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Thermochimica Acta 448 (2006) 111–116
thermochimica acta
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Model-free kinetics applied to sugarcane bagasse combustion

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Received 27 April 2006; received in revised form 30 June 2006; accepted 1 July 2006

Abstract

Vyazovkin's model-free kinetic algorithms were applied to determine conversion, isoconversion and apparent activation energy to both dehydration and combustion of sugarcane bagasse. Three different steps were detected with apparent activation energies of 76.1 ± 1.7, 333.3 ± 15.0 and 220.1 ± 4.0 kJ/mol in the conversion range of 2–5%, 15–60% and 70–90%, respectively. The first step is associated with the endothermic process of drying and release of water. The others correspond to the combustion (and carbonization) of organic matter (mainly cellulose, hemicellulose and lignin) and the combustion of the products of pyrolysis.

Keywords: Thermal analysis; Model-free kinetics; Sugarcane bagasse

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1. Introduction

In the tropics, sugarcane constitutes a major raw material for the production of sugar and alcohol. Brazil is one of the world's largest producers of sugarcane. During processing, however, a number of by-products are generated. These substrates include molasses, filter mud and sugarcane bagasse. Vinasse is regarded as a secondary by-product [1]. Sugarcane bagasse, the residual fibre, is obtained after the pressing of the sugarcane. Bagasse is usually burned to supply electric energy and steam for the process. However, 10% surplus bagasse still remains. Due to its high content in xylose, it can be used for the production of furfural. Furthermore, a few results about the production of active carbon from bagasse have also been reported [2].

The characterization of the properties of bagasse allows both their appropriate use as well as their increased use as an energy source. Thermal analysis methods are widely employed in the characterization of many materials. Among the methods of thermal analysis, differential scanning calorimetry (DSC) and thermogravimetry (TG) are significantly prominent, the common advantage of both techniques being the simplicity of sample preparation. Thermogravimetric analysis (TGA) techniques have a number of advantages that are relevant to the study of any reaction in which there is a weight loss or gain, the temperature can be controlled more accurately than by almost any other technique and, most importantly for rate studies, the chosen reaction temperature may be reached very quickly [3]. Kinetic investigations are nowadays one of the most important applications of thermal analysis. Knowledge of kinetic parameters, such as the reaction rate and activation energy, is one of the keys to determining reaction mechanisms in solid phases. Solid-state kinetic data are of major and growing interest in many technological processes. These processes include, for instance, thermal decomposition of crystalline solids and energetic materials, thermal oxidation and decomposition of polymers and coal, crystallization of glasses and polymers, and pyrolysis and combustion of biomass resources. There are numerous papers in the literature that include these kinetic studies in which these techniques are applied [3–19]. The aim of the present study is to determine the kinetic parameters for bagasse oxidation using Vyazovkin's model-free kinetics methodology.

2. Experimental

The cane bagasse sample used in this study was obtained from the Cruz Alta mill in Olimpia, São Paulo State, Brazil. It

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doi:10.1016/j.tca.2006.07.001

Nomenclature

A	pre-exponential factor
E	activation energy
$f(\alpha)$	reaction model
$g(\alpha)$	integrated reaction model
$k(T)$	temperature-dependent constant
R	gas constant
t	time
T	temperature
Greek symbols	
α	extent of reaction
β	heating rate

was placed in a sealed sample box to avoid contamination and then dried in an oven at a temperature of 105 °C for 3 h, close to the moisture equilibrium value of bagasse in contact with ambient air. The bagasse sample was subsequently classified into two fractions: fibres and powder [20,21]; the sample was screened for 30 min, after which it was separated into fibres and powder bagasse types. The sample used in the analyses was the powder-type cane bagasse. Its elemental chemical composition, obtained via three repetitions in a C–H–N Perkin-Elmer model 2400B elemental analyzer was: C, 45.4%; H, 5.3%; N, 1.5%.

A Mettler-Toledo TGA/SDTA851^{e} and a DSC822^{e} were used for the thermal analyses in oxygen (or nitrogen) dynamic atmosphere (50 ml/min) at a heating rate of 10 °C/min. For the kinetics measurements, the TG experiments were carried out in an oxygen atmosphere at heating rates of 5, 10 and 20 °C/min. In all cases, 1–2 mg of powder sugarcane bagasse sample was thermally treated. In TGA tests under oxygen, a Pfeiffer Vacuum ThermoStar^{TM} GSD301T mass spectrometer was used to determine the evacuated vapours. The masses 18 (H_2O), 44 (CO_2) and 46 (NO_2) were tested by using a detector C-SEM, operating at 1400 V, with a time constant of 0.5 s.

2.1. Determination of kinetic parameters and modelling

The rate of heterogeneous solid-state reactions can generally be described by:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \qquad (1)$$

where t is time, $k(T)$ the temperature-dependent constant and $f(\alpha)$ a function called the reaction model, which describes the dependence of the reaction rate on the extent of reaction, α.

The temperature dependence of the rate constant is described by the Arrhenius equation. Thus, the rate of a solid-state reaction can generally be described by:

$$\frac{d\alpha}{dt} = A\,e^{-E/RT}f(\alpha) \qquad (2)$$

where A is the pre-exponential factor, E the activation energy and R the gas constant.

The above rate expression can be transformed into non-isothermal rate expressions describing reaction rates as a function of temperature at a constant heating rate, β:

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\,e^{-E/RT}f(\alpha) \qquad (3)$$

Kinetics analysis is traditionally expected to produce an adequate kinetic description of the process in terms of the reaction model and the Arrhenius parameters. These three components ($f(\alpha)$, E, and A) are sometimes called the “kinetic triplet”.

There are many methods for analysing solid-state kinetic data [22]. These methods may be classified according to the experimental conditions selected and the mathematical analysis performed. Experimentally, either isothermal or non-isothermal methods are employed. The mathematical approaches employed can be divided into model-fitting and isoconversional (free model) methods.

The earliest kinetics studies were performed under isothermal conditions [22,23] the concepts of solid-state kinetics being established on the basis of these experiments. A major problem of the isothermal experiment is that a sample requires some time to reach the experimental temperature. The situation is especially aggravated by the fact that, under isothermal conditions, a typical solid-state process has its maximum reaction rate at the beginning of the transformation. However, the advantages of the non-thermal experimental technique are at least partially compensated by serious computational difficulties associated with the kinetic analysis.

In the model-fitting method, the $f(\alpha)$ term is determined by fitting various reaction models to experimental data. Subsequently, the $k(T)$ can be evaluated by the chosen form of $f(\alpha)$. Historically speaking, model-fitting methods were the first and most popular methods, especially for isothermal experiments. They were widely used because of their capacity to directly determine the kinetic triplet. However, these methods suffer from several problems, among which two are of particular importance. The first is that non-isothermal experiments provide information on both $k(T)$ and $f(\alpha)$, but not in a separate form. Thus, almost any $f(\alpha)$ can satisfactorily fit data at the cost of drastic variations in the Arrhenius parameters that compensate for the difference between the assumed form $f(\alpha)$ and the true, but unknown kinetic model. That is to say, the method is unable to provide a unique reaction model. The second problem is that only a single pair of Arrhenius parameters results from each application of the model-fitting method. The majority of solid-state reactions are not simple one-step processes, and thus a combination of serial and parallel elementary steps should result in an activation energy that changes during the course of the reaction. Consequently, the popularity of these methods has recently declined in favour of isoconversional methods, which can compute kinetic parameters without modelling assumptions [24–26].

Model-free isoconversional methods allow the activation energy to be estimated as a function of α without choosing the reaction model. The basic assumption of these methods is that the reaction rate for a constant extent of conversion, α, depends only on the temperature [27–30]. Hence, constant E values may be expected in the case of single-state decomposition, while a multi-step process E varies with α due to the variation in the relative contributions of the single step to the overall reaction rate.

In non-isothermal kinetics, several isoconversional methods are used. To use these methods, a series of experiments has to be conducted at different heating rates [31,32].

Vyazovkin et al. developed an isoconversional method that allows both simple and complex reactions to be evaluated [33]. Integrating up to conversion, α, Eq. (3) gives:

$$\int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)} = g(\alpha) = \frac{A}{\beta}\int_{T_0}^{T} \mathrm{e}^{-E/RT}\,\mathrm{d}T \tag{4}$$

Since $E/2RT \gg 1$, the temperature integral can be approximated by:

$$\int_{T_0}^{T} \mathrm{e}^{-E/RT}\,\mathrm{d}T \approx \frac{R}{E}T^2\,\mathrm{e}^{-E/RT} \tag{5}$$

Substituting the temperature integral and taking the logarithm, we have that:

$$\ln\frac{\beta}{T_\alpha^2} = \ln\left[\frac{RA}{E_\alpha g(\alpha)}\right] - \frac{E_\alpha}{R}\frac{1}{T_\alpha} \tag{6}$$

To apply the method, it is necessary to obtain at least three different heating rates (β), the respective conversion curves being evaluated from the measured TG curves [34]. For each conversion value (α), $\ln(\beta/T_\alpha^2)$ plotted versus $1/T_\alpha$, gives a straight line with slope $-E_\alpha/R$, and thus the activation energy is obtained as a function of the conversion. The sole evaluation of E_α dependence is enough to predict the isothermal kinetics from non-isothermal data, as in Eq. (7) [29,35]:

$$t_\alpha = \frac{\int_0^{T_\alpha} \mathrm{e}^{(-E_\alpha/RT_0)}\,\mathrm{d}T}{\beta\,\mathrm{e}^{(-E_\alpha/RT_0)}} \tag{7}$$

The time (t_α) at with a given conversion (α) will be reached at an arbitrary temperature (T_0) is computed by Eq. (7).

3. Results and discussions

The TG and DTG curves of powder-type sugarcane bagasse, under both nitrogen and oxygen atmospheres, are presented in Fig. 1. The drying process takes place in the initial stage at a temperature below 100 °C. Subsequently, at $T = 210$ °C for nitrogen and 200 °C for oxygen, the sample starts to loss mass. In the case of the nitrogen atmosphere, the maximum mass loss rate occurs at approximately $T = 350$ °C. Finally, at $T = 600$ °C, a black residue of approximately 35% full mass is obtained which is related to graphitic carbon. These results are in good agreement with those obtained by García-Pérez et al. [36]. In TG–DTG analysis of lingocellulosic materials, two or three peaks appear. These peaks can be assigned to cellulose, hemicellulose and lignin, indicating that, although there are interactions between fractions, their basic identity is maintained [37–39]. The TG in an oxygen atmosphere presents a maximum mass loss rate at 320 °C followed by a second step at $T > 350$ °C (DTG-curve relative minimum at 440 °C). In a reactive atmosphere, the residue at 600 °C is less (about 15%) than that obtained in an inert atmosphere, because total combustion of the organic matter takes place.

The DSC curves are presented in Fig. 2. The curve in an inert atmosphere, under nitrogen, is similar to the reactive-atmosphere curve, under oxygen, at $T < 100$ °C, although this behaviour changes at higher temperatures. Under nitrogen, relative to endothermic band, the first one, at $T < 100$ °C indicates the water desorption process, the other, between 200 and 400 °C, should be due to hemicellulose and cellulose desorption. In addition, a new, very narrow endothermic band appears at approximately 573 °C that can be associated with the quartz $\alpha \rightarrow \beta$ phase transition. The endothermic process due to organic matter desorption, observed when an inert atmosphere is employed, transforms into two exothermic bands in an oxygen atmosphere (a similar profile to the invested DTG-curve) due to the combustion reactions taking place.

In this study, in an oxygen atmosphere, the activation energy (E), the conversion and the degradation decomposition time were estimated as a function of temperature using both TG experimental data and Vyazovkin's model-free kinetics.

Model-free kinetics requires at least three dynamic curves with different heating rates. In the present study, these were 5, 10 and 20 °C/min. The total interval of temperatures of the curve (25–1000 °C) was chosen for model-free kinetics calculations. The respective conversion curves were calculated from TG experimental data. Fig. 3 shows the conversion curves versus temperature. Fig. 4 shows the apparent activation energy versus thermal process conversion, obtained by Vyazovkin's model-free kinetics methodology. There are three steps, which correspond to the TG curve carried out in the presence of oxygen. In the first, the activation energy is low and should be associated with water loss. The other two steps should be associated with

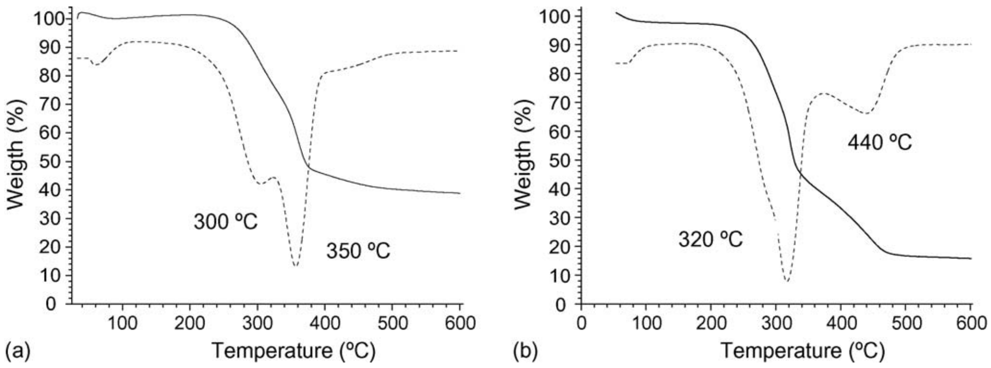

Fig. 1. TG (—) and DTG (. . .) curves for sugarcane bagasse in a dynamic atmosphere of (a) nitrogen and (b) oxygen.

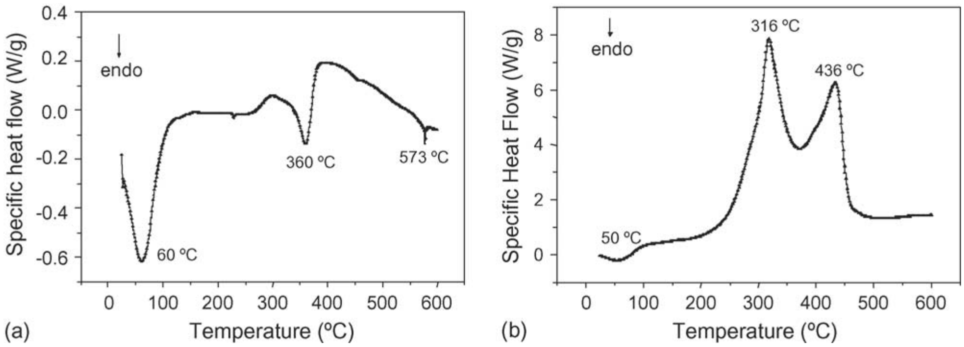

Fig. 2. DSC curves for sugarcane bagasse in a dynamic atmosphere of (a) nitrogen and (b) oxygen.

the combustion of the organic compounds presents in the bagasse sample. The apparent activation energies in the 2–5% conversion range have a value of 76.1 ± 1.7 kJ/mol. In the 15–60% conversion range, this value increases to 333.3 ± 15.0 kJ/mol, and, finally, when the conversion is 70–95%, it has a value of 220.1 ± 4.0 kJ/mol.

Mass spectrometry analysis is used to determine the H_2O, CO_2 and NO_2 concentration from a sample of the expelled vapour (Fig. 5). The conjunction of experimental results (Fig. 6) confirms that the first step (2–5% conversion) is solely related to the release of water. Subsequently, at 15–60% conversion ($T = 200–350\,^{\circ}C$), both combustion and carbonization of organic matter takes place, with the formation of water and carbon (and

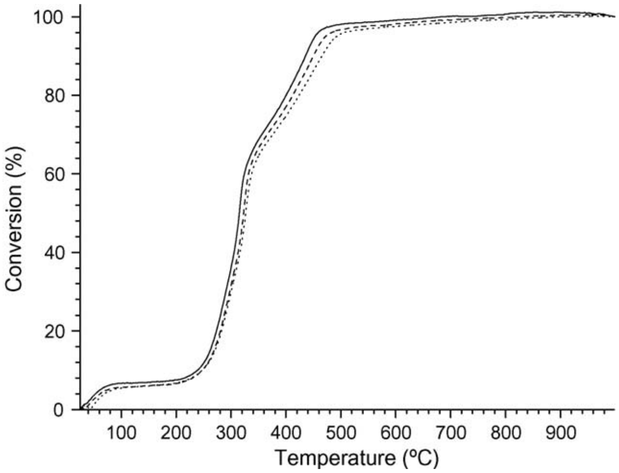

Fig. 3. Conversion curves as a function of temperature (in °C/min): 5 (solid line), 10 (dotted line), and 20 (dashed line).

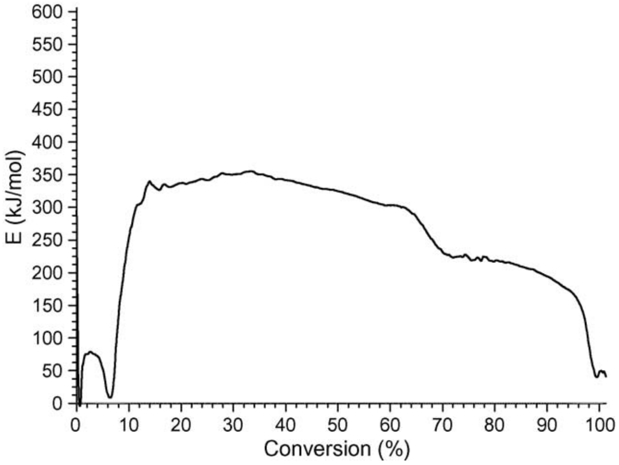

Fig. 4. Apparent activation energy as a function of conversion.

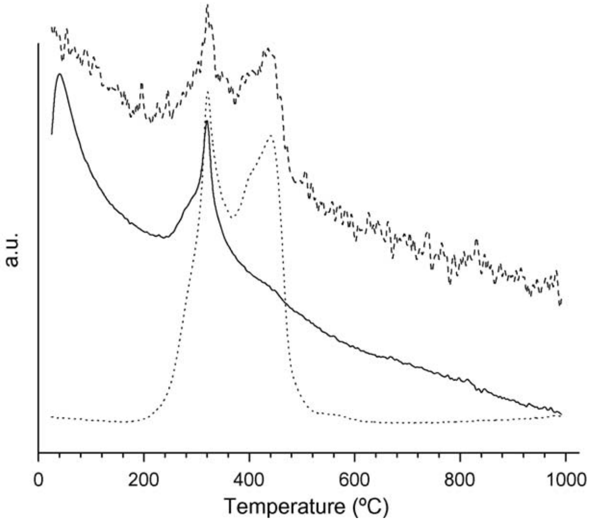

Fig. 5. Mass spectrometry analysis of evacuated vapours as a function of temperature: H_2O (solid line), CO_2 (dotted line) and NO_2 (dashed line).

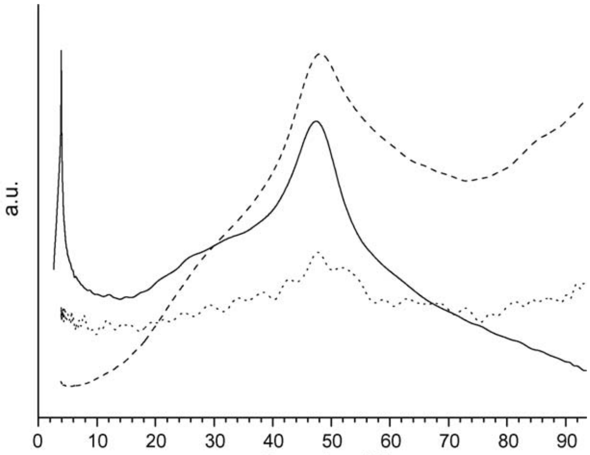

Fig. 6. Mass spectrometry analysis of evacuated vapours as a function of conversion: H_2O (solid line), CO_2 (dotted line) and NO_2 (dashed line).

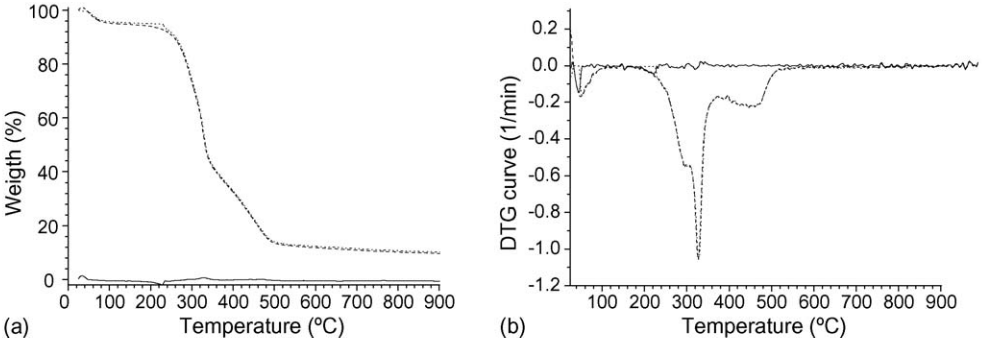

Fig. 7. Experimental (dashed line), simulated (dotted line), and difference (solid line) profiles at 20 °C/min heating rate: (a) TG and (b) DTG data.

nitrogen) oxide. Finally, in the third stage (70–95% conversion, $T = 400$–600 °C), the combustion of the pyrolysis products is observed, and the formation of appreciable quantities of water not being detected in the evacuated gases.

Vyazovkin's method allowed us to plot simulated TG-curves from the apparent energy activation data shown in Fig. 4. Previously, it is necessary to know the pre-exponential factor, A. This parameter can be calculated via artificial isokinetic relationship [35,40]. Next, knowing the values of E and A, it is easy to reconstruct the reaction model by using the Eq. (3). Thus, in Fig. 7a, we simulate the curve with a heating rate of 20 °C/min. Fig. 7b shows the calculated data in their derived form. In both cases (TG and DTG) the differences between experimental and calculated curves are negligible. Furthermore, by using Eq. (7), with non-isothermal kinetic data, is possible the prediction of sample behaviour in isothermal conditions (Fig. 8 and Table 1).

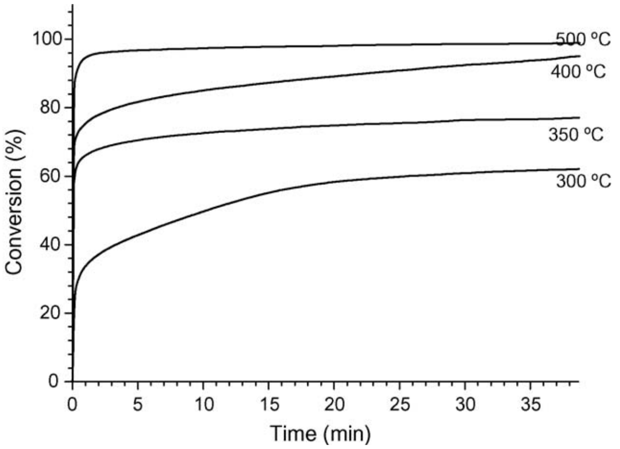

Fig. 8. Estimated conversion curves at different temperatures as a function of time.

Table 1
Isoconversion kinetic parameters for sugarcane bagasse sample: temperature (in °C) to which each conversion percentage is reached in the selected time

Conversion (%)	Time (min)		
	10	15	30
5	43.2	37.0	26.9
10	223.8	220.5	215.0
20	259.8	257.0	252.2
30	276.8	273.9	269.0
40	291.3	288.1	282.9
50	300.2	296.8	291.8
60	308.6	304.9	298.5
70	337.9	332.4	323.3
80	381.7	375.1	364.1
90	416.4	408.0	394.2
100	910.5	805.6	663.6

4. Conclusions

The present study shows that under non-isothermal conditions, in which the sample was heated at three different constant heating rates, model-free kinetics analysis is a good alternative for estimating the apparent activation energy to combustion of sugarcane bagasse. The apparent activation energy was ca. 76, 333 and 220 kJ/mol in the conversion range of 2–5% (dehydration), 15–60% (combustion and carbonization) and 70–95% (combustion), respectively.

Acknowledgements

The authors wish to thank CNPq (Proc. 142135-2003-8 and Proc. 305720/2003-1) and Fapesp (Proc. 2001/14302-1) in Brazil, and the Consejería de Educación y Cultura (Principado de Asturias, Research Project No. PC-04-06) in Spain, for their financial support.

References

[1] H. Lutz, K. Esuoso, M. Kutubuddin, E. Bayer, Biomass Bioenerg. 15 (2005) 155.
[2] R. Costales, J. García, G. Ocampo, Sobre los Derivados de la Caña de Azúcar 23 (1989) 30.
[3] J.R. Opfermann, E. Kaisersberger, H.J. Flammersheim, Thermochim. Acta 391 (2002) 119.
[4] A.S. Araujo, V.J. Fernandes, J. Marcelo, J. Valter, J.B. Souza, A.O.S. Silva, J.M.F.B. Aquino, Thermochim. Acta 413 (2004) 235.
[5] T.B. Brill, K.J. James, Chem. Rev. 93 (1993) 2667.
[6] A.K. Burnham, R.K. Weese, Thermochim. Acta 426 (2005) 85.
[7] R. Turcotte, M. Vachon, Q.S.M. Kwok, D.E.G. Jones, Thermochim. Acta 433 (2005) 105.
[8] A.C. Lua, J. Su, Polym. Degrad. Stabil. 91 (2006) 144.
[9] J. Reguera, J.M. Lagarón, M. Alonso, V. Reboto, B. Calvo, J.C. Rodríguez-Cabello, Macromolecules 36 (2003) 8470.
[10] A.N. García, R. Font, Fuel 83 (2004) 1165.
[11] M. Shui, L. Yue, Y. Hua, Z. Xu, Thermochim. Acta 286 (2002) 43.

[12] M.V. Kok, Energy Sour. 25 (2003) 1007.
[13] J.J.M. Orfao, J.L. Figueiredo, Thermochim. Acta 380 (2001) 67.
[14] P. Stolarek, S. Ledakowicz, Thermochim. Acta 433 (2005) 200.
[15] R. Capart, L. Khezami, A. Burnham, Thermochim. Acta 417 (2004) 79.
[16] H.-S. Shim, M.R. Hajaligol, V.L. Baliga, Fuel 83 (2004) 1495.
[17] I. Majchrzak-Kuceba, W. Nowak, Thermochim. Acta 413 (2004) 23.
[18] H. Polli, L.A.M. Pontes, A.S. Araujo, J. Therm. Anal. Calorim. 79 (2005) 383.
[19] S. Vecchio, R.D. Rocco, C. Ferragina, S. Materazzi, Thermochim. Acta 435 (2005) 181.
[20] J.M. Paturau, By-products of the Cane Sugar Industry, 2nd ed., Elsevier, Amsterdam, 1982.
[21] S.A. Nebra, Pneumatic Drying of cane bagasse, Ph.D. Thesis, State University of Campinas (in Portuguese), 1985.
[22] S. Vyazovkin, Int. Rev. Phys. Chem. 17 (1998) 407.
[23] G.N. Lewis, Z. Phys. Chem. 52 (1905) 310.
[24] S. Vyazovkin, C.A. Wight, Thermochim. Acta 340–341 (1999) 53.
[25] A. Khawam, D.R. Flanagan, Thermochim. Acta 429 (2005) 93.
[26] A. Khawam, D.R. Flanagan, J. Phys. Chem. B 109 (2005) 10073.
[27] H. Friedman, J. Polym. Sci. C 6 (1965) 195.
[28] T. Ozawa, Bull. Chem. Soc. Jpn. 38 (1965) 1881.
[29] J.H. Flynn, L.A. Wall, J. Res. Natl. Bur. Stand. Sect. A 70 (1966) 487.
[30] S. Vyazovkin, D. Dollimore, J. Chem. Inf. Comput. Sci. 36 (1996) 42.
[31] A. Abdel-Kader, S.I. Saleh, Thermochim. Acta 181 (1991) 203.
[32] S. Vyazovkin, J. Comput. Chem. 18 (1997) 393.
[33] S. Vyazovkin, N. Sbirrazzuoli, Anal. Chim. Acta 355 (1997) 175.
[34] S. Vyazovkin, C.A. Wight, Ann. Rev. Phys. Chem. 48 (1997) 125.
[35] S. Vyazovkin, Int. J. Chem. Kinet. 28 (1996) 95.
[36] M. García-Pérez, A. Chaala, J. Yang, C. Roy, Fuel 80 (2001) 1245.
[37] J.A. Caballero, J.A. Conesa, R. Font, A.J. Marcilla, J. Anal. Appl. Pyrol. 42 (1997) 159.
[38] K. Raveendran, A. Ganesh, K. Khilar, Fuel 75 (1996) 987.
[39] T. Fisher, M. Hajaligol, B. Waymack, D. Kellogg, J. Anal. Appl. Pyrol. 62 (2002) 331.
[40] S. Vyazovkin, W. Linert, Chem. Phys. 193 (1995) 109.