J Therm Anal Calorim (2012) 109:967–974
DOI 10.1007/s10973-011-1773-5

Thermal stability during pyrolysis of sunflower oil produced in the northeast of Brazil

Iara M. S. Correia · Marcelo J. B. Souza · Antônio de S. Araújo · Elisa M. B. D. Sousa

Received: 28 April 2011 / Accepted: 24 June 2011 / Published online: 17 July 2011

Abstract This study aims to analyze thermal stability and make a rheological assessment of sunflower oil produced in the Northeast of Brazil, resulting from the pyrolysis process. Oil samples were submitted to thermal degradation and the reaction was evaluated by the thermogravimetric technique, at temperatures between 30 and 900 °C. Apparent activation energy was determined using the model-free kinetics theory. The coaxial cylinder system at operating temperature of 40 °C was used to obtain rheological parameters. Oil was characterized by gas chromatography. The lipid profile of the oil exhibited good quality. The activation energy of the sunflower oil was 201.2 kJ mol^{-1}. Results showed the influence of physical–chemical characteristics of vegetable oil on the thermal decomposition process. Rheological analyses confirmed Newtonian rheological behavior. The high potential of the "Catissol" variety produced in Northeast Brazil as raw material for biofuel production using pyrolysis was also demonstrated.

Keywords Sunflower · Thermogravimetry · Rheology · Pyrolysis

I. M. S. Correia · E. M. B. D. Sousa (✉)
Department of Chemical Engineering, Federal University of Rio Grande do Norte, Natal, RN 59078-970, Brazil
e-mail: elisa@eq.ufrn.br

M. J. B. Souza
Department of Chemical Engineering, Federal University of Sergipe, São Cristóvão, SE 49100-000, Brazil

A. de S. Araújo
Department of Chemistry, Federal University of Rio Grande do Norte, Natal, RN 59078-970, Brazil

Introduction

The use of fossil fuels is a major contributor to climate change provoked by the greenhouse effect. In light of growing concern about environmental questions and reduced oil reserves, exploiting vegetable oils for biofuel production is a promising alternative to fossil fuels, in addition to promoting social inclusion and regional development through agribusiness.

Oils and fats of plant, animal, or microbiological origin are practically insoluble in water. Fatty acids contain from 8 to 24 carbons along the chain, with different degrees of unsaturation [1]. Vegetable oils have emerged as an alternative source for biofuel production. Several vegetable oils obtained from soybean, castor, sunflower, cotton, corn, palm and others, are widely applied on biodiesel production [2]. The most traditional method of producing biodiesel is by tryglyceride transesterification with methanol or ethanol, obtaining a mixture of fatty acid methyl or ethyl esters. The transesterification reaction is composed of three consecutive reversible reactions, in which diglycerides and monoglycerides are formed as intermediates [3].

However, several other techniques to convert plant oils into biofuels are being studied, including pyrolysis. It consists of macromolecular material degradation by heating in the absence of oxygen [4, 5]. Conversion of plant oils or animal fats composed predominantly of triglycerides using the pyrolysis reaction represents a potential option for the production of renewable fuels [6].

The sunflower (*Helianthus annus L.*, famíly *Compositae)* is a plant that adapts to different climatic conditions and can be grown in any region. It is currently grown on all continents, in areas encompassing approximately 18 million hectares. It ranks fourth in grain production and fifth in cultivated area worldwide [7]. However, the plant is little exploited in Northeast Brazil owing to unfavorable climatic conditions.

In the state of Rio Grande do Norte, the Agrienergy Program was launched in February 2008. Under this program 13,000 hectares of sunflower and 15,000 of cotton are destined to biodiesel production. Investments total approximately 5 million dollars, benefitting around 12,500 small farmers [8]. In addition to promoting oleaginous seed production, such as sunflower and cotton, the program stimulates complementary industries. For example, plume cotton can be used by the textile industry and sunflower seed cake can be used for fish and animal feed [9]. The goal of the program is to promote oleaginous plant cultivation by small farmers, aimed at biodiesel production, as well as ensuring financial sustainability of producers and competitive production costs. As a preliminary step, pilot studies were conducted to evaluate sunflower in Rio Grande do Norte [10]. Productive behavior of different cultivars were evaluated for grain production, oil content and other agronomic characteristics, identifying the most promising types for oil production and biofuel manufacture. Of those available, we found that the Catissol-01 variety exhibited high-potential productivity, with mean grain yield of 2245 kg/ha.

The thermal analysis technique considers several scientific applications and is an efficient tool to measure thermodynamic properties such as enthalpy, heating capacity, and phase change temperature of substances. Thermal analysis has been successfully used to determine certain properties, study chemical reactions, and investigate oil stability [11]. Thermal analysis is a well established analytical method for investigation of temperature-dependent properties and thermal decomposition [12].The thermogravimetry (TG) is a thermal analysis technique based on the study of sample mass variation, as function either of time as of temperature. The most important parameters of TG analysis are initial decomposition temperature, the maximum temperature of conversion and final decomposition temperature [2]. The shape of the thermogravimetric curve is a function of the reaction kinetics and can hence be used to evaluate kinetic parameters for reactions involving mass changes [13].The DTG curve is defined as the differentiate curve from TG, in which the sample mass loss is proportional to the area under the derivative peak [2].

The potential of vegetable oil pyrolysis for biofuel production has been shown in a number of literature studies [14–16], ranging from type of raw material and reactor used. Thermoanalytical methods (including thermogravimetry) has several advantages, since they are accurate, sensitive, rapid and use a small amount of sample [17, 18]. Isoconversion processing of thermoanalytical data requires different heating rates to calculate activation energy as a function of conversion. Isoconversion application showed that the method can be used to explore the reaction mechanism and predict process kinetics. These two characteristics form the basis of isoconversion kinetic analysis or model-free kinetics [19].

Pyrolysis thermogravimetric kinetics of sunflower oil was evaluated in a study carried out under helium atmosphere at different heating ratios [17, 18]. Thermogravimetric curves (TG) and the kinetic method proposed in the literature [20] were used to estimate activation energy, conversion rates, and degradation time as a function of temperature. Oil produced in the pyrolysis of sunflower bagasse was characterized in a fixed-bed reactor [21]. The effects of particle diameter (0.42–1.8 mm), reaction temperature (400–700 °C) and heating rate (7–40 °C/min) were evaluated. The pyrolysis product was characterized by chromatography and spectroscopy. Results showed that the best output was obtained with particle pyrolysis of 0.425–0.850 mm, with a heating rate of 7 °C/min and nitrogen at a rate of 100 cm^3/min.

Production and characterization of the product obtained from pyrolysis of sunflower press bagasse were also analyzed [22]. Experiments were conducted in a fixed-bed tubular reactor under nitrogen atmosphere at a temperature range of 400–700 °C and heating rate of 5 °C/s. Chemical characterization of the oil obtained (using gas chromatography) for different gas flow levels (25–400 ml/min) showed that this material can be potentially used as fuel.

A thermoanalytical and kinetic study of sunflower oil with and without antioxidant (citric acid) was carried out using thermogravimetry [23]. Thermal analyses were conducted in air (20 mL/min), with heating rates of 2, 5, 10, and 20 °C/min. It was found that the mean activation energy of sunflower oil was higher with antioxidant than without it, indicating that the antioxidant (citric acid) provokes an increase in thermal stability of the oil under study. Thermogravimetric analysis of the thermal stability of comestible oil was conducted using samples of corn oil, sunflower, rice, canola, and olive oil, under air atmosphere at 20 mL/min and heating rate of 10 °C/min until reaching 800 °C [24]. Thermal stability was measured as a function of initial decomposition temperature. Results indicate that the thermal stability of oil depends on the percentage of fatty acids in its composition and the presence of antioxidants.

Considering the growing use of vegetable oils to obtain biodiesel and the need to evaluate the quality of sunflower oil produced in Northeast Brazil (Catissol), this study aimed to assess the thermal degradation and rheology of this important raw material in the production of biofuels derived from the pyrolysis process.

Materials and methods

Raw material and sample characterization

“Catissol” sunflower seeds were obtained from the EMPARN (Agricultural Research Institute of Rio Grande do Norte) Experimental Station in the municipality of Ipanguaçu. BUNGE® refined sunflower oil (lot 0908) was used in this study.

Sunflower seeds were characterized for moisture [25] and apparent density [26, 27].

Oil extraction

Crude sunflower oil (CSO) was obtained by the cold extraction process using a helicoidal mini press (ECIRTEC MPE-40- Brazil, with capacity for 40 kg/h), adjusted by means of spacers placed between the 12 disks that make up the compression chamber. After pressing, the oil was left standing for 5 days to remove residue by decantation, which was followed by filtration.

Thermogravimetry

Pyrolysis study was conducted by microscale thermogravimetry (TG), using a thermogravimetric analyzer as reactor. A Mettler—TGA 851 thermobalance was used at a temperature range of 30–900 °C, under helium atmosphere, flow rate of 25 mL min^{-1} and heating rates of 5, 10, and 20 °C min^{-1}. 60 mg of oil sample mass was used for each experiment. An aluminum crucible (100 mg capacity) was used to allow better distribution of the temperature gradient in the sample. All thermal conversion data were recorded in a computer coupled to the thermoanalytical equipment and evaluated by Mettler STAR software.

Determination of kinetic parameters

Thermogravimetric analyses were carried out to determine conversion values (α) from the difference between initial and final sample mass (TG curves). Initial mass was defined as the mass at ambient temperature and final mass by the DTG (derived thermogravimetric) curve.

This study used model-free kinetics to determine pyrolysis kinetic parameters of the reaction. In this method, the kinetic model assumes that the variation of a given conversion with temperature and apparent activation energy is constant. Starting from the basic equation for non-isothermal kinetics, we have:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{k}{\beta}\cdot f(\alpha) \quad (1)$$

where k is the velocity constant (s^{-1}); β is the heating rate (°C s^{-1}); α is the degree of conversion (%) and $f(\alpha)$ is the expression of the reaction rate equation expressed in terms of conversion α. Expressing k as a function of the Arrhenius equation and considering that $E/RT \gg 1$:

$$\ln\frac{\beta}{T_\alpha^2} = \ln\left[\frac{R.k_0}{E_\alpha g(\alpha)}\right] - \frac{E_\alpha}{R}\frac{1}{T_\alpha} \quad (2)$$

One of the significant advantages of this model is that for each conversion (α), $\ln(\beta/T_\alpha^2)$ is plotted against $1/T\mathrm{B}_\alpha$, generating a straight line whose slope corresponds to a $-E_\alpha/R$. Thus, activation energy can be calculated by the angular coefficient, isolating function g (α) in the linear coefficient, given that this function is difficult to determine, especially in complex events [28]. The mathematical equations of this model were inserted as algorithms into Star software developed by Mettler. Thus, we could obtain isoconversion and apparent activation energy data from the pyrolysis reaction of the oils under study.

Rheology

Absolute or dynamic viscosity was determined in a HAAKE MARS oscillation rheometer (Modular Advanced Rheometer System Thermo Electron Corporation) at a temperature of 40 °C. The coaxial cylinder system was used to obtain rheological parameters (shearing rate and shear stress), where 12 mL of sample is sheared between the cylinder walls. Shearing rates and shear stress were calculated as a function of the radii of the rotor and the body. Haake RheWin 3 software was used to analyze experimental data.

Sample behavior was assessed by applying the Ostwald de Waale model, Eq. 3, fit to stress and shearing rate data.

$$\tau = \kappa\gamma^m \quad (3)$$

In which τ is shear stress (Pa), κ is the fluid consistency index (Pa.s^n), γ is deformation or shear rate (s^{-1}), and m is the fluid behavior index. The Newtonian model was tested, where the behavior index has a unitary value. Equation 4 can therefore be simplified to Eq. 4, in which κ is now the fluid viscosity value (η).

$$\tau = \eta\gamma \quad (4)$$

Chromatographic analyses

Sunflower oil samples were esterified in accordance with the AOAC 963-33 method [29]. The fatty acid profile of the samples was determined from gas chromatography conducted in a gas chromatograph with a Varian CP-3800 flame ionization detector, equipped with a Perkin Elmer Elite—225 capillary column (50% cyanopropylphenyl–methylpolysiloxane, 30 m × 0.25 mm × 0.25 μm). The following chromatographic conditions were used: (i) oven temperature gradient: initial temperature of 60° C for 1 min, increasing from 60 to 180° C at a heating rate of 20 °C min^{-1} and from 180 to 215 °C t a rate of 3 °C min^{-1}, remaining for 70 min; (ii) injector and detector temperature was 250 and 280 °C, respectively; (iii) entrainment gas used was argon (at flow rate of 1 ml min^{-1}) and an injected sample volume of 1 μL. Data were collected and analyzed with Varian Star Chromatography Workstation. Fatty acids in the samples were identified by comparing the spectra of the standards (Sigma) determined under the same conditions.

Results and discussion

Sunflower seed characterization

Sunflower seed was characterized for moisture and apparent density. Results are presented in Table 1. Values obtained represent the mean of three determinations. Moisture content ranged between 6.65 and 6.70%. These results are compatible with moisture values of Catissol sunflower seeds obtained in the literature, which ranged from 5.7 to 7.1% [30], and 6 to 7% [31]. The result obtained in the apparent density test showed a mean value of 0.40 g/cm^3, in accordance with the value obtained by [32] for the same variety of sunflower seed (0.41 g cm^{-3}).

Figure 1 shows rheological behavior of sunflower oil press-extracted at 40 °C, where the shear stress (Pa) diagram is presented as a function of shearing rate or deformation (1/s). For comparison purposes, Fig. 2 exhibits rheological behavior for refined sunflower oil (with the addition of antioxidant).

A variation in viscosity values can be observed for low shearing rates (<10 s^{-1}), indicating non-Newtonian behavior and Bingham plastic fluid, where oil shows a linear relationship between shear stress and deformation rate, but only from the moment of initial or minimum shear stress is reached. This behavior was also found in [33] in a study to determine the viscosity of different vegetable oils.

Table 1 Sunflower seed characteristics

Property	Results
content moisture/%	6.6716 ± 0.0298
Apparent density/g cm^{-3}	0.40 ± 0.0045

Newtonian behavior is observed for shearing rates above 10 s^{-1}, given that viscosity tends towards a constant value for any shearing rate. The Newtonian model fit the two cases perfectly, exhibiting linear correlation coefficients of 0.9999 and 0.9998 for crude (CSO) and refined (RSO) sunflower oil, respectively.

Table 2 gives dynamic viscosity results of crude and refined sunflower oil. Vegetable oil viscosity increases with the length of triglyceride fatty acid chains, as a function of molecule dimensions and orientation [34]. The values in Table 2 suggest that crude oil contains a higher percentage of unsaturated fatty acids, since its viscosity is lower than that of refined oil.

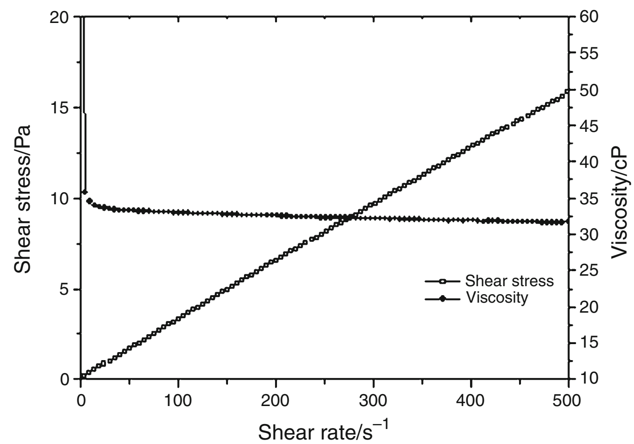

Fig. 1 Rheological behavior of CSO at 40 °C

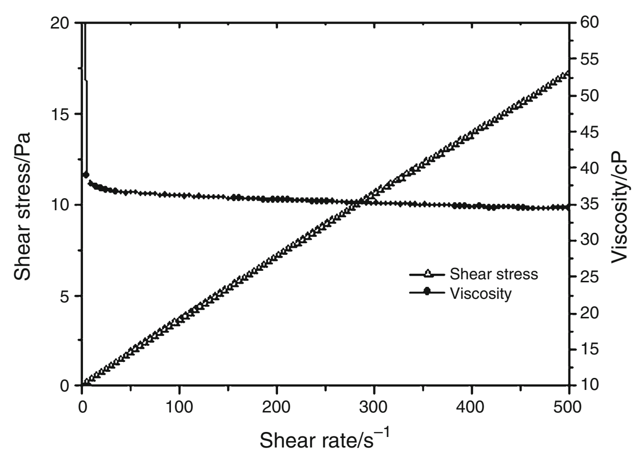

Fig. 2 Rheological behavior of RSO at 40 °C

Table 2 Dynamic viscosity of sunflower oil

Property	Refined sunflower oil	Crude sunflower oil
Dynamic viscosity at 40 °C/cP	34.52	31.67

Table 3 Lipid profile of sunflower oil

Fatty acids	Crude sunflower oil (CSO)/%	Refined sunflower oil (RSO)/%
(C16:0) Palmitic	4	5.92
(C18:0) Stearic	1.47	2
(C18:1) Oleic	49.02	21.27
(C18:2) Linoleic	45.35	70.81
Others	0.11	–

Table 3 shows chromatographic results for fatty acid composition of crude and refined oils, respectively. According to the literature [35], the percentage of linoleic and oleic acids is approximately 90% of total fatty acids in sunflower oil, values confirmed by chromatographic analyses of the two types of oil studied (92.08 and 94.37% for refined and crude oil, respectively).

Table 3 shows that oleic acid was the predominant fatty acid in crude sunflower oil. There may be an inverse relationship between the main fatty acids in sunflower oil that is strongly influenced by environmental conditions, especially temperature, during the seed development phase. At high temperatures, for example, oleic acid levels increase while linoleic acid decreases [36].

Analyses revealed that crude oil extracted from sunflower seeds cultivated in the state of Rio Grande do Norte had a relatively high oleic acid index (49.02%), when compared to oil from seeds produced in other parts of the country. This is likely due to climatic differences among regions (for example 14.6% oleic acid in oil obtained from IAC-Iarama sunflower seeds cultivated in the state of São Paulo-Brazil) [37].

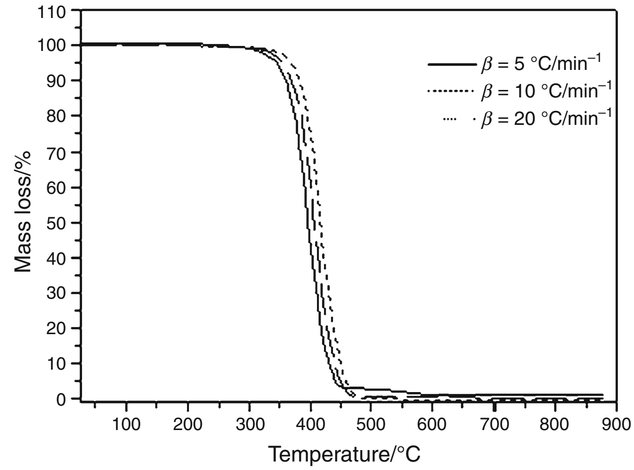

Fig. 3 TG curves of refined sunflower (RSO)

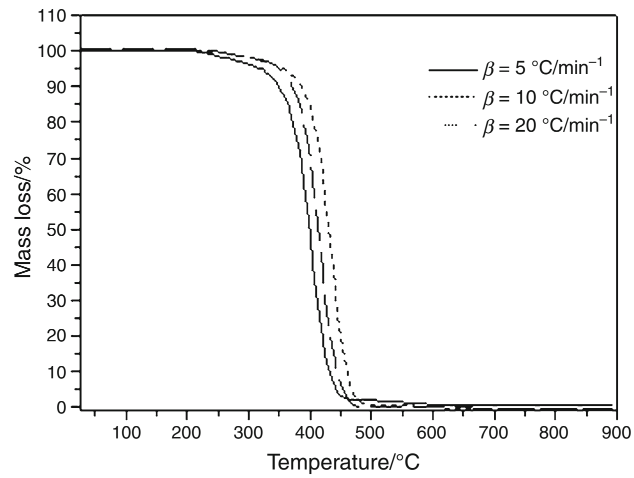

Fig. 4 TG curves of crude sunflower oil (CSO)

Thermogravimetric analyses

The thermal decomposition process of both samples (crude and refined oil) were investigated at a temperature range between 25 and 900 °C, in order to have a better understanding of sunflower oil pyrolysis. Thermogravimetric curves of the decomposition process are shown in Figs. 3 and 4.

Experimentally, the thermal decomposition reaction of oils at heating rates of 5, 10, and 20 °C min^{-1} occurs at a single well-defined stage, with less than 1% residue remaining at around 600 °C. DTG curves (Figs. 5, 6) depict peak profiles that confirm this single decomposition stage. These results may be related to the presence of artificial antioxidant (citric acid) in the composition of refined sunflower oil, which may provide greater stability and in turn higher activation energy for the decomposition to occur.

The TG curves indicate that crude sunflower oil (CSO) requires lower temperatures for pyrolysis, that is, CSO was degraded/volatilized more rapidly than refined sunflower oil under the same conditions. This can be confirmed by the significant decomposition event that occurs between 270 and 500 °C for crude oil and from 320 to 590 °C for refined oil, even though they exhibit similar total mass loss profiles.

Triglycerides, which constitute 96–98% of vegetable oils, produce volatile compounds during heating, which are removed by the resulting steam formed. These products are primarily created by thermal reactions of unsaturated fatty acids [17]. Vegetable oil pyrolysis initiates at 350 °C, where triglycerides decompose, leading to the formation of carboxylic acid, acrolein and ketenes [3]. Since ketenes and acrolein are less stable than carboxylic acid, they are easily decomposed, resulting in the formation of esters, carboxylic acid, and hydrocarbons. Decarbonylation or decarboxylation may then occur after thermal decomposition of carboxylic acids. Water, CO, and a hydrocarbon with new

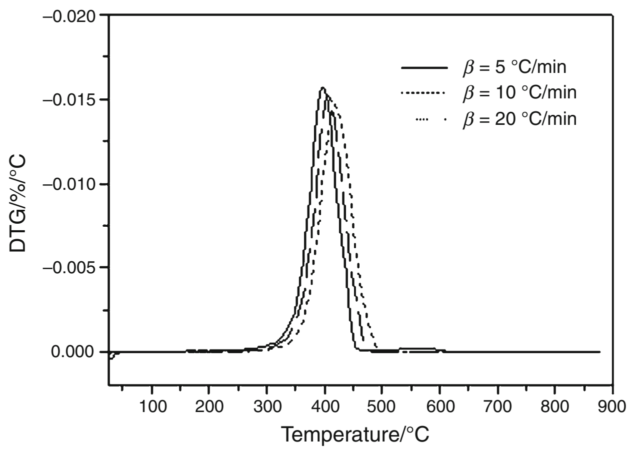

Fig. 5 DTG of refined sunflower oil (RSO)

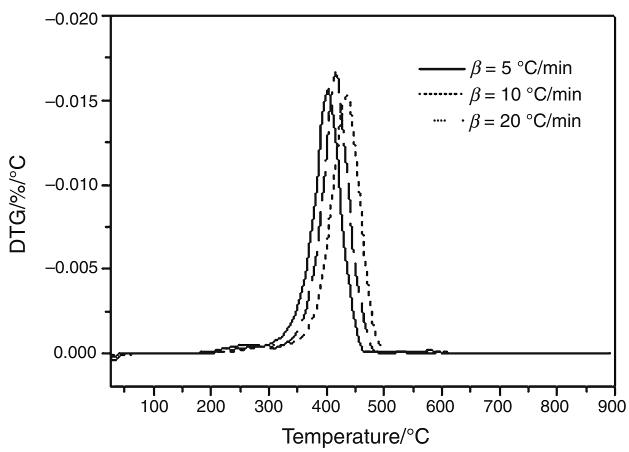

Fig. 6 DTG curves of crude sunflower oil (CSO)

terminal unsaturation are formed during decarbonylation. CO_2 and a hydrocarbon are generated in decarboxylation, without the formation of new unsaturations [3, 38].

It was observed that an increase in heating rate led to a temperature shift at higher values. This occurs because of less uniform heat distribution in the sample, causing the temperature gradient to increase. Heating rate is an important factor that directly affects the thermal decomposition of oil. A higher heating rate can decrease the distribution of heat from oil molecules, which may initiate decomposition at higher temperatures. As a consequence, initial decomposition on the TG curves increases with heating rate.

Determination of kinetic parameters

Figure 7 depicts the relationship between apparent energy activation as a function of conversion. Refined oil exhibited activation energy of 237 kJ mol^{-1}, while for crude sunflower oil it was 210 kJ mol^{-1}. These results may be related

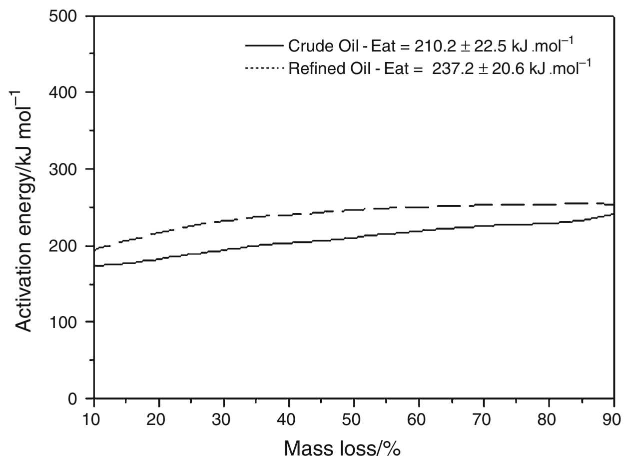

Fig. 7 Activation energy as a function of conversion for CSO and RSO

Table 4 Isoconversion parameters for CSO and RSO

Time/min	Conversion/%				
	10	30	60	90	99
CSO					
10	332.41	359.12	378.57	403.62	435.22
30	313.75	340.89	361.3	386.69	418.75
60	302.56	329.92	350.86	376.44	408.75
90	296.21	323.69	344.92	370.59	403.03
120	291.79	319.34	340.77	366.50	399.03
RSO					
10	340.96	364.77	383.91	409.29	438.2
30	323.80	349.16	368.53	392.92	419.6
60	313.46	339.69	359.19	383.00	408.36
90	307.58	334.28	353.85	377.32	401.95
120	303.47	330.51	350.11	373.36	397.47

to the presence of antioxidant in refined sunflower oil (citric acid), which could provide it with more stability and in turn higher activation energy to allow the decomposition process to occur. The activation energy value obtained (207.7 kJ mol^{-1}) is compatible with that found in the literature for commercial sunflower oil without antioxidants [24].

Table 4 shows isoconversion data of refined and crude sunflower oil samples. For example, to degrade 70% of refined sunflower oil in 60 min requires a temperature of approximately 365 °C. Under the same time and conversion conditions, the temperature needed to degrade crude sunflower oil is about 357 °C. Thus, isoconversion data are a powerful tool for estimating the temperature required to degrade a given amount of oil as a function of time and may also serve as starting parameters for designing pyrolytic reactors.

A comparative assessment of the different oils determines which of these displays better potential as raw material. To that end, it is essential to know thermal behavior and kinetic parameters of the biomass evaluated during the thermal conversion process. Thermal analysis techniques, particularly thermogravimetric analysis (TG) and derived thermogravimetric analysis (DTG) provides this information simply and rapidly [39].

Conclusions

Thermogravimetry is a technique that can be used to monitor the thermal decomposition reaction of vegetable oils, showing the influence of oil characteristics on the pyrolysis reaction. The results obtained by thermogravimetry clearly demonstrated the thermal behavior of the oil under study. Results obtained in pyrolysis tests exhibited a main thermal decomposition stage initiating at 350 °C, which may be related to the onset of triglyceride decomposition for the formation of fatty acids and fatty acids in hydrocarbons.

With this method, it is possible to determine activation energy for the thermal decomposition reaction of sunflower oil that occurs at this temperature range. The sunflower oil under study (CSO) obtained lower activation energy than that of refined sunflower oil (RSO), that is, in the pyrolysis process CSO requires less energy than RSO to reach the same conversion rate. Application of model-free kinetics involving decomposition of this oil proved to be a reliable method. Results were consistent, demonstrating that vegetable oil with more antioxidant requires a greater amount of energy to decompose. CSO needs lower temperatures to decompose to a good conversion level compared to RSO.

The results confirm the high potential of Catissol sunflower produced in Rio Grande do Norte for vegetable oil production, with favorable characteristics for use as raw material in biofuel production via pyrolysis.

Acknowledgements To the National Council of Scientific and Technological Development (CNPq) for financial support.

References

1. Conceição MM, Fernandes VJ, Bezerra MC, Silva MCD, Santos IGM, Silva FC, Souza AG. Dynamic kinetic calculation of castor oil biodiesel. J Therm Anal Calorim. 2007;87(3):865–9.
2. Freire LMS, Bicudo TC, Rosenhaim R, Sinfrônio FSM, Botelho JR, Carvalho Filho JR, Santos IMG, Fernandes VJ Jr, Antoniosi Filho NR, Souza AG. Thermal investigation of oil and biodiesel from *Jatropha curcas* L. J Therm Anal Calorim. 2009;96:1029–33.
3. Suarez PAZ, Meneghetti SMP, Meneghethi MR, Wolf CR. Transformação de triglicerídeos em combustíveis, materiais poliméricos e insumos químicos: Algumas aplicações da catálise na oleoquímica. Quim Nova. 2007;30(3):667–76.
4. Meier D, Faix O. State of the art of applied fast pyrolisis of lignocellulosic materials-a review. Bioresour Technol. 1999;68:71–7.
5. Mohan D, Pittman CU, Steele PH, Energ Fuel, 2006; 20:248. doi:10.1021/ef0502397.
6. Maher KD, Bressler DC. Pyrolysis of triglyceride materials for the production of renewable fuels and chemicals. Bioresour Technol. 2007;98:2351–68.
7. Embrapa. In: Tecnologias da Produção de Girassol. http://www.cnpso.embrapa.br/producaogirassol. Accessed 13 Jun 2008.
8. Ministério do Desenvolvimento Agrário. http://www.mda.gov.br/portal/Index/Show/Index/Cod/134/Codinterno/15763. Accessed 13 Dez 2008.
9. Emater. http://www.rn.gov.br/sistemnoticias/noticias.Asp?idnoticia=13093. Accessed 12 Nov 2008.
10. Lira MA, Carvalho HWL, Carvalho CGP, Lima JMP. Medeiros AA Avaliação de Cultivares de Girassol no Estado do Rio Grande do Norte. Artigos Científicos: Emparn-Empresa de Pesquisa Agropecuária do RN; 2007.
11. Rodríguez RP, Sierens R, Verhelst S. Thermal and kinetic evaluation of biodiesel derived from soybean oil and higuereta oil. J Therm Anal Calorim. 2009;96:897–901.
12. Geißler R, Saraji-Bozorgzard M, Streibel T, Kaisersberger E, Denner T, Zimmermann R. Investigation of different crude oils applying thermal analysis/mass spectrometry with soft photoionisation. J Therm Anal Calorim. 2009;96:813–20.
13. Arias S, Prieto MM, Ramajo B, Espina A, García JR. Model-free kinetics applied to the vaporization of caprylic acid. J Therm Anal Calorim. 2009;98:457–62.
14. Alencar JW, Alves PB, Craveiro AA. Pyrolysis of tropical vegetable oils. J. Agr. Food Chem. 1983;31(6):1268–70.
15. Fortes ICP, Baughb PJ. J Brazil Chem Soc. 1999;10:469.
16. Lima DG, Soares CD, Ribeiro EB, Carvalho DA, Cardoso ECV, Rassi FC, Mundim KC, Rubim JC, Suarez PAZ. Diesel-like fuel obtained by pyrolysis of vegetable oils. J Anal Appl Pyrol. 2004;71:987–96.
17. Santos JCO, Santos IMG, Conceição MM, Porto SL, Trindade MFS, Souza AG, Prasad S, Fernandes VJ Jr, Araújo AS. Thermoanalitical, kinetic and rheological parameters of commercial edible vegetable oils. J Therm Anal Calorim. 2004;75:419–28.
18. Garcia CC, Franco PIBM, Zuppa TO, Antoniosi Filho NR, Leles MIG. Thermal stability studies of some cerrado plant oils. J Therm Anal Calorim. 2007;87:645–8.
19. Vyazovkin S, Sbirrazzuoli N. Isoconversional kinetic analysis of thermally stimulated processes in polymers. Macromol Rapid Commun. 2006;27:1515–32.
20. Vyazovkin S, Goryachko V. Potentialities of software for kinetic processing of thermoanalytical data by the isoconversion method. Thermochim Acta. 1992;30:221–30.
21. Yougun S, Sensoz S, Koçkar OM. Characterization of pyrolysis oil produced in the slow pyrolysis of sunflower-extracted bagasse. Biomass Bioenerg. 2001;20:141–8.
22. Gerçel FH. Production and characteriation of pyolisys liquids from sunflower-pressed bagasse. Bioresour Technol. 2002;85:113–7.
23. Souza MJB, Silva AOS, Aquino JMFB, Fernandes VJ, Araujo AS. Kinetic study of template removal of MCM-41 nanostructured material. J Therm Anal Calorim. 2004;2:693–8.
24. Santos JCO, Dantas JP, Souza AG, Conceição MM. Kinetic parameters on thermal degradation of edible vegetable oils by thermogravimetric In: Congresso Brasileiro de Plantas Oleaginosas, Óleos, Gorduras e Biodiesel, 2, Anais do Congresso,Varginha, 2005,582–586.
25. Esteves W; Golçalves L; Arellano DB. Compilação da metodologia padrão Alemã para análise de gorduras e outros lipídeos.

(Translation of: Deutsche Einheitsmethodem zur Untersuchung von Fetten, Fettprodukten, Tensiden und verwandten Stoffen Abteilung A, B, C, F). Campinas, 1995.
26. Nip WK. Development and storage stability of drum dried guava and papaya-taro flakes. J Food Sci. 1979;44(1):222–5.
27. Carvalho AV, Garcia NHP, Wada JKA. Caracterização físico-química e curvas de solubilidade protéica de sementes, amêndoas fermentadas e torradas de cupuaçu (Theobroma grandiflorum Schum). Br J Food Technol. 2005;8(2):127–34.
28. Vyazovkin S, Wright CA. Model-free and model-fitting approaches to kinetic analysis of isothermal and nonisothermal data. Thermochim Acta. 1999;340:53–68.
29. AOCS. American Oil Chemists' Society. Official methods and recommended practices of the American oil chemists' society (5 edn) Champaign, 2002.
30. Aguiar RH. Avaliação de Girassol Durante o Armazenamento, para Uso Como Semente ou Extração de Óleo. Dissertação de mestrado em Engenharia Agrícola. Departamento de Engenharia Agrícola, Universidade Estadual de Campinas, Campinas. 2001.
31. Telles MM, Caracterização dos Grãos, Torta e Óleo de Três Variedades de Girassol (Helianthus Annus L.) e Estabilidade do Óleo Bruto. Dissertação de mestrado em Ciências dos Alimentos. Universidade Federal de Santa Catarina, Florianópolis, 2006.
32. Bagnis CG. Isolado Protéico de Girassol – Obtenção e Propriedades. Dissertação de mestrado em Tecnologia de Alimentos. Universidade Estadual de Campinas. São Paulo. Campinas. 1984.
33. Brock J, Nogueira MR, Zakrzevski C, Corazza FC, Corazza ML, Oliveira JV. Determinação experimental da viscosidade e condutividade térmica de óleos vegetais. Ciênc Tecnol Aliment. 2008;28(3):564–70.
34. Moretto E. Fett R. Tecnologia de Óleos e Gorduras Vegetais. São Paulo: Livraria Varela; 1998.
35. Mandarino JMG. Características bioquímicas e nutricionais do óleo e do farelo de girassol. EMPRAPA-CNPSo, Documentos n.52, p 25. Londrina, 1992.
36. Castiglioni VBR, Balla A, Castro C, Silveira JM. Fases de desenvolvimento da planta de girassol. Londrina: EMBRAPA, CNPSo. Documento n.59, 1997.
37. Pighinelli ALMT. Extração mecânica de óleos de amendoim e de girassol para a produção de biodiesel via catálise básica. Dissertação de mestrado em Engenharia Agrícola. Universidade Estadual de Campinas, Campinas. 2007.
38. Santos FC, Ferreira JCN. Decomposição catalítica de óleo de soja em presença de diferentes zeólitas. Quim Nova. 1998;21(5):560–3.
39. Seye O, Cortez LAB, Gómez EO. Estudo cinético da biomassa a partir de resultados termogravimétricos. In: Encontro de Energia no Meio Rural, 3, Campinas. Anais. São Paulo, 2000.