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Use of Genetic Algorithm and Particle Swarm Optimization in The Estimation of Kinetic Parameters of Green Coconut Biomass

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The development of more economically and energy-efficient processes for the sustainable production of fuels and chemicals is becoming increasingly necessary. In this context, it is relevant to understand the behaviour of thermal degradation of different biomasses in oxygen free atmosphere to investigate the breakdown of polymer chains, which can be converted into new products. Good effects on the acceleration of degradation of organic molecules can be achieved with the use of catalysts in these breaking processes, thus increasing the yield of bio-oil production. In this work, fiber of crushed and sifted green coconut shell, submitted to thermogravimetry analysis (TG), was used as biomass. Some types of a catalyst were incorporated into the biomass, based on cobalt ferrite, Fe_2CoO_4. The design of a biomass pyrolysis reactor requires knowledge of kinetic parameters, activation energy (Ea), pre-exponential factor (k_0) and order of reaction (n). In this context, the present study aimed to perform the thermogravimetric (TG) analysis in an inert atmosphere of pure nitrogen, and to determine the kinetic parameters involved in the lignin pyrolysis process, to assist in the design of biomass conversion reactors. This work presents a solution to obtain the kinetic parameters for thermogravimetric reaction of lignin breaking present in the biomass of the green coconut. Two computational methods were used: genetic algorithm and particle swarm optimization. The results obtained for activation energy, pre-exponential factor and order reaction are in the range of values found in the literature.

1. Introduction

The use of renewable plant materials is a promising alternative for production of chemicals (Kumar, 2015, Strubinger, 2017). The growth of green coconut water consumption and the natural tendency for its industrialization have caused difficulties for final disposal of the residue generated, that is, the fruit peels (Rosa et al., 2001). Hydrothermal pyrolysis is a feasible alternative to this reuse, where matter decomposes in an inert atmosphere generating gases, liquids and solid residues (Carrijo et al., 2002). After cooling the solution and condensing the vapors, it is possible to observe the formation of a brown liquid called bio-oil. Lignocellulosic biomass is mostly composed of three main components consisting of about 30-50% cellulose, 15-35% hemicellulose and 10-20% lignin (Schena, 2015). For a suitable use of this biomass, it is extremely important to know their thermal behavior during thermoconversion process. The biomass, when subjected to high temperatures, undergoes thermal decomposition of its components (hemicelluloses, cellulose and lignin), undergoing a carbonization process under inert atmosphere (Raad, 2006). The knowledge of such process is fundamental for monitoring processing conditions of these materials (Ahmad et al., 2017). Thermogravimetric analysis technique (TGA) makes possible to obtain this information in a simple and fast way. Changes in its surface properties with increasing calcination time may influence the catalytic activity of the breakdown reactions of lignocellulosic components (Barbosa, 2014). Thermogravimetric tests, using biomass mixtures and catalysts with different calcination times in the final stage of preparation, are of fundamental importance to

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find a catalyst capable to generate real catalytic effect, accelerating the thermal degradation of the polymeric structures present, and which can be applied in a hydrothermal liquefaction (HTL) route.
An equation for the kinetic mechanism of lignin carbonization present in green coconut biomass was obtained by equations proposed by Speyer (1994) and by the thermogravimetry of green coconut samples in a mixture with cobalt ferrite catalyst. The design of a reactor using the biomass pyrolysis process requires knowledge of kinetic parameters of Arrhenius equation (activation energy Ea, pre-exponential factor k_0 and apparent order of reaction n). The techniques of thermal analyses, in particular the thermogravimetric (TG) analysis, allow to obtain kinetic information in a simple and fast way.
Kinetic modelling of a reaction system is important to better comprehend the whole system and to improve it, for example using initial conditions responsible to achieve higher conversions. However, to select optimal initial conditions in laboratory or industrial scale through mathematical modelling is necessary to have a reliable model. The model is trustable if it is capable to represent well the experimental data available, the procedure used to adjust the model's prediction to experimental data by manipulating model parameters is known as parameter estimation, which is an optimization procedure, and uses an objective function that weighs the distance between the model`s prediction and the experimental data. Application of stochastic optimization methods are highly indicated in parameter estimation problems, like genetic algorithm (GA) and particle swarm optimization (PSO) (Kumar, 2009) and they are based on empirical evolutionary rules that frequently mimic successful optimization strategies found in nature.
Genetic algorithm is an optimization technique based on Darwin evolution theory. In the last years, its application in chemistry is increasing significantly due the special characteristics for optimization of complex systems (Costa Filho, 1999). Initially, a random set of individuals is formed. At each iteration, this population in evaluated and ranked according to its adaptability. One part of the most fit individuals is retained, while the other is discarded. Among the individuals maintained, a group is selected that will be submitted to the genetic operators like mutation or crossover and will have their characteristics altered, generating better descendants for the next generation. This process is repeated until a set of satisfactory solutions are found (Goldberg, 1989 and Beasley et al.,1993).
Particle swarm optimization (PSO) is related to evolutionary computation procedures and has strong ties with genetic algorithm. However, the population of candidate solutions to the optimum of the problem are called particles. The objective of the technique is to move these particles in the search space taking into account their position and speed. PSO is based on the simulation of simplified social models, such as bird flocking, fish schooling and the swarming theory (Kennedy & Eberhart, 1995). The PSO has been widely studied by several authors in numerous fields (Ourique, 2002). Parameter estimation and parameters confidence region construction by PSO were discussed by Schwaab et al. (2008).
The objective of the current work is to perform thermal analysis of pyrolysis process of the component lignin under an inert atmosphere of pure nitrogen and to estimate the kinetic parameters of lignin thermal decomposition through genetic algorithm and particle swarm optimization techniques to provide information for designing biomass thermo-conversion reactors.

2. Material and Methods

2.1 Thermogravimetric Analysis

To obtain thermogravimetry data, a TG Netzsch STA 449 F3 Jupter was used, in the temperature range of 20 °C to 1000 °C, under nitrogen (inert) atmosphere, under a flow of 20 $mL.min^{-1}$ and heating rate of 20 $°C.min^{-1}$ in a crucible. Before starting the analysis, temperature stabilization of the equipment on a bath was carried out with minimum duration of 3 hours for the temperature stabilization just above room temperature. After that analysis were initiated. The empty crucible was added for reference weighing and only then the nitrogen cylinder and the valves were opened. Three purges with nitrogen gas were made so that all the oxygen inside the apparatus was removed before starting the real tests. For each analysis, a blank was run with an empty crucible for the same duration of sample analysis, 60 minutes, and a heating rate of 20 ° C / min^{-1}. In the equipment control software, analysis conditions, initial heating temperature, final temperature and heating rate are defined. Thus, the analysis began, first with the empty crucible and then, following the same procedure, with the sample to be analysed. Firstly, the samples used for thermogravimetric analysis were only of biomass in the form of powder and, after that, were done tests with proportions of catalyst and biomass
The catalyst used was cobalt ferrite calcined during 9 h in oven at 1000 °C. After the thermogravimetry test, data of temperature, mass loss and derivative of mass loss were taken from TG software and transferred to an excel sheet.

2.2 Decomposition kinetics from thermogravimetric analyses

Based on the premise that the parameters of a given kinetic mechanism are valid for both the constant temperature and the variable temperature processes, the kinetic parameters *"k_0" (*pre-exponential factor), "*Ea*" (activation energy) and "*n*" (reaction order) can be obtained from TG data. A kinetic study using the method described by Speyer (1994) was done in the temperature range of thermogravimetry defined as possibly being lignin thermal decomposition. Several techniques for determining kinetic mechanisms use of TG data obtained at several different heating rates, which makes the analysis more time consuming and cumbersome (Kan-Sen, 1984). Speyer et al. (1994) elucidated the development of a kinetic model for decomposition reactions with data collected from TG to obtain activation energy, pre-exponential factor and order of reaction without the need for extra analysis at different heating rates.
The general reaction rate for the study of decomposition kinetics can be described as:

$$\frac{dX}{dt} = -k * X^n \tag{1}$$

where *X* is the mass of the reactant, *t* is the time, *k* is the kinetic constant and *n* is the order of reaction. This expression may be related to the information that is taken from TG:

$$X = m_0 - m_0 * \left(\frac{w}{w_0}\right) \tag{2}$$

where *m* is the mass of the initial sample, w_0 is the initial mass loss and *w* is the mass loss at each time t. Before the start of the reaction, $w = 0$ and $X = m_o$. After the end of the reaction, $w = w_\infty$ and $X = 0$. The derivative of Eq(2) yields:

$$\frac{dX}{dt} = -\left(\frac{m_0}{w_\infty}\right) * X^n \tag{3}$$

where w_∞ is the maximum mass loss. Substituting Eq(3) in Eq(1) results:

$$\frac{dw/w_\infty}{dt} = k * {m_0}^{n-1} * \left(1 - \frac{w}{w_\infty}\right) * n \tag{4}$$

Eq(4) can be simplified by equating $f = w / w_\infty$ and assuming the reaction rate constant *k* follows the Arrhenius temperature dependence, resulting in the following expression. The terms *f* and *df/dt*, may be obtained directly from the TG output.

$$\frac{df}{dt} = k_0 * {m_0}^{n-1} * (1-f)^n * exp\left(\frac{-Ea}{R * T}\right) \tag{5}$$

2.3 Parameter Estimation Procedure

A genetic algorithm is a search heuristic that is inspired by Charles Darwin's theory of natural evolution. The basic genetic algorithm involves five steps: variable coding, initial population creation, response evaluation, crossover, and mutation. In this way, the proposed algorithm assimilates much to the natural evolutionary process. The process optimization was performed in MATLAB R2018a using the GA functions available in the Global Optimization Toolbox. With the chosen data, it was used trial and error technique to find the best search range of the model parameters. The program was run repeatedly, modifying the population size, the number of generations migration fraction and the crossover fraction. In addition, initial kicks were also proposed for the lower and upper limits of the parameters to be found and, from them, one can narrow the search range. In the proposed work, the genetic algorithm technique was used to estimate the kinetic parameters of lignin decomposition, reaction order, pre-exponential factor and activation energy. A second parameter estimation procedure was performed in Python to estimate the same kinetic parameters set but, this time, particle swarm optimization was applied. This algorithm uses information about the best solution found by each particle and all particles. Likewise, in the proposed work, through Python programming language, particle swarm optimization was used to estimate the kinetic parameters of lignin decomposition. As in the prior estimation, the use of trial and error is required to search for better model parameters. The performance of the two models were evaluated by the coefficient of determination (R^2) and the sum of the quadratic error (SSE).

3. Results and Discussion

3.1 Qualitative analysis

The thermoanalytical tests were carried out in a laboratory of Department of Chemical and Materials Engineering (DEQM/PUC-Rio). Calibrations and daily checks of the thermobalance were required before thermogravimetric tests. A blank was made with an empty crucible for each condition evaluated. The thermogravimetric analysis of the sample (fiber plus catalyst) with a mass fraction of Fe_2Co_4 equal to 50 % was performed. The experiment was also carried out in inert atmosphere of nitrogen with a heating rate of 20 ºC/min, between 20 and 1000 ºC, 42.2 mg of fiber was initially used and the catalyst added was calcined before thermogravimetric assays for 9 h in an oven at 1000 ºC.

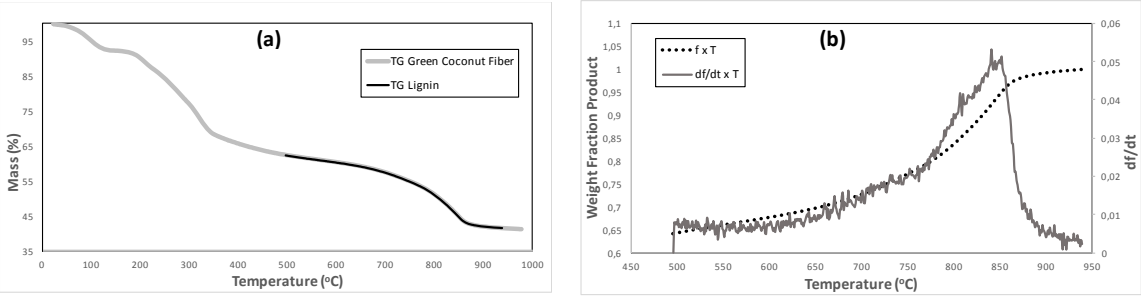


Figure 1: (a)Thermogravimetric characterization of green coconut fiber plus catalyst (50/50) in an inert atmosphere of N_2 for 9 h, calcination at 1000 ºC. (b) Method for determining f and its derivative through data obtained from lignin curve.

In Figure 1(a), the TG signals from blends (50% w/w) of the catalyst calcined at 1000 ^{o}C (9 h) are presented, suggesting that degradation of lignin begins at a lower temperature than without the presence of the catalyst. The catalytic activity is involved in a decomposition mechanism that allows the fixed carbon not to be the priority, but combustible gases and bio-oils. Without the catalyst, for kinetic reasons, instead of the organic structure decomposing to form hydrocarbon molecules, it increases the amount of fixed carbon formed (Monteiro, 2018).
In Figure 1(a), the darker line shows the thermogravimetric result for lignin and includes the data used for calculation of *f*, which is defined as the mass fraction of product at that particular time and temperature (500 to 950 ^{o}C). The graph was constructed as a percentage of mass by the temperature in Celsius. As aforementioned, the terms *f* and *df / dt* can be derived directly from the TG data and their derivative. With this, the graphs of *f* by temperature and derivative of *f* by temperature were constructed, as can be seen in Figure 1(b).

3.2 Genetic algorithm and Particle Swarm Optimization comparison

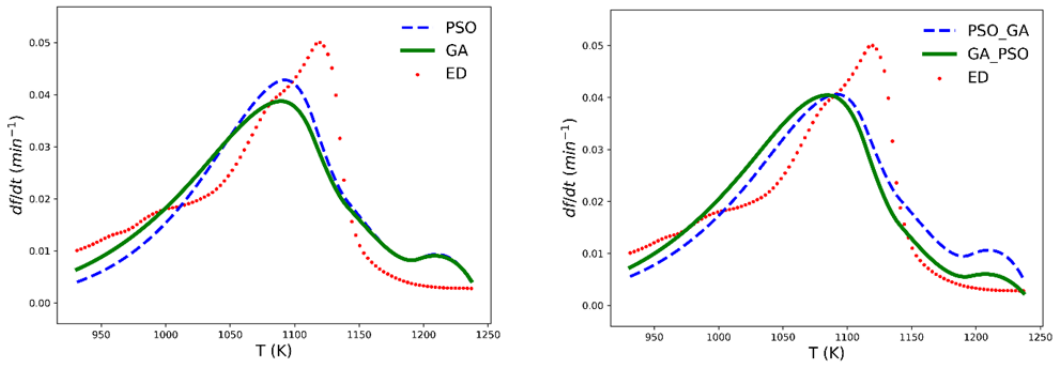
Initially, a data treatment with Python programming language was performed to reduce the number of floating points that make the curve noisy and turn difficult to obtain the derivatives. The final data set, considered in the estimation procedures, is made of 100 experimental points. Thus, with the values of *f* and *df / dt*, through a MATLAB programming, genetic algorithm was used to estimate kinetic parameters of lignin decomposition. The genetic algorithm used a population of 5000 individuals with 7500 generations, crossover rate in 70%, migration rate in 40% and migration interval in 10 individuals. The values for the order of reaction, pre-exponential factor and activation energy found were 0.9546 (considered first order reaction), 91.95 x 10^4 s^{-1} and 13.54 x 10^4 J.mol^{-1} respectively.
Then, a particle swarm optimization (*PSO*) model was also run for estimation of the kinetic parameters of lignin decomposition. The Python programming language was used to run the proposed model, 250 particles were used and 350 iterations were performed with a numerical tolerance of 0.0001 for the objective function. For this case, the result obtained for the reaction order was 1.1073, for the pre-exponential factor was 48.19 x 10^6 s^{-1} and for the activation energy of 17.21 x 10^4 J.mol^{-1}.
With the values of order of reaction, two new estimation procedures were done. The first one, named *GA_PSO*, fixed the order value of reaction, *n*, with the value found by *PSO* method, and estimated through *GA* the activation energy and the pre-exponential factor. The second procedure, named *PSO_GA*, used *PSO* method to estimate the same two parameters (*Ea* and k_0) with the value of *n* fixed by the one found by *GA*. *GA_PSO* method estimated for k_0 and *Ea* the values of 95.83 x 10^4 s^{-1} and 13.71 x 10^4 J.mol^{-1} respectively.

However, for the *PSO_GA* method, the estimated values for the pre-exponential factor and activation energy were 30.53 x 10^5 s^{-1} and 14.58 x 10^4 J.mol^{-1} respectively. All estimated parameters can be seen in Table 1.

Table 1: Values of kinetic parameters found for each optimization model (k_0 in s^{-1} and Ea in J.mol^{-1}).

GA		PSO		GA_PSO		PSO_GA	
k_0	91.95 x10^4	k_0	48.19 x 10^6	k_0	95.83 x 10^4	k_0	30.53 x 10^5
Ea	13.54 x 10^4	Ea	17.21 x 10^4	Ea	13.71 x 10^4	Ea	14.58 x 10^4
n	0.9546	n	1.10734	n	1.10734	n	0.9546

Figure 2 shows how the data obtained through the optimization models, *GA* and *PSO*, approached the experimental data available. The performance of the kinetic models presented was evaluated through the coefficient of determination (R2) for each variable and the sum of quadratic error (SSE), using minimization of the objective function to achieve the smallest possible error as shown in Table 2.



(a) *(b)*

Figure 2: Experimental and estimated data for: (a)GA and PSO models, (b) GA_PSO and PSO_GA models.

Table 2: Comparison between R2 values and error index values (SSE) for the models studied.

GA		PSO		GA_PSO		PSO_GA	
R^2	0.763351	R^2	0.771488821	R^2	0.70733146	R^2	0.771012599
SSE	0.00454332	SSE	0.0045903	SSE	0.0046289	SSE	0.0047698

According to Riegel et al. (2008), the activation energy value found in the literature for the pyrolysis of lignocellulosic compounds is in the range of 15 x 10^4 – 20 x 10^4 kJ.mol^{-1}, indicating that the values found for all the models are in accordance with literature data.

Some works using thermogravimetry to obtain kinetic parameters have already been produced, but as far we have knowledge, few studies were found using genetic algorithms and particle swarm for estimation of kinetic parameters of thermal degradation of lignocellulosic biomass. These methods can be very useful if the objective is to estimate parameters with greater accuracy and error minimization, besides allowing comparisons between the models and verification of the accuracy of the results found.

As an example of proposed work to search for kinetic parameters using thermal decomposition, Rueda-Ordóñez (2018) had as objective to study the kinetics of sugarcane straw thermal decomposition by non-isothermal thermogravimetry. Kinetics of the system was analyzed by three consecutive reaction schemes, obtaining activation energies of 130, 200 and 56 kJ.mol^{-1}. The consecutive reaction scheme allowed an excellent agreement between experimental and model data, providing an adjustment quality similar to that obtained with the independent parallel reaction scheme. Therefore, among many techniques for parameter estimation, use of GA and PSO is of great help in the search for kinetic parameters from thermogravimetry.

4. Conclusions

The application of *GA* and *PSO* to estimate the kinetic parameters of green coconut fiber lignin breaking using two different estimation methods was considered in the current work. Through the kinetic equation proposed by Speyer, thermogravimetric data were found and the results obtained by the different optimization models

were compared with the values published in the literature. This procedure confirmed that both optimization methods are promising techniques from the point of view of estimating and correlating predicted and actual data. Posterior studies must be performed to improve the kinetic model equations and to better understand the catalysis involved in the process under investigation. Use of GA and PSO as global search methods was satisfactory but the kinetic model considered herein might not be the best one for this system.

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