyrolysis.

heat of combustion of vegetable oils, biofuels and diesel/biofuel blends.

2. Experimental

2.1. Samples

Soybean oil and palm tree oil (*Elaeis* sp.) were obtained from commercial sources and used without further purification. The compositions of these oils were determined by GC-FID in a previous work [21] and these data are displayed in Table 1. The biofuels were obtained by pyrolysis (diesel-like fuel) and by transesterification (biodiesel) of palm tree and soybean oils according to methods previously reported [3,22].

2.2. Pyrolysis reaction

Pyrolysis experiments were carried out at temperatures ranging from 350 to 400 °C with a 5 L stainless steel batch unit, as detailed described before [3]. 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 vapour feed left the reactor 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 fraction and an organic fraction. These fractions were separated by decantation and the organic phase distilled by standard oil laboratory techniques [3]. The distillates were separated into four fractions with distillation temperature ranges: (a) $\Delta T < 80\,°C$; (b) $80\,°C \leq \Delta T < 140\,°C$; (c) $140\,°C \leq \Delta T < 200\,°C$; (d) $200\,°C \leq \Delta T$ (heavy fraction). The different fractions were weighed and the heaviest one was analyzed by gas chromatography (GC), FTIR, and other ASTM standard methods for petroleum fuels as described before [3] and similar results were obtained.

Table 1
Vegetable oil composition

Vegetable oil	Fat acid (wt.%)				
	Palmitic	Stearic	Oleic	Linoleic	Linolenic
Soybean	14	4	24	52	6
Palm tree	35	6	44	15	–

2.3. Transesterification reaction

The methanolysis of soybean oil and palm tree oil catalyzed by KOH were carried out using mass ratio of 100:33:1 (vegetable oil:MeOH:KOH), as previously reported [22]. 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 reactor and the reaction mixture was maintained under stirring at 5000 rpm for 2 h at room temperature (23 ± 1 °C). For the palm tree oil, the mixture was stirred during 4 h due to its higher viscosity. After 2 h (4 h for palm tree oil) for the reaction completion, the mixture was allowed to stand and the two phases (one rich in glycerin and the other one in methyl ester) were separated. The excess of methanol in the methyl ester phase was removed by rotary evaporation at 70 °C. The methyl ester was then washed twice with a phosphoric acid water solution (5% v/v) and with brine until a clear phase (methyl ester) was obtained. The biodiesel products were analyzed by high-pressure liquid chromatography (HPLC) using a Perkin-Elmer Series 200 LC-pump and a refractive index

Table 2
Heats of combustion of biofuel/diesel blends

Biofuel/diesel blends (%)	Palm tree (MJ/kg)		Soybean (MJ/kg)	
	Transesterificated	Pyrolised	Transesterificated	Pyrolised
0	46.65 ± 0.20	46.65 ± 0.20	46.65 ± 0.2	46.65 ± 0.2
2	46.64 ± 0.20	45.77 ± 0.32	46.01 ± 0.29	45.95 ± 0.35
5	45.84 ± 0.15	45.85 ± 0.27	45.46 ± 0.22	45.46 ± 0.27
10	45.33 ± 0.46	44.95 ± 0.13	44.48 ± 0.19	44.82 ± 0.31
20	44.37 ± 0.41	44.28 ± 0.12	43.75 ± 0.19	44.35 ± 0.18
50	42.13 ± 0.20	43.19 ± 0.12	41.93 ± 0.11	42.39 ± 0.19
100	37.86 ± 0.46	38.89 ± 0.17	38.09 ± 0.31	39.67 ± 0.21

Series 200 detector and controlled by a PC with a software package (Perkin-Elmer Turbochrom Navigator). A Zorbax Eclipse XDB-C18 column (4.6 mm × 250 mm × 5 μm) was used and the mobile phase was an acetone/acetonitrile mixture (70:30 v/v) at a flow rate of 0.7 mL/min. The biodiesel samples were diluted with acetone (HPLC grade) and the injection volume was 20 μL [23]. This method also allows the quantification of the monoglyceride, diglyceride, and triglyceride contents in biodiesel. The reaction was repeated two or three times until purity of more than 99 mass% in methyl esters were detected by GC. For the consecutive reactions a similar procedure was followed, using the reaction product instead of vegetable oil as reagent and the same amounts of methanol and KOH. The methyl esters were finally stored in amber flasks in a refrigerator at 6 °C.

Arrays of biofuel/diesel blends were obtained by mixing 2.0%; 5.0%; 10.0%; 20.0% and 50.0% (w/w) of biofuel in diesel, using a roller mixer spinning at constant speed for 30 min, in order to produce B2, B5, B10, B20 and B50 blends, respectively.

2.4. Heat of combustion

An oxygen bomb calorimeter (Parr 1241) was used to obtain the heat of combustion of oil, diesel, biofuel, biodiesel and biofuel/diesel blends. The Parr 1241 is a static and manual calorimeter with temperature resolution of 0.002 °C, capable of oxygen charging pressures up to 40 atm, and can liberate up to a maximum 33,400 J per charge.

The fuel samples were placed directly in a stainless steel capsule (2.5 cm of diameter and 1 cm of deep) and burned with oxygen at a pressure of 3.0 MPa according to ASTM method D240 [24,25].

Calibration of the calorimeter was done by burning 1.0 g benzoic acid pellets (Parr). Heats combustion for diesel, transesterified soybean oil, pyrolysed soybean oil, crude soybean oil, transesterified palm tree oil, pyrolysed palm tree oil and crude palm tree oil were determined.

All experiments were done in triplicate.

3. Results and discussion

Experimental performance of the blends was somewhat better than predicted, systematically showing a small positive synergistic effect when testing blends. As observed by the error limits, however, observed differences were greater than the experimental repeatability.

The heat of combustion data of palm tree oil and soybean oil were 41.28 ± 0.31 and 41.88 ± 0.31 MJ/kg, respectively.

All heats of combustion of blends are summarized in Table 2. The heat of combustion decreases linearly with the addition of the biofuel in commercial diesel. It is also clear that the heat of combustion of biofuel obtained by pyrolysis is higher than produced by alcoholysis.

The addition of biofuels derived from soybean oil to diesel follow a similar behaviour to addition of biofuels derived from palm-tree oil. For biofuels obtained from both vegetable oils, the diesel-like compounds obtained from pyrolysis presented a heat of combustion higher than biodiesel obtained from transesterification, explained by presence of more alkene groups in biofuels obtained from pyrolysis.

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