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A STUDY OF PYROLYSIS OF MACADAMIA NUT SHELL: PARAMETRIC SENSITIVITY ANALYSIS OF THE IPR MODEL

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Abstract - The macadamia tree is known for producing fruit high in fats, enclosed in very hard woody shells. Macadamia nut shell, considered as a by-product from macadamia nut processing, may be a suitable option for pyrolysis. These residues are constituted of cellulose, hemicellulose, lignin and extractives. The Independent Parallel Reaction (IPR) Model has been applied in this work to study the pyrolysis of macadamia nut shell from thermogravimetric experiments. The kinetic parameters and mass fraction of each component were estimated using the Differential Evolution Algorithm. The influence of the model parameters was also analyzed by means of sensitivity studies. The results showed that the decomposition of the macadamia nut shell is more sensitive to the parameters related to the decomposition of lignin. The results of sensitivity analysis also showed that the activation energy affects the total biomass conversion more strongly than the other parameters and the contribution of extractives in the IPR model is as important as the hemicellulose.

Keywords: Macadamia nut shell; Biomass; Pyrolysis.

INTRODUCTION

Macadamia is a small evergreen tree, native to eastern Australia. The tree is known for producing a fruit (nuts), enclosed in very hard, woody shells. Macadamia nuts are extremely nutritious, with a high amount of beneficial fatty acids, as well as calcium, iron and B vitamins.

Hawaii is the major producer of macadamia nuts, followed by Australia. Other producers include Brazil, South Africa, Guatemala, Kenya, Costa Rica, Malawi, Mexico, New Zealand and China (Penoni *et al*., 2011).

Environmental awareness has increased, and various strategies have been employed to reduce the environmental load produced by the discarded waste. However, over the past decades, the total amount of waste has increased significantly and the sources have become increasingly diverse (Arabiourrutia *et al*., 2007; Lopez *et al*., 2009). For each ton of macadamia nut produced 70 to 77% of shell residues are generated (Penoni *et al*., 2011). Macadamia nut shells can be burned at very high temperatures to produce activated carbon (Conesa *et al*., 1999) or directly used as charcoal. Even with these applications, disposal of the macadamia waste shells has created a serious problem for the nut processing industries (Poinern *et al*., 2011). Macadamia nut shells are known to have a higher surface area than other nut

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shells and their ash contents are very low (less than 1%). In this context shell residues can be seen as a promising option for use in biomass pyrolysis.

Knowledge of kinetic parameters is important for the design and optimization of any future pyrolysis process of macadamia nut shell. The kinetics of biomass pyrolysis are complex and involve a large number of parallel and serial reactions. The literature contains several kinetic models, e.g., the single reaction model (Radmanesh *et al*., 2006), the consecutive reaction (CR) model (Mui *et al*., 2008; Santos *et al*. 2012a) and the independent parallel reaction (IPR) model (Gómez, 2006). The Independent Parallel Reaction (IPR) kinetic model, or the n-pseudo-component model, is more accurate than the others, because this model (IPR) considers that the pseudo-components are degraded individually, ensuring a possibly simultaneous decomposition. Therefore, the rate of weight loss is calculated considering the individual reaction rates and their respective mass fraction.

The parametric sensitivity analysis provides a systematic procedure to estimate the accuracy and robustness of a mathematical model (Lira *et al*., 2009). Sensitivity analysis is a useful means of determining whether values of theoretically identifiable parameters can be reliably obtained from experimental data. Kinetic models usually have high parametric sensitivity (Barrozo *et al*., 1996), so that variations in some parameters may lead to completely different results (Arnosti Jr *et al*., 1999, Ribeiro *et al*., 2005). Thus, determining the influence of these parameters on the response variable of the model can help to indicate what parameters must be estimated with greater accuracy. The DASPK 3.0 code has been used in the optimization of several large-scale engineering problems (Barrozo *et al*., 2006; Lira *et al*., 2010). However, there are very few studies on the use of this technique applied to the sensitivity analysis of kinetic parameters.

In this paper, the Independent Parallel Reaction (IPR) kinetic model has been used to estimate the kinetic parameters during pyrolytic decomposition of macadamia nut shell from TGA tests. The activation energy, the pre-exponential factor of the Arrhenius equation and the mass fraction of each subcomponent of the biomass were calculated. In addition, parametric sensitivity analysis, using the DASPK 3.0 code, was also performed to evaluate the effect of incremental changes in each kinetic parameter.

In a previous work (Santos *et al*., 2012b), it was shown that the IPR model for sugarcane bagasse is more strongly affected by activation energies, followed by the pre-exponential factors of the Arrhenius equation and mass fractions. However, in lignocellulosic biomass, despite having the same principal components (extractives, hemicellulose, cellulose and lignin), these are present in quite different amounts. Thus, the main objective of this work is to show that biomass composition modifies the way in which the IPR model is influenced by its parameters.

MATERIAL AND METHODS

Material

Macadamia nut shell used in the experiments came from São Mateus-ES, southeastern Brazil.

Elemental analysis was performed with a Leco CHNS-932 Element Analyzer with samples of about 1.5 mg. The real density was determined by gas pycnometry using a Micromeritics Accupyc 1331 with 10^{-4} $g.cm^{-3}$ sensitivity, under a helium atmosphere. Moisture content was estimated gravimetrically before and after oven-drying at 378±3K for 24 h. The ash content was determined according to the standard ASTM D1762-84. All of these tests were run in triplicate.

Thermogravimetric Analysis

The thermogravimetric data were obtained from a Shimadzu TGA-50H, with an inert atmosphere of N_2 applied at a flow rate of 50 mL min^{-1}. Macadamia nut shell samples of approximately 26 mg with a particle diameter < 1 mm were used in all tests. The TGA tests were performed in triplicate for each operating condition. The dynamic tests were performed starting at room temperature to reach 1173K at various heating rates: 5, 10, 20 and 30 $K.min^{-1}$. The residual weight of the sample and the derivative of weight in terms of time and temperature (DTG analysis) were recorded using TGA software.

Kinetic Model

The kinetic parameters of Macadamia nut shell pyrolysis were determined using the Independent Parallel Reaction model (IPR). It was assumed that the macadamia nut shell contains four pseudo-components (extractives, hemicellulose, cellulose and lignin) that degraded individually and simultaneously in the same temperature range.

The degree of transformation or conversion is expressed by:

$$X = \frac{m_0 - m}{m_0 - m_\infty} \tag{1}$$

where m is the mass of biomass and the subscripts 0 and ∞ refer to the initial and residual amounts, respectively.

The rate of reaction of each pseudo-component is:

$$\frac{dX_i}{dt} = k_{0i} \exp\left(-\frac{E_{ai}}{RT}\right)\left(1 - X_i\right)^{n_i} \tag{2}$$

where, for each pseudo-component i, X_i *is* the conversion, k_{0i} is the pre-exponential factor, E_{ai} is the activation energy, and n_i the reaction order, t is time, and T is temperature.

First order reaction kinetics were assumed for the extractives, cellulose and hemicellulose (Lira *et al.*, 2010; Hu *et al.*, 2007). The pyrolysis of lignin cannot be modeled by first-order kinetics (Gómez *et al.*, 2004). Several papers in the literature report that the pyrolysis of lignin is better described by third-order reaction kinetics (Gómez, 2006; Gómez *et al.*, 2004; Manyà and Araùzo, 2008). Thus, in this work third order reaction kinetics was assumed for the pyrolysis of lignin.

The total rate of reaction in the IPR model is the linear combination of the rates of the partial reactions, considering the mass fraction c_i of each of the pseudo-components of Macadamia nut shell:

$$\frac{dX}{dt} = -\sum_{i=1}^{N} c_i \frac{dX_i}{dt} \tag{3}$$

Consequently, the mass loss with time is calculated using the following relationship:

$$\frac{dm^{calc}}{dt} = -\left(m_0 - m\right)\sum_{i=1}^{N} c_i \frac{dX_i}{dt} \tag{4}$$

The IPR model unknown parameters were determined by evaluation of experimental data, which can be done either from the mass loss curve (TG) or its derivative (DTG). In this work, the objective function to be minimized consists of the sum of squares of the residuals for the DTG curve (Equation (6)).

$$O.F._{TG} = \sum_{j=1}^{N}\left(m(t)_j^{obs} - m(t)_j^{calc}\right)^2 \tag{5}$$

$$O.F._{DTG} = \sum_{j=1}^{N}\left(\left(dm/dt\right)_j^{obs} - \left(dm/dt\right)_j^{calc}\right)^2 \tag{6}$$

In order to assess the quality of fit parameters of the IPR model and compare them with results presented in the literature, the fit between the experimental and estimated data was calculated as the deviation in TG and DTG, respectively, defined as:

$$FIT_{TG}(\%) = 100\sqrt{\left(O.F._{TG}\right)/N} \Big/ \max\left(\left|m_j^{obs}\right|\right) \tag{7}$$

$$FIT_{DTG}(\%) = 100\sqrt{\left(O.F._{DTG}\right)/N} \Big/ \max\left(\left|\left(dm/dt\right)_j^{obs}\right|\right) \tag{8}$$

A program in MATHLAB was implemented to estimate the kinetic parameters of the IPR model using the Differential Evolution Method. Differential evolution (DE) is a mathematical method of optimization of multidimensional functions which belongs to the class of evolution strategy optimizers. DE finds the global minimum of a multidimensional multimodal (i.e., exhibiting more than one minimum) function with good probability (Storn *et al.*, 2005; Lobato *et al.* 2008).

Sensitivity Analysis

In this work, sensitivity analysis was performed by calculation of the sensitivity coefficient. It is basically the ratio of the change in output to the change in input while all other parameters remain constant:

$$\mathrm{s_i} = dy/dp_i \tag{9}$$

where s_i is the absolute sensitivity coefficient of variable y relative to parameter p_i. This method offers the advantage of determining the sensitivity along the temperature evolution, providing a much more accurate evaluation of each parameter.

In order to compare the sensitivities of the parameters together, the normalized sensitivity coefficients were calculated by multiplying the absolute sensitivity coefficients by p_i/X. Using this procedure, all sensitivities can be compared with each other on the same basis.

After estimating the values of the parameters, the normalized sensitivity coefficients and the differential equations of the IPR model were solved using DASPK 3.0 code. This code, developed in FORTRAN, offers several methods to solve DAEs or ODEs systems and to calculate absolute sensitivity coefficients. Analyses and comparisons of the several methods are presented by Li *et al.* (2000).

RESULTS

The results of the elemental composition, real density, ash and moisture content of the macadamia nut shell used in this work are presented in Table 1.

It can be seen that there is a low ash content. This is interesting for pyrolysis, because high ash content, especially of potassium, sodium and calcium, can act as a catalyst, promoting secondary decomposition reactions of volatiles and char formation, leading a low conversion (Di Blasi, 2008).

Table 1: Analytical characteristics of macadamia nut shell.

Elemental Analysis				Ash (%)	Moisture (%)	Density (g.cm^{-3})
C (%)	H (%)	N (%)	O (%)			
47.00	6.10	0.36	46.52	0.22±0.04	10.47±0.15	1.45

Figure 1 shows the curves of the rate of mass loss (differential thermogravimetric, DTG) of macadamia nut shell pyrolysis, in dynamic tests, as a function of temperature at different heating rates. As expected, the maximum rate of pyrolysis increases with increasing heating rate. From DTG curves it can be observed that the macadamia nut shell devolatilization consists of two visible peaks, and a flat tailing section. Each peak corresponds to the maximum degradation of one subcomponent of biomass. The lower temperature shoulder represents the decomposition of hemicellulose present in the macadamia nut shell and the higher temperature peak corresponds to the decomposition of cellulose. The flat tailing section of the conversion rate curves at higher temperatures corresponds to lignin. Lignin is known to decompose slowly and in a wider range of temperature (Manyà and Araùzo, 2008). Besides, macadamia nut shell also contains a small amount of extractives, which also influence its overall thermal degradation rate.

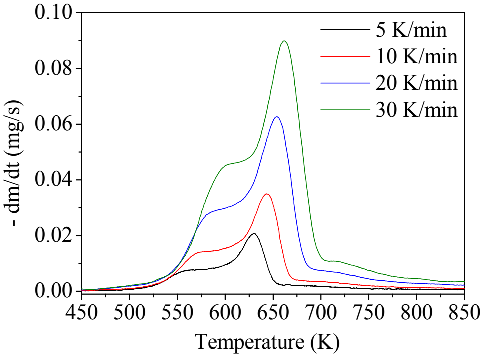


Figure 1: Rate of mass loss (DTG) as function of reaction temperature and heating rate.

These DTG curves (Figure 1) showed major peak shifts to higher temperature when the heating rate is increased. At lower heating rates the decomposition reactions are minimized by the superposition of events that are shifted to lower temperatures (Riegel *et al*., 2008). Thus, it is possible to infer that higher rates will have higher equilibrium temperatures with lower temperature rise times, both parameters being important to define pyrolysis type, because different values may favor the formation of different compounds (Moldoveanu, 2010).

Figure 2-(a) shows the DTG curve (experimental and calculated) of macadamia nut shell pyrolysis at a heating rate of 10 K min^{-1}. It can be seen that the results from the IPR model are in good agreement with the experimental data. It can also be observed that the first fitted peak corresponds to the evaporation of extractives, while the second, third and fourth peaks correspond to the hemicellulose, cellulose and lignin thermal degradation, respectively. Figure 2-(b) was extracted from Santos *et al*. (2012b) for Sugarcane bagasse pyrolysis at the heating rate of 5 K min $^{-1}$. It is clear the importance of the presence of extractives in the DTG curve. In the first figure, Figure 2-(a), extractives and hemicellulose overlap, contributing to a smooth and flatter peak in the DTG curve. In the second figure, Figure 2-(b), hemicellulose defines the first peak of the DTG curve. In Santos *et al*. (2012b), extractives are less than 1% of the total

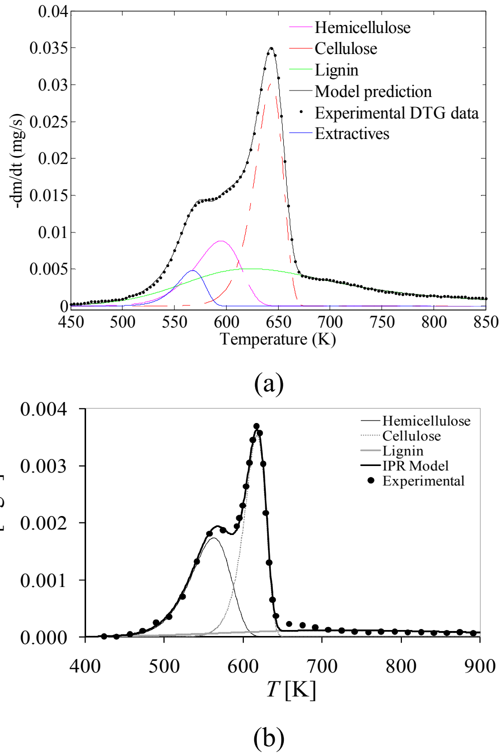


Figure 2: Experimental and predicted DTG curves: (a) Macadamia nut shell pyrolysis at the heating rate of 10 K min^{-1} and (b) Sugarcane bagasse pyrolysis at the heating rate of 5 K min^{-1} extracted from Santos *et al*. (2012b).

composition of sugarcane bagasse; on the other hand, macadamia nut shell has on average 6% extractives. This shows that, when there is a significant amount of extractives, this should be considered in the IPR model; otherwise, the mass loss estimation can be compromised between 550 and 650 K.

Table 2 shows the results of the parameter estimation of the IPR Model using the Differential Evolution method. The mass fraction of the hemicellulose (c_H), cellulose (c_C), lignin (c_L) and extractives (c_E), as well as the parameters of the Arrhenius equation (k_0 and E_a) for each subcomponent have been calculated for all heating rates. As the pyrolysis reaction mechanisms are different for different heating rates, it is expected that parameters of the Arrhenius equation are also different, as shown in Table 2. Nevertheless, the values of activation energy estimated in this work are in good agreement with data reported in the literature that also used the IPR model (Hu *et al*., 2007; Vamvuka *et al*., 2003; Manyà and Araùzo, 2008; Órfão *et al*., 1999; Santos *et al*., 2012b). It can be seen that the calculated setting errors were less than 0.40% and 0.70% for TG and DTG curves, respectively, showing that the model can adequately predict the macadamia nut shell pyrolysis kinetics. The estimated mass fractions fell within a range of 0.14–0.17 for hemicellulose, 0.36–0.38 for cellulose, 0.39–0.42 for lignin and 0.05–0.07 for extractives. These mass fraction values have a small standard deviation (since it is the same biomass) and they are similar to macadamia nut shell compositions reported by literature (Antal *et al*., 2010; Toles *et al*., 1998).

The IPR kinetic model, along with the sensitivity coefficients, was solved using the DASPK 3.0 code. The normalized sensitivity coefficients of the macadamia nut shell conversion (X) were obtained using perturbations of 1% in each parameter of the Independent Parallel Reaction model. The parameters studied here were: pre-exponential factors (k_{0i}), activation energies (E_{ai}), mass fractions of subcomponents (c_i) and orders of reaction (n_i). Figure 3 shows the normalized sensitivity coefficients of the IPR model parameters for the heating rate of 10 K min^{-1}.

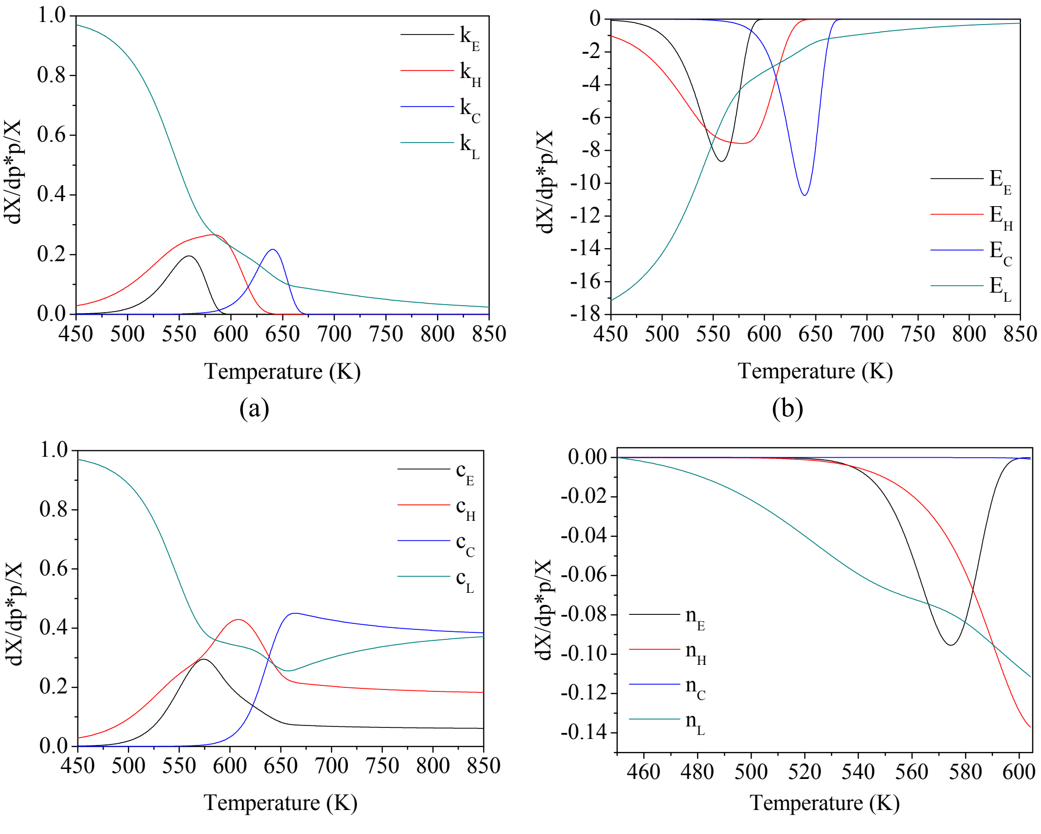
Figure 3 shows, as expected, that the pre-exponential factors and mass fractions of subcomponents have positive sensitivity, while the activation energies and orders of reaction have negative sensitivity. A positive sensitivity coefficient implies an increase in the measurement with a given increase in the parameter p_i. Similarly, a negative sensitivity coefficient implies a decrease in the measurement given an increase in the same parameter p_i.

Among the parameters investigated, the highest sensitivities are those with respect to activation energies; mass fractions of subcomponents and pre-exponential factors of the Arrhenius equation result in a moderate sensitivity, while reaction orders give the lowest sensitivities. For a parameter to be reliably identifiable, the macadamia nut shell conversion should be highly sensitive to changes in this parameter, as with the activation energies. The lower the sensitivity coefficient, the more difficult it is to assign a single value for the parameter. This may have contributed to the higher standard deviation of the estimates of the pre-exponential factor. It is worth remembering that, in this work, the reaction orders were not estimated. Values suggested in the literature were used.

Table 2: IPR model parameters estimated by the Differential Evolution technique.

β (K. min^{-1})	Component	k_0 (s^{-1})	E_a (kJ.mol^{-1})	c_i	FIT (%)
5	Hemicellulose	1.5x10^{10}	140.2	0.16	0.11[a]
	Cellulose	8.2 x10^{19}	265.7	0.37	0.50[b]
	Lignin	2.7 x10^{2}	62.8	0.40	
	Extractives	1.2 x10^{15}	183.6	0.07	
10	Hemicellulose	2.9 x10^{9}	132.2	0.17	0.20[a]
	Cellulose	1.1 x10^{19}	258.3	0.37	0.40[b]
	Lignin	8.7 x10^{2}	65.8	0.40	
	Extractives	2.8 x10^{16}	199.5	0.06	
20	Hemicellulose	5.3 x10^{9}	133.4	0.15	0.25[a]
	Cellulose	8.9 x10^{15}	221.2	0.38	0.55[b]
	Lignin	4.3 x10^{3}	71.1	0.42	
	Extractives	3.3 x10^{16}	201.3	0.05	
30	Hemicellulose	1.8 x10^{11}	150.6	0.15	0.31[a]
	Cellulose	1.6 x10^{16}	225.5	0.38	0.64[b]
	Lignin	1.0 x10^{4}	74.5	0.42	
	Extractives	1.0 x10^{17}	208.2	0.05	

[a] TG FIT
[b] DTG FIT



(c) (d)

Figure 3: Sensitivity of the IPR model to the following parameters: (a) pre-exponential factors; (b) activation energies; (c) mass fractions of subcomponents; (d) orders of reaction.

It also can be observed that the parameters associated with lignin are significant in the first stage of macadamia nut shell decomposition, while for the other components they are significant in the specifics ranges of conversion. This occurs because lignin decomposition occurs over a wide temperature range and its contribution to the macadamia nut shell degradation is greater at the beginning when the other components have not yet started to decompose.

In this work, the IPR kinetic model for pyrolysis of macadamia nut shell has a component that is normally not considered in the literature for other biomass, the extractives, because they are present in small amounts when compared with other components. Although macadamia nut shells contain 5-7% of extractives, Figure 2 shows that their contribution is almost as important as the hemicellulose in rate of mass loss. Furthermore, the presence of extractives modifies the way the model is influenced by hemicellulose, when compared to the work of Santos *et al*. (2012b). This modification decreases the intensity of the relative sensitivity coefficients for the three most important parameters (activation energy, mass fraction of subcomponent and pre-exponential factor of Arrhenius equation), while the temperature range is not changed.

CONCLUSIONS

The pyrolysis kinetics of macadamia nut shell can be successfully described by the independent parallel reaction model. The parametric sensitivity analysis of the IPR model showed that the activation energies affect the conversion of the material to a greater extent than the other parameters, followed by the mass fractions of subcomponents and pre-exponential factors of the Arrhenius equation. The IPR kinetic model has only a very slight sensitivity to the reaction orders. The parametric sensitivity study also showed that rate of mass loss of the macadamia shell was more sensitive to the parameters related to lignin. In addition, the contribution of extractives in the IPR model is as important as that of hemicellulose.

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