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Application of Artificial Neural Networks for Identification of Catalysts Used in Thermogravimetry Lignocellulosic Biomass

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In recent decades there has been a growing need to develop efficient processes in economic and energetic terms for the sustainable production of fuels and chemical products. In this context, it is important to understand the thermal degradation behaviour of different biomass in an inert atmosphere to investigate the breakdown of polymer chains into smaller chains, which could be converted into new products. Catalysts can be used in these breaking processes, since they generate good effects in accelerating the degradation of organic structures and with this increases the yield of bio-oil production. In this work the fiber of crushed and sifted green coconut shell, submitted to the thermogravimetry analysis (TG), was used as biomass. Types of a catalyst were incorporated into the biomass, based on cobalt ferrite, Fe_2CoO_4. The analysis revealed distinct profiles of mass loss of the green coconut fiber with and without the catalysts. To detect possible instrumentation and/or preparation failures of the experimental samples, models were developed with the help of artificial intelligence. The strategy chosen was the use of artificial neural networks (ANN) feedforward because it is a set of mathematical procedures that seek an intelligent way (inspired in by the network of biological neurons) to manage and analyze systems. The RNA model was developed from the import of the TG data to the MATLAB R2017a software, identifying data inputs/outputs. The inputs were loss of mass (mg), derived from the loss of mass and temperature (°C). The training algorithms were: Levenberg-Marquardt (*trainlm*) and Levenberg-Marquardt with Bayesian regularization (*trainbr*) that avoids over-adjustment. The activation functions used were the hyperbolic tangent (*tansig*) and logistic (*logsig*) to activate the intermediate layers of the model. The results of the model involving mass loss information were satisfactory to identify the type of catalyst with a topology of 3-6-4-1. The evaluation of the SSE error rates of 0.882 and the MSE of 6.85E-04, confirmed the good fit of the neural network, since the values are close to zero. Thus, the model can be used in conjunction with TG analysis, preventing possible measurement failures.

1. Introduction

Reducing conventional resources, environmental regulations and increased fuel demand has increased the need to find alternative energy sources to fossil fuels. Renewable plant materials are one promising alternatives for fuels and chemicals production (Strubinger, 2017). The growth of the consumption of green coconut water and the natural tendency for its industrialization have caused difficulties of final disposal of the residue generated, that is, the fruit peels (Rosa et al., 2001). A viable alternative to this reuse is the production of bio-oil through pyrolysis or hydrothermal pyrolysis. In this process the matter decomposes in an inert atmosphere generating gases, liquids and solid residue (Carrijo et al., 2002). After cooling and condensation of the vapors, a dark brown liquid is formed, which is called a bio-oil. The great majority of lignocellulosic biomass is basically composed of three main components consisting of about 30-50 % cellulose, 15-35 % hemicellulose and 10-20 % lignin (Schena, 2015). In the present study, the thermal degradation of lignocellulosic materials showed the following trend: moisture, hemicellulose, cellulose and finally lignin degradation confirming that found by Chumpoo and Prasassarakich (2010).

For these biomass to be well utilized, it is extremely important to know their thermal behavior during the thermoconversion process. The knowledge of such process is fundamental for the monitoring of the processing conditions of these materials (Tomczak et al., 2007). The techniques of thermogravimetric analysis (TGA), make it 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 the lignocellulosic components (Barbosa, 2006). Thermogravimetric tests using biomass mixtures and catalysts with different calcination times in the final stage of preparation are of fundamental importance in order to find a catalyst that can generate a real catalytic effect, accelerating the thermal degradation of the polymeric structures present, and which can be used later on a Hydrothermal liquefaction (HTL) route.
In order to help researchers make decisions faster and prevent possible failures or variations in experimental conditions, intelligent models can be used. Artificial neural network (ANN) can be an example of intelligent model. ANN is a mathematical system that simulated biological neural networks and was often described as a massively interconnected network structure consisting of many simple processing elements (neurons) with the ability to perform parallel computation for data processing (Agatonovic-Kustrin et al., 1998) and also as tools for optimisation (Baş and Boyacı, 2007). ANN is capable of handling multiple independent and dependent variables simultaneously and to do this prior knowledge on the functional relationship did not need to be known. Each neuron received information through input connections, processed the information and produced the output, which was distributed through output connections. A neural network in its basic form was usually composed of several layers of neurons, there being one input layer, one output layer and at least one hidden layer. A growing literature within the field of chemical engineering describing the use of artificial neural networks (ANN) has evolved for a diverse range of engineering applications such as fault detection, signal processing, process modelling, and control, as can be seen in Ahmad et al. (2017)
In this work we intend to use temperature and mass loss data in the construction of a neural network in order to predict the catalyst used that can increase the yield in the thermogravimetric processes of lignocellulosic biomass, in the sense of facilitating the breaking of the organic chains.

2. Material and Methods

2.1 Thermogravimetric Analysis

The thermogravimetric analysis was performed in a TG Netzsch STA 449 F3 Jupter, 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 the beginning of the analysis, a bath of stabilizing the temperature of the balance must be carried out in the equipment with the minimum duration of 3 hours so that the temperature stabilizes just above the ambient temperature. After the temperature is stabilized, the procedures for conducting the analysis are started. The empty crucible is added for reference weighing and the nitrogen cylinder and valves are opened. Three purges with the nitrogen will be made so that all the oxygen inside the apparatus is removed before the tests. For each analysis, a blank with the empty crucible with the same duration of the sample analysis, 60 minutes, and a heating rate of 20 °C/min shall be performed. In the equipment control software, the analysis conditions, the initial heating temperature, the final temperature and the heating rate are defined. Thus, the analysis begins, first with the empty crucible and then, following the same procedure, with the sample to be analysed.

2.2 Acquisition of thermogravimetry data

Three types of catalysts were used, calcined cobalt ferrite at 3h, 6h and 9h in oven at 1000 °C. After the thermogravimetry tests, for each type of catalyst, data of temperature, mass loss and derivative of mass loss were taken from the TG software and transferred to an excel sheet. These data were used for testing and training artificial neural networks. The temperature, the mass loss and the mass loss derivative were used as inputs and the type of catalyst as output.

2.3 Artificial neural network architecture

Artificial Neural Networks (ANN) technology offers an alternative method for the generation of process models. The advantages of using Artificial Neural Networks to represent a system are its ability to perform a nonlinear mapping between inputs and outputs and the necessity of requiring minimal prior knowledge of the system (Kumar, 2015). The objective of the development of a feedforward neural network model was to predict the type of catalyst used in the study of the thermogravimetry of the green coconut fiber at various temperatures and time periods. Thus, networks trained by the optimization algorithm Levenberg-Marquardt and Levenberg-Marquardt with Bayesian regularization were developed and also the use of activation functions *logsig* and *tansig*. The neural networks were used with two hidden layers. The whole simulation was performed with MATLAB R2017a. To determine the number of neurons in the hidden layer, different networks were trained

with training data and tested with the test data. The performance of the ANN was evaluated by the error indexes sum squared error (SSE), as shown Equation 1, and mean squared error (MSE), as shown Equation 2. In addition, other aspects such as value of Coefficient of Determination (R2), as shown Equation 3, and number of effective parameters were evaluated.

$$SSE = \sum_{i=1}^{n}(Y_{observed} - Y_{predicted}) \quad (1)$$

$$MSE = \frac{1}{n}\sum_{i=1}^{n}(Y_{observed} - Y_{predicted}) \quad (2)$$

$$R^2 = 1 - \frac{\sum_{i=1}^{n}(Y_{observed} - Y_{predicted})^2}{\sum_{i=1}^{n}(Y_{observed} - Y_{mean})^2} \quad (3)$$

3. Results and discussion

3.1 Qualitative analysis

The thermoanalytical tests were carried out in a laboratory of the Department of Chemical and Materials Engineering (DEQM/PUC-Rio). Calibrations and daily checks of the thermobalance were required before the thermogravimetric tests. A blank was made with the empty crucible for each condition evaluated. The thermogravimetric analysis of the samples (fiber plus catalyst) with a mass fraction of Fe_2Co_4 equal to 50 % were performed. These experiments were also carried out in an inert atmosphere of nitrogen with a heating rate of 20 ºC/min, between 20 and 1000 ºC. But the catalysts were varied, differentiated by the calcination time at which they were produced. Calcination times of 3 h, 6 h and 9 h all were studied at a temperature of 1000ºC.

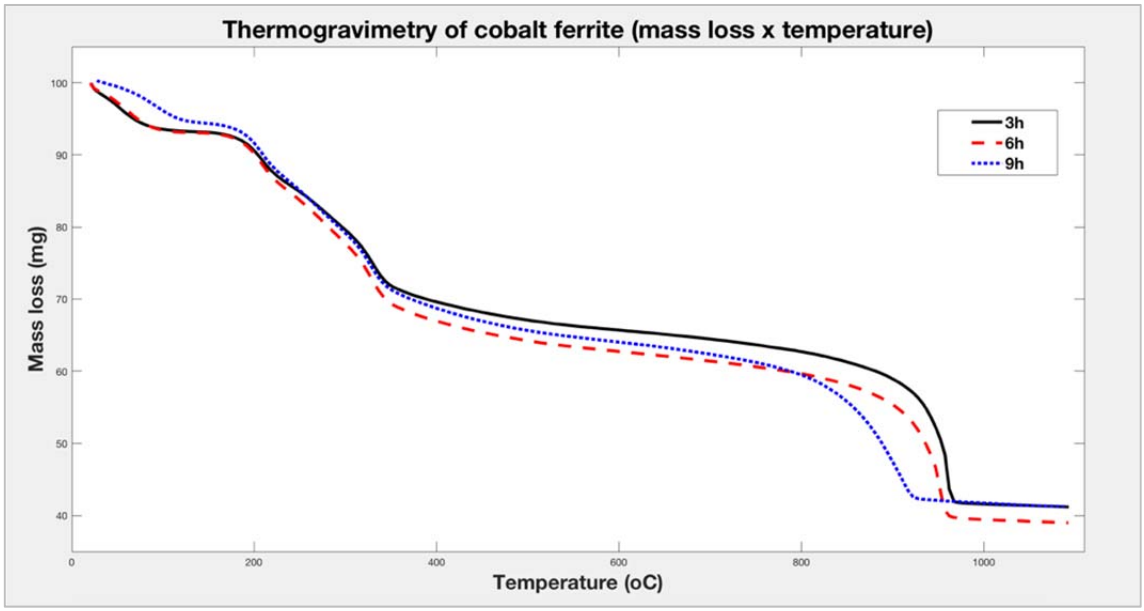

Figure 1: Thermogravimetric characterization of the green coconut fiber plus the catalyst (50/50) in an inert atmosphere of N2 for 3 h, 6 h and 9 h, calcination at 1000 ºC.

On Figure 1 the TG signals of mixtures (50% w/w) of the catalyst calcinated at different times at 1000 ^{o}C (3, 6 and 9h) are present, suggesting for the sample with the oxide calcinated for 9 h the final degradation of liginin starts at a lower temperature (from 750 ^{o}C), suggesting a superior catalytic activity. Therefore, the catalytic activity should be associated only to the process, whereas lignin is fully converted to volatile molecules. In this sense it can be said that the presence of Fe2CoO4 crystals activates another mechanism for the lignin degradation, where no fixed carbon results. It is noticeable from the data of Figure 1, that through enhancing the calcination time from 3 to 9h, there was a gain regarding the observed catalytic activity.
The sample produced with mixing under agate mortar crucible, promoting a better contact between catalyst and biomass, and stimulating the desired catalytic effect.

Arumugasamy et al. (2015) used neural networks to study the effects of temperature and reaction time on the biochar yield in a thermogravimetry study. It was noticed that with the increase of the temperature the coal yield decreased as the mass loss was higher, due to the initial amount of volatiles that were released. Then a lower temperature was used for a better biochar yield. An ANN model was then developed with input experimental data (reaction time and temperature) and output data (mass loss). Thus, the loss of mass predicted by the network versus the experimental output were plated and a 2-20-1 network showed the best yield.

3.2 ANN training and testing

The experimental data used in this study were collected from thermogravimetric analysis. The programming was then divided into two sections: training, which used about 50% of the data and the neural network test, which used the rest of the data provided. A total of 5163 data sets were used, where 2583 were used for training and 2580 were used for the tests. Table 1 displays some ANN modelling results for each studied case, with different amounts of neurons in the first and second hidden layers, activation functions and training algorithms. Several scenarios of topologies were performed, but some are shown in the table. The R^2, SSE and MSE values were analyzed for the selection of the best model. This ANN, in addition to presenting a better correlation coefficient, presents SSE and MSE error indexes satisfactory.

Table 1: Some ANN topologies used in the model proposed in the TG process of three types of cobalt ferrite catalysts, besides the activation function, training algorithm and the adjustment values obtained for each case

Neurons (hidden layer 1)	Activation Function	Neurons (hidden layer 2)	Activation Function	Training algorit	R2	SSE	MSE
6	tansig	4	tansig	trainlm	0.25687	24.40	0.00945
6	tansig	4	logsig	trainlm	0.40123	67.00	0.02594
6	logsig	4	tansig	trainbr	0.59579	18.00	0.00697
6	**logsig**	**4**	**logsig**	**trainbr**	**0.99976**	**0.88**	**0.00034**
5	tansig	4	tansig	trainlm	0.51852	29.70	0.01150
5	tansig	4	logsig	trainlm	0.49089	21.30	0.00825
5	logsig	4	tansig	trainbr	0.00680	26.60	0.01030
5	logsig	4	logsig	trainbr	0.07000	26.50	0.01026
4	tansig	4	tansig	trainlm	0.53042	27.20	0.01053
4	tansig	4	logsig	trainlm	0.25754	29.40	0.01138
4	logsig	4	tansig	trainbr	0.34496	13.50	0.00523
4	logsig	4	logsig	trainbr	0.53905	21.10	0.00817

The model concerns the prediction of the catalyst used in different calcination times. ANN models were studied using 3 neurons in the input layer, corresponding to temperature, mass loss and mass loss derivative value. The topology studied in this step comprised 6 neurons in the first hidden layer, 4 neurons in the second hidden layer and 1 neuron in the output layer. The activation functions applied to the neurons of the first hidden layer, the second hidden layer and the output layer, were *logsig*, *logsig* and *purelin*, respectively. The training algorithm applies was the *trainlm*.

Figure 2(a) shows the topology used, as well as the training algorithm and the SSE error index obtained. Figure 2(b) shows the R^2 values for the ANN topologies studied for the predictor model of the catalyst used and how the predicted data behave in relation to the observed data of each sample for the test step. The topology presented R^2 equal to 0.9974, an SSE performance value of 0.882 and MSE of 0,000341, with a total of 57 effective parameters.

Working with neural networks opens up a range of possibilities for parameter matching. In this study we could still work with other configurations for topology, changing, for example, the training algorithm and the function of activation of the output layer. But the objective was reached with the previous simulations, because a relatively simple and robust topology was obtained. With this simulation it was realized that the model is suitable to be used in conjunction with TG tests, to predict the type of catalyst to be used, avoiding possible

measurement failures, identifying with more than 99% safe the experimental conditions used during the process. The model predicts satisfactorily the experimental data, allows faster decision making about the process or the development of more advanced strategies in the system

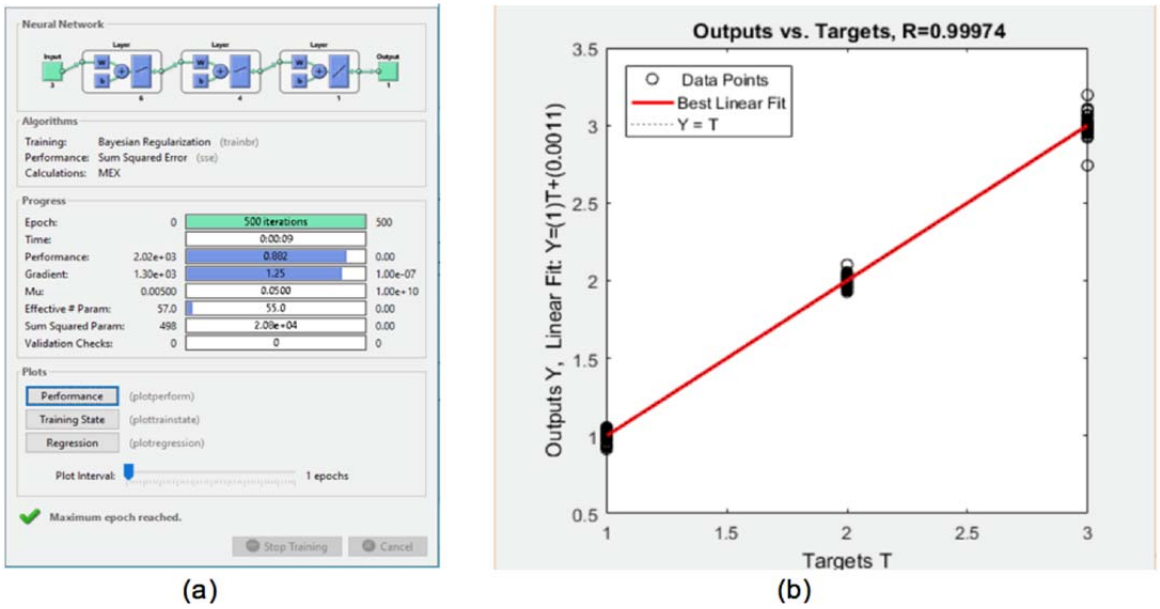

Figure 2: (a) Image obtained from MATLAB R2017a software that shows the ANN topology, as well as the training algorithm and the SSE error index obtained during the training stage. (b) Regression diagram for the ANN test stages used to predict the type of catalyst used in thermogravimetry analysis.

4. Conclusions

The data extracted from the thermogravimetric analysis were implemented for training and testing of the artificial neural network. For the proposed model, the chosen topology of ANN is considered adequate, presenting satisfactory performance confirmed by the observed values of SSE, MSE and R2. The model involving mass loss information were adequate to identify the type of catalyst with a topology of 3-6-4-1. Thus, the model can be used in conjunction with TG analysis, avoiding possible measurement failures, identifying with 99.87% safety the experimental conditions used during the process.

In this work the cobalt ferrite was used as catalyst, but for other studies could be done with other oxides that can have this catalytic effect in lignocellulosic biomass. One suggestion for a possible future work would be the use of thermogravimetric input data, such as temperature and process time for the construction of an artificial neural network in order to predict the loss of mass of the green coconut fiber in these thermogravimetry processes.

Acknowledgements

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