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DYNAMIC KINETIC CALCULATION OF CASTOR OIL BIODIESEL

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Diesel oil has an important role in the field of urban traffic as well as in the transportation of products. However, the amount of the non-renewable sources is continuously decreasing. This fact and the environmental requirements brought the necessity to search for other, renewable sources. This paper aimed the dynamic kinetic calculation of thermal decomposition of castor oil, methanol biodiesel and ethanol biodiesel using Coats–Redfern, Madhusudanan and Ozawa methods. On the base of the thermogravimetric curves the following thermal stability order could be established: castor oil>ethanol biodiesel>methanol biodiesel. Kinetic data presented coherent results. Methanol biodiesel presented lower activation energy than ethanol biodiesel, suggesting that methanol biodiesel has a better quality for combustion.

Keywords: *biodiesel, castor oil, Coats–Redfern, kinetic, Ozawa*

Introduction

Most of the energy consumed in the world originates from petroleum, coal and natural gas, mainly petroleum derived fuels. In USA, in 2004, the overall energy consumption was around $105.8\cdot10^{18}$ J, in which fossil fuels represented around 86%, where the contribution of petroleum was 40% the natural gas was 23% and coal was 23%. The amount of nuclear energy was 8%. The renewable sources amounted to only 6.0%, where 2.7% corresponds to hydroelectric power, 2.7% to biomass and the remaining 0.5% to solar, geothermal and wind energy sources [1, 2].

Since the fossil fuels' sources are exhaustible (164 years for coal, 67 years for natural gas and only 40 years for petroleum [2]) searching for other, renewable sources has more and more interest. Vegetable oils, animal fats after their transformation to fatty acid esters (biodiesels) can be alternative sources to substitute the diesel oil in compression ignition engines [3].

Oils and fats derived from animal, vegetable or having even microbial origin are practically insoluble in water. They are basically glycerin-derived esters mixtures, where the fatty acids contain 8–24 carbon atoms long chains, with different degrees of unsaturation. The composition of a determined vegetable oil is important since it influences the physical properties e.g. viscosity, melting point, thermal stability and cetane number of the oil [4].

Vegetable oils contain in average 95% of triacylglycerides, 0.1% of diacylglycerides and 2% of monoacylglycerides. Tri-, di- and monoacylglycerides are constituted by a glycerine molecule linked to three, two or one molecules of fatty acids, respectively. Besides the fatty acids linked to the glycerin molecules, there are fatty acids that are not linked to the glycerin, denominated as free fatty acids. Their amount can be 0.3–2.0% in the vegetable oil or even higher in used oils. Free fatty acids are responsible for the acidity of oils and fats [4].

Different types of oleaginous plants results oils with different degree of unsaturation and chemical composition. Depending on the quality of the oil, substances such as peroxides, free fatty acids, phosphatides, carotenoids, terpenes and phytosterols can be associated to the glycerides,. The term 'lipids' embraces a variety of chemical substances. In addition to triglycerides, it also includes mono- and diglycerides, phosphatides, cerebrosides, sterols, terpenes, fatty alcohols, fatty acids, fat-soluble vitamins and other substances [5].

Biodiesel is a renewable fuel produced from the reaction of vegetable oils or animal fats and alcohol. Biodiesel is a fuel that can be used either as pure (B100) or blended with different amounts of petrodiesel (BX, whose *X* denotes the volume per-

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centage of biodiesel) in diesel engines. It brings also advantages in pollutant emission and engine wear, too. One of the most important biodiesel sources is the castor oil. Transformation of castor oil to biofuel brings the benefits of producing a fuel locally and generates thousands of jobs from planting to the diesel production and commercialization.

The environmental benefits can also generate economical advantages. Brazil can include biodiesel in the frame of 'Kyoto Agreement' in the guidelines of the Clean Development Mechanisms. There is the possibility of selling carbon quotas by means of Prototype Carbon Fund to reduce the emission of pollutant gases and also carbon sequestration credits through the Bio Carbon Fund (both funds managed by the World Bank) [6–9].

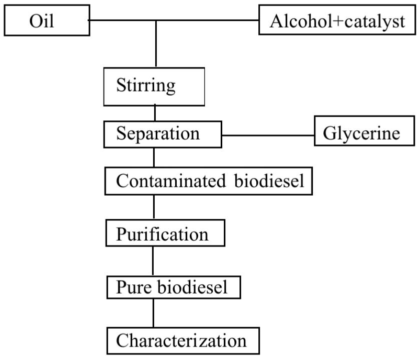
Combustibility and application of a substance as fuel depends on how easily it undertakes combustion, and, besides how much is the gained mechanical energy. In diesel engines combustibility is related to fuel properties, such as viscosity, which is an intrinsic property of vegetable oils and biodiesel. It remarkably influences the operation of the fuel injection system and the fuel atomization mechanism. This is also reflected in the combustion process which influences the amount of the maximum power developed by the engine upon its operation [10–13].

Castor was used in Egypt for lamp oil about 6000 years ago. It is indigenous to eastern Africa, and most probably originated in Ethiopia. In the production of castor beans India has 70% contribution, the remaining being produced in China, Brazil, Russia, Thailand and some African countries [14]. Today in many countries, among them Brasil [12, 13] more and more effort is paid for the production of biodiesels originating from environmentally friendly sources [15].

The aim of this work is the kinetic study of the thermal decomposition of castor oil and its biodiesel (methanol and ethanol routes), using the Coats–Redfern, Madhusudanan and Ozawa dynamic methods.

Experimental

Castor oil was converted to biodiesel using alkaline transesterification. In this reaction 1% catalyst (potassium hydroxide) was dissolved in alcohol (methanol and ethanol routes), with 1:6 oil:alcohol molar ratio and this mixture was added to the oil. The reaction mass was stirred at room temperature for 30 min. After the decantation process, the glycerine was removed and the biodiesel was purified with the addition of water, then the biodiesel was dried and characterized (Scheme 1).



Scheme 1 Production of biodiesel

Biodiesel samples were analyzed using gas chromatography to verify the conversion of triacylglycerides to the corresponding methyl and ethyl esters upon the transesterification reaction. Varian 3800 Gas Chromatograph was used with split/splitless injector, FID detector, column of 5% phenyl and 95% polydimethylsiloxane, (30.0×0.25×0.25 mm). The injector temperature was 290°C, the detector temperature was 300°C and 1:50 flow ratio was applied.

Thermogravimetric curves were obtained using Shimadzu TGA-50 Thermobalance, using 10, 15 and 20°C min^{-1} dynamic heating rates between room temperature up to 900°C with synthetic air purging.

Results and discussion

The compositions of methanol and ethanol biodiesels obtained by gas chromatography are presented in Tables 1 and 2. It can be observed that the transesterification process resulted 99.36% conversion of methyl esters and 99.60% conversion of ethyl esters. These values are higher than the requested 96.5% by the European standard EN 1403.

Thermogravimetric results

TG/DTG curves of the castor oil, (recorded at a heating rate of 10°C min^{-1}) show three steps of mass loss, attributed to the volatilization and/or combustion of the

Table 1 Ester composition of castor oil biodiesel (methanol route)

Ester	Methanol biodiesel/%
Methyl ricinoleate	85.79
Methyl stearate	4.88
Methyl oleate	3.87
Methyl palmitate	1.20
Methyl linoleate	0.81
Methyl linolenate	0.06
Others	2.75
Total	99.36

Table 2 Ester composition of castor oil biodiesel (ethanol route)

Ester	Ethanol biodiesel/%
Ethyl ricinoleate	85.48
Ethyl stearate	1.17
Ethyl oleate	0.97
Ethyl palmitate	0.32
Ethyl linoleate	0.24
Ethyl linolenate	1.67
Others	9.75
Total	99.60

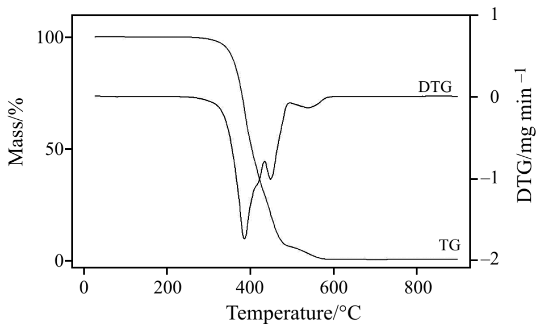


Fig. 1 TG/DTG curves of castor oil

triacylglycerides. The temperature ranges of these steps were 261–436, 436–49 and 498–60°C, with mass losses of 71.1, 22.7 and 5.6%, respectively (Fig. 1).

Thermogravimetric curve of the castor oil biodiesel (methanol route) at a heating rate of 10°C min^{-1} presented two mass loss steps, attributed to the volatilization and/or combustion of the methyl esters, whose main component is methyl ricinoleate (Table 1). These steps appeared between 150–334 and 334–513°C resulting 97 and 3% mass losses, respectively (Fig. 2). The first step involved the evaporation of methyl ricinoleate (its boiling point is (185–212°C) and oxidative degradation of esters.

Thermogravimetric curve of castor oil biodiesel (ethanol route) presented two thermal decomposition steps, ascribed to the volatilization and/or combustion of the ethyl esters, whose main component is ethyl ricinoleate (Table 2). These steps occurred in the 159–309 and 309–506°C temperature ranges with the respective mass losses of 95.3 and 4.7% (Fig. 3). These steps are related to the boiling point of ethyl ricinoleate and oxidative degradation of esters.

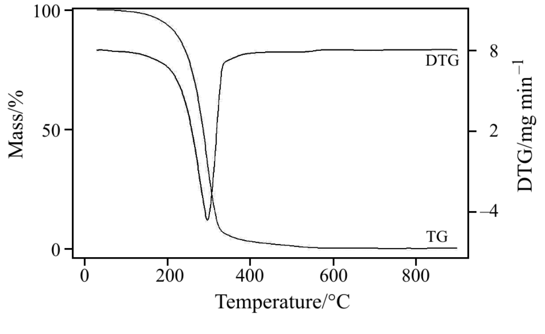


Fig. 2 TG/DTG curves of the methanol biodiesel

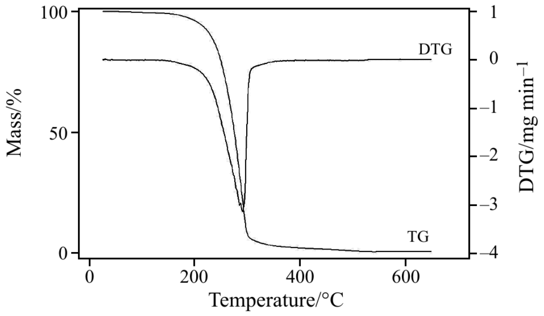


Fig. 3 TG/DTG curves of the ethanol biodiesel

It can be observed that the initial temperature of the thermal degradation of castor oil is higher than that for methanol and ethanol biodiesel. This is due to cleavage of triacylglyceride molecules during the transesterification reaction during the biodiesel production.

Kinetic study

The dynamic kinetic calculation is based on the following equation:

$$g(\alpha)=\frac{A}{\phi}\int_{0}^{T} e^{-E/RT}\mathrm{d}T \qquad (1)$$

where $g(\alpha)$=kinetic model; T=temperature; ϕ=heating rate; E=activation energy; A=pre-exponential factor; R=gas constant.

The first term of Eq. (1) is easy to solve, whereas the integral of exponential does not present an exact solution, even though, various approximations for the calculation of this integral have been proposed, originating different methods for calculation of the kinetic parameters. These solutions are classified on the basis of mathematical methods. Various equations of approximation and integration methods e.g. Coats–Redfern and Madhusudanan [16, 17] were proposed.

These mathematical methods are somehow subjected to a certain degree of inaccuracy, which influences the precision of the results. Thus, such methods should be used carefully. One possible way to avoid having false kinetic parameters is to investigate the process at different heating rates and to use at least three different methods. If the estimated kinetic parameters are in agreement with each other the kinetic parameters are true [18, 19].

The kinetic study [20–22] was carried out in the step corresponding to the beginning of thermal decomposition of castor oil, methanol biodiesel and ethanol biodiesel, using dynamic thermogravimetric curves at heating rates of 10, 15 and 20°C min^{-1}. The determination of the kinetic model was performed in the decomposed fraction (α) of 0.10–0.90, using the program of thermal decomposition mechanisms by the Coats–Redfern dynamic method [16].

The kinetic model that best fitted the experimental curves for the ethanol biodiesel was the one-dimensional phase-boundary controlled model (R1). For the castor oil and methanol biodiesel the kinetic model that best fitted the experimental data was the two-dimensional phase-boundary controlled model (R2).

Ozawa method (Eq. (2)) was also used in the kinetic studies [23]. This method is based on the Doyle's approximation, which proposed a method that determines the value of activation energy (E) from several dynamic thermogravimetric curves obtained with different heating rates (ϕ) independently of the knowledge of the reaction mechanism.

$$\log\phi = \log\left[\frac{AE}{Rg(\alpha)}\right] - 2.315 - 0.4567\frac{E}{RT} \qquad (2)$$

If the value of the decomposed fraction (α) is kept constant, a graph of $\log\phi$ *vs*. $1/T$ should result a straight line allowing the determination of the activation energy (E). The values of E can be calculated from several values of the decomposed fraction (α). The most probable value of the activation energy is taken from the average of these results.

Table 3 Kinetic data obtained for castor oil

Kinetic parameter	Method		
	Coats–Redfern	Madhusudanan	Ozawa
n	0.50	0.53	0.40
E/kJ mol^{-1}	115.1	116.3	129.7
A/s^{-1}	$1.0\cdot10^{8}$	$1.5\cdot10^{8}$	$6.7\cdot10^{9}$
r	0.9999	1.0000	–

Table 4 Kinetic data obtained for methanol biodiesel

Kinetic parameter	Method		
	Coats–Redfern	Madhusudanan	Ozawa
n	0.48	0.45	0.50
E/kJ mol^{-1}	85.6	88.7	71.8
A/s^{-1}	$2.0\cdot10^{6}$	$1.5\cdot10^{6}$	$1.9\cdot10^{6}$
r	0.9999	1.0000	–

Table 5 Kinetic data obtained for ethanol biodiesel

Kinetic parameter	Method		
	Coats–Redfern	Madhusudanan	Ozawa
n	0.32	0.33	0.20
E/kJ mol^{-1}	92.4	93.0	80.9
A/s^{-1}	$4.2\cdot10^{6}$	$5.2\cdot10^{6}$	$9.8\cdot10^{6}$
r	1.0000	1.0000	–

The kinetic parameters, reaction order (n), activation energy (E) and pre-exponential factor (A) were determined by the Coats–Redfern, Madhusudanan and Ozawa methods [16, 17, 23]. The kinetic parameters of castor oil, methanol biodiesel and ethanol biodiesel are summarized in Tables 3–5, respectively.

The Ozawa graphs of these samples at heating rates of 10, 15 and 20°C min^{-1} presented a good correlation due to similarity of the angular coefficients (Figs 4–6).

Kinetic data obtained by Coats–Redfern, Madhusudanan and Ozawa methods presented coherent results. Particularly the agreement between the Coats–Redfern and Madhusudanan methods was very good. Castor oil presented higher activation energy than ethanol and methanol biodiesel indicating that castor oil has higher stability.

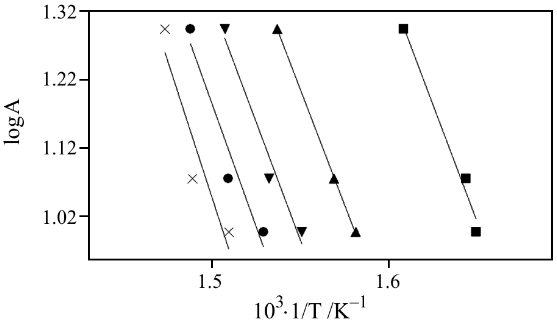


Fig. 4 Ozawa graph of castor oil

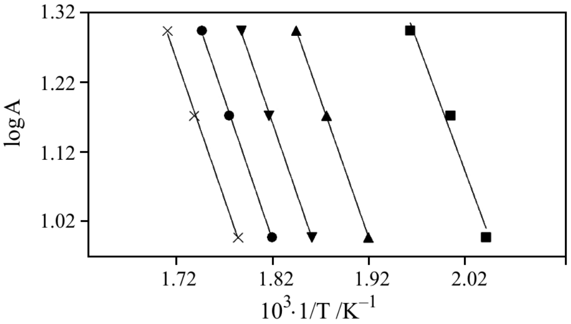


Fig. 5 Ozawa graph of methanol biodiesel

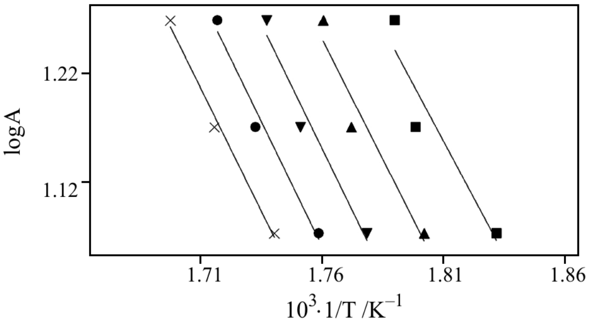


Fig. 6 Ozawa graph of ethanol biodiesel

Conclusions

On the base of the thermogravimetric curves the following thermal stability could be established: castor oil>ethanol biodiesel>methanol biodiesel. The transesterification process leads to a higher volatility of biodiesel compared to castor oil.

Kinetic data obtained by Coats–Redfern, Madhusudanan and Ozawa methods presented coherent results. Particularly the agreement between the Coats–Redfern and Madhusudanan methods was very good. Methanol biodiesel presented lower activation energy than ethanol biodiesel indicating that methanol biodiesel has better combustion properties.

Acknowledgements

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References

1 Renewable Energy Annual 2004 Edition, Official Energy Statistics from the U.S. Government, Energy Information Administration, available at the site http://www.eia.doe.gov/cneaf/solar.renewables/page/rea_data/rea_sum.html, accessed in July 5, 2006.
2 Putting energy in the spotlight, BP Statistical Review of World Energy June 2005.
3 R. A. Ferrari, V. S. Oliveira and A. Scabio, Quim. Nova, 28 (2005) 19.
4 P. M. G. Felizardo, Instituto Superior Técnico, Lisboa, Portugal 2003.
5 Food Fats and Oils, Chapter 1–4, The Institute of Shortening and Edible Oils, available at the site http://www.iseo.org/ffo_1-4.htm, accessed in July 5, 2006.
6 K. Piyaporn, N. Jeyashoke and K. Kanit, J. Am. Oil Chem. Soc., 73 (1996) 471.
7 U. Schuchardt, R. Sercheli and R. M. Vargas, J. Braz. Chem. Soc., 9 (1998) 199.
8 E. G. Shay, Biomass Bioenergy, 4 (1993) 227.
9 D. Wysham, A Carbon Rush at the World Bank, FPIF Special Report February 2005, available at the site http://www.fpif.org/papers/0502wbank.html, accessed in July 5, 2006.
10 S. Stournas, E. Lois and A. Serdari, J. Am. Oil Chem. Soc., 72 (1995) 436.
11 G. F. Zagonel and L. P. Ramos, Rev. Quim. Ind., 717 (2001) 17.
12 M. M. Conceição, R. A. Candeia, H. J. Dantas, L. E. B. Soledade, V. J. Fernandes Jr. and A. G. Souza, Energy Fuel, 19 (2005) 2185.
13 M. M. Conceição, R. A. Candeia, F. C. Silva, A. F. Bezerra, V. J. Fernandes Jr. and A. G. Souza, Ren. Sustain. Energ. Rev., In press.
14 Site http://www.cyberlipid.org/glycer/glyc0054.htm, accessed in July 6, 2006.
15 A. Srivastava and R. Prasad, Ren. Sustain. Energ. Rev., 4 (2000) 111.
16 A. W. Coats and J. P. Redfern, Nature, 201 (1964) 68.
17 P. M. Madhusudanan, K. Krishnan and K. N. Ninan, Thermochim. Acta, 221 (1963) 13.
18 J. Šesták, Talanta, 13 (1966) 567.
19 J. H. Flynn and L. A. Wall, J. Res. Nat. Bur. Stand., 70A (1966) 487.
20 M. M. Conceição, A. M. L. Melo, N. Narain, I. M. G. Santos and A. G. Souza, J. Therm. Anal. Cal., 67 (2002) 273.
21 M. M. Conceição, V. J. Fernandes Jr., F. S. M. Sinfrônio, J. C. O. Santos, M. C. D. Silva, V. M. Fonseca and A. G. Souza, J. Therm. Anal. Cal., 79 (2005) 461.
22 M. M. Conceição, A. G. Souza, M. F. S. Trindade, T. G. Nascimento, C. F. S. Aragão and R. O. Macedo, Thermochim. Acta, 433 (2005) 163.
23 T. Ozawa, J. Thermal Anal., 2 (1970) 301.

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