Neural fuzzy model applied to autohydrolysis of *Paulownia trihybrid*

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Key words

Neural fuzzy modeling; Paulownia; autohydrolysis; glucan; xilan; oligosaccharides;

1. INTRODUCTION

Fuzzy modelling, which is based on the pioneering idea of Zadeh[1], is a powerful tool for describing non-linear behaviour in complex systems. Since the 1980s, the theory of fuzzy logic has been successfully used by a number of researchers to simulate and control fermentation and anaerobic digestion processes[2].

Neural networks, which were developed by analogy with the functioning of neurons in living beings[3], constitute one other powerful tool for modelling complex systems. The most salient feature of neural networks is their ability to exactly map non-linear behaviour via a series of input (independent variable) and output (dependent variable) data without the need for an exact knowledge of the functional relationships between the two data sets[4]. Neural networks have provided good results in the assessment of various biological systems including anaerobic digestions, stability predictions of oxidizing vegetable oils from compositions and contents in endogenous oil components, lifetime predictions in milk, predictions of *trans* isomer formation and changes in unsaturated fatty acids during the hydrogenation of vegetable oils, fermentation processes and kinetic analyses[5].

The combination of fuzzy logic and neural networks provides an even more useful modelling tool than either in isolation. Specifically, neural fuzzy systems have been successfully used to model organosolv delignification of raw materials such as vine shoots and tagasaste in chemical and industrial systems allowing the exploitation of lignocellulosic biomass[6–8].

In this work, we used neural fuzzy methodology to model fractionation sequences for lignocellulosic materials (LCM) with a view to the integral exploitation and isolation of their major fractions (cellulose, hemicellulose and lignin) with reduced production of waste and increased production of valorizable by-products –and maximum profitability as a result. One of the earliest fractionation steps in the process is that involving dissolution of hemicellulose, which is accomplished hydrothermally. This treatment, which provides a liquid fraction and a solid fraction amenable to conversion into products with a high added value, relies on autohydrolysis and is thus clean and environmentally benign. Hydrothermal processes exploit the ease with which hemicellulose can be hydrolysed relative to cellulose[9].

The raw material used was a trihybrid clone of Paulownia, a tree which originated in China and cultivation of which has subsequently expanded vastly worldwide by virtue of its rapid growth and high biomass production –which facilitates recovery, control and stabilization of soil erosion and makes it an effective sink for carbon dioxide[10–13]. Paulownia biomass is typically used to obtain energy and cellulose pulp[14, 15].

In this work, we used a single-configuration neural fuzzy method to model and optimize the amount of sugars and oligomers extracted as a function of the process variables temperature and time in an experimental process involving the autohydrolysis of the Paulownia trihybrid (*elongata*, *fortunei* and *tormentosa*).

2. MATERIALS AND METHODS

2.1. Raw material. Provision and characterization

A trihybrid variety of Paulownia (*Elongata* x *Fortuneii* x *Tormentose*) has been used in this work. The studied material was an hybrid clone obtained by in vitro replication that was harvested after three years of growth in plantations used to exploit biomass or energy crops in Extremadura (southwestern Spain). The material was supplied by the firm Vicidex Europa.

Paulownia wood trimmings samples were milled to pass a 5 cm screen. The chips were cold-ground again to pieces 0.2 to 10 mm long in order to prevent alterations of their components and fines removed by sieving through 0.6 mm mesh. Samples were airdried, homogenized in a single lot to avoid differences in composition among aliquots, and stored.

Aliquots from the homogenized wood (without compounds extraibles) lot were subjected to moisture determination (drying at 105 ºC to constant weight), quantitative acid hydrolysis with 5 ml of 72% sulfuric acid for an hour (Tappi T-248-em-85), and quantitative posthydrolysis with 4% sulfuric acid (adding water until 148.67g) at 121 ºC and 2 atm during 60 min in order to ensure quantitative conversion of oligomers into monomers[16]. Before HPLC analysis, the solid residue from posthydrolysis process was recovered by filtration and considered as Klason lignin. The monosaccharides and acetic acid contained in hydrolysates were determined by HPLC in order to estimate (after corrections for stoichiometry and sugar descomposition) the contents of samples in cellulose (as glucan), hemicelluloses (xylan + araban), and acetyl groups. The moisture of wood was considered as water in the material balances. Chromatographic determination was performed using an Agilent 1100 HPLC equipped with an ion-exchange resin BioRad Aminex HPX-87H column under the following conditions: mobile phase, 0.005 mol·L-1 of sulphuric acid; flow rate, 0.6 mL·min-1; and column temperature, 50 °C. The volume injected was 20 μL.

2.2. Autohydrolysis process and oligosaccharides determination

Wood chips and water were mixed in the desired proportions and reacted in a 2 L stainless steel Parr reactor fitted with double four-blade turbine impellers. The vessels were heated up to maximum temperatures in the range 160 to 200ºC with external electric heaters. The temperature of the process was automatically controlled via an internal cooling coil equipped with circuit-opening electrovalves which was used to cool the reactor after the highest temperature and operating time were reached.

Several experiences from isothermal autohydrolysis were carried out in order to study the effect of the process on the xyloolygomer production and cellulose degradation. Based on previous experiences on *Paulownia Fortunei* and others lignocellulosic materials[17-21], the operations were carried out at temperatures and times of process indicated in the experimental design.

Two preliminary tests were conducted under the central operating conditions (a temperature of 180 °C and a processing time of 15 min) that were followed by others involving temperatures from 165 to 195 °C and times over the range 0–30 min. A constant hydromodulus of 12 (g/g) was used in all tests in order to ensure efficient mixing in the digester. The model used prescribed the development of 8 experiments around a central one conducted in duplicate and 2 additional experiments –the last were used in conjunction with one of the central experiments to check data from the neural fuzzy model.

At the end of treatment, the solid residue was recovered by filtration and washed with distilled water for gravimetric yield determination. An aliquot of liquors was filtered through 0.45 μm membranes and used for direct HPLC determination of monosaccharides and acetic acid. A second aliquot of liquors (25 ml) was subjected to quantitative posthydrolysis (with 4% sulfuric acid at 121 ºC and 2 atm during 60 min) before HPLC analysis. Operation conditions in HPLC are described in previous section for raw material. The increase in the concentrations of monosaccharides and acetic acid caused by posthydrolysis measured the concentrations of oligomers and acetyl groups bound to oligosaccharides and the sum of glucan, xylan and araban contents can be considered as holocellulose contents[22].

2.3. Neural fuzzy modelling

The integration of fuzzy systems and neural networks combines the advantages of the two systems and provides an especially powerful modelling tool, viz. the neural fuzzy system, which uses neural networks as tools in fuzzy systems.

The variation of liquor properties as a function of the operational variables of the autohydrolysis process can be predicted by using the following expression[23]:

$$Y_e = \frac{\sum_{l=1}^{m} y^l \cdot \left[\prod_{l=1}^{n} \mu^l_{Fi}(x_i, \theta^l_i) \right]}{\sum_{l=1}^{m} \left[\prod_{l=1}^{n} \mu^l_{Fi}(x_i, \theta^l_i) \right]} \qquad (1)$$

Where:

Y_e is the estimate value of output variable,

M the number of rules,

n the number of input variables,

y^l the defuzzifier and,

$\mu^l_{Fi}(x_i, \theta^l_i)$ the membership-function.

In this paper, $\left[\prod_{i=1}^{n} \mu^l_{\mathrm{Fi}}(x_i, \theta^l_i)\right]$ will be denoted by R_l which is known as a fuzzy rule.

In this sense, R_l is defined by the product of n membership functions (one per independent variable). Then, Eq. (1) could be expressed as

$$Y_{\mathrm{e}} = \frac{\sum_{l=1}^{m} y^{l} \cdot R_l}{\sum_{l=1}^{m} R_l} \qquad (2)$$

Independent variables with three levels (low, medium and high) are selected in order to get improve the fitness of the experimental values. In this sense, Gaussian membership functions for variables with three levels have been selected to perform the response of the system since they provide the best results at validating the model. Three levels for one independent variable. The mathematical equations which respond to Gaussian membership functions are:

$$\mu(low) = \exp\cdot(-0{,}5\cdot(\frac{x - x_{low}}{L})^{2}) \qquad (3)$$

$$\mu(medium) = \exp\cdot(-0{,}5\cdot(\frac{x - x_{medium}}{L})^{2}) \qquad (4)$$

$$\mu(high) = \exp\cdot(-0{,}5\cdot(\frac{x - x_{high}}{L})^{2}) \qquad (5)$$

where x_{low}, x_{medium} and x_{high} are the low, medium and high values of the temperature (165, 180 and 195 ºC), time (0, 15 and 30 min). The introduction of three levels for a variable is justified since a high increase on the fitness is observed by introducing those for one specific variable and not for the others. The proposed combinations of the membership functions are clearly defined in the tables exposed in the result section.

The parameters and constants in the previous equation were estimated by using the ANFIS (Adaptative Neural Fuzzy Inference System) Edit tool in the Matlab 6.5 software suite. In that form, membership function parameters are not trained since they have previously been defined in order to provide a uniform distribution of the membership function within the independent variable range. The constants c_l are trained in order to minimize the mean square error.

3. RESULTS AND DISCUSSION

3.1. Properties of the raw materials

Table 1 shows the chemical properties of the Paulownia trihybrid and the materials used as references (*Paulownia fortunei* and *Eucalyptus globulus*)[14, 17, 24–27]. The table also includes the data for Paulownia previously obtained by Caparrós *et al.* (2008) and Jiménez *et al.* (2005) for comparison.

The holocellulose content of the Paulownia trihybrid, 65.2%, is very similar to that of *Eucalyptus globulus* (66.9%) and falls in the range spanned by reported values for *Paulownia fortunei*. This, together with its fast growth, makes Paulownia an interesting species for pulp and paper production in addition to various other industrial uses.

The glucan content of the trihybrid, 44.4%, is high relative to that of eucalyptus (46.8–53.8%), which is the most widely assessed species for industrial purposes and hence a natural reference for comparison. On the other hand, the lignin content of the trihybrid, 27.8%, is similar to that of the Paulownia species and higher by 21.4% than that of eucalyptus.

The xylan content of the Paulownia trihybrid, 15.7%, is one of the lowest among the species studied here, but similar to that of eucalyptus (14.2–16.6%) in any case.

The proportion of araban (1.1%) is 1.8–2.7 times higher than those of the tree species studied, but lower than those of the grasses and bushes (*miscanthus*, kenaf). However, this compound is scant in the raw material, which abounds with other sugars such as glucan, holocellulose and xylo-oligomers.

3.2. Autohydrolysis of the Paulownia trihybrid

Table 2 shows the yield, and the glucose, xylose, arabinose, acetyl group and xylo-oligomer contents of the liquors, from the autohydrolysis process obtained under the different experimental conditions.

The experimental data in Table 2 were processed with the ANFIS Edit tool in MATLAB 6.5 to estimate the parameters and constants (y^j) in eq. (1). The independent variables (temperature and time) were processed with Gaussian membership functions at three levels (low, medium and high), which were those best fitting the experimental values. Therefore, the functions R_i in eq. (2) were given by eqs (3)–(5). The body of combinations of the two independent variables led to an equation with nine terms in the numerator and as many in the denominator: eq. (2). Table 3 shows the results for parameters (y^j) and L, and the mean error for each dependent variable.

The estimations of the neural fuzzy models used departed little from their experimental counterparts: by less than 1% for yield, glucose, xylose and arabinose; less than 2.1% for acetyl groups; and less than 5.6% for xylo-oligomers. Therefore, the mathematical model used provides accurate estimations of the experimental results.

Unlike other modelling methods such as polynomial multiple linear regression, neural fuzzy modelling enables physical interpretation of constants (y^j) inasmuch as they represent the average value of each property (Y_e) under the conditions defined by the specific neural fuzzy rule. Also, neural fuzzy models enable assessment of the influence of each operational variable on the properties of the material[28]. This can be easily illustrated with the variation of yield (Table 3). Thus, the highest yields were obtained at low temperature and time levels (rule 1), and the lowest at high levels of both independent variables (rule 9). As can be inferred from the results of rule 3 (69.82%), which involves a low time and a high temperature, and rule 7 (81.26%), based on a high time and a low temperature, the temperature has a stronger influence of the yield than has the time.

The yield in soluble compounds in the autohydrolysis liquor, or as expressed in the autohydrolysis solid residue, is influenced in a Gaussian manner by changes in the independent variables (Fig. 1). Increasing the time and, especially, the temperature raises the contents of the liquor.

The glucose content of the autohydrolysis liquor also exhibits Gaussian dependence on both variables; it peaks at medium temperatures and is favoured by a high time. This does not contradict the widely accepted assumption that cellulose polymers are substantially hydrolysed above 200 °C[29, 30] –a temperature, however, which was never reached in our experimental design. As can be seen from Fig. 2, the time during which the material is kept at a given temperature has a stronger influence than the temperature itself in the low range of the latter variable. In theory, the cellulose degradation rate should increase with increasing temperature[31]; this, however, does not seem to be the case judging from the figure. Also, the curve drops above 180 °C in any time range, which suggests that increasing the temperature reduces the amount of glucose reaching the liquor by hydrolysis of cellulose –which only starts after all hemicellulose has been hydrolysed. This effect must inevitably be associated with the autohydrolysis time; also, the “non-influence” of the autohydrolysis temperature is only relative as it merely reflects the prevalence of the effect of the autohydrolysis time[32]. This effect is very interesting with a view to preserving the integrity of the cellulose polymer in the autohydrolysis residue with a view to obtaining quality cellulose pulp and can be maximized by using an optimal combination of high temperatures and short operating times in the autohydrolysis treatment in order to maximize oligomer extraction and preserve cellulose polymers intact as far as possible.

The xylose content of the autohydrolysis liquor (Fig. 3) is more markedly dependent on the temperature, particularly at long processing times; therefore, it peaks at high levels of both variables. This clearly departs from the trend in the glucose content and suggests a strong dependence of the ease of hydrolysis or degradation of hemicellulose on the autohydrolysis temperature and, to a lesser extent, also on the autohydrolysis time.

This allows one to dwell on the previous hypothesis regarding the need to use autohydrolysis temperatures in the upper range and autohydrolysis times in the lower range in order to preserve the integrity of cellulose polymers while maintaining the xylose and xylo-oligomer yields in the liquor as far as possible.

The equation used to model the acetyl group content includes the same terms, with the same signs and weights, as that for xylose. This confirms the strong correlation between the contents in both types of compounds. The previous comments on the results for xylose also apply here.

The Gaussian effect of the autohydrolysis temperature on the content in the monomeric sugar arabinose is more marked than that of the processing time and depends on whether a long or short processing time is used. Thus, the temperature has a negative effect at long times and a positive time at short times; the peak concentration is obtained at medium temperatures and times, which suggests the need to operate in the central regions of the operating ranges. Probably, this is a result of the production of arabinose degradation products at increased temperatures or times –and its hindering accurate assessment of the influence of the two independent variables and its nature.

Finally, the results for xylo-oligomers (Fig. 4) can be interpreted in the light of the starting hypothesis that increasing the temperature and time of the autohydrolysis process increases their presence in the liquor; however, there is the added effect of the simultaneous or subsequent hydrolysis of these compounds to monomeric sugars or degradation products when values of the independent variables in the upper ranges are used. Whether one effect prevails over the other or vice versa determines the relative significance of the terms in the equation used to model the xylo-oligomer content. The Gaussian effects of both process variables are very typical, which suggests the need to operate in the central regions of the respective ranges of variation in order to maximize extraction of xylo-oligomers.

4. CONCLUSIONS

The Paulownia trihybrid studied, which comprises the species *fortunei*, *elongata* and *tormentosa*, is amenable to both autohydrolysis and delignification on account of its similarities to other non-wood raw materials (particularly, its high content in holocellulose and acceptable content in lignin).

Also, the trihybrid is a useful lignocellulosic material for biorefining purposes on account of the high content in sugars of its autohydrolysis liquor and the potential of its solid residue for producing cellulose pulp of acceptable quality.

Yields and sugar extraction were modelled as a function of the operating conditions with the aid of the ANFIS Edit tool in MATLAB 6.5. Based on the results, the optimum operating conditions for this raw material are medium–high temperatures and medium times. Such conditions minimize degradation of the solid residue, which is rich in cellulose, while maximizing xylose recovery via an extraction liquor containing large amounts of xylose and xylo-oligomers. In addition, the autohydrolysis treatment increases the proportion of lignin in the solid residue and the amount of hemicellulose obtained.

ACKNOWLEDGEMENTS

The authors acknowledge financial support from the Grupo Empresarial ENCE, S.A. (San Juan delPuerto factory, Huelva, Spain) and VICIDEX EUROPA S.L., and the CICYT-FEDER (Science and Technology Inter Ministerial Commission, Spanish Government – European Regional Development Fund), projects numbers CTQ2006-10329/PPQ and AGL2009-13113 for their support, and to the “Ramón y Cajal”, “Juan de la Cierva” and FPU Programs of the Spanish Ministry of Science and Innovation.

Table 1

Chemical composition of Paulownia trihibrid and other materials*

	Paulownia trihibrid	*Paulownia fortunei*		*Eucalyptus globulus*		Miscanthus	Kenaf	Aspen
		[19]	[14]	[20]	[21]	[22]	[21]	[23]
Holocellulose	65.2**	56.9	71.0	66.9	n.d	n.d	n.d	n.d
Klasson lignin	27.8	27.2	22.4	22.9	n.d	n.d	13.4	19.3
Glucan	44.0	34.2	37.4	46.8	53.4	39.5	40.0	36.3
Xylan	15.7	18.3	n.d	16.6	14.2	19.0	19.0	22.7
Araban	1.10	1.1	n.d	0.5	0.4	1.8	1.8	0.6
Acetyl groups	4.40	3.3	n.d	3.6	n.d	n.d	n.d	n.d

* Percentages oven dry matter basis.

** Holocellulose as: glucan + xylan + araban + acetyl groups

Table 2

Values of independent variables and composition of the liquid fractions and solid yield obtained in the autohydrolysis process using the proposed experimental design.

t	**T^a**	**Yield %**	**Glucose %**	**Xylose %**	**Arabinose %**	**Acetyl Groups %**	**Xylo-oligomers %**
15	180	74.5	0.99	1.45	0.56	0.10	9.30
30	195	66.0	0.98	4.47	0.26	0.31	1.82
30	165	81.0	0.98	0.81	0.52	0.09	7.51
0	195	70.3	0.87	2.59	0.39	0.17	8.81
0	165	92.7	0.88	0.49	0.13	0.06	0.61
30	180	71.7	1.02	2.39	0.54	0.17	8.16
0	180	79.2	0.94	0.92	0.45	0.08	7.81
15	195	67.0	0.93	3.32	0.41	0.22	7.45
15	165	84.2	0.93	0.57	0.40	0.07	5.93

Cheking data from neural fuzzy model

t	**T^a**	**Yield %**	**Glucose %**	**Xylose %**	**Arabinose %**	**Acetyl Groups %**	**Xylo-oligomers %**
15	180	74.0	1.00	1.37	0.59	0.13	9.27
22.5	188	69.8	0.97	2.93	0,39	0.20	8,26
7.5	173	87.7	1.08	0.55	0,34	0.06	3,91

Table 3 Values of the constants ci and membership functions in the neural fuzzy model for dependent variables with 9 rules

Xt	XT	Yield	Glucose	Xylose	Arabinose	Acetyl Groups	Xylo-oligomers
Low	Low	93.97	0.871	0.472	0.091	0.056	0.002
Low	Medium	79.01	0.944	0.811	0.469	0.072	8.81
Low	High	69.82	0.860	2.66	0.384	0.171	8.94
Medium	Low	84.28	0.924	0.516	0.400	0.066	5.96
Medium	Medium	74.07	0.998	1.36	0.590	0.088	9.82
Medium	High	66.22	0.925	3.42	0.412	0.223	7.61
High	Low	81.26	0.979	0.733	0.526	0.084	7.54
High	Medium	71.12	1.03	2.43	0.559	0.169	8.56
High	High	65.46	0.979	4.68	0.232	0.323	1.02
L		6.37	6.37	6.37	6.37	6.37	6.37
	L	6.37	6.37	6.37	6.37	6.37	6.37
Medium error %		< 1%	< 1%	< 1%	< 1%	2.07%	5.54%

Membership functions are defined by

Low

$$\mu(medium)=\exp\cdot(-0{,}5\cdot(\frac{x-x_{medium}}{L})^{2})$$

Medium

$$\mu(low)=\exp\cdot(-0{,}5\cdot(\frac{x-x_{low}}{L})^{2})$$

High

$$\mu(high)=\exp\cdot(-0{,}5\cdot(\frac{x-x_{high}}{L})^{2})$$

Esto lo voy a sacar de la tabla y lo pongo en cuadros de texto, que son más fáciles de centrar

Membership functions are defined by

Low

$$\mu(medium)=\exp\cdot(-0{,}5\cdot(\frac{x-x_{medium}}{L})^{2})$$

Medium

$$\mu(low)=\exp\cdot(-0{,}5\cdot(\frac{x-x_{low}}{L})^{2})$$

High

$$\mu(high)=\exp\cdot(-0{,}5\cdot(\frac{x-x_{high}}{L})^{2})$$