



Model-free kinetics applied to volatilization of Brazilian sunflower oil, and its respective biodiesel

Anne G.D. Santos^{a,**}, Antonio S. Araujo^{a,*}, Vinícius P.S. Caldeira^a, Valter J. Fernandes Jr.^a, Luiz D. Souza^b, Allan K. Barros^c

^a Federal University of Rio Grande do Norte, Department of Chemistry, 59078-970 Natal RN, Brazil

^b State University of Rio Grande do Norte, Department of Chemistry, 59610-210 Mossoró RN, Brazil

^c National Agency of Petroleum, Natural Gas and Biofuels, Av. Rio Branco 65, 20090-004 Rio de Janeiro RJ, Brazil

ARTICLE INFO

Article history:

Received 13 October 2009

Received in revised form 17 April 2010

Accepted 22 April 2010

Available online 29 April 2010

Keywords:

Thermogravimetry

Biodiesel

Oil sunflower

Kinetics

Model-free kinetics

ABSTRACT

Model-free kinetic studies for volatilization of Brazilian sunflower oil and its respective biodiesel were carried out. The biodiesel was obtained by the methylic route using potassium hydroxide as catalyst. Both sunflower oil and biodiesel were characterized by physicochemical analyses, gas chromatography, simulated distillation and thermogravimetry. The physicochemical properties indicated that the oil and biodiesel samples are in accordance with the specifications of the Brazilian National Agency of Petroleum, Natural Gas and Biofuels (ANP). Gas chromatography indicated that the biodiesel was obtained with a content of ester of ca. 97.35 wt%. The TG curves indicated that the temperatures for volatilization of biodiesel are lower than for sunflower oil, which is explained by their different compositions and properties. The value of the apparent activation energy for the volatilization process, as determined by the Vyazovkin Method, was higher for sunflower oil than for biodiesel.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The major part of all energy consumed worldwide comes from fossil sources. Diesel fuels have an essential function in the industrial economy of a developing country. Economic growth is always accompanied by commensurate increase in the transport. The huge energy demand in the industrialized world and the pollution problems caused due to the widespread use of fossil fuels has made it increasingly necessary to develop alternative sources of energy to resolve these questions. Alternative diesel fuels must be acceptable, economically competitive, environmental acceptable and easily available [1–3]. 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 [4].

Oils and fats derived from vegetable, animal or from microbial origin are practically insoluble in water. Fatty acid contains 8–24 carbon atoms long chains, with different degrees of unsaturation [5]. The fatty acid composition of a determined vegetable oil is important since it influences the physical properties. Vegetable oils are composed primarily of triacylglycerides, diacylglycerides

and monoacylglycerides, in decreasing order, respectively. Different types of oleaginous plants result in oils with different degree of unsaturation and chemical composition [6,7]. Vegetable oils present higher viscosity than diesel, normally 25 times, as also 8–10 times greater than the corresponding methyl biodiesel. This problem is solved by the transesterification reaction, decreasing the molecular mass of the oils, consequently decreasing the viscosity [2].

The commonly used method for biodiesel production is transesterification of vegetable oils. This process, also called alcoholysis, is the reaction of triglycerides with alcohols to produce methyl or ethyl esters and glycerol as a by-product. A catalyst is usually used to improve the reaction rate and yield. The transesterification reaction consists in three equivalents, consecutive and reversible reactions. The triglyceride is converted stepwise to diglyceride, monoglyceride and finally glycerol. According the stoichiometry, at each reaction step, one molecule of methyl or ethyl ester is produced for each molecule of methanol or ethanol consumed [8,9]. The advantages of use of biodiesel include renew ability, biodegradability, higher flash point, inherent lubricity, reduction of most regulated exhaust emissions, as well as miscibility with petrodiesel. Various specifications that a biodiesel fuel must have are contained in biodiesel standards, such as *American Society for Testing and Materials* (ASTM) and EN 14214 in Europe.

Thermal analysis is concerned with a lot of scientific applications. It provides efficient tools for measuring thermodynamic

* Corresponding author. Tel.: +55 8432119240; fax: +55 8432119240.

** Corresponding author.

E-mail addresses: anne_gabriela@hotmail.com (A.G.D. Santos), asa-ufrn@usa.net (A.S. Araujo).

Table 1
Physicochemical analysis of sunflower oil and its biodiesel obtained by the methylic route.

Property	Methods	Sunflower oil	Sunflower biodiesel	Limits ^a (ANP)
Kinematic viscosity, mm ² s ⁻¹	ASTM D 445	33.2	4.3	3.0–6.0
Specific mass, kg m ⁻³	ASTM D 4052	918.8	883.6	850–900
Flash point, °C	ASTM D 93	314.0	178.0	≥100
Combustion point, °C	–	320.0	182.0	–
Total sulfur, mg kg ⁻¹	ASTM D 5453	0.2	0.4	50
Acid value, mg KOH g ⁻¹	EN 14104	0.32	0.032	≤0.5
Iodine value, g I ₂ 100 g ⁻¹	EN 14111	135.4	125.2	–

^a Specifications according to the ANP Brazilian agency.

properties such as enthalpies, heat capacities and temperature of phase transitions [2]. From thermogravimetry (TG) it is possible to follow the kinetics of thermally stimulated processes, like volatilization, decomposition, oxidation, reduction, crystallization, polymerization and combustion.

Isoconversional methods require experiments with different heating rates in order to calculation of the activation energy as a function of conversion. The potential applications of the isoconversional methods have been studied by Vyazovkin showing that it can be used to explore reaction mechanisms and process kinetics prediction. These two features make a foundation of isoconversional kinetic analysis or so-called “*model-free kinetics*” [10].

The purpose of this work is the kinetic study of the thermal volatilization of Brazilian sunflower oil and its biodiesel obtained from the methylic route. The model-free kinetics method proposed by Vyazovkin [11–13] has been previously applied to determine the kinetic parameters of some chemical reactions, such as the apparent activation energy (E_a) and conversion rates.

2. Experimental

A sample of Brazilian sunflower oil was converted to biodiesel using alkaline transesterification. The sample of biodiesel was prepared in 1:6 molar ratio of oil/methanol. In this reaction 1 wt% of catalyst (potassium hydroxide) in relation to oil was dissolved in methanol, and then added to the oil being stirred at a constant temperature for 2 h. 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.

The analyses of the pure biodiesel (B100) were performed in accordance with the standards of the *American Society for Testing and Materials* (ASTM) and *Brazilian Association of Technical Standards* (ABNT), as indicated by the Resolution No. 7 of ANP, the Brazilian National Agency of Petroleum, Natural Gas and Biofuels [14]. The obtained sunflower biodiesel was analyzed by gas chromatography (GC) with a flame ionization detector, in order to determine the conversion of triacylglyceride to methyl esters of the corresponding fatty acids upon the transesterification reaction. A Thermo Trace GC-FID gas chromatograph was used. The FID detector temperature was 250 °C. The oven program to carry out the analysis of ester content has initial temperature 150 °C for 6 min, next, the first heating rate was 10 °C min⁻¹ up to 210 °C for 5 min, finally a second heating rate was 5 °C min⁻¹ up to 240 °C for 2 min.

Also, the *SIM*ulate *DI*stillation (*SIMDIS*) gas chromatography analysis for sunflower oil and biodiesel was performed according to ASTM D 2887. An equipment Varian 450-GC with CP-8400 autosampler, FID detector, operating at temperature of 390 °C with a column Varian CP-SimDist was used. The temperature range used was from 35 to 390 °C with a heating rate of 10 °C min⁻¹. The carrier gas was helium and the total analysis time was 39 min.

The thermogravimetry (TG) experiments were carried out using a thermobalance Mettler-STGA 851 model, in the temperature range of 30–600 °C, under nitrogen atmosphere flowing in a rate of 25 mL min⁻¹, and heating rates of 5; 10 and 20 °C min⁻¹. To each

experiment, a mass of ca. 70 mg of sample was used. For this amount of oil and biodiesel a pan with capacity of 100 mg was used in order to avoid the gradient of temperature on the sample.

The reaction rate of a thermal and catalytic reaction depends on conversion (α); temperature (T) and time (t). The methods that make use of the isoconversional principle which states that at a constant extent of conversion, the reaction rate is a function only of the temperature so that:

$$\left[\frac{d \ln(d\alpha/dt)}{dT^{-1}} \right] = -\frac{E_a}{R} \quad (1)$$

In Eq. (1), E_a is Arrhenius parameters (apparent activation energy), R is the gas constant, T is the temperature, t is the time, and α is the extent of conversion, which can be determined from analysis TG as a fractional mass loss [10].

The model-free kinetics is a program based on the Vyazovkin theory for decomposition studies of complex reaction. The approach follows all points of conversion from multiple experiments instead of a single one. A chemical reaction is measured at least in three different heating rates (β) [15].

3. Results and discussion

The results of the physicochemical analyses for sunflower bio-products are displayed in Table 1. The biodiesel samples obtained by the methyl route are in accordance to the specifications established by ANP Brazilian agency [14].

It can be seen that the sulfur content in the biodiesel is negligible; this confers a great advantage to biodiesel, in that no sulfur bearing compounds are produced upon its combustion in Diesel engines. For the kinematic viscosity, it is observed a significant decreasing in the biodiesel when compared to sunflower oil, which is a positive factor; because the high viscosity of the oil reduces the fuel atomization and increases fuel spray penetration. The results of iodine value indicate the unsaturation in the oil and biodiesel. This unsaturation was coimproved by gas chromatography. The difference between oil and biodiesel for iodine value can be attributed to the inaccuracy of the method.

The obtained biodiesel was analyzed by gas chromatography, in order to assess the conversion of the triglycerides into their methyl esters. Table 2 presents the main methyl ester of sunflower biodiesel. The results, as expected by the sunflower oil composi-

Table 2
Chromatographic data of sunflower biodiesel.

Methyl ester (% m/m)	Biodiesel
Palmitate (C16:0)	8.40
Oleate (C18:1)	26.96
Linoleate (C18:2)	49.47
Linolenate (C18:3)	2.64
Docosanoic (C22:0)	1.75
Others	8.130
Total	97.35

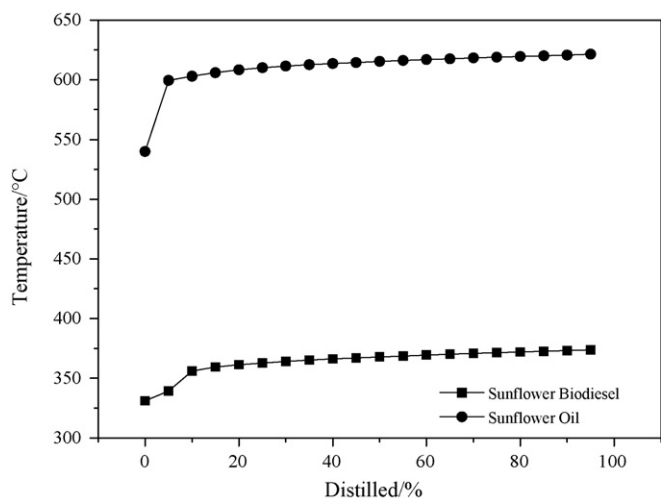


Fig. 1. Distillation characteristics of sunflower oil and biodiesel via simulated distillation.

tion, indicated the prevalence of the methyl linoleate and oleate, respectively. The conversion of 97.35 wt% of sunflower oil in methyl esters confirms the efficiency of the conversion of the fatty acids into esters by the adopted procedure. This value is higher than that requested by the European standard EN 1403, which is 96.5 wt%. It is considered that gas chromatography is an efficient technique to evaluate if the conversion into esters was complete and mainly if the biodiesel production was complete.

By SIMDIS (Fig. 1), one can evaluate the distillation curve of the studied samples. Sunflower Biodiesel has a range of distillation temperature of 300–370 °C, this result is in agreement with reported in the literature [16]. Considering the distilled volume, it can be noted that about 80% of the distillate occurred in the temperature ranging from 361 to 369 °C, suggesting that the sunflower biodiesel consists mainly of methyl esters with 18 carbon atoms. The results are in agreement with the literature [17]. For sunflower oil, the boiling temperatures were higher than that of biodiesel, indicating that it has a higher molecular weight, diffculting the evaporation and thus needing more energy to volatilization.

In order to have a better understanding of the sunflower oil and biodiesel, the thermal volatilization behavior of both samples was investigated. In this study, typical TG curves of the volatilization process are shown in Figs. 2 and 3. Experimentally, the thermal volatilization of samples at heating rates of 5, 10 and 20 °C min⁻¹,

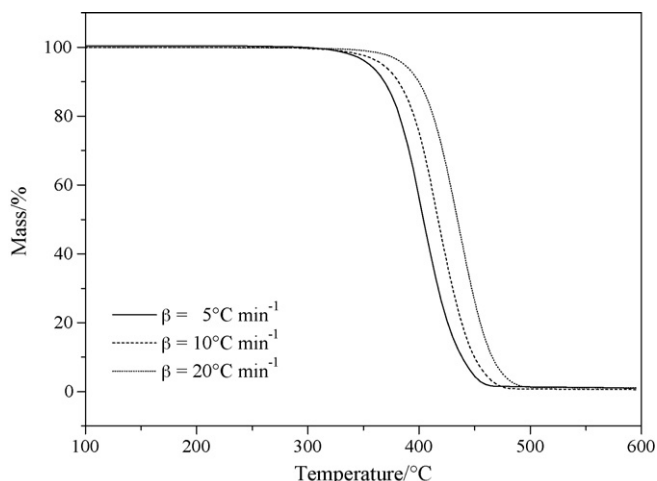


Fig. 2. TG curves of sunflower oil at different heating rates.

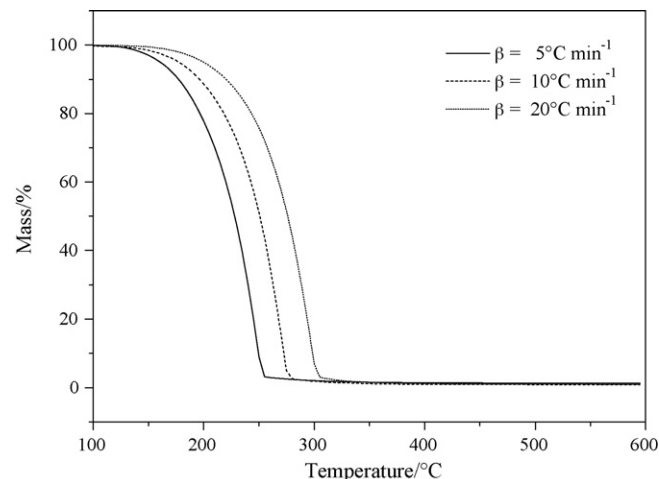


Fig. 3. TG curves of sunflower oil biodiesel at different heating rates.

occurs in a single well-defined step. The volatilization of sunflower oil and its biodiesel occurs in the range of 320–490 and 130–320 °C; with mass losses of 98.7 and 98.1 wt% and residue mass of 1.3 and 1.9 wt%, respectively. These mass losses were attributed to the volatilization of the methyl esters, mainly of the methyl linoleate (48.5 wt%) and methyl oleate (25.9 wt%), the most abundant components in the biodiesel, in agreement with the high concentration of linoleic and oleic acids in sunflower oil. The volatilization process of the sunflower oil initiates and finishes in temperatures higher than to the respective biodiesel. This is explained by the fact that sunflower oil presents a higher molecular weight, with viscosity and intermolecular forces stronger than for its respective biodiesel. The observed temperatures for biodiesel are closer to the volatilization of conventional diesel temperatures. Hence, sunflower oil biodiesel is confirmed as a potential alternative fuel [10]. The heating rate is a crucial factor affecting the volatilization results. The higher heating rate may decrease the distribution of the heat in the biodiesel molecules, thus the volatilization start at higher temperature. As a consequence, in the shape of the TG curves, it is observed that the initial volatilization increases with the heating rates.

Table 3 shows the correlation between the properties that are linked to the process of volatilization of the oil and sunflower biodiesel. It can be observed that for Flash Point, Combustion Point and SIMDIS analysis, the obtained values were practically the same, suggesting a correlation of the data, when compare the ratio values of oil to biodiesel. The correlation value for the property SIMDIS obtained was lower than that of other properties. However, the difference is insignificant and does not compromise the results.

The plots of $\ln(\beta/T_2)$ vs. $1000/T$ to conversion levels from 0.05 to 0.90 at different heating rates for samples were done and obtained average correlation coefficients for 0.9998 and 0.9914 to biodiesel and oil, respectively. It can be seen that there is a considerable degree of parallelism for the lines obtained for both samples, which

Table 3
Correlation between the properties of volatilization of the oil and sunflower biodiesel.

Sunflower sample	Property			
	Flash point	SIMDIS ^a	TG ^a	Combustion point
Oil	314	616.2	440	320
Biodiesel	178	368.7	250	182
Ratio: oil/biodiesel	1.76	1.67	1.76	1.76

^a The heating rate used was 10 °C min⁻¹.

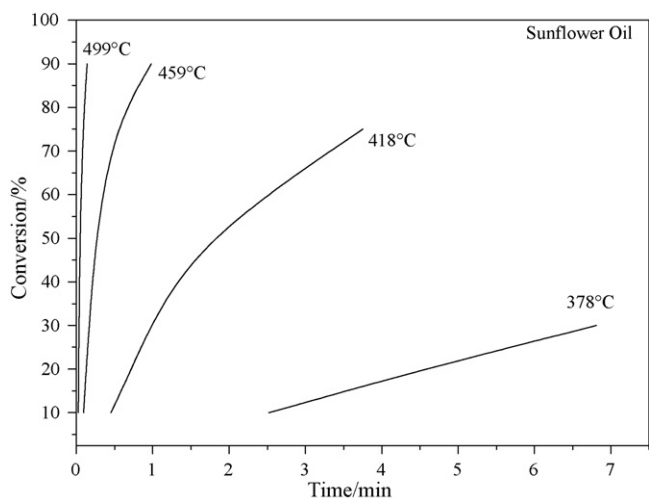


Fig. 4. Conversion of sunflower oil as a function of time at different temperatures.

it means that only one phenomenon is happening, in this case, the volatilization process. The linearity also demonstrates that the model-free method can be used to evaluate the thermal behavior of oil and biodiesel from sunflower.

Figs. 4 and 5 show the conversion curves for sunflower oil and biodiesel. For both samples were considered four isotherms, oil (378, 418, 459 and 499 °C) and biodiesel (200, 251, 302 and 354 °C). It can be observed that in the case of biodiesel, at a temperature of 251 °C there was a complete evaporation in a time of 5.4 min, with a conversion of about 90%. As for sunflower oil, for the same percentage of conversion, the volatilization time was 1.0 min at a temperature of 459 °C. This rapid and complete volatilization resulted in production of a small residual mass, as seen in data from TG. Performing a comparative analysis of sunflower oil and biodiesel, it can observe the influence of molecular weight during the process.

The apparent activation energy (E_a) for the thermal volatilization process of sunflower oil and biodiesel predicted by the model-free kinetics theory is shown in Fig. 6. According to the theory of Vyazovkin, the E_a was estimated by the slope of each straight lines ($0.05 < \alpha < 0.90$) the curve $\ln(\beta/T^2)$ vs. $1000/T$, as shown in Eq. (1). The values for E_a obtained as a function of the conversion for the volatilization process are in the ranges of ca. 50–75 kJ mol⁻¹ for

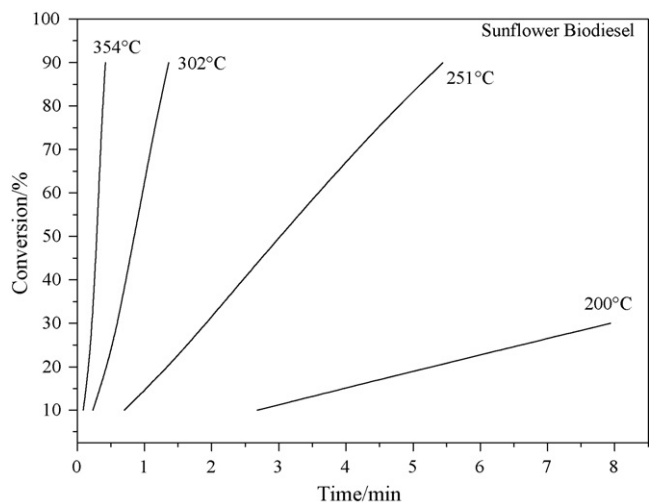


Fig. 5. Conversion of sunflower biodiesel as a function of time at different temperatures.

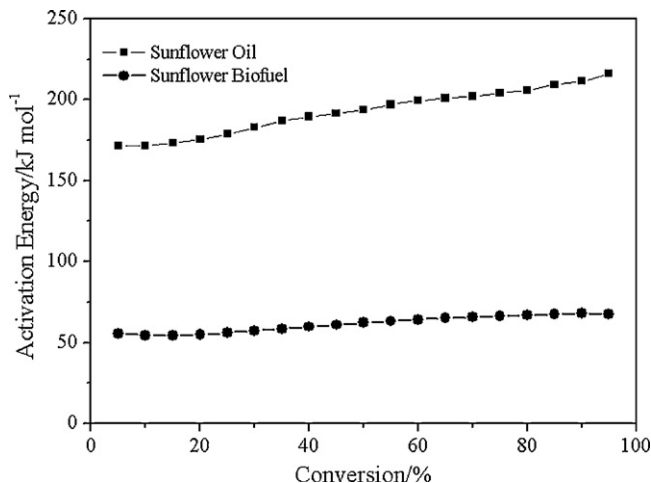


Fig. 6. Activation energy as a function of conversion for volatilization of sunflower oil and biodiesel using the model-free kinetics.

sunflower biodiesel, and ca. 170–210 kJ mol⁻¹. The E_a for sunflower oil is much higher than for biodiesel, suggesting the high stability of sunflower oil for application as raw material for biodiesel production.

4. Conclusions

The model-free kinetics applied in the research has proven to be a reliable method for the study of volatilization process of the sunflower oil and its biodiesel. The values of apparent activation energies for the volatilization processes of sunflower oil were higher than those found to the biodiesel. These values are consistent, evidencing that compounds with the higher molecular weight and viscosity, require high energy to the volatilization. Also, it was observed that biodiesel requires smaller temperature to volatilize to a good degree of conversion than that sunflower oil. Significant results for the correlation between the methods applied to the process of volatilization also, it was observed that biodiesel requires smaller temperature to volatilize to a good degree of conversion than that oil. Significant results for the correlation between the methods applied to the process of volatilization were obtained.

Acknowledgements

The authors are gratefully acknowledged to Brazilian National Agency of Petroleum, Natural Gas and Biofuels (ANP), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), CAPES and FINEP, for financial support.

References

- [1] J.R.O. Lima, R.B. Silva, E.M.C.V.R. Moura, *Fuel* 87 (2007) 1718.
- [2] R.P. Rodrigues, S. Verhelst, *J. Therm. Anal. Calorim.* 96 (2009) 897.
- [3] V.V. Bokade, G.D. Yadav, *Process Saf. Environ. Protect.* 85 (2007) 372.
- [4] J.M. Lujan, V. Bermudez, P.B. Tormos, *Biomass Bioenerg.* 33 (2009) 948.
- [5] M.M. Conceição, V.J. Fernandes, M.C. Bezerra, M.C.D. Silva, I.G.M. Santos, F.C. Silva, A.G. Souza, *J. Therm. Anal. Calorim.* 87 (2007) 865.
- [6] J.M. Encinar, J.F. González, A.R. Reñares, *Fuel Process. Technol.* 88 (2007) 513.
- [7] K.G. Georgogianni, M.G. Kontominas, P.J. Pomonis, D. Avlonitis, V. Gergis, *Fuel Process. Technol.* 89 (2008) 503.
- [8] N.C.O. Tapanes, D.A.G. Aranda, J.W.M. Carneiro, O.A.C. Antunes, *Fuel* 87 (2008) 2286.
- [9] M.G. Kulkarni, A.K. Dalai, N.N. Bakhshi, *Bioresour. Technol.* 98 (2008) 2027.
- [10] S. Vyazovkin, N. Sbirrazzuoli, *Macromol. Rapid Commun.* 27 (2006) 1515.
- [11] S. Vyazovkin, *Int. J. Chem. Kinet.* 28 (1996) 95.
- [12] S. Vyazovkin, N. Sbirrazzuoli, *Anal. Chim. Acta* 335 (1997) 175.

- [13] S. Vyazovkin, C.A. Wight, *Thermochim. Acta* 340–341 (1999) 53–68.
- [14] Resolution ANP No. 7, of 13.3.2008. Available at: <http://www.anp.gov.br>.
- [15] M.J.B. Souza, A.O.S. Silva, J.M.F.B. Aquino, V.J. Fernandes, A.S. Araujo, *J. Therm. Anal. Calorim.* 2 (2004) 693.
- [16] H. Polli, L.A.M. Pontes, M.J.B. Souza, V.J. Fernandes, A.S. Araujo, *J. Therm. Anal. Calorim.* 86 (2006) 469.
- [17] C. Bachler, S. Schober, M. Mittelbach, *Energy Fuels* 24 (2010) 2086.