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Neural Network Modeling for Prediction of Oxidized Lignin Content by Delignification of Sugarcane Bagasse Through Hydrogen Peroxide with RAMAN Spectroscopy Data

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Sugarcane bagasse has great capacity for conversion into new products, resulting from a more noble application of the residue. Hydrogen peroxide delignification is an alternative to conventional processes that provide energy and environmental demands for a cleaner process in terms of product generation. In this study, the experiments, performed in duplicate, consist of batchings with combinations of temperature values (25, 35 and 45 ° C) and hydrogen peroxide concentration values (1,5, 3,0, 4,5 and 7 , 5% v / v). The performance of the delignification process was evaluated by the RAMAN analytical spectroscopy technique, by verifying the oxidized lignin content. It was possible to collect a large amount of information on the samples submitted to each established condition. Thus, it was advantageous to use the artificial neural networks (ANN) as a method of predicting information for the lignin / cellulose ratio, since the ANNs are fast implementation and high performance learning methodologies, presenting high recognition and association of patterns. Pretreatment models with hydrogen peroxide were proposed for the prediction of oxidized lignin content. An ANN topology was selected and the performance was evaluated by the correlation coefficient (R^2) and error indexes (MSE and SSE). The model developed from the neural network was satisfactory, since the R^2 value was 0.92 and the error index values were 0.277 for SSE and 0.0046 for MSE.

1. Introduction

The lignocellulosic material is composed of three main fractions, represented by cellulose, lignin and hemicellulose. The fractions are fixed to each other. In order to make the lignocellulosic fractions raw material for other processes of transformation and generate products with greater applicability and economic value, such as cellulosic ethanol (Lopes et al., 2017), lactic acid (Grewal et al., 2018) and polymers, blends and lignin-based compounds (Naseem et al., 2016) require a fiber delignification step, which will make the fractions available for later steps in the synthesis.
Delignification is a critical step in promoting the separation of lignin from lignocellulosic biomass. If executed successfully, it ensures the good performance of the later stages. The pre-treatment of biomass with hydrogen peroxide, as recently confirmed (Santos-Rocha et al., 2017), appears as an alternative to classical processes, which require reagents with great potential for pollution and generate a large amount of intermediate residues.
Lopes et al. (2017) shows the use of sugarcane as a good source of biomass because several countries generate large volume of bagasse as a by-product of production. According to data from UNICA (2016), sugar cane is an agricultural crop of great importance for the Brazilian sugar and alcohol production industry. To evaluate the delignification performance of cane bagasse, analytical methods such as Raman spectroscopy (FT-Raman) and Fourier transform infrared spectroscopy (FTIR) can be applied to identify organic materials such as lignin and cellulose.

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Raman spectroscopy is a qualitative analysis technique that allows precise investigations and is therefore widely used for the characterization of carbonaceous materials by means of the identification of the existing types of chemical bond and by information on the degree of disorder of the crystalline lattice. The technique uses a monochromatic light source that reaches an object and is scattered, this dispersion is related to the electronic states and is characteristic of each material. It is this energy difference that is measured in the analysis and for this work it is possible to evaluate the efficiency of delignification with sugarcane bagasse with hydrogen peroxide.

In addition to identifying a composite of the samples, Raman spectroscopy allows quantifying these results through mathematical manipulations. In this same context, Miyafuji et al. (2017) uses Raman spectroscopy to quantify the lignin contents of various wood species through the calibration curve from the standard sample. Agarwal et al. (2003) used Raman spectroscopy to determine lignin concentration in bleached and partially bleached pine pulps and thus to develop a new method for measuring Kappa number.

Most of the engineering processes present strong non-linearities, making it difficult to obtain phenomenological models. The volume of data obtained and the long time required by the experimental and analytical methods point to the application of artificial neural networks (ANNs) as support for the development of engineering processes.

ANN is a fast, high-performance implementation technique for learning arbitrary non-linear mappings with high pattern recognition and associative capability that enables complex problem solving and provides security resolution through predictive and behavioural data of the technological process. In this context, Di Domenico et al. (2017) use ANN to optimize the process of convective drying of foods and reduce energy consumption. However, for the success of modeling and process control through a generalized model it is necessary to know strongly the main variables of the process and a database of good quality for the desired domain, since the parameters of the network will be adapted by the data set.

2. Materials and Methods

2.1 Preparation of biomass

Sugarcane bagasse obtained through free trade fairs in the city of Rio de Janeiro was washed with running water and subsequently dried at 45º C for 48 h at room temperature as confirmed (Rabelo et al., 2014). Then, the lignocellulosic biomass was particularized in an electric crusher and reserved in a place for later use.

2.2 Process of sugarcane bagasse delignification with Hydrogen Peroxide

Aliquots of 1g the treated lignocellulosic biomass were added to the 250 mL Erlenmeyer followed by 25 mL of 30% hydrogen peroxide solution in alkaline medium at different concentrations. The reactors were placed in Shaker with constant stirring for 1 hour at a set temperature.

For the delignification reaction of the lignocellulosic biomass, the conditioning temperature and the concentration of hydrogen peroxide (v/v) are important variables that influence the process, so, in order to facilitate the process, these variables were evaluated by means of experiments. The experiments aimed at combining values of temperature and concentration of hydrogen peroxide to condition the biomass delignification reactor. The different concentrations of hydrogen peroxide used in the experiments were: 1.5% (v/v), 3.0% (v/v), 4.5% (v/v), and 7.5% (v/v). Each batch of tests was performed with three conditioning temperatures: 25ºC, 35ºC and 45 ºC. Rabelo et al., (2014) has reported that the best pH adjustment for the tests is 11.5, carried out with 5M potassium hydroxide.

2.3 Analysis in Raman spectroscopy

The lignin samples obtained through the different process conditions of lignocellulosic biomass delignification were submitted to qualitative analysis with Raman spectroscopy system. However, prior preparation of these lignin samples fixed under a silicon foil and with the addition of a thin top layer of polyethylene glycol (PEG) was required. This is due to the high characteristic fluorescence of the compound investigated, attributed to the presence of aromatic rings in its chain. Raman spectra were obtained through a Witec® alpha300 SR Confocal Raman Microscope. The laser used as excitation source was Nd: YAG with wavelength 532nm and maximum power of 100 mW. The instrument was operated with 50x lenses. The spectrometer was operated with a diffraction grating of 600 slots / mm. The spectra between 1300 cm^{-1} and 1700 cm^{-1} were corrected for the background contribution and intensities of the bands at 1600 cm^{-1} and 1378 cm^{-1} were calculated with the baseline method. Peak-height and band-area were calculated for each band by Guassian peak functions. All samples were analyzed at least twice so that data with mean values could be used for ANN construction.

2.4 Artificial neural network architecture

In this study, MATLAB R2016b was used to predict was used to perform an ANN topology selected to predict the conditions of the delignification process through the intensity values provided by Raman spectroscopy. The activation functions for the hidden layer neurons tested were tansig and logsig and the training algorithms were trainbr and trainlm.

To evaluate the performance of the ANN, the error indexes SSE (Sum of Squared Errors) and MSE (Mean Squared Error) were observed. In addition, other aspects such as value of Coefficient of Determination (R^2) and number of network parameters were evaluated.

3. Results and Discussion

3.1 Raman analyses

With the treated Raman spectra, safe measures of lignin content can be realized. Agarwal et al., (2003) has reported the main lignin feature is seen at 1600 cm^{-1} region. Most other bands are attributable to cellulose confirmed (Ji et al., 2013). The 1378 cm^{-1} region was chosen to be attributed to cellulose because it was expressive in the generated Raman spectra. Region`s intensity was calculated by peak-heigh and band-area. To measure the efficiency of each of the pretreatment conditions tested, a ratio was calculated between the intensity referring to 1600 cm^{-1} and the intensity referring to 1378 cm^{-1} as shown in Table 1.

Table 1: Raman intensity data and oxidized lignin ratio for test conditions in lignin (1600 cm-^{1}) and cellulose (1378 cm^{-1}) regions.

T (ºC)	Concentration H_2O_2 % (v/v)	intensity 1600cm^{-1} (lignin)	intensity 1378 cm^{-1} (cellulose)	1600 cm^{-1} intensity / 1378 cm^{-1} intensity
25	1.5	0.5889	0.6009	0.9801
	3.0	0.7988	0.8224	0.9714
	4.5	0.7831	0.7698	1.0173
	7.5	0.6946	0.6982	0.9950
35	1.5	0.1281	0.1245	1.0282
	3.0	0.2705	0.2604	1.0385
	4.5	0.4623	0.4440	1.0414
	7.5	0.2075	0.1987	1.0442
45	1.5	0.6654	0.2851	2.3337
	3.0	0.0107	0.0095	1.1308
	4.5	0.6134	0.5853	1.0480
	7.5	0.7650	0.7701	0.9934

The lignin/cellulose ratio expressed the content of oxidized lignin and allows comparing the performance between the tests equivalently. Among the values of the lignin / cellulose ratio, 2.3337 is relevant for the condition of 45ºC for temperature and 1.5% (v/v) for hydrogen peroxide concentration, indicating that this is the most suitable condition for the process.

Figure 1 shows the Raman spectra of sugarcane bagasse after pretreatment for the test conditions at 35 ° C and 45 ° C for all tested hydrogen peroxide concentrations (1.5, 3.0, 4.5, 7.5% v / v). These are the process conditions tested that presented the best values for the lignin / cellulose ratio, which expresses the oxidized lignin content.

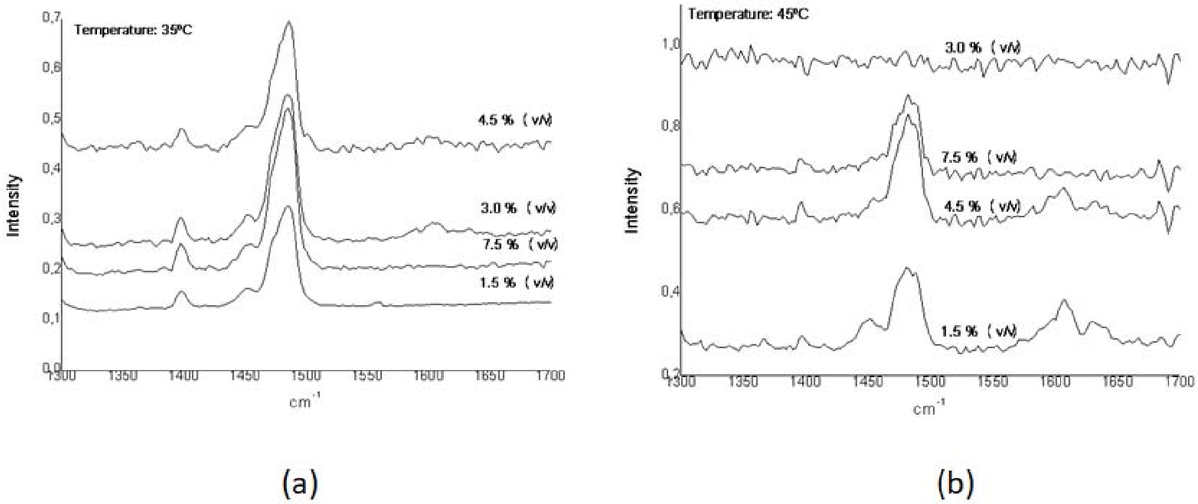

Figure 1: FT-Raman spectra of sugarcane bagasse after pretreatment with hydrogen peroxide in the condition of 35 ºC for the four concentrations evaluated (a) and 45ºC for the four concentrations evaluated (b).

3.2 Artificial neural network

The Raman spectroscopy analysis performed on the samples generated a database with 80 arrays, where 75% were used for ANN training and 25% for testing.

The variables used as neurons in the input layer were the temperature and the concentration of hydrogen peroxide defined in each experimental condition. The variable used as neuron in the output layer was the oxidized lignin content. To avoid overfitting in the ANN, the maximum number that could be used in the hidden layer was 14 neurons.

Table 2 shows some ANN topologies developed in this work.

Table 2: Some ANN topologies used in the model proposed in the process of delignification of sugarcane bagasse with hydrogen peroxide, besides the activation function, training algorithm and the adjustment values obtained for each case.

Number of neurons in the hidden layer	Activation Function	Training Algorithm	R^2	SSE	MSE
6	Tansig	trainlm	0.930	0.650	0.0108
4	tansig	trainlm	0.888	1.230	0.0205
6	logsig	trainlm	0.920	0.277	0.0046
6	logsig	trainbr	0.896	1.540	0.0257
4	logsig	trainlm	0.879	0.314	0.0052
6	tansig	trainbr	0.905	1.650	0.0275
8	logsig	trainlm	0.932	0.667	0.0111

The selected ANN has only 6 neurons in the hidden layer, presenting 25 effective parameters. ANN topologies with lower number of neurons in the hidden layer tended to present higher values for error indices or lower correlation coefficient. Topologies with higher number of neurons in the intermediate layer did not show significant improvement in the value of the correlation coefficient and error indexes, and its use it is not recommended, given the increase in the number of effective parameters.

Similar applications of artificial neural networks (ANN) can be found in Santos et al., (2017), Valim et al., (2017), Villarrubia et al., (2018) and Pappu et al., (2016).

Figure 2 shows the R^2 values of 0.920 for the testing stage obtained for the applied ANN topology. This ANN presented an SSE performance value of 0.277 and MSE of 0.0046.

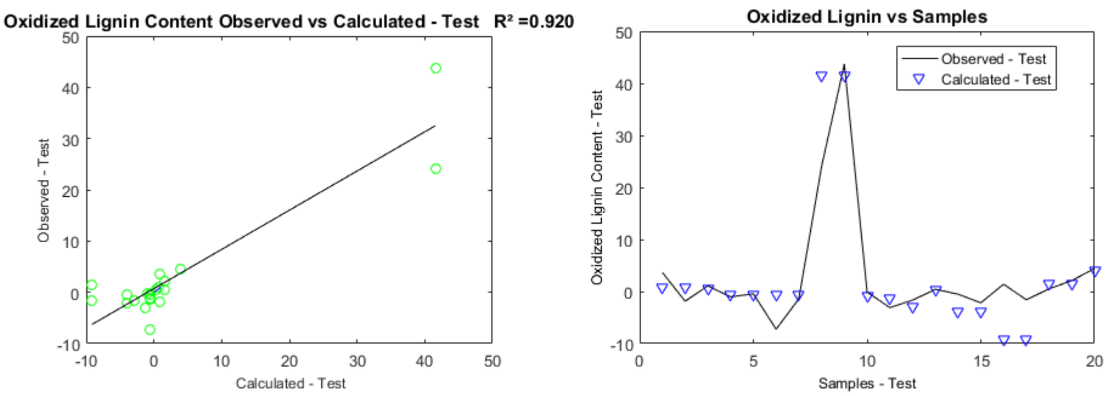

Figure 2: Regression diagram and representation of the behavior of the predicted data in relation to the observed data of each sample, for the ANN test stage used to predict the percentage of oxidized lignin of the sugarcane bagasse after the pre-treatment with hydrogen peroxide.

4. Conclusions

In order to evaluate two important variables involved in the process of delignification, effect of process temperature and concentration of hydrogen peroxide in the reaction medium, a qualitative identification technique was combined with a computational tool. Thus, an intelligent mathematical model was developed, which made it possible to indicate the optimum conditions of the lignocellulosic biomass delignification process. The FT-Raman approach can be used to obtain stable measurements of oxidized lignin by pretreatment with hydrogen peroxide. Through this method, the process condition that stands out most is temperature of 45ºC and concentration of hydrogen peroxide the value of 1.5% (v/v). The difficulty of the method is the high characteristic fluorescence of the lignocellulosic fraction, heterogeneity of the samples and the necessity of a high volume of experimental data. In this way the mathematical model developed through the ANN applications is an important alternative tool to experimental tests. It allows detecting the values of the lignin/cellulose ratio for different experimental conditions. Data extracted from the analyses were essential for the ANN training and testing. Regarding the predictions, the proposed ANN topology is considered adequate, since it presented satisfactory performance, confirmed by SSE, MSE and R^2 values. The use of the combined technology was motivated by the volume of data provided by the FT-Raman qualitative analysis, which developed a mathematical modeling that identified two of the most indicated process conditions in terms of performance. This work pioneered the use of combined techniques and supports later stages of qualitative analysis for the development of an optimal process that can be applied on an industrial scale.

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