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Kinetic study of thermal processing of glycerol by thermogravimetry

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Abstract Over the past years, the production of biodiesel has significantly increased in Brazil due to its obligatory use in the composition of diesel for vehicle use. As a result, in the most ordinary processes, a hundred thousand tons of glycerol is produced as by-product per 1 billion liters of biodiesel. Glycerol has already been widely studied. Nonetheless, the quantity produced today demands new proposals for uses, such as a fuel. In this aim, the authors studied the kinetics of the thermal processing of glycerol. In this research, thermogravimetry (TG), derivative thermogravimetry (DTG), and differential thermal analysis (DTA) were used to provide the experimental data. Kinetic parameters were calculated by Kissinger method for the global process observed during the heating of the samples from the room temperature up to 600 °C, both in open and in sealed crucibles (with a little hole). Kinetic data were also determined at different isoconversion conditions during heating, by applying Ozawa–Flynn–Wall and Blazejowski methods to TG data. Results show that glycerol heated from 30 to 600 °C, under normal pressure, does not experience simple volatilization. The activation energies calculated at different conversion degrees by these methods show that only volatilization occurs when the mass loss of glycerol is lower than 40% and that for higher conversion degrees, partial thermal decomposition and/or dissociation of glycerol are occurring as well. These facts are also confirmed by the volatilization enthalpies estimated using another method developed by Blazejowski based on Van't Hoff equation.

Keywords Glycerol · Thermal processing · Kinetics · TG–DTG–DTA

Introduction

Biodiesel is industrially produced by the reaction of vegetable oils or animal fats with methanol or ethanol, to generate mono-alkyl-esters and glycerin [1, 2]. Presently, due to the Brazilian 11097/2005 law obligating the addition of biodiesel to the diesel consumed in Brazil, 1 billion liters of biodiesel are produced per year and, in most ordinary processes, with a co-production of 1 hundred thousand tons of glycerol [3, 4].

Glycerol is a polyalcohol, and the three hydroxyls are responsible for the hydrogen bonds, for its high boiling point (290 °C) and also for the infinite solubility in water and ethanol [5, 6]. In environmental conditions, this polyalcohol is liquid, colorless, odorless, viscous, sweet, and has many uses. It has been utilized in industries such as cosmetics, food, tobacco, drugs, and also as a raw material for hundreds of other products, as in explosives, polymers (e.g., as a plasticizer [7]), and biotechnology industries [7, 8]. Owing to its large use, glycerol has been widely studied; however, the growing production demands new proposals. In some industries, for instance, it is already used as a source of energy when it is burned, thus replacing part of

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the combustible oil [9]. The aim of this work is to study the thermal behavior of glycerol, from kinetic analysis mainly of TG and DTG analysis data.

The Kissinger method [10] is one of the first free kinetics model applied to thermal analysis data of chemical decomposition reactions. It was initially developed for differential thermal analysis (DTA) data and based on the Arrhenius equation:

$$k = \mathrm{d}\alpha/\mathrm{d}t = A \cdot \mathrm{e}^{(-E/RT)} \tag{1}$$

where A is the pre-exponential factor, E is the activation energy, R is universal gas constant (8.314 J K^{-1} mol^{-1}), T is the absolute temperature, and α is the conversion degree. The reaction rate $\mathrm{d}\alpha/\mathrm{d}t$ reaches its maximum value at a specific temperature (T_m), which depends on the heating rate (β) and which can be determined by the temperature where the DTA or DTG peak maximum signals occur [11]. In the present case, the heat flow consumed by a glycerin sample for its volatilization with or without dissociation or decomposition is directly proportional to the mass loss and actually, T_m values are more precisely measured from derivative thermogravimetric (DTG) data. In fact, mass losses are measured faster than thermal effects, because while mass change effects are immediately detected, detection of thermal effects depend on the capacity of thermal exchange between sample and temperature sensors, which in turn have to transmit the signal to the recording devices. Leiva [12] used thermogravimetry to determine the activation energy of combustion of fuel oils and compared the results with those obtained by ASTM E-1641 kinetic analysis method, concluding that the Kissinger method applied to thermogravimetry is perfectly satisfactory.

During the heat treatment of a sample that can undergo volatilization or pyrolysis (with dissociation or decomposition), the mass loss rate is directly proportional to the heat flow that the sample receives, and the heat of transformation is a function of the operating temperature. During a dynamic thermal analysis, the equipment controller acts changing the heating power in order to maintain the same heating rate throughout the analysis. This power increases as a function of temperature for a same heating rate, which may be used for volatilization and/or decomposition mechanisms depending on the thermo chemical properties of the sample.

The method developed by Kissinger for dynamic thermal analysis at constant heating rates is independent of the reaction mechanism and is based on the application of Eq. 2:

$$\ln\left(\beta/T_\mathrm{m}^2\right) = -E/(RT_\mathrm{m}) + \ln(AR/E), \tag{2}$$

where β is the heating rate and T_m, A, and E were previously defined. The experimental data are analyzed for at least three heating rate conditions, to confirm linearity between (β/T_m^2) versus $1/T_\mathrm{m}$ data, allowing one to calculate the mean activation energy for all the transformation process. Paine III et al. [13] report that when glycerol is submitted to 650–675 °C in inert atmosphere, it produces large quantities of acetaldehyde and formaldehyde. Walliyappan et al. [14] also report that in N_2 atmosphere, glycerin heated to 650–800 °C under 1 atm pressure produces between 70 and 93% of syn gas (H_2 and CO) in addition to CO_2, CH_4, and C_2H_4.

Provided that glycerol may undergo not only a simple volatilization process during heating, but more than one different competing mechanisms, each with its own activation energy, the Ozawa–Flynn–Wall free-kinetics isoconversion method equation was applied [15], where $C(\alpha)$ is a function of the conversion degree α:

$$\ln(\beta) = C(\alpha) - E_\alpha/(RT). \tag{3}$$

Applied for at least three values of heating rate (β) for different and same values of α, it allows to investigate whether the mechanism of the overall conversion is changing with the conversion degree, estimating the respective activation energy E_α at a conversion degree α.

According to Williams [16], for a non-volatile substance, such as glycerol, the heating causes a competition between the decomposition and volatilization, the former being favored since the activation energy to break the intramolecular bonds is lower than that required for the intermolecular bonds.

Analyzing the thermodynamics of volatilization processes under dynamic non-isothermal conditions with or without dissociation and based on Van't Hoff equation, Blazejowski [17] developed a method to estimate the vaporization enthalpy (ΔH_v) through Eq. 4:

$$\ln\alpha = -\Delta H_\mathrm{v}/(nRT) + \Delta H_\mathrm{v}/(nRT_\mathrm{v}), \tag{4}$$

where α is the vaporized fraction, which is equivalent to the vaporization degree, ΔH_v is the vaporization enthalpy, T is the absolute temperature at a conversion degree equal to α, T_v is the vaporization temperature at atmospheric pressure, and n is the number of moles of substances that are formed in vapor phase per each mole of substance being vaporized. If vaporization occurs without dissociation (or decomposition) of the molecule, the value of n is 1. If vaporization occurs with dissociation, n is an integer higher than 1. Admitting initially that in the case of glycerol heating only vaporization occurs, Eq. 4 was tested by using $n = 1$.

Blazejowski [17] also developed a method to estimate the activation energy (E) in non-isothermal vaporization processes through Eq. 5:

$$g(1-\alpha) = (ZT/\beta)e^{--E/(nRT)}, \tag{5}$$

where $g(1-\alpha)$ represents the kinetic model, n is defined as in Eq. 4, and Z is a constant. Equation 5 can be rewritten as shown in Eq. 6:

$$\ln(\beta/T) = Z/g(1-\alpha) - E/(nRT). \tag{6}$$

For a defined value of α, the first term of the right-hand side of equation is constant. Thus, applying Eq. 6 for thermogravimetric data obtained at least three values of heating rate (β) for different and same values of α, the respective activation energy E_α at different conversion degrees was also estimated, which change indicates change in the mechanism of mass loss.

As will be shown, comparison of the results obtained by the above methods indicates that until 40% of conversion degree, practically only vaporization occurs. For higher conversion rates, results indicate that dissociation and/or decomposition reactions occur.

Experimental

For the experiments *Pro Analysis* (PA) glycerol from VETEC has been used. The water content of the samples was 0.57%, determined by a method developed by the authors and described in a previous paper [18]. The thermal analyses of 10–20 mg samples were performed in simultaneous TA Instruments TG-DTA equipment, model SDT 2960, at 10, 15, and 20 °C min^{-1} constant heating rates from 30 to 600 °C, by using 100 mL min^{-1} flow of nitrogen as the purge gas. These analyses were conducted in both open and sealed aluminum crucibles with holes of approximately 0.6-mm on the top.

Isothermal analyses were also performed in thermogravimetric equipment developed by Dweck and Souza Santos and described previously [19–21], where larger samples can be used. Samples of approximately 1 g were used and analyzed at 260, 290, 300, and 400 °C in ceramic crucibles. In order to provide the inert ambient during heating, quartz covers with 1 mm holes were used.

Kinetic data analysis for non-isothermal analyses is presented and discussed first using Kissinger method and Ozawa–Flynn–Wall free-kinetics isoconversion model. Then volatilization enthalpies and kinetic parameters obtained using Blazejowski methods are presented and discussed.

Results and discussion

Analysis performed in open crucibles

Figure 1 demonstrates an example of a set of DTA curves of pure glycerol, obtained at 10, 15, and 20 °C min^{-1} heating rates.

The activation energy calculated by Kissinger method, for the global transformation, is 104.84 kJ mol^{-1}. Since volatilization is a process that occurs with mass loss and heat absorption simultaneously, the gravimetric effect can be measured (in TG/DTG curves) before the temperature difference effect between the sample and the reference (in DTA curves). Consequently, the activation energy of the volatilization of glycerol was also studied through the DTG curves obtained from the heating programs of 10, 15, and 20 °C min^{-1} (Fig. 2), and the value calculated for these data is 107.03 kJ mol^{-1}. The activation energy calculated is apparently low, in both cases, suggesting that the global process during the heating of glycerol is mainly a physical one, similar to the volatilization. On the other hand, a typical value for these types of transformation is about 83 kJ mol^{-1} [22–25]; therefore, the calculated activation energy for the global thermal process indicates that other phenomena are occurring as chemical reactions.

While Kissinger method uses only the point of maximum conversion rate, the Ozawa–Flynn–Wall isoconversion method assumes that the conversion rates may be different in each part of the global conversion, which can be seen when the activation energy changes along the

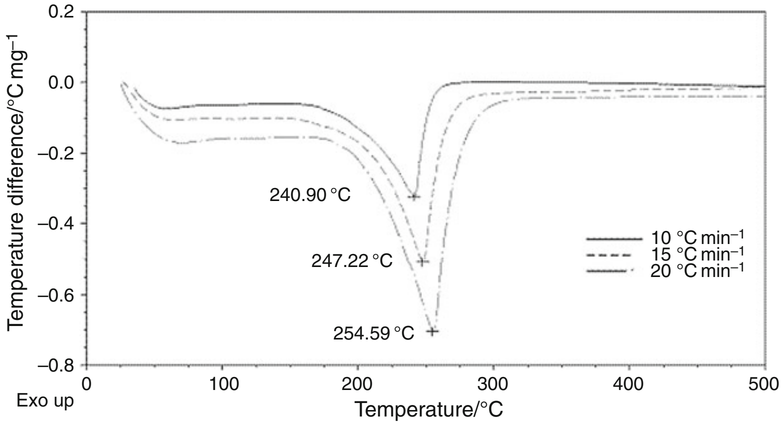


Fig. 1 DTA curves of pure glycerol performed in open aluminum pans

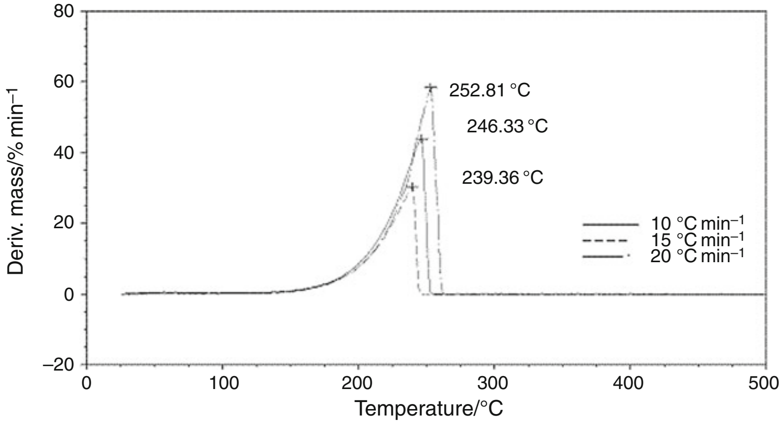


Fig. 2 DTG curves of pure glycerol in open aluminum pans

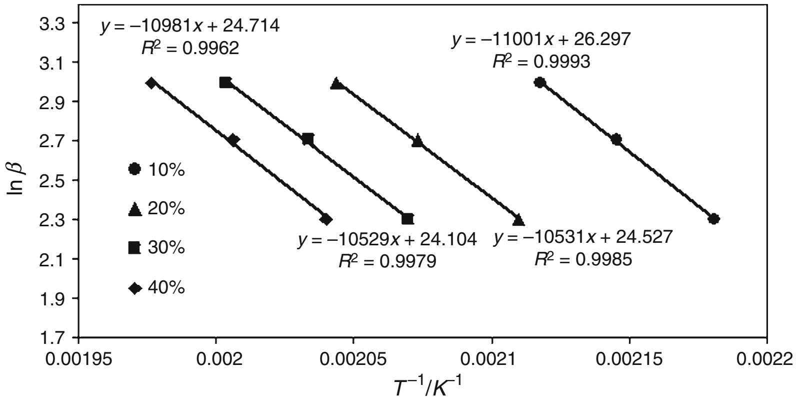


Fig. 3 Ozawa–Flynn–Wall isoconversion method applied to the thermal processing TG data of glycerol in open pans within 10–40% of conversion

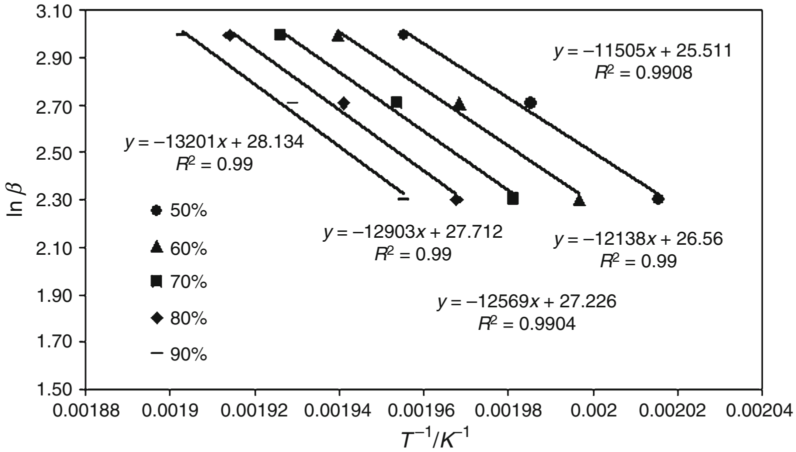


Fig. 4 Ozawa–Flynn–Wall isoconversion method applied to the thermal processing TG data of glycerol in open pans within 50–90% of conversion

observed transformation. Figures 3 and 4 show this behavior in correlations obtained from TG/DTG curves.

The results show that glycerol presents two different types of behavior under thermal processing: one from 10 to 40% of conversion and another from 50 to 90%. It is possible to see that in the first case (Fig. 3), the angular coefficients are lower, which lead to lower activation energies. As a result, between 10 and 40% conversion, it can be considered that the predominant phenomenon is volatilization; however, in the 50–90% conversion range, chemical reactions compete with the volatilization by increasing the activation energy of the overall transformation, as temperature increases.

Isothermal analyses at 260, 290, 300, and 400 °C were performed to estimate apparent activation energy and to verify the linear correlation, between the natural logarithm of the average speed of vaporization ($\ln d\alpha/dt$), where α is the mass% of glycerol lost by the sample and the inverse of absolute temperature (T^{-1}) for each temperature analysis. This was verified only for $\alpha < 40\%$ by the expression ln

$(d\alpha/dt) = -10612T^{-1} + 13.031$, based on Eq. 1, with a correlation coefficient equal to 0.9278. From these data, activation energy of volatilization of 88.19 kJ mol^{-1} was estimated, which is very close to the vaporization heat of glycerin, which is 88.03 kJ mol^{-1} (at 55 °C) and 75.95 kJ mol^{-1} (at 195 °C) [25]. The value of the activation energy obtained for the range of isothermal vaporization within the 260–400 °C temperature range is consistent, because the activation energy represents the energy required to promote a shift in the case of endothermic transformations and usually is larger than the heat of vaporization.

Analysis performed in sealed crucibles (with a pin hole)

Figures 5 and 6 show, respectively, DTA and DTG curves of glycerol. The respective activation energies calculated by Kissinger method, were 160.73 and 170.19 kJ mol^{-1}.

The activation energy is lower when the analysis conducted in the open crucibles, because the purge nitrogen gas quickly carries the vapors produced during the conversion. As a consequence, this also decreases the partial pressure of the formed gases in vapor phase accelerating their formation. This phenomenon is less likely to happen in a sealed crucible with a hole, because the vapor produced is prevented from leaving the vicinity of the sample, which only occurs after reaching the values of vapor pressure required to overcome the resistance to flow out of the hole. Such event reinforces the notion that the generated vapor, once closed in the crucible, delays the volatilization process to higher temperature conditions, providing conditions for chemical reactions to occur simultaneously. Figures 7 and 8 illustrate this behavior, presenting the isoconversion analysis for these data.

The change in the slope of the straight lines is quite clear after 40% of conversion. The activation energy calculated for the conversions from 10 to 40% is between 83.37 and 93.74 kJ mol^{-1}, whereas from 50 to 90% it is between 113.67 and 162.84 kJ mol^{-1}.These results, with significantly higher activation energy values indicate that, for the higher conversion range, vaporization is occurring with other simultaneous decomposing or dissociative phenomena.

Vaporization enthalpy estimates by Blazejowski method

Blazejowski method to estimate vaporization enthalpy in non-isothermal experiments with constant heating rate was

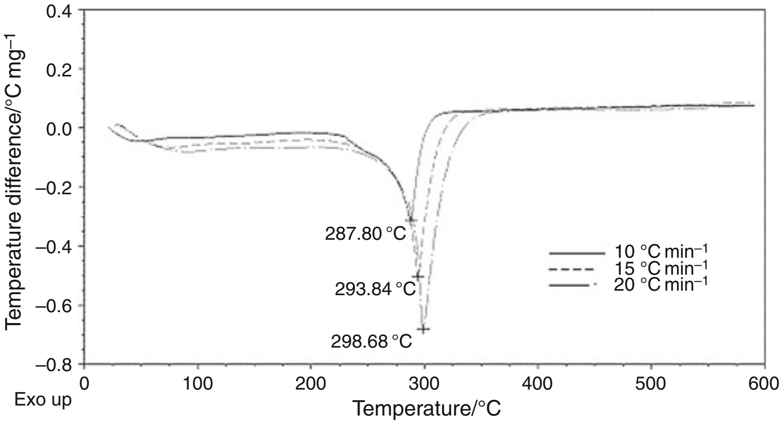


Fig. 5 DTA curves of glycerol in sealed aluminum crucibles with a little hole

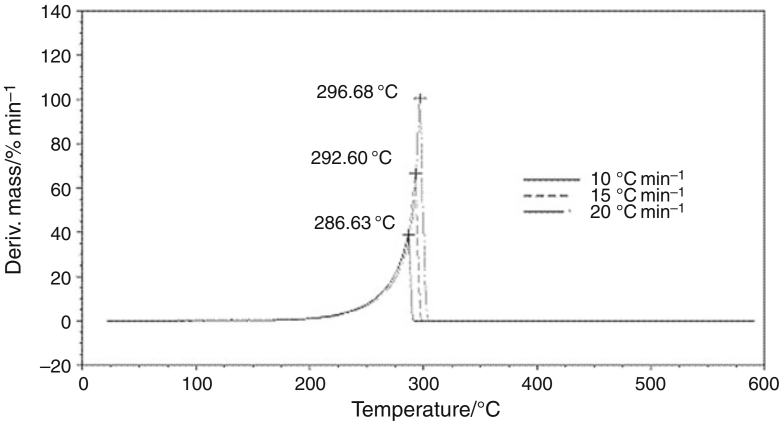


Fig. 6 DTG curves of glycerol in sealed aluminum crucibles with a little hole

Fig. 7 Ozawa–Flynn isoconversion method data for the thermal processing of glycerol in sealed crucibles with a pin hole within 10–40% conversion range

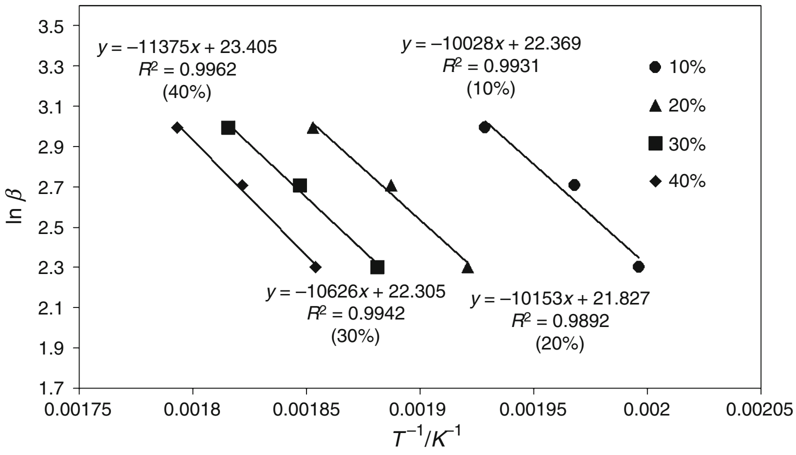


Fig. 8 Ozawa–Flynn isoconversion method data for the thermal processing of glycerol in sealed crucibles with a hole within 50–90% conversion range

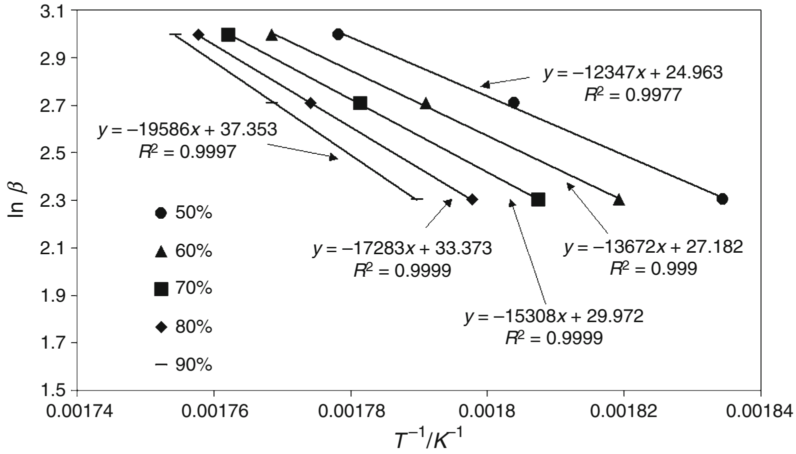
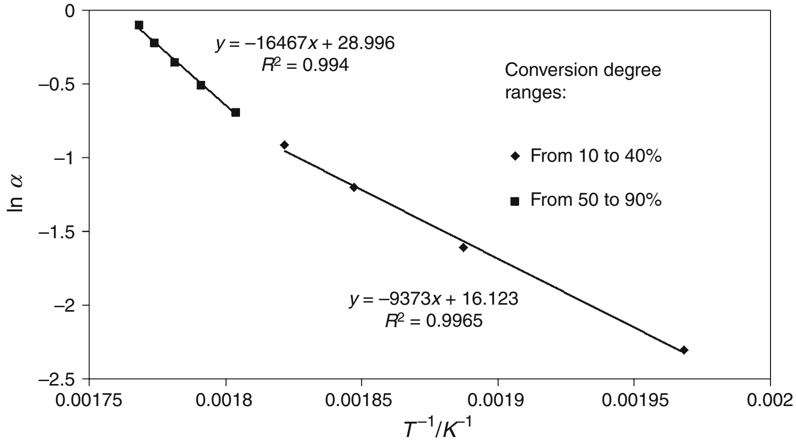


Fig. 9 Blazejowski correlations used to estimate glycerol vaporization enthalpies



applied to the two ranges of glycerol conversion degrees. Data obtained at the mean heating rate of 15 °C min^{-1} were used for these estimates. Considering as a first hypothesis that only vaporization occurs, we assumed $n = 1$. Thus, the angular coefficient of the linear correlation of ln α versus T^{-1} given by Eq. 4 is equal to $-\Delta H_{\mathrm{v}}/T$. Figure 9 shows that ΔH_{v} for the 10–40% conversion range is 77.89 kJ mol^{-1}, which is a compatible value with the vaporization enthalpy values of the literature of 88.03 kJ mol^{-1} at 55 °C and 75.95 kJ mol^{-1} (at 195 °C) [25], as previously mentioned. However, for the 50–90% conversion range, the angular coefficient is significantly different from that of the lower conversion range, which gives an apparent volatilization enthalpy of 136.84 kJ mol^{-1}. This indicates that the hypothesis considering that within the higher conversion range only volatilization occurs is not valid.

Kinetic parameters estimation by Blazejowski method

Figures 10, 11, 12, and 13 show the correlations obtained applying Blazejowski method, in the form of Eq. 6, for constant and different values of conversion of the TG data obtained at three different heating rates from glycerol analysis in open and sealed pans with a pin hole in nitrogen flow.

Comparison between the kinetic results

Figure 14 presents the different values of the activation energies obtained for Ozawa–Flynn and Blazejowski isoconversion methods from the analyses performed in SDT equipment in both cases (open crucibles or sealed crucibles with little holes), depending on the temperature at which

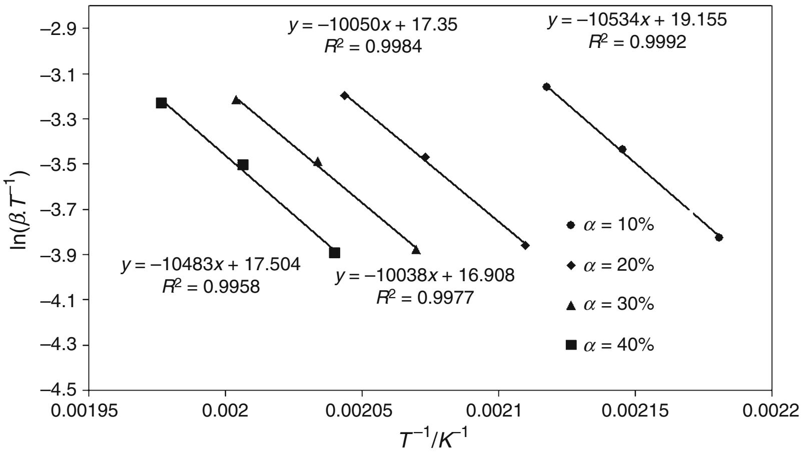


Fig. 10 Blazejowski isoconversion method applied to the thermal processing TG data of glycerol in open pans within 10–40% of conversion range

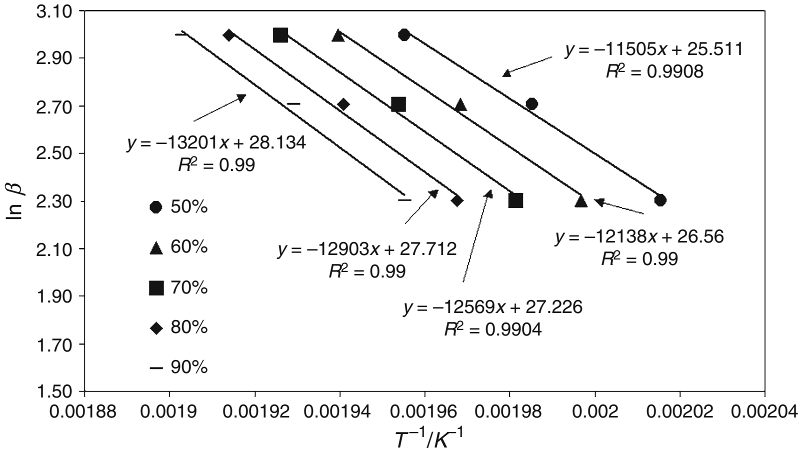


Fig. 11 Blazejowski isoconversion method applied to the thermal processing TG data of glycerol in open pans within 50–90% of conversion range

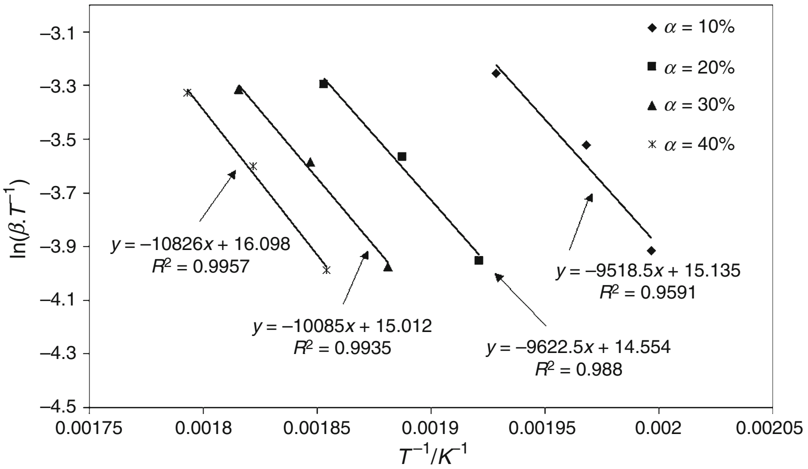


Fig. 12 Blazejowski isoconversion method applied to the thermal processing TG data of glycerol in sealed pans with pin hole within 10–40% of conversion range

Fig. 13 Blazejowski isoconversion method applied to the thermal processing TG data of glycerol in sealed pans wit pinhole within 50–90% of conversion range

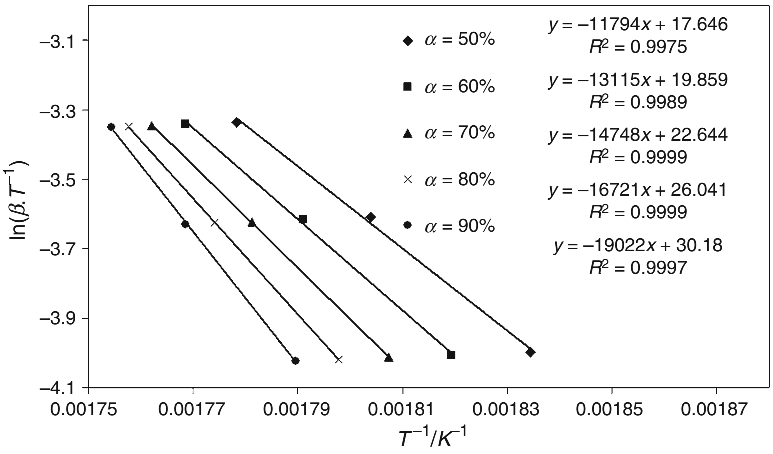


Fig. 14 Activation energies obtained from the TG/DTG analyses, at each degree of conversion as a function of the corresponding temperatures of the runs performed at 15 °C min^{-1}

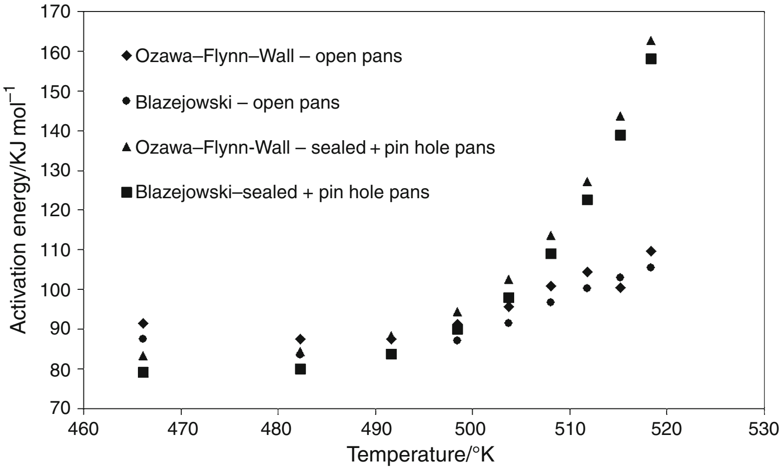
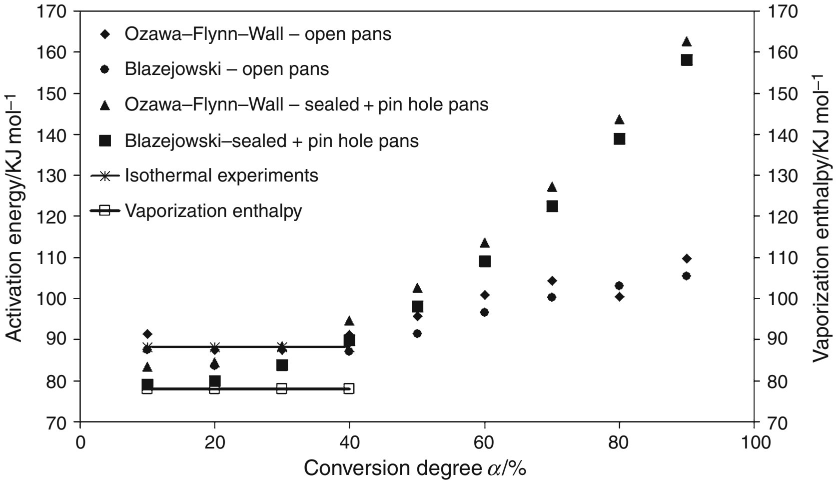


Fig. 15 Comparison between the activation energies for each degree of conversion of glycerol in open or sealed crucibles (with a hole) and for the 10–40% of conversion range in isothermal analyses



each degree of conversion occurred in the analyses at a 15 °C min^{-1} heating rate. This heating rate was selected because of its intermediate value compared to the three ones used for the present study and shows practically how the sealed (with a pin hole) condition changes the temperatures and activation energies where the same conversion occurs, as a consequence of the increase of partial pressure of the released gases in vapor phase.

It can be seen that both isoconversion methods give same order of magnitude of activation energies for the different conversion degrees at respective temperatures and type of pans. Open pan conditions show higher activation energy than in sealed pans for conversion degrees lower than 40%. For higher conversion degrees, the opposite occurs.

Figure 15 shows the comparison between the activation energies calculated by the isoconversion method in each degree of conversion of liquid glycerol to gaseous phase obtained from the analyses in open crucibles and sealed crucibles with a pinhole. It also presents the activation energy obtained for its volatilization in the range of 10–40% conversion from isothermal analysis data, as well as the vaporization enthalpy obtained from Blazejowski correlation for this conversion range. It is possible to notice that in this range of conversion, glycerol undergoes simple volatilization, regardless of the analysis conditions and the activation energies are little higher than the vaporization enthalpy estimated by Blazejowski correlation.

It can be seen that the activation energies in the range of 50–90% of conversion are similar for a same type of used pan, regardless of the temperatures at which they occurred, but always the values estimated by Ozawa–Flynn isoconversion method being little higher than those predicted by Blazejowski method. The higher is the temperature, the higher is the activation energy in open or sealed pans with a pin hole, and this effect is much more evident in the last case. During glycerol thermal processing, the sealed crucible with a little hole prevents the released molecules to be eliminated by the purge gas, which is a characteristic of open crucibles. This promotes greater interaction between them, thus making dissociation and/or decomposition reactions to happen. It is important to note that after the isothermal experiments, which were performed with a much higher mass than SDT experiments, a little carbonaceous residue was covering the bottom of the inner part of the crucibles, indicating that partial thermal decomposition of the glycerol occurred during its volatilization.

Conclusions

- Glycerol heated to temperatures above ambient and up to 600 °C and under normal pressure does not undergo only a volatilization.
- The activation energies calculated demonstrate that volatilization is the predominant process in the range of 10–40% conversion.
- In a sealed pan with a pinhole, the process occurs at temperatures higher than those in an open pan, and above 40% of conversion chemical reactions occur simultaneously with the volatilization.
- Above 40% of conversion decomposition and/or dissociation reactions compete with volatilization in larger extensions as the temperature increases. This effect is higher when glycerol is heated in sealed pans with a pinhole, which force the need of higher temperatures than in case of open pans to have a same volatilization degree.
- The two different isoconversion methods used to estimate the kinetic parameters presented very good correlation coefficients and similar activation energies for the different conversion degrees of glycerol. Their values were always higher than the glycerol vaporization enthalpy.

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References

1. ANP. National Agency of Petroleum. Resolution No. 30 (Sept. 20 2004):1–3 (in Portuguese).
2. ASTM American Society for Testing and Materials ASTM D6751/2002: Terminology.
3. Brazilian—Mines and Energy Ministry. 11097 Law, Official Union Journal, Jan 14th 2005; 8 (in Portuguese).
4. Biodieselbr. In www.biodieselbr.com/noticias/biodiesel/glicerina-gerada-producao-biodiesel-novos-usos-29-03-07.htm. Accessed Aug 15th 2008.
5. Morrison R, Boyd R. Organic chemistry. 6th ed. Lisbon: Calouste Gulbenkian Foundation; 1978.
6. Allinger N. Organic chemistry. 2nd ed. Rio de Janeiro: Livros Técnicos e Científicos; 1979.
7. Schlemmer D, Oliveira ER, Sales MJA. Polystyrene/thermoplastic starch blend with different plasticizers. J Therm Anal Calorim. 2007;87(3):635–8.
8. Ma F, Hanna MA. Biodiesel production: a review. Bioresour Technol. 1999;70:1–15.
9. Bouças C (2007) Glycerin from biodiesel floods the country's market and drops prices. Valor J. B7 (in Portuguese).
10. Kissinger HE. Reaction kinetics in differential thermal analysis. J Anal Chem. 1957;29(11):1702–6.
11. Dweck J, Aderne RS, Shanefield DJ. Aluminum nitride oxidation by simultaneous TG and DTA. J Therm Anal Calorim. 2001;64(3):1163–9.
12. Leiva CRM. The employment of thermogravimetry to obtain the activation energy of combustion of fuel oils. Quim Nova. 2006;29(5):940–6.
13. Paine JB III, Pithawalla YB, Naworal JD, Thomas CE Jr. Carbohidrate pyrolysis mechanisms from isotopic labeling. Part 1: the pyrolisis of glycerin: discovery of competing fragmentation mechanisms affording acethaldehyde and formaldehyde and the implications for carbohydrates pyrolisis. J Anal Appl Pyrolisis. 2007;80:297–311.
14. Walliyappan T, Bakhshi NN, Dalai AK. Pyrolisis of glycerol for the production of hydrogen or syn gas. Bioresour Technol. 2008;99:4476–83.
15. Sbirrazzuoli N, Vecchio S, Catalani A. Isoconversional kinetics study of alachlor and metolachlor vaporization by thermal analysis. Int J Chem Kinet. 2004;37:74–80.

16. Williams BW, Irsa AP, Zmora H, Beuhler RJ. Kinetics of volatilization in rapid heating mass spectroscopy: activation energies for some hydrogen-bonding species. J Phys Chem. 1983;87:2185–90.
17. Janiak T, Blazejowski J. Thermal features, thermochemistry and kinetics of the thermal dissociation of hexachlorostannates of aromatic mono-amines. Thermochim Acta. 1989;156:27–43.
18. Castelló ML, Dweck J, Aranda DAG. Thermal stability and water content determination of glycerol by thermogravimetry. J Therm Anal Calorim. 2009;97:627–30.
19. Dweck J, Santos PS. Prototype of thermogravimetric equipment. Ceramics. 1989;239:169–73 (in Portuguese).
20. Dweck J, Santos PS. Some applications of the prototype equipment for thermogravimetric analysis in ceramic materials and processes. Ceramics. 1998;250:84–8 (in Portuguese).
21. Dweck J. Fundamentals and thermal analysis equipment used in environmental engineering. In: Seminary on prevention and control of pollution. University of São Paulo, São Paulo; 2005. p. 2 (in Portuguese).
22. Keller JU, Staudt R. Gas absorption equilibria: experimental methods and adsorptive isotherms. New York: Springer; 2005. p. 19.
23. Lowell S. Characterization of porous solids and powders: surface area, pore size, and density. Particle technology series. vol 16, 4th edn. New York: Springer, 2004. p. 213.
24. Martins JBL. Equilibrium and chemical kinetics. Theoretical physical-chemistry. Brasilia: Institute of Chemistry, University of Brasília; 2005. p. 18 (in Portuguese).
25. Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed, vol 11. New York: Wiley-Interscience Publications; 1980.