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Characterization of polyacrylonitrile thermal stabilization process for carbon fiber production using intelligent algorithms

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ABSTRACT

Composite materials have widened their application range in recent years. The polymeric composite reinforced with carbon fibers can be described as a high-performance structural material which merges two important features: low weight and mechanical stability. Carbon fiber production which uses polyacrylonitrile as precursor is composed of many stages such as polymerization, spinning, thermal stabilization, carbonization, and surface treatment. Thermal stabilization is the critical stage of this production process, during which aromatic rings are generated, and therefore the main factor for the carbon fiber structure definition and thus for this material quality. A thermal stabilization model using intelligent algorithms was developed aiming a possible optimization of the production process and consequent cost reduction. This work was based on real experimental data obtained from a composite material production pilot plant. A qualitative analysis was initially performed using Self-Organizing Maps trained with variables of fiber production reagents and process. Thereafter, a supervised training with feedforward backpropagation neural network was used for a quantitative analysis. Based on this quantitative analysis, the carbon fiber thermal stabilization process was simulated, obtaining 2.98% and 2.48% mean errors relative to experimental results of Volumetric Density and FTIR Conversion index, respectively.

1. Introduction

Carbon fibers are usually defined as a set of microfilaments which comprises a cable. These fibers, when used together with polymers, result in a compound usually called polymeric composite reinforced with carbon fiber, which exhibits excellent physicochemical properties such as chemical resistance and low density. These characteristics are important to low weight applications. Besides these, they present exceptional chemical and mechanical properties such as high tensile strength, elasticity module and chemical resistance [1].

The low weight and mechanical stability combination is an ideal feature for a material intended to high performance applications. These properties are mainly useful in low weight designs which aim energy efficiency and environmental sustainability and are currently applied in aeronautic, nuclear, civil, naval, oil and gas, automotive, biomedical, and sportive areas [2]. Considering this wide application, carbon fiber has attracted worldwide attention as a promising material. Global demand is predicted to significantly increase in coming years [3].

Carbon fibers can be obtained by several precursors such as pitch, rayon and polyacrylonitrile (PAN). The polyacrylonitrile acrylic fiber is the main precursor that is commonly used due its interconnected carbon chain with rigid structure, which is insoluble and strongly resistant [4].

The carbon fiber production based on polyacrylonitrile has different stages: polymerization, spinning, thermal stabilization, carbonization, and surface treatment [5]. The process is based on the increase of carbon-content structure, molecular orientation, incorporation, and elimination of oxygen atoms through gaseous products as can be seen in Fig. 1 [6].

This work was mainly based in the study of the thermal stabilization obtained in air atmosphere varying between 200 and 300 °C, transforming the fiber into ladder structured and consequently into a non-flammable material. This stage involves a combination of reactions that occur simultaneously: oxidation, dehydrogenation, and cyclization [3].

The stabilization is the harshest production stage on account of being the most energy and time consuming. This stage is comprised of the main chemical reactions that are the major causes of fiber orientation and, therefore, essential for carbon fiber properties. Furthermore, its heating rate and temperature control is fundamental to avoid rupture or overheating [6].

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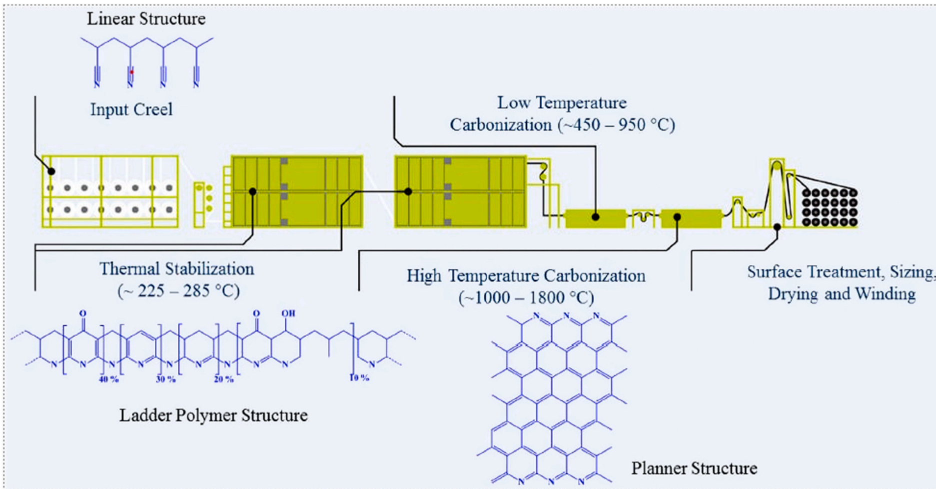

Fig. 1. Scheme of a carbon fiber conversion unit from Carbon Nexus, Australia, published by Nunna et al. [6].

The optimization of process complexity should reduce the production costs as well as improve the fiber quality. A tool to obtain process optimization using computer simulation was recently published [7–9]. In these works, the production process is emulated minimizing energy consumption based on prediction of product quality.

The stability process is influenced both by fiber chemical structure and process conditions. The chemical structure is related to the comonomers composition in the polyacrylonitrile polymer. These comonomers are reaction catalysts and are also responsible to reduce the polyacrylonitrile homopolymer defects. The comonomers also increase the distance of the chains and reduce the polymer density, raising the oxygen diffusion into the fiber [10,11].

Stability process conditions are mainly influenced by some parameters as: heating rate, oven temperatures, recirculating air speed, exhaustion suction, amount of input air during recirculation, dwell time, concentration of flue gases inside the oven, fiber tension, air flux rate and heating atmosphere [3]. Despite so many parameters, Khayyam et al. [3] selected only three key parameters to optimize thermal stabilization process: oven temperatures, dwell time and applied tension to filaments. The dwell time and applied tension to filaments are proportional to drive speed in this stage. Therefore, oven temperature and heating rate correspond to the oven temperature sequence.

This work chose drive speed and oven temperature as the parameters to obtain a thermal stabilization model using artificial neural networks (ANNs). ANNs were developed based on biological nervous system behavior [12] and have been an important tool to simulate the behavior of systems in different application areas [13]. Ramin and Farsani [14] have developed a model and optimization scheme for a carbon fiber production based on polyacrylonitrile using a hybrid learning system combining fuzzy logic with artificial neural networks. Chen et al. [15] have also used hybrid algorithms to the same purpose.

In present work, a simulation model of the thermal stability process was developed based on two steps: a previous qualitative analysis using an unsupervised training with Self-Organizing Maps on an available experimental database, followed by a quantitative analysis using supervised learning through a standard feedforward backpropagation neural network.

The Self-Organizing Maps (SOMs) usually organize database based on competitive algorithms, possibly obtaining clusters based on data similarities [16]. The input data must be multidimensional, and the obtained output maps in shorter dimension (usually two-dimensional maps), often called Kohonen maps [17]. These maps exhibit spatially organized regions usually corresponding to data clusters established by the classification, visualization, and aggregation capability [18] of these neural networks.

Based on the previous analysis, the more significant variables were used as input to a standard feedforward neural network. This network promotes the training of interconnected layers of artificial neurons, where connection weights are the free parameters to be optimized according to the minimization of target errors. In this work, the neural networks were trained using a standard backpropagation unsupervised method to optimize network weights through an iterative adjustment, minimizing the differences between actual output and desired output [19].

In summary, intelligent algorithms were applied to an experimental database from a real carbon fiber production plant to simulate the stability stage of a carbon fiber production based on polyacrylonitrile (PAN).

2. Experimental

The methodology was composed of two stages: the first, collecting samples from experimental analysis and creating a database, and the second, training and developing an artificial network simulation. The artificial network simulation was also composed of two steps: a qualitative analysis using SOMs and a quantitative analysis employing feedforward backpropagation network.

2.1. Polyacrylonitrile (PAN), oxidized polyacrylonitrile (PANOX) and stability parameters

The samples were obtained from a university pilot carbon fiber plant. There were three different sample types: raw material samples, polyacrylonitrile (PAN) samples, and the stability stage product samples, also called oxidized polyacrylonitrile (PANOX), which were collected in different operational conditions.

The used polyacrylonitrile had itaconic acid and methyl acrylate as comonomers and was produced with dimethylformamide wet-spinning process containing 5500 filaments.

The input database was composed of all thermal stabilization parameters that were related to the process conditions and to the properties of the fibers. The selected parameters were the heating rate, oven temperatures, fiber tensioning and dwell time. The heating rate and oven temperatures are related to the sequence of temperatures of the oven tube and of the chamber. It is important to emphasize that fiber tensioning and dwell time are proportional to drive speed.

2.2. Fiber's characterization (output database)

The main techniques used to the fiber characterization were

(a) (b)

Fig. 2. Kit 33360 Mettler Toledo (Archimedes principle)- ASTM D3800.

Table 1
Database variables.

Input	v1	PAN linear density	
	v2	Chamber temperature	Zone 1
	v3	Average tube temperature	
	v4	Set point temperature	
	v5	Chamber temperature	Zone 2
	v6	Average tube temperature	
	v7	Set point temperature	
	v8	Chamber temperature	Zone 3
	v9	Average tube temperature	
	v10	Set point temperature	
	v11	Chamber temperature	Zone 4
	v12	Average tube temperature	
	v13	Set point temperature	
	v14	Average speed	
Output	v15	PANOX volumetric density	
	v16	PANOX linear density	
	v17	FTIR conversion index	
	v18	DSC aromatization index	

Table 2
SOM training parameters.

number of neurons	*epochs*		
12	9000	1100	1300
14	7000	9000	1100
16	5000	7000	8000

volumetric and linear density. Furthermore, Differential Scanning Calorimetric (DSC) and Fourier Transformed Infrared Spectroscopy (FTIR) methods were used to check the stabilization stage efficiency.

2.2.1. Volumetric and linear density

The solid material volumetric density (ρ) analyses were performed, in triplicate, through Archimedes Principle based on fluid immersion as shown in Fig. 2. This method is oriented by ASTM [20]. Due to PANOX strong hydrophilic behavior, absolute ethanol was used and, posteriorly, a correlated factor dependent on the sample saturation was applied. This factor is a relation between wet and dry densities according to Morgan (2005). Considering the Morgan (2005) correlated factor calculated for 4 and 5% saturation level, this work evaluated, by extrapolation, a factor for each saturation condition, obtained from Equation (1).

$$s = \frac{w_s - w_d}{w_d} * 100, \tag{1}$$

where w_s is the saturated fiber weight and w_d is the dry fiber weight. According to Archimedes Principle, the density was obtained considering the immersed sample weight (w_i) in a fluid, absolute ethanol, using Equation (2). Afterwards, this density was corrected by applying the previously evaluated saturation correlated factor.

$$\rho_{solid} = \frac{w_d}{w_d - w_i} * \rho_{fluid} \tag{2}$$

The linear density (μ) was derived from the weight per length (L) and could be obtained by dry sample weighing such as described in Equation (3).

$$\mu_{solid} = {w_d}/{L}. \tag{3}$$

2.2.2. Differential scanning calorimetric (DSC)

The PAN and PANOX samples were pricked and weighed using analytical balances to establish an approximate 3 mg size. The precursor experiment was performed with a 10°C-per-minute rate and an initial temperature varying from 25 °C to 350 °C; the PANOX experiment was performed using a 10 to 440 °C temperature ramp with a 10°C-per-minute rate. Both analyses were performed under inert atmosphere, using a 50 ml-per-minute nitrogen flux in a DSC 3 equipment from Mettler Toledo.

The DSC analyses lead to a heat-flow-versus-temperature graph, which represents the cyclization process considering the input (PAN) and output (PANOX) materials. The graph integration using the STARe software [21] produced input and output enthalpies, which enabled the aromatization degree measurement. Thus, the thermal stability extension could be evaluated by comparing the relation between PAN and PANOX released heat reactions.

Since the enthalpy was derived from differential scanning calorimetric experiments, in accordance with Hameed at. al [22,23], it was possible to calculate the aromatization index using the following equation:

$$AI = \frac{\Delta H_{PAN} - \Delta H_{PANOX}}{\Delta H_{PAN}} * 100\% \quad , \tag{4}$$

where:

ΔHPAN = PAN fiber exothermic heat ($J.g^{-1}$); and
ΔHPANox = PANOX fiber exothermic heat after the oxidative stabilization ($J.g^{-1}$).

2.2.3. Fourier Transformed Infrared Spectroscopy (FTIR)

Spectra were collected at room temperature in a Thermo Scientific 4700 Nicolet Fourier Transformed Infrared (FTIR) Spectrometer equipped with an Attenuated Total Reflection (ATR) accessory using a zinc selenide (ZnSe) crystal at 45° angle. This technique offers high transfer rate and precision scanning in the range between 5100 cm^{-1} and 500 cm^{-1}, which covers the spectral region of interest (4000 cm^{-1} to 400 cm^{-1}). The analyses were performed with 40 scans using a resolution of 4 cm^{-1} in the absorbance mode. All the spectra were analyzed with Omnic Software [24].

Fourier Transformed Infrared Spectroscopy (FTIR) was used to recognize the functional groups in fiber sample. Ouyang et al. [25] and Karacan and Erdögan [26] have reported the polyacrylonitrile samples have a representative C≡N group in 2243 cm^{-1} band and that, after thermal stabilization, there is another significant band between 1595 and 1580 cm^{-1}. This last band occurs due to combination of C=C and C=N vibrations, and to the bending/inclination of NH group on the stabilized PAN (PANOX) structure plane. Therefore, the conversion

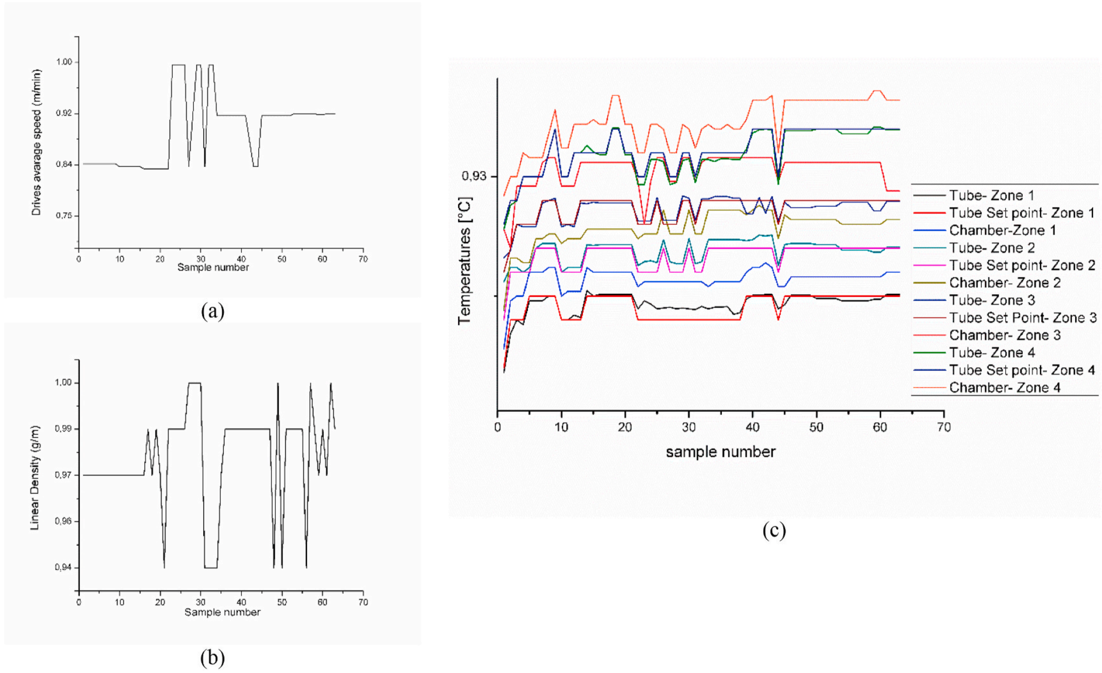

Fig. 3. Behavior of input vectors in relation to 63 samples. Variable values are normalized.

Table 3
Volumetric and linear density evaluation variables. Each variable was parameterized on PANOX commercial values.

Sample	Dry fiber weight	Wet fiber weight	Humidity	Correction factor	Immersed wire	Immersed (fiber + wire)	Saturated volumetric density	Dry volumetric density	Volumetric density average	Linear density	Linear density average
1	0,9651	0,9060	0,4621	0,9995	0,9834	0,8976	0,9316	0,9412	0,9594	0,9406	0,9381
	0,9591	0,9007	0,4650	0,9993	0,9834	0,9028	0,9389	0,9485		0,9347	
	0,9636	0,9031	0,4482	1,0000	0,9834	0,8838	0,9229	0,9329		0,9391	
2	0,9528	0,9287	0,7786	0,9871	0,9635	0,9632	0,9709	0,9688	0,9924	0,9285	0,9307
	0,9606	0,9341	0,7575	0,9879	0,9635	0,9724	0,9746	0,9734		0,9362	
	0,9516	0,9239	0,7450	0,9884	0,9635	0,9684	0,9785	0,9777		0,9274	
3	0,9504	0,9493	0,9905	0,9788	0,9635	0,9925	0,9802	0,9699	1,0030	0,9262	0,9278
	0,9564	0,9263	0,7241	0,9892	0,9635	0,9960	1,0000	1,0000		0,9321	
	0,9494	0,9442	0,9519	0,9803	0,9635	1,0000	0,9900	0,9811		0,9253	
4	0,9211	0,8926	0,7289	0,9890	0,9302	0,8993	0,9486	0,9484	0,9719	0,8976	0,9019
	0,9286	0,8964	0,6952	0,9903	0,9302	0,9120	0,9563	0,9574		0,9050	
	0,9265	0,9015	0,7626	0,9877	0,9302	0,9148	0,9552	0,9538		0,9029	
5	0,8665	0,8498	0,8317	0,9850	0,9934	0,8987	0,9692	0,9651	0,9853	0,8444	0,8389
	0,8640	0,8512	0,8694	0,9835	0,9934	0,9056	0,9743	0,9687		0,8421	
	0,8520	0,8405	0,8817	0,9830	0,9934	0,8930	0,9712	0,9651		0,8303	
6	0,8861	0,8781	0,9206	0,9815	0,9302	0,8349	0,9077	0,9007	0,9683	0,8635	0,8622
	0,8849	0,8766	0,9179	0,9816	0,9203	0,9350	0,9919	0,9843		0,8624	
	0,8831	0,8742	0,9118	0,9819	0,9203	0,9091	0,9711	0,9639		0,8606	
7	0,9425	0,9068	0,6675	0,9914	0,9834	0,9171	0,9462	0,9483	0,9979	0,9185	0,9187
	0,9407	0,9052	0,6688	0,9914	0,9834	0,9643	0,9860	0,9881		0,9168	
	0,9449	0,9087	0,6633	0,9916	0,9834	0,9804	0,9972	0,9996		0,9209	
8	0,9567	0,9317	0,7705	0,9874	1,0000	0,9730	0,9717	0,9699	0,9847	0,9324	0,9361
	0,9603	0,9357	0,7749	0,9872	1,0000	0,9879	0,9810	0,9790		0,9359	
	0,9645	0,9397	0,7739	0,9873	1,0000	0,9522	0,9501	0,9482		0,9400	
9	0,9407	0,9322	0,9208	0,9815	0,9834	0,9954	0,9921	0,9844	0,9889	0,9168	0,9189
	0,9428	0,9343	0,9212	0,9815	0,9834	0,9764	0,9749	0,9673		0,9188	
	0,9452	0,9360	0,9139	0,9818	0,9834	0,9655	0,9651	0,9578		0,9212	
10	0,9322	0,9253	0,9342	0,9810	0,9834	0,9787	0,9833	0,9751	1,0026	0,9085	0,9160
	0,9437	0,9140	0,7238	0,9892	0,9834	0,9879	0,9996	0,9996		0,9197	
	0,9437	0,9338	0,9079	0,9820	0,9834	0,9850	0,9823	0,9752		0,9197	
11	0,9998	0,9981	0,9849	0,9790	0,9336	0,9502	0,9229	0,9133	0,9274	0,9744	0,9731
	1,0000	1,0000	1,0000	0,9784	0,9336	0,9433	0,9172	0,9072		0,9746	
	0,9958	0,9948	0,9913	0,9788	0,9336	0,9399	0,9176	0,9079		0,9704	
Commercial PANOX								1,0000	1,0000	1,0000	1,0000

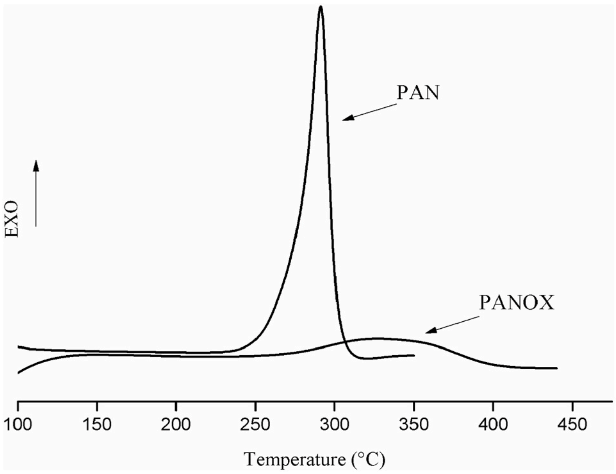

Fig. 4. DSC curve for PAN and PANOX samples.

index can be evaluated using Equation (5) [26]:

$$CI_{FTIR} = \frac{Abs_{1585}}{Abs_{1585} + Abs_{2243}} * 100\% \quad , \tag{5}$$

where:

Abs_{1585} = C═N group absorbance for region between 1595 and 1580 cm^{-1} band; and Abs_{2243} = C≡N group absorbance for region between 2235 and 2246 cm^{-1} band.

2.3. Database

A database was created by selecting process parameters and results from characterization analyses for each sample. This database was constituted by 18 chosen variables which are associated with the quality of fibers and stability process as shown in Table 1.

2.4. Qualitative analysis

The qualitative analysis was performed using each variable behavior in relation to the samples. Based on a previous selection, the data were used as input to a Self-Organizing Map (SOM) neural network using the Kohonen and CP-ANN [27] software.

Different SOM configurations were tested using variations of training parameters:

- number of neurons;
- training *epochs*;
- SOM topologies.

The hexagonal topology was chosen and used with SOM parameters used as described in Table 2.

The obtained SOM maps and corresponding prototype vectors were analyzed, and the more representative stabilization-process output variables were selected. This selection result will be described in section 3.3.

2.5. Quantitative analysis

Based on previous qualitative analysis, the created database was used to train a feedforward backpropagation neural network using the neural network toolbox from MATLAB® [28]. This neural network was trained using the following parameters:

input samples: 51;
number of neurons: 10;
number of layers: 5;
number of epochs: 1000;
gradient: 10^{-7};
transfer function: hyperbolic tangent sigmoid;
data initialization: random;
training algorithm: Levenberg-Marquardt;
performance parameter: mean squared error; and
number of validation checks: 1000.

The trained networks were used to simulate the previously selected variables relative to thermal-stabilization process output. A set of 1000 validation tests were performed using 12 samples and relative error was estimated based on experimental data.

The 'holdout' cross-validation technique [29] was applied by

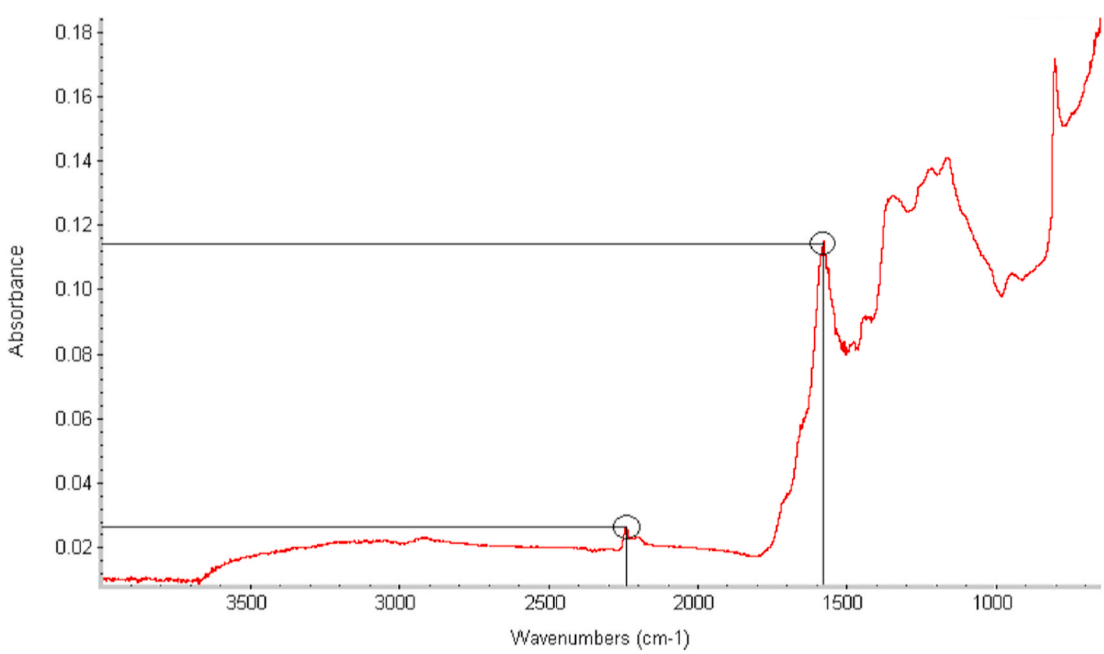

Fig. 5. PANOX FTIR spectrum with peaks identification.

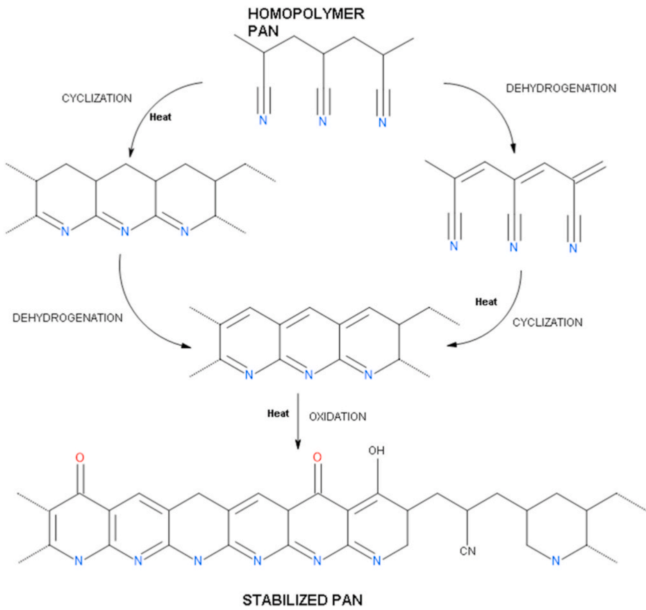

Fig. 6. Reactions involved in PAN thermal stabilization [7] (adapted).

randomly selecting 30 mutually exclusive subassemblies from overall database. Thereafter, a statistical analysis was performed to estimate the model relative error using R Software [30].

3. Results

3.1. Input data

The input data were collected according to criteria described on section 2.1. The behavior of these variables in relation to 63 different samples is exemplified in Fig. 3.

Fig. 3 shows the input data behavior. It was not possible to identify significant correlation between the 'Linear Density' (a) and the 'Average Speed' (b) variables, indicating they could contain independent information about the process. The process temperatures for each zone (Fig. 3 (c)) exhibit considerable correlation. Variable values are shown normalized due confidentiality questions. Despite this considerable correlation, the temperature variables were considered, independently, to construct the model. These variables implicitly contain information from all ovens and also represent the heating rate for the thermal stabilization process.

Heating rate control was considered as a fundamental variable taking into account that generated heat, arisen from these reactions, can promote a fiber rupture and consequent interruption of all productive process. This heat is mainly derived from complex and exothermic thermal stabilizing reactions. Continuous process control is, therefore, especially important since possible fiber ruptures should affect orientation and tensioning of fibers. Carbon fiber quality is a direct result of these factors and heating rate is a key parameter in thermal stabilization stage.

3.2. Fiber's characterization- output data

3.2.1. Volumetric and linear density

The volumetric density was calculated using Archimedes Principle

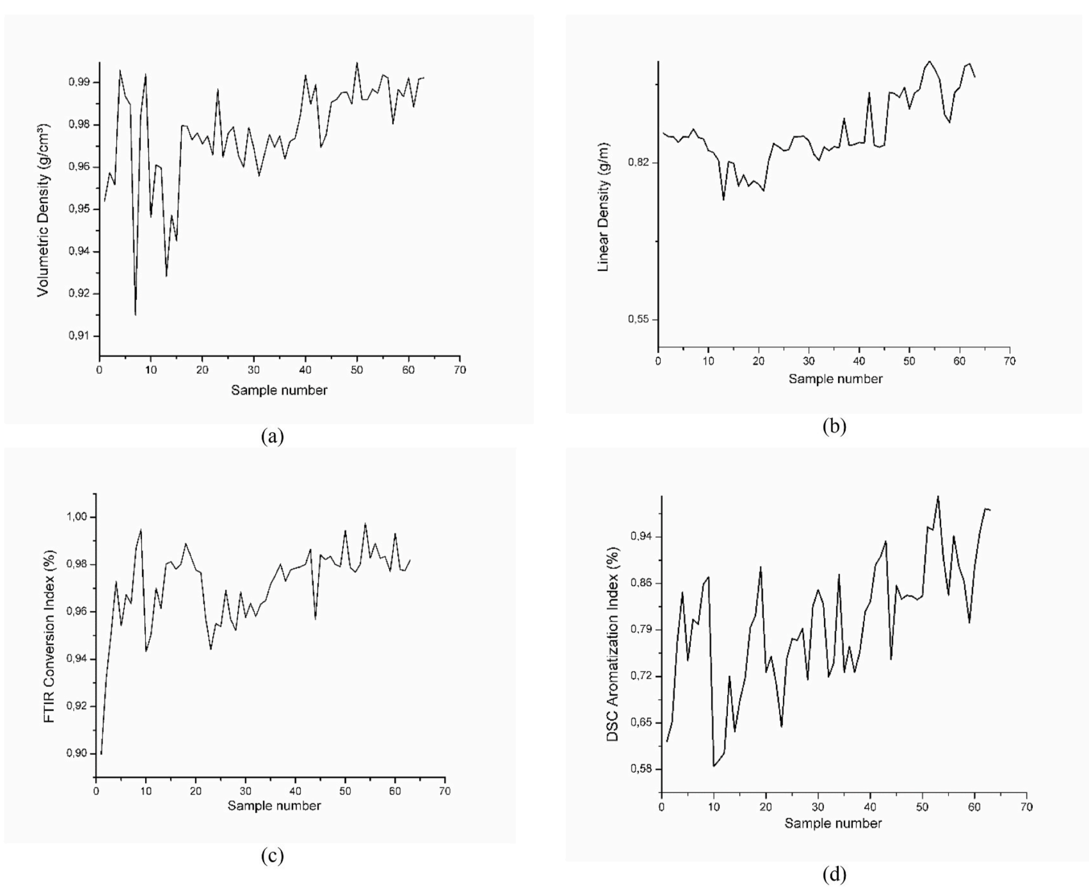

Fig. 7. Output variables behavior: (a) Volumetric Density, (b) Linear Density, (c) FTIR Conversion Index and (d) DSC Aromatization Index.

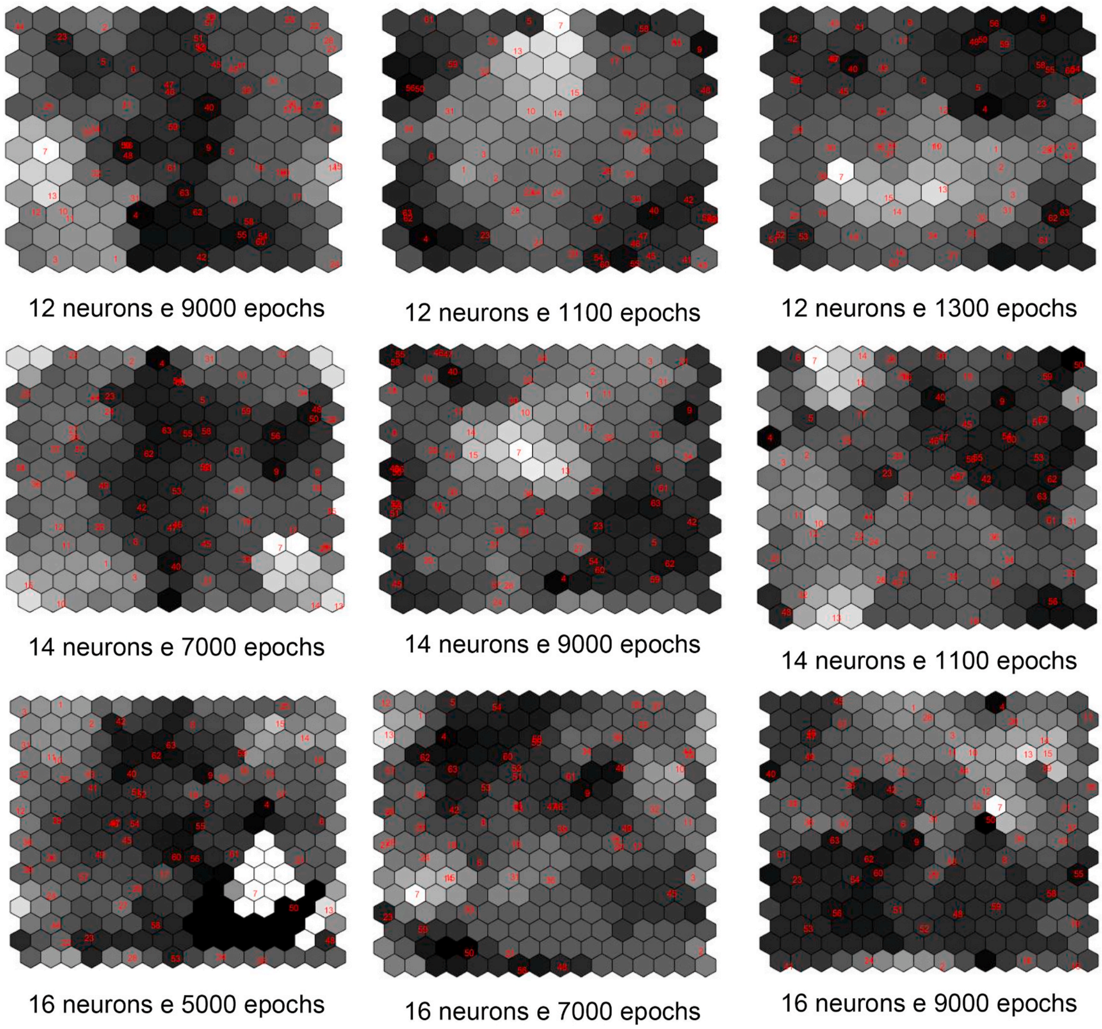

Fig. 8. Volumetric density (v15) U-matrix SOM maps obtained for 12 × 12, 14 × 14 and 16 × 16 map sizes trained for 1100 to 9000 epochs.

and the linear density was obtained from 63 samples. Table 3 exhibits volumetric and density variables measured and calculated values for a subset of 11 samples. This subset was chosen for exemplification in this paper. The results were parameterized based on PANOX commercial values due to absolute values confidentiality [31].

The obtained results shown in Table 3 attested the quality of PANOX samples. The density properties of the samples are similar to a commercial oxidized polyacrylonitrile fiber from SGL Carbon. The volumetric-density results varied in the 0,21% to 7,26% range. The linear density had a greater fluctuation between 6,19% and 16,11%.

Despite this variation, both parameters were subsequently used to simulate the thermal stabilization process considering the significance of these physical properties. According to Badii et al. [32], density, as a key property, plays a decisive role in the optimization of the thermal stabilization process of the PAN precursor, therefore this is an important property to characterize the material. The density significance is mainly due to considerable modifications that occur on polyacrylonitrile structure after the oxidation, dehydrogenation, and cyclization reactions.

3.2.2. Differential scanning calorimetric (DSC)

Differential Scanning Calorimetric (DSC) is a thermal analysis method based on the temperature difference between the sample and a standard material. This technique is based on heat transfer in differential flow over a temperature gap. The measured temperature differences obtained through the thermocouples are proportional to the variation of enthalpy, to the heat capacity and to the heat flow thermal resistance [33]. The conversion from PAN precursor to oxidized fiber is characterized by the formation of nitrile group cyclic chains and by the connection of oxygen element structures for exothermic stabilization reactions.

DSC analysis has been used to investigate PAN thermal stability since it is possible to calculate the heating reaction (ΔH) for different thermal process conditions [26,34,35]. The enthalpy values were evaluated for precursor and stabilized samples using differential scanning calorimetric. Fig. 4 shows the thermogram of analyzed samples.

DSC curves shown in Fig. 4 exhibit a single exothermic peak corresponding to the oxidized PAN. The reaction enthalpy values were obtained integrating the curve inside the exothermal reaction interval. Aromatization index was evaluated using PAN and PANOX enthalpies using equation (4) according to Haamed et al. [22]. These values were added to the database to be used in the following analyses.

The enthalpy behavior during the thermal stabilization process can be seen in Fig. 4. The exothermic peak is related to the reaction velocity of the activity centers involved in dehydrogenation, cyclization, and oxidation. Therefore, the cyclization of fibers and aromatization reactions decrease the enthalpy as the thermal treatment stabilizes polymeric chains.

3.2.3. Fourier Transformed Infrared Spectroscopy (FTIR)

Fig. 5 shows the spectrum of a PANOX sample which presents the absorbance peak corresponding to the C≡N functional group near the

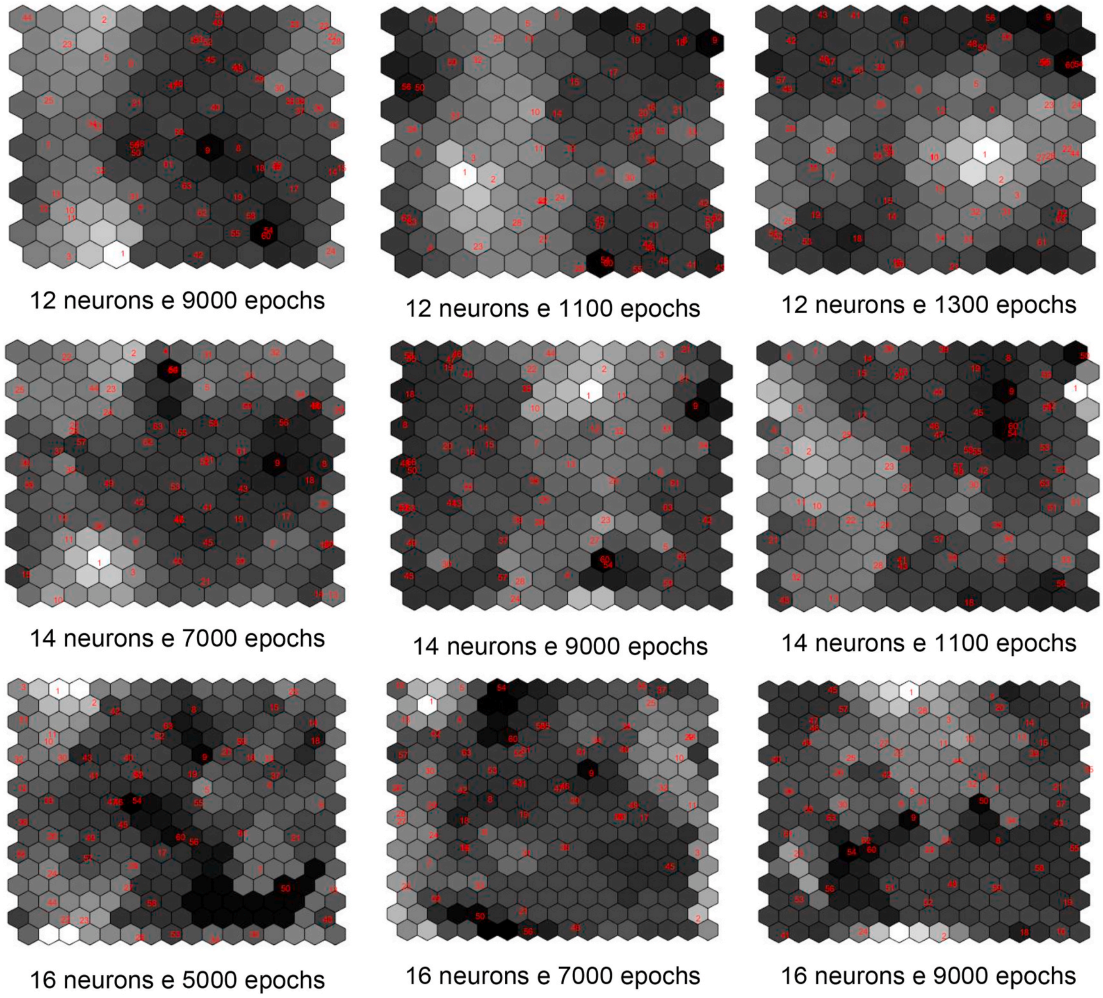

Fig. 9. FTIR conversion index (v17) U-matrix SOM maps obtained for 12 × 12, 14 × 14 and 16 × 16 map sizes trained for 1100 to 9000 epochs.

2243 cm^{-1} wavelength. The spectrum also presents a peak in the 1595 - 1580 cm^{-1} wavelength range that corresponds to the combination of C=C and C=N vibrations and also to the flexion of NH function group in PANOX structure plane [26]. Observing a gradual and continuous C≡N intensity reduction expresses the occurrence of cyclization reactions during thermal stabilization. The conversion index was evaluated based on the absorbance peaks identified in Fig. 5 and using Karacan and Erdögan equation (Equation (5)).

During thermal stabilization process, three different reactions occur simultaneously: oxidation, cyclization, and dehydrogenation (Fig. 6). The reaction represented in Fig. 6 shows the functional groups identified in the FTIR spectrum (C≡N, C=C and C=N), thus it is possible to demonstrate the thermal stabilization progress obtained in the tested sample (Fig. 5).

Considering that the variables used to calculate the conversion index are correlated with the thermal stabilization reactions, it also possible to deduce a relation between the FTIR conversion index and the thermal stabilization process, which will be applied to the artificial intelligence modelling in the following item.

3.3. Qualitative analysis

The output variables behavior for different samples is presented on Fig. 7 bellow.

Fig. 7 shows the behavior of the output variables for the 63 samples. Volumetric density (v15), FTIR conversion index (v17) and DSC aromatization index (v18) were the variables used for SOM training based on described criteria (section 2.4). The linear density variable (v16) was not selected to SOM training because it did not present significant variation for different samples. Besides that, it also presented important fluctuation when compared to commercial PANOX properties as indicated in Table 3. Therefore, this parameter was not considered to be suitable to characterize the thermal stabilization stage.

A set of self-organizing maps were trained using Kohonen and CP-ANN Toolbox [27] based on the above selection criteria. The obtained SOM maps enabled the cluster distribution visualization as shown in Figs. 8–10. The darker regions denote the grade of proximity of prototype vectors and, consequently, indicate the best vectors which could represent the data behavior [17].

Fig. 8 and 9 show trained SOM maps with better defined clusters for volumetric density (v15) and FTIR conversion index (v17) (as described in section 2.4). The DSC aromatization index (v18) maps (Fig. 10) did not present considerable tone differences. Based on this qualitative analysis, 'volumetric density' and 'FTIR conversion index' were considered more suitable to represent the thermal stabilization process in the following neural network model.

3.4. Quantitative analysis

Based on previous selection, a cross validation procedure was performed using 30 mutually exclusive subgroups within 51 samples in order to train a feedforward backpropagation network. This training was performed using the Neural Network Toolbox for MATLAB® [28], where the output volumetric density (v15) and conversion FTIR index

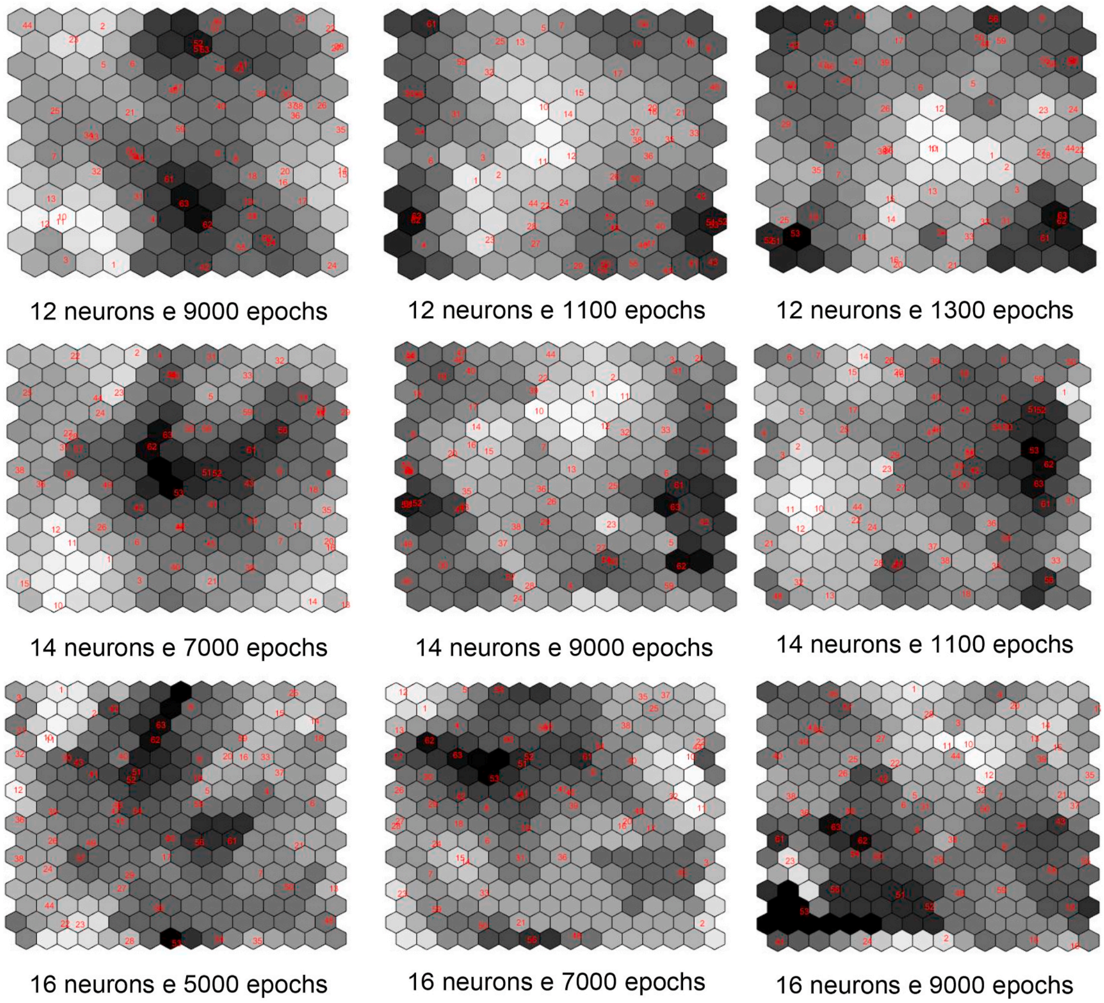

Fig. 10. DSC aromatization index (v18) U-matrix SOM maps obtained for 12 × 12, 14 × 14 and 16 × 16 map sizes trained for 1100 to 9000 epochs.

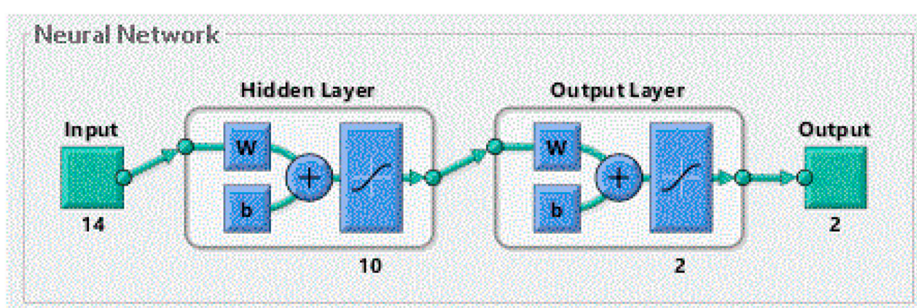

Fig. 11. Neural network feedforward backpropagation scheme from MATLAB® [28].

(v17) were used as output and the 14 variables described on Table 1 as input, as illustrated in Fig. 11.

The simulation results were statistically analyzed using the remaining 12 different experimental data sets. The obtained relative errors for volumetric density (v15) simulation were 2,98 ± 0,01% in average. FTIR conversion index (v17) errors were 2,48 ± 0,02% in average. Those results have shown good agreement with experimental measurements and, therefore, to be a good model to thermal stabilization stage of carbon fiber production process.

Fig. 12 exhibits the relative errors density distribution and boxplots for these results. Fig. 12 (a) and (b) graphs show that the highest relative errors are concentrated between 0% and 2%. The volumetric density error distribution (Fig. 12(a)) presents other 2 peaks between 4% and 8% presenting thus, a greater variation than FTIR conversion index. Boxplot graphs also show wider variation for volumetric density (Fig. 12 (c)). Volumetric density relative error distribution has a 2,74% median, indicating that half of the errors were between 1% and 3% and the other half, between 3% and 5%. The FTIR conversion index boxplot shown in Fig. 12(d), presents a 0,96% median value, indicating that half of simulated FTIR index relative errors were lower than 1%.

The 'FTIR conversion index' showed to best represent the thermal stabilization process according to this statistical analysis. The 'volumetric density' simulation also presented a good prediction performance which is consistent with its importance as an industrial parameter for

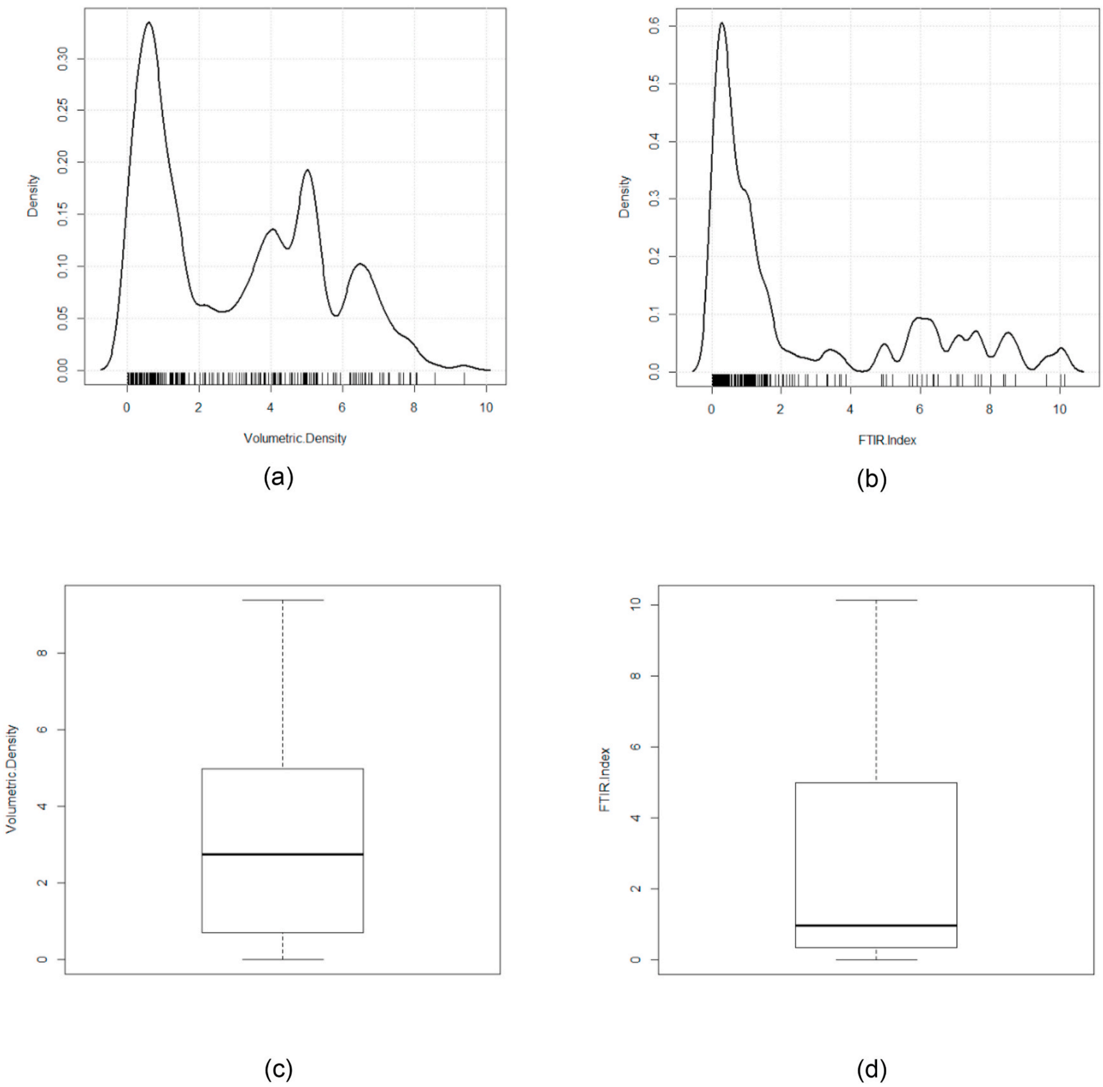

Fig. 12. Simulation relative error statistical analysis. (a) Volumetric density distribution. (b) FTIR conversion index distribution. (c) Volumetric density boxplot. (d) FTIR conversion index boxplot.

this process.

4. Conclusion

There has been an improving industry demand for fiber carbon utilization. This growth is mainly due to its unique properties that fit a wide range of potential lightweight applications. The carbon fiber produced by polyacrylonitrile has been considered as one of the most important and has been the mainly used precursor for carbon fiber manufacturing.

Carbon fiber production consists of many stages such as polymerization, spinning, thermal stabilization, carbonization, and surface treatment. Thermal stabilization stage is the most critical one as it is the longer phase and the one which contains the main chemical reactions. Different reactions occur simultaneously during precursor stabilization steps such as oxidation, dehydrogenation, and cyclization. Those are responsible for the filament structure definition and orientation and, consequently, directly decisive for the carbon fiber quality.

This work analyzed the influence of key variables in a pilot thermal stabilization process such as temperature, heating rate, time, and tension. A simulation model, using intelligent algorithms, was developed using experimentally measured reagent (PAN precursor) and product (PAN oxidized) characterization analyses. This model was mainly based on reaction conversion indexes evaluated on experimental data obtained from Differential Scanning Calorimetric (DSC) and Fourier Transformed Infrared Spectroscopy (FTIR). The measurements were performed on a thermal stabilization stage of a pilot production plant.

An initial qualitative analysis was performed to select the best suited variables to construct the model. A comparison of available measured variables was performed through self-organizing map tests. This analysis selected ‘volumetric density’ and ‘FTIR conversion index’ as the more appropriate variables.

Subsequently, a quantitative analysis was performed to simulate the thermal stability stage, training a feedforward backpropagation network through cross validation technique using these selected variables. This kind of computer-based modelling has the unique property of correctly predict, with low error, product material properties for such production stage. The success of such modelling effort is especially important to estimate possible results of carbon fiber obtainment when using different precursors and process parameters, primarily when there is not an available analytical model. This simulation obtained a 2,98 $\pm$ 0,01% average relative error for volumetric density and a 2,47 $\pm$ 0,01% average relative error for FTIR conversion index. The statistical analysis also showed the distribution and regularity of these relative errors, which ranged from 0 to 2%. Therefore, the model showed good representativeness for a thermal stabilization stage in a polyacrylonitrile carbon fiber production process.

This simulation can be a starting point to further development of methods to reduce the gap between laboratory and industrial standards used on carbon fiber production. The results specifically reaffirm that good computer-based nonlinear prediction models can be constructed based on 'volumetric density' and 'FTIR conversion index' and, therefore, could be a basis to develop intelligent systems to control thermal stabilization process quality.

It is noticeable that thermal stabilization is the most energy and time-consuming stage in the whole carbon fiber manufacture process. Hence, computer-based systems to simulate such processes using key parameters as 'volumetric density' and 'FTIR conversion index' should contribute significantly as tools to implement a cost reduction and quality development program in carbon fiber production and development systems.

Data availability

The raw and processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymertesting.2021.107238.

Author statement

Bruna Mota Terra: Conceptualization, Methodology, Software, Investigation, Formal analysis, Resources, Data curation, Writing – original draft. Delvonei Alves de Andrade: Conceptualization, Software, Writing – review & editing. Roberto Navarro de Mesquita: Conceptualization, Software, Formal analysis, Writing – review & editing, Visualization, Supervision, Project administration and Funding acquisition.

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