

Thermal and kinetic evaluation of biodiesel derived from soybean oil and higuiereta oil

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Abstract The purpose of this work is to evaluate the thermal and kinetic behavior of biodiesel derived from soybean and higuiereta oils. The thermogravimetric profiles of biodiesels indicated one step associated with decomposition of the ethyl esters. The thermal profiles were compared with reference diesel. Kinetic parameters were obtained by thermal analysis, estimating reaction order, pre-exponential factor and activation energy. For estimation of the kinetic parameters the Coats & Redfern method was used. The selection criterion of best fit was based on the correlation coefficient of the linear regression and the compensation effect of the kinetic parameters.

Keywords Thermal analysis · Biodiesel · Activation energy · Kinetics · Thermogravimetry

Introduction

As the conventional fossil fuel sources are decreasing, and in the last two years their prices have the risk of been growing, it is necessary to find energy alternatives, especially renewable energy sources. With respect to the bio-fuels, there are many reports of their tests and use in

internal combustion engines. The most important fuels used for this purpose are vegetable oils and biodiesel from different natural sources. Biodiesel (BD) can be obtained by the reaction between an ester and alcohol (methanol or ethanol) in the presence of a catalyst, producing methyl or ethyl ester (biodiesel) and glycerin, a byproduct. The chemical reaction is called transesterification. The molecular mass close to diesel and similar physical-chemical properties make biodiesel a good substitute for diesel. Vegetable oils are other biofuels, more problematic mainly due to higher viscosity than diesel, normally 25 times. This problem is efficiently solved by the transesterification reaction that decreases the molecular mass of the oils increasing the volatility and decreasing the viscosity, or using a pre-heating system [1, 2].

Thermal analysis is concerned with a lot of scientific applications. It provides efficient tools for measuring thermodynamic properties such as enthalpies, heat capacities and temperature of phase transitions [3]. The methods of thermal analysis make it possible to follow the kinetics of thermally stimulated processes like decomposition, oxidation, reduction, crystallization, polymerization and combustion.

The purpose of this work is to investigate two different biodiesel samples by thermogravimetry (TG) and derivative thermogravimetry (DTG), and to compare with the thermogravimetric profile of diesel fuel. One sample was of biodiesel from soybean oil (BD-soy), an edible oil and the other from higuiereta oil (BD-hig), a non edible oil. Both were obtained by ethanol transesterification of their respective oils. The application of thermogravimetry to liquid fuels like diesel and biodiesel is not usually found in reports. Only few reports describe the use of this technique in liquid fuels. Most papers have been focused on solid fuels.

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Thermal analysis

Thermal analysis is a widely used technique to evaluate kinetic parameters of solid-state decomposition processes, but has also been used for liquid fuels. There are reports of this technique applied to sunflower oil [4], palm oil [5], cotton oil biodiesel [6] and corn oil biodiesel [7].

A number of methods have been developed to obtain kinetic parameters from TG data in order to study the reaction mechanisms. The most widely used are Coats-Redfern [8], Horowitz-Metzger, Kissinger, Madhusudanan, and Model Free-Kinetics [9, 10]. It is possible with these methods to obtain kinetic parameters from thermal data such as activation energy (E_a), reaction order (n) and the pre-exponential factor (A). The so-called Coats & Redfern method [8] was selected in order to obtain all kinetic parameters from the thermogravimetric data from single heating-rate experiments but working at four heating rates. This method makes it possible to evaluate different reaction order values e.g. 1/2, 2/3, 1, 3/2. The correct order is presumed to lead to the best linear regression coefficient.

The method is based on the following equations:

$$\ln \left[\frac{-\ln(1-\alpha)}{\tau^2} \right] = \ln \left[\frac{AR}{\beta E_a} \left(1 - \frac{2RT}{E_a} \right) \right] - \frac{E_a}{RT} \quad \text{for } n = 1 \quad (1)$$

$$\ln \left[\frac{1 - (1-\alpha)^{1-n}}{(1-n)\tau^2} \right] = \ln \left[\frac{AR}{\beta E_a} \left(1 - \frac{2RT}{E_a} \right) \right] - \frac{E_a}{RT} \quad \text{for } n \neq 1 \quad (2)$$

where α represents the conversion degree, R the universal gas constant, β the heating rate and T the absolute temperature. After determination of E_a from the slope of the plot, using Coats & Redfern (CR), it is possible then to calculate the corresponding A from the intercept of the linear regression assuming different reaction orders. The model with the best correlation coefficient should bring the adequate value of n . In this work the compensation effect criterion for the adequate model selection is also used, which means that the obtained pair of parameters of activation energy and the logarithm of the pre-exponential factor ($\ln A$) must be correlated by a compensation effect [7, 11]. A discussion about the meaning of this effect was published by Brown [11]. The compensation effect is mathematically described by Eq. 3, where β is an index, representing in our study the experimental heating rate, which causes a variation in the values of the kinetic parameters [3, 11].

$$\ln A_\beta = a + bE_{a\beta} \quad (3)$$

The correct order is presumed to lead to the best linear plot and the best compensation effect. Every good kinetic

model must show this compensation effect that means, an increase in E_a is correlated through a linear fit with the logarithm of the pre-exponential factor [7, 11].

Experimental procedures

Standard diesel and biodiesel obtained through ethanol transesterification reaction from two natural sources were used, soybean and higuera (ricino ricinus communis). The equipment for the TG analysis was a thermobalance Shimadzu model 51H. This device works from room temperature to 450 °C with heating rates between 5 and 30 °C min⁻¹. The atmosphere used was air at 100 mL min⁻¹, at atmospheric pressure. Samples with an initial mass between 25 and 30 mg were inserted. The samples were tested at heating rates of 5, 10, 20 and 30 °C min⁻¹. The thermal profiles were obtained from the TG curves. The experimental procedure involves the placing of the sample, setting the heating rate and the flow rate of the purge gas (air) and then starting the experiment.

The activation energy for different fuels was obtained from the slope of the linear regression applying the CR method. This is a single heating rate method but in this case applied at four different heating rates. Only data into the 10–90% decomposition range was processed. This limited range is because of the uncertainty associated with the measurements at conversion levels lower than 10% and higher than 90%.

Results and discussion

The thermal profiles (TG-DTG curves) presented in all cases only one mass loss step. In case of diesel this happens between 50 and 250 °C (Fig. 1), due to decomposition processes of its compounds. Thus diesel is thermally stable in air up to 50 °C. The smoothness of the curve of mass loss and the unique peak obtained for the derivative of mass suggest a single-step reaction. In these thermal profile figures the TG curve is represented in dash line and the derivative curve in solid line. The same behavior was observed at the other three heating rates, except for a slight displacement of the plot to the region of higher temperatures.

In the case of soybean and higuera biodiesels (Figs. 2 and 3) the same general behavior was observed. Both biodiesels were more thermally stable than diesel, starting the decomposition reaction only at 185 °C and ending near 300 °C. The thermal profile for BD-hig is quite similar to BD-soy. The derivative peak in these cases is attributed to decomposition of the ethyl esters. The onset temperatures

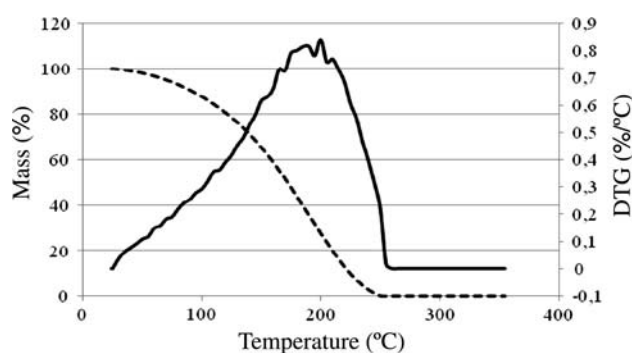


Fig. 1 TG-DTG curves of diesel at 5 °C min^{-1} in air (dash line: TG, solid line: DTG)

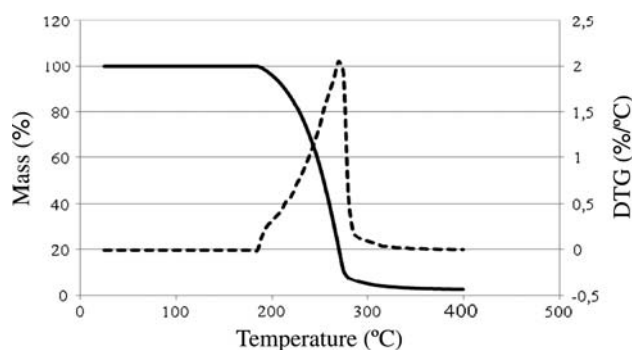


Fig. 2 TG-DTG curves of BD-soy at 5 °C min^{-1} in air (dash line: TG, solid line: DTG)

of both are the same (near 185 °C), very stable with respect to diesel which starts reacting before 50 °C . All the samples were totally degraded around 300 °C . Also an evidence of single-step reaction for biodiesels was observed.

The lower onset temperature shows that diesel is less stable than biodiesels. This result is in accordance with Goodrum [12], where the volatility of methyl and ethyl esters from different oil sources were compared with a reference diesel using thermal data. Chemically there are some important differences between diesel and these biodiesel samples. Ethyl esters have oxygen in their composition while diesel has not. Diesel is composed on average of 75% saturated hydrocarbons and 25% aromatics. Furthermore diesel is composed of saturated non-branched molecules with carbon atoms ranging from C_{12} to C_{18} and aromatics. Biodiesel is a mixture of fatty acid ethyl esters (ethanol route) with a composition according to the oil source. Soybean oil contains on average 16% of saturated fatty acids, 24% of mono-unsaturated and 60% of poly-unsaturated. Higuera oil contains on average 4% of saturated, 5% of mono-unsaturated and 1% poly-unsaturated, but it has 90% of ricinoleic acid, which is not present in soybean oil. Biodiesels obtained from the oils will have the same proportion of the ethyl esters [12]. The formula range for the biodiesel composition is $C_{15-25}H_{28-48}O_2$ [2].

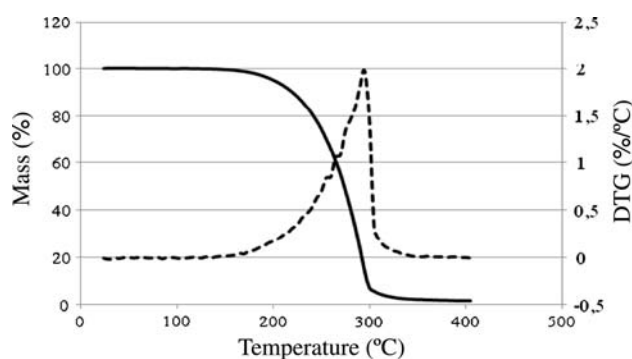


Fig. 3 TG-DTG curves of BD-hig at 5 °C min^{-1} in air (dash line: TG, solid line: DTG)

There are some important things to point out in the obtained fuels thermal profiles. The onset temperature is lower for diesel, about 50 °C and the same for both biodiesels. This is the temperature when the mass loss is starting and demonstrates the higher thermal stability of the ethyl esters with respect to diesel. The burn-out temperature is almost the same for the fuels. The real difference between them is in the onset and peak temperatures, quite different for diesel with respect to the biodiesels. The lower stability of diesel can be due to its content of aromatic compounds and some organic volatile compounds that are not present in biodiesel. The real composition of the fuel depends of factors like oil source or methods used to produce the fuels, but generally the length chains are larger for biodiesel fuels, increasing the onset temperature of the fuel.

The difference between these biodiesel samples is in the poly-unsaturated fatty acid composition that is about 60% in BD-soy and 1% in BD-hig [2]. But there are no differences between these biofuels in relation to their thermal profile as is observed in Figs. 2 and 3. The peak temperature is assumed as the physical value when the derivative of mass has its maximum value. The higher value is for BD-hig. A thermal comparison between the fuels is shown in Fig. 4, showing substantial differences between diesel and the biofuels.

The obtained TG curves for all the fuels show an influence of the heating rate on the thermogravimetric profile, shifting the thermogravimetric curves to higher temperatures. The increase of the heating rate leads to a less uniform heat distribution and a higher temperature gradient, shifting the curves toward higher temperatures. Also the values of activation energy (E_a), pre-exponential factor (A) and reaction order (n) were estimated from TG data. The activation energy values obtained were different depending on the fuel. All the kinetic parameters estimated using Coast & Redfern are shown in Table 1.

The calculated thermal parameters shown in Table 1 correspond to the best compensation effect obtained. In

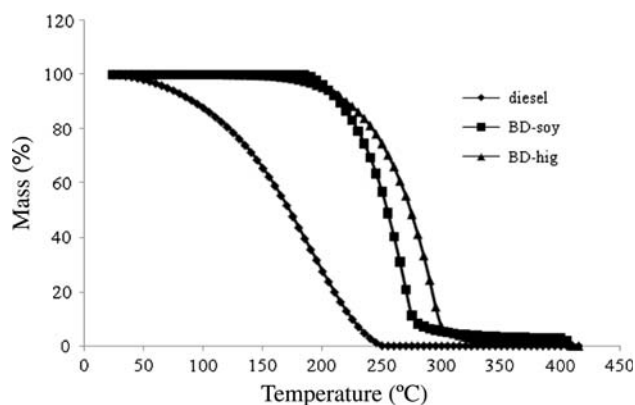


Fig. 4 TG curves for the fuels at 10 °C min^{-1}

case of soybean biodiesel the correlation coefficient for the compensation effect plot was $r = 0.9905$ corresponding to $n = 0.5$ as is shown in Fig. 5. For higuiereta biodiesel $r = 0.9980$ was obtained corresponding to $n = 0.7$ and for diesel $r = 0.9981$ corresponding to $n = 0.5$. The selection combined the best observed compensation effects and the best linear regression coefficients for the CR method plots. This compensation effect was analyzed for all fuels substituting different values of n in the model equations. The analyzed n values were 0, $1/2$, $2/3$, 1 and $3/2$. The compensation effect can also be applied to compare or correlate kinetic parameters obtained with different kinetic methods [13]. The differences observed in Table 1 are in the obtained E_a values of diesel, lower than the obtained for BD-soy and BD-hig which are similar.

Souza [6] tested cotton oil BD with four different methods included CR, reporting values of n between 0.25 and 0.44 in an air atmosphere. Dantas [7] reported E_a between $74\text{--}82\text{ kJ mol}^{-1}$ and $0\text{--}2/3$ of reaction order for

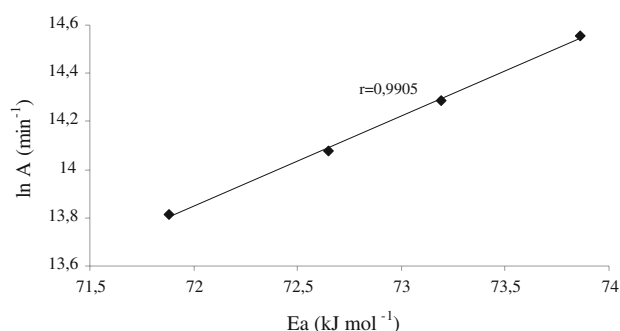


Fig. 5 Kinetic compensation effect for BD-soy for $n = 0.5$

corn biodiesel. These results are in the same range of the ones obtained in this work for BD-soy and BD-hig. Dantas [7] also noticed a linear relationship between $\ln A$ and E_a . The study was made at three different heating rates. Respect the use of CR method to evaluate the kinetic parameters, Olivella [13] reported the use of the CR method to the study of oil shales at four heating rates. Kök reported the use of CR for oil shales and silopi asphaltites at four different heating rates [14, 15] while Souza [6] report the use of CR at a single heating rate for cotton oil biodiesel. Aragão [16] reported the use of CR applied to Warifteine thermal data at four different heating rates. Lopez-Fonseca [17] applied CR at four different heating rates to diesel soot surrogates and assures that kinetic methods based on results obtained from single-rate run experiments do not permit an unambiguous determination of E_a , however these pair of E_a and A factor could be fitted according to a linear relationship defined by the compensation effect.

There are reports of the use of CR method to study the thermal data of sunflower oil [4], where three decomposition steps were observed. The TG was also applied to corn oil biodiesel [18]. The authors observed one step for the decomposition of corn oil in nitrogen atmosphere with methanol reaction and three steps in air atmosphere through methanol reaction. They observed two steps in air through ethanol reaction. These results in air are not in accordance with our results but it should be considered that these are biodiesels from different natural sources. The paper mentioned reports one decomposition step for reference diesel with the decomposition starting at 50 °C and the peak temperature near 200 °C at 5 °C min^{-1} , in accordance with our results for diesel. The report for corn biodiesel shows reaction orders between 0.15 and 0.42 and activation energy between 73 and 85 kJ mol^{-1} using CR. Our results for the activation energy as shown in Table 1 are mainly covered in this range. However our obtained reaction orders for both tested biodiesel samples are higher than the reported by Dantas [18]. It is reported the

Table 1 Kinetic parameters for fuels decomposition

Fuel	Kinetic parameter	Heating rate (°C min^{-1})			
		5	10	20	30
BD-soy	E_a (kJ mol^{-1})	73.86	73.19	71.88	72.65
	A (min^{-1})	$2.1 \cdot 10^6$	$1.6 \cdot 10^6$	10^6	$1.3 \cdot 10^6$
	n	0.5	0.5	0.5	0.5
	r	0.9990	0.9985	0.9975	0.9956
BD-hig	E_a (kJ mol^{-1})	73.50	77.77	76.55	87.15
	A (min^{-1})	10^6	$2.4 \cdot 10^6$	$2 \cdot 10^6$	$12 \cdot 10^6$
	n	0.7	0.7	0.7	0.7
	r	0.9955	0.9965	0.9978	0.9944
Diesel	E_a (kJ mol^{-1})	21.62	22.30	22.76	22.87
	A (min^{-1})	$1.2 \cdot 10^4$	$2.7 \cdot 10^4$	$5.5 \cdot 10^4$	$6.1 \cdot 10^4$
	n	0.5	0.5	0.5	0.5
	r	0.9985	0.9982	0.9990	0.9998

evaluation of biodiesel from soybean oil blends with only one step observed in air and nitrogen atmospheres [19]. The use of CR method is reported for the study of the kinetic behavior of castor oil biodiesel and it is compared with other two methods [20]. Santos [21] reported for the babassu biodiesel a start of the decomposition process around 52 °C obtained methanol route, contrasting with the thermal profiles shown in Figs. 2 and 3 for our biodiesel samples. In the other hand Dantas [22] observed three steps in air for the corn biodiesel ethanol route.

Conclusions

Thermogravimetry is an appropriate thermal analysis technique to study the decomposition process of biodiesel from higereta oil and soybean oil.

The obtained thermogravimetric profiles in the air atmosphere for diesel, soybean oil biodiesel and higereta oil biodiesel indicate one mass loss step. In case of biodiesel this is associated to the decomposition of the ethyl esters. For diesel it is due to decomposition or pyrolysis of the saturated hydrocarbons.

Diesel has a smaller onset decomposition temperature than biodiesels indicating that biodiesels samples are more thermally stable than diesel.

The obtained kinetic parameters for BD-hig and BD-soy are similar to the reported for biodiesel produced from other natural sources. The application of the Coats & Redfern method indicates $n = 0.5$ for diesel and soybean biodiesel, and $n = 0.7$ for higereta biodiesel. The activation energy of biodiesel is in both cases higher than diesel.

With varying heating rates, a linear relationship was observed between activation energy and pre-exponential factor for all the analyzed fuels.

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