

# Furfural production from *Eucalyptus globulus*: Optimizing by using neural fuzzy models.

García-Domínguez M.T.<sup>1</sup>; García-Domínguez J.C.<sup>2</sup>; Feria, M.J.<sup>2</sup>; Gómez-Lozano, D.M.<sup>3</sup>; López, F.<sup>2</sup>; Díaz, M.J.<sup>2</sup>

<sup>1</sup>Agrifood Campus of International Excellence (CeIA3). Parque Huelva Empresarial. 21007 Huelva.

<sup>2</sup>PRO2TEC- Chemical Engineering Department. Campus "El Carmen". Universidad de Huelva. 21071 Huelva. Spain.

<sup>3</sup>ACCIONA INFRAESTRUCTURA Dirección de Innovación Tecnológica. C/ Valportillo II, 8. Polígono Industrial Alcobendas. 28108 Alcobendas (Madrid)

\*Corresponding author. Tel.: +34988387075. Fax: +34988387001. E-mail: dblanco@uhu.es

## SUMMARY

Samples of *Eucalyptus globulus* were subjected to isothermal autohydrolysis (temperature: 220-250°C and isothermal residence time 0-250°C). The effect of the H factor on the sugar yield and composition of both liquid and solid phases obtained after the treatments has been studied. The furfural concentration and composition has been determined. A central composite experimental design, in conjunction with the neural fuzzy model, was used to the furfural content maximization under isothermal autohydrolysis. A variation range, involving two independent variables at three different levels, was established for each process variable (viz. temperature and autohydrolysis time). The obtained models reproduced the experimental results of the dependent variables with errors below 6%. Under optimum experimental conditions, the yield of furfural (4.4 g/100 g raw material) could be obtained at 60 minutes and 220°C).

Key words: autohydrolysis, furfural, xylan, eucalyptus globules.

## INTRODUCTION

Lignocellulosic materials are the most abundant renewable resources in the world. Over the last decade, there has been a growing interest in the potential of lignocellulosic biomass as an alternative for petroleum resources; this is because of its abundance as a feed stock and its carbon neutrality. However, the strong crystalline structure of cellulose and the complex structure of lignin and hemicelluloses with cellulose in lignocellulosic material also make it complicate to use them as feedstock for the chemical industry. Due to the development in chemical technology and biotechnology, it will possible to convert lignocellulosic materials into such platform chemical as ethanol, succinic acids, fumaric, maleic, etc. at a commercial scale in the near future (Cheng and Zhu, 2008)

One compound that shows a lot of promise is furfural. It is an important product of lignocellulosic materials because of its numerous possible applications in oil refining, plastics and pharmaceuticals. Its annual production volume is more than 200.000 t (Kottke, 2006). Furfural is a significant product of the prehydrolysis step and it results from the degradation, through intermediates, of xylose. It is the only organic compound derived from biomass that can replace the crude oil based organics used in industry (Dalin Yebo Trading 2004). Moreover, it is an important compound in the fragrance industry, pharmacy, agriculture, and in leather manufacture and it is used widely in the petrochemical and fine-chemical industries. The molecular formula is  $C_5H_4O_2$ . Its synonyms are: 2-furancarboxaldehyde, furaldehyde, 2-furaldehyde, 2-furfuraldehyde, fural, furfurol. In this sense, the importance of furfural and its derivatives has increased due to its very wide applications and this has made it

imperative for the search for cheap, renewable and always available feedstock for the production of furfural (Wankasi et al., 2011).

The ability for hydrolysis to hydrolyze hemicellulose, producing furfural from the pentosans of woody materials is well known (Klemola, 1976). This can occur without the use of mineral acids due to the liberation of acetic acid from the acetyl groups of the hemicelluloses of many woods. However, industrial production of furfural requires a minimum content of 15-20% of pentosans and only about one third of the pentosans in the raw materials can be converted into furfural (Zerbe and Baker, 1987, Yahyazadeh, 2011). Furthermore, furfural itself can also degrade to an array of decomposition products. The actual furfural obtention involved in the production of furfural from agricultural wastes as a source of hemicellulose or pentosan is by acid catalyzed hydrolysis (Sproull et al., 1985, 2007, Wankasi et al., 2011, Rong et al., 2012) and steam pressure (Lee et al., 2008).

Sustained employment of lignocellulosic resources involves necessarily its fractionation. In that form, lignocellulosic materials are sequentially fractionated to obtain the main components (cellulose, hemicelluloses and lignin) in separated streams for an individualized profit of each. This fractionation could be performed by hydrolysis methods (Garrote et al., 1999, Binder et al., 2010), alkaline extraction (Schild et al., 2010; Cheng et al., 2010), enzymatic hydrolysis (Martin-Sampedro et al., 2012), etc.

Among the treatments of lignocellulosic biomass at moderate conditions, autohydrolysis is presented as energy efficiency suitable hemicellulose extraction process for producing hemicellulose-derived oligosaccharides with reasonable yield and purity (Garrote et al., 2002) with clear economic

advantages. Moreover, compared to other pretreatment methods, hydrolysis is useful for the conversion of maximum hemicellulosic fraction into xylose and other sugars, which can be fermented into ethanol by specialized microorganisms (Chandel et al., 2011).

On the other hand, attending to dynamic modelling methods, the neural fuzzy modelling accuracy seems to be a suitable system to obtain an adequate mathematical model for industrial lignocellulosic applications (Alfaro et al., 2009, Chen et al., 2004, Yang, 2006, Chaibakhsh et al., 2011, Wang et al., 2011). Nevertheless, a few references have been found in hydrolysis applications (Capparós et al., 2007, Barakat, 2012).

The aim of this study is to optimize furfural processing technology by using neural fuzzy models to obtain optimum furfural yields from *Eucalyptus globulus* autohydrolysis. Material balances and compositions of solid and liquid phases were evaluated, with especial attention to furfural concentration and liquid phase composition.

## 2. MATERIALS AND METHODS

### 2.1. Raw material

*Eucalyptus globulus* samples from local plantations (Huelva, Spain) were milled to pass an 8 mm screen, since in preliminary studies no diffusional limitations were observed for this particle, air-dried, homogenized in a single lot to avoid differences in compositions among aliquots, and stored.

### 2.2. Analysis of raw material and solid residues from hydrothermal treatment

Aliquots of raw material or solid residue were milled to particle size < 0.5 mm and subjected to moisture and determination of extractable compounds (TAPPI T-264-om-88) and to Quantitative Acid Hydrolysis with 72% H<sub>2</sub>SO<sub>4</sub> following standard methods (T-249-em-85). The solid residue after hydrolysis was recovered by filtration and considered as Klason lignin. The compounds (glucose, xylose and arabinose, furfural and 5-hydroxymethylfurfural [HMF]) and acetic acid contained in the hydrolysates were determined by HPLC, so the HPLC features are below mentioned. Ashes were determined by calcination (T-244-om-93). Composition of raw material is shown in **Table 1**.

### 2.3. Hydrothermal processing of wood samples

Raw material and water were mixed in the desired proportions and treated in a 600 cm<sup>3</sup> stainless steel reactor (Parr Instruments Company, Moline, Illinois, USA) using a liquid/solid ratio (LSR) of 8 kg water/kg raw material, on dry basis (the moisture content of material was considered as water). The liquid/solid ratio had been recognized as an important factor in furfural yield at low acid concentration and its optimal value (8-10) has been found in previous studies (**Yahyazadeh, 2011**). The reactor was fitted with four-blade turbine impellers, heated by an external fabric mantle and cooled by cool water circulating through an internal loop. The reaction media stirred at 150 rpm and heated to reach the desired temperature, time zero was considered to be the beginning of the isothermal stage. **Figure 1** show heating profile of the reactor.

After treatment, solid residues were recovered by filtration, washed with water, air-dried, weighted for yield determination. Aliquots of the solid residues were assayed for moisture and composition (duplicate) using the same methods as

for raw material analysis. An aliquot of the liquors was oven-drying to constant weight to determine the dry content (DC, g non volatile compounds/g liquid phase). A second aliquot was filtered through 0.45 mm membranes and used for direct HPLC determination of monosaccharides, furfural, hydroxymethylfurfural (HMF) and acetic acid. A third aliquot was subjected to quantitative posthydrolysis with 4% H<sub>2</sub>SO<sub>4</sub> at 121 °C for 45 min, before 0.45 mm membranes filtration an HPLC analysis. The increase in monosaccharide and acetic acid concentration caused by posthydrolysis provided a measure of the oligomer concentration. HPLC analyses were performed using a BioRad Aminex HPX-87H colum at 30° C eluted with 0.01 M H<sub>2</sub>SO<sub>4</sub> at a flow rate of 0.6 mL min<sup>-1</sup>.using a Refractive Index detector to quantify glucose, xylose, arabinose, acetic acid, HMF and furfural.

The H-factor is a kinetic model that expresses isothermal residence time and temperature as a single variable. It was developed to predict the temperature or isothermal residence time needed to obtain a given lignocellulosic severity process. The H-factor is given by the eq. 1.

$$H = \int_0^t e^{\left(43.181 \frac{16115}{T(t)}\right)} dt \quad (\text{Eq. 1})$$

Where time (t) is in hours and the temperature (T) is given in degrees Kelvin (Sixta, 2006). The numerical constants in the expression are related to the universal gas constant and activation energy for removal of lignin during process.

2.4. Experimental design and Statistical analysis by adaptative neural fuzzy inference system (ANFIS)

In order to be able to relate the dependent (glucan, xylan, araban, acetyl groups, hydroxymethylfurfural, furfural) and independent variables (isothermal residence time and temperature) with the minimum possible number of experiments, a three levels full factorial design was used (Akhnazarova, and Kafarov, 1982). These levels are called “high”, “medium” and “low” or “+1”, “0” and “-1”, respectively. This experimental design (Table 2) enabled the construction of non-linear fuzzy models.

The independent variables used in the equations relating to both types of variables were those having a statistically significant coefficient (viz. those not exceeding a significance level of 0.05 in Student's t-test and having a 95% confidence interval excluding zero). The isothermal temperature and time used in the factorial design were 220, 235 and 250°C for temperature and 0, 30 and 60 min for isothermal residence time.

On the other hand, fuzzy modeling is a powerful tool to describe the behaviour of non-linear complex systems and fuzzy theory has been successfully applied to the simulation, and control of several biological processes. Another powerful tool for modeling these complex systems is neural network (NN), which was developed from the analogies to the properties of biological neurons. The integration of fuzzy systems and neural network can combine the merits of both systems, offering a more powerful tool for modeling. It uses NNs as a tool in fuzzy systems. In that form, Adaptive network based fuzzy inference system (ANFIS), proposed by Jang (1993), is based on the first order Sugeno-fuzzy model. The NN paradigm used is a multilayer feed forward back-propagation network. The detailed architecture, learning procedure for ANFIS can be found in related literature (Jang and Sun 1995).

The mathematical equation which responds to different rules is:

$$y_e = \frac{\sum_{l=1}^m y_l \cdot R_l}{\sum_{l=1}^m R_l} \quad (\text{Eq. 2})$$

$y_e$ = estimate value of output variable (glucan, xylan, araban, acetyl groups, hydroxymethylfurfura, furfural %),

$m$ = number of rules,

$y_l$ = defuzzifier.

$R_l$  is the product of the selected membership functions.

In that form, the simplification of Eq. 2 for the variables studied under 9 fuzzy rules (three levels for isothermal residence time and temperature respectively) is

$$y_e = \frac{\sum_{l=1}^{48} c_l \left[ \prod_{i=1}^3 x_i \right]}{\sum_{l=1}^{48} \left[ \prod_{i=1}^3 x_i \right]} \quad (\text{Eq 3})$$

where “ $c_i$ ” is a linear equation (defuzzifier equation),

The parameters, constants in the equation 4 were estimated by using the ANFIS tool in the Matlab (Fuzzy Logic Toolbox Version 2.2.2, Neural Network Toolbox Version 4.0.6) software suite.

### 3. RESULTS AND DISCUSSION

#### 3.1. Raw material composition

The raw material composition of the *Eucalyptus globulus* (EG) was analyzed as described in the experimental section, and the results are detailed in [Table 1](#).

For EG, the amounts of lignin and cellulose, measured as Klason lignin and glucan, respectively, were 21.2% and 42.8% of the total material. The xylan



represented 17.1% of the EG. Moreover, the composition was 0.4% for arabinan and 3.5% for acetyl groups. As can be seen, the compositions of the selected materials were similar to others EG reported in the literature.

### 3.2. Effect of the H factor on *Eucalyptus globulus* solubilization under hydrothermal treatment

In Table 2, the experimental conditions used for the studied H factor range is shown. In that form, **Figure 2** shows the xylose, glucose, arabinose and acetyl groups contents of the studied samples and degradation products found (furfural and HMF) as a function of the H factor. As expected, an increase in H factor produces an increase in hemicellulose content in the liquor and the subsequent reduction in its solid phase. The principal component in the hydrolyzed extracts from EG was acetyl groups. A light increases in this compound is observed with the progressive increase in H factor. In autohydrolysis, where water is the only reactive added to substrate, catalysts of hydrolysis are in a first stage hydronium ions coming from water auto-ionization that lead to depolymerization of hemicelluloses by selective hydrolysis of both glycosidic linkages and acetyl groups. In a second stage, hydronium ions coming from acetic acid also act as catalysts, improving reaction kinetics and in this form the contribution of hydronium ions from acetic acid is higher than that from water autoionization (**Palmqvist and Hahn-Hagerdal, 2000; Carvalho et al., 2008**). Moreover, previous studies indicated that lignocellulosic material itself may have a neutralizing effect on the acid due to the buffering effect of the mineral salts contained in the wood particularly at low hydronium ion concentrations (**Springer and Harris, 1985, Parajó et al., 1995**).

The xylose concentration was significantly higher in water extracts under low H factor values than under higher H factor values. And lower xylose contents is found under higher H factor. These results suggested that xylose reactions to other degradation products (vs. furfural) in hydrothermal pretreatment are happening at high factor H values. Many manuscripts have found that the xylose hydrolysis rate is not uniform and under high extraction levels the rate slows (Maloney et al., 1985, Garrote et al., 2004, Rodriguez-Chong et al., 2004) and have been explained by the different intrinsic reactivity of the different xylose fractions; product inhibition arising from a decreasing H<sup>+</sup> concentration with isothermal residence time as a result of the furfural's ability to act as a base which reacts with H<sub>3</sub>O<sup>+</sup> to form stable, protonated furfural. This causes the acid concentration to decrease and the reaction rate to drop (Antal et al., 1991). It is known that these reactions were controlled by oligomeric xylose decomposition, while acid-catalytic reactions in dilute acid pretreatment were controlled by monomeric xylose decomposition (Shen and Wyman, 2011). The greatest concentration of xylose, 4% with respect to initial raw material, was generated in water extracts at 3111 hrs H Factor. After that, the xylose transformation to degradation other products was generated in significant quantities (Binder et al., 2010).

Arabinose is a minor constituent of hardwood hemicellulose which is dissolved into the extract solution. Arabinose removal was found to have a maximum of 0.4% which was achieved in water extracts at all H factors tested. It was inferred from these results that all of the available arabinose most likely had been removed at the lowest H factor. Then, similar behaviour than that found for

xylose is observed for arabinose. nevertheless, this compound gets higher resistance to breakdown to that observed for xylose (Carvalho et al., 2005).

Moreover, in Figure 2 is observed that the nonglucose carbohydrate portion of the lignocellulosic biomass is much more sensitive to acid hydrolysis than the glucose portion (Chamy et al., 1994). The low glucose concentrations present in the hydrolyzed extract originating from autohydrolysis would be detrimental to the pulp yield (Garrote et al., 2003). Figure 2 indicates that under high H factor begins to impact them negatively as far as yield loss in the solid phase (Table 2). The hydrolysis of the glucan fraction during hydrolysis involves solubilization and partial destruction of the glucose produced. Therefore, glucose concentration does not increase in equivalent proportion that the H factor is increasing. These decreases are probably due to the degradation of glucose, which results in hydroxymethyl-furfural (Antal et al., 1991).

The yield of furfural increased with increasing the H factor to 10000 hrs H Factor (Figure 3). A prolonged temperature or isothermal residence time resulted in a decrease in the furfural content due to degradation that occurred in this compound (Chandel, et al., 2011). These results indicate that, when the reaction H factor was fixed at low values could be considered as optimum conditions for the production of furfural. Moreover, as shown in Figure 3, HMF concentration in the hydrolyzate increased with H factor and only degradation has been observed under high H factor values.

### 3.3 Solid phase composition after hydrothermal treatments

Table 2 shows the fraction of the constitutive biopolymers that remains in the solid residue after autohydrolysis at the different hydrolysis conditions tested. As can be observed, in the case of cellulose (expressed as glucan), around

90% remained unaltered under low H factor values. However, the reaction conditions do affect this behavior and only 1.9% of this component is found at 264127 hrs H factor. In the case of xylan, arabinan and acetyl groups this unaltered component percentage was lower, varying between 0–10%, independent of the reaction conditions. That is, these components have been extracted in significant quantities even at low H factor levels.

In all studied conditions, the amount of the cellulose remained in the solid was significant (63.9 - 45.2%), so can be considered that the cellulose remaining in the solid could be separated in subsequent processes.

### 3.4. Optimizing isothermal autohydrolysis conditions for maximizing furfural yield in liquor

There are several factors which affect the production of furfural from xylan-containing hemicellulose such as the initial xylose concentration, temperature and isothermal residence time, are important variables in autohydrolysis processes (Dutta et al., 2012). In previous studies of the hydrolysis it was found that high temperatures and times (high pressures) would increase the soluble xylan concentration and hence increase furfural production (Yang et al., 2006) however some authors have suggested that pentosans are released better at slightly lower temperatures. Therefore an efficient optimization *Eucalyptus globulus* is necessary to carry out.

In the final liquor composition modeled (Figures 4-7), it was observed that release of xylose and glucose in the hydrolyzate was dependent on experimental operating conditions.

As can be seen in **Figure 4**, isothermal residence time is the variable most influential in glucose extraction during the autohydrolysis process. In that form, high glucose values could be found under low process time. After that a high degradation of this compound has been observed. With respect to temperature, lower statistical influence than that observed for isothermal residence time can be distinguished and similar behavior to that detected for isothermal residence time is examined in temperature. In that form low glucose values in liquor could be found under high isothermal residence time and temperature. Then, the dehydration of glucose at high isothermal residence time and temperature resulted in substantial glucose decomposition.

**Figure 5** shows a similar effect with respect to the independent variables (isothermal residence time and temperature ) on xylan evolution during the autohydrolysis process than those found in **Figure 4** for glucose evolution. Moreover, increasing the isothermal residence time and temperature decreases the rate of decomposition of xylan (**Figure 5**), similar behavior has been found for **Dutta et al., (2012)** with similar biomass. Maximum concentration of xylose, 3.8% (o.d.b.) was achieved when reaction was carried out at 220°C for isothermal residence time period of 0 min in this temperature (only the of reactor warming-up time to the selected temperature has been the reaction time).

Among glucose decomposition products, HMF could be the most important component (**Carvalho, et al., 2008**). In general HMF (**Figure 6**) increased with time under all studied temperatures to reach a maximum (3.6% o.d.b. at 30 min and 250°C) after that isothermal residence time high HMF decomposition is

found. When temperature has low values higher HMF contents is observed with respect to medium-to-high values.

Maximizing furfural in the final liquor could be critical due to the high decomposition of this component (Binder et al., 2010). These processes were governed mainly by volatilization/degradation of furfural under severe conditions. From **Figure 7** high statistical influence of temperature with respect to isothermal residence time is found for this component. Therefore, it presents a different behavior to the other hydrolyzed studied. Furfural content was highly affected by the temperature than the isothermal residence time. In **Figure 7**, a continuous increase for furfural content with respect to time and a high statistical decrease with respect to temperature can be observed. Subsequently, the optima isothermal autohydrolysis conditions within the studied range in this work to obtain high furfural content (4.4% o.d.b.) could be found at 60 minutes and 220°C.

#### **4. CONCLUSIONS**

Isothermal autohydrolysis of *Eucalyptus globulus* could be used as a appropriate process for furfural production.

Isothermal autohydrolysis showed that the maximal yield in the production of xylooligosaccharides at 220°C. At this temperature *Eucalyptus globulus* gave a maximum yield of xylose (3,8% with respect initial raw material). An almost quantitative extraction for arabinose and acetyl groups has been found at this temperature.

In *Eucalyptus globulus* the increase in the hydrolysis temperature yielded liquor with higher contents of furfural and low xylan contents. Consequently, optima

isothermal autohydrolysis conditions to obtain high furfural content (4.4% o.d.b.) could be found at 60 minutes and 220°C.

## **5. ACKNOWLEDGEMENTS**

The authors acknowledge financial support for this investigation has been provided by CDTI (CENIT-E-CDTI-BioSos-CEN-2009-1040) and supported by Ministry of Economy and Competitiveness, "Local Investment fund for employment" and the business group ACCIONA INFRAESTRUCTURAS, S.A.

## REFERENCES

- Akhnazarova, S., Kafarov, V., (1982) Experiment optimization in chemistry chemical engineering. Mir Publisher, Moscow.
- Alfaro, A., Pérez, A. García, J.C. López, F. Zamudio, A.M. and Rodríguez, A. 2009. Ethanol and soda pulping of tagasaste wood: Neural fuzzy modeling. *Cellulose Chem. Technol.*, 43 (7-8), 295-306.
- Antal, M. J., Leesomboon, T., Mok, W. S. & Rochards, G. N. (1991) Mechanism of the formation of 2-furaldehyde from D-Xylose. *Carbohydrate Research*, 217, 71-85.
- Barakat, A., Monlau, F., Steyer, J.P. Carrere, H. (2012) Effect of lignin-derived and furan compounds found in lignocellulosic hydrolysates on biomethane production. *Bioresource Technology*. 104: 90–99.
- Binder, J.B., Blank, J.J., Cefali, A.V. and Raines R.T. (2010) Synthesis of Furfural from Xylose and Xylan. *ChemSusChem* 3, 1268-1272.
- Binder, J.B., Blank, J.J., Cefali, A.V. Raines, R.T. 2010. Synthesis of Furfural from Xylose and Xylan. *ChemSusChem* 3, 1268-1272.
- Caparrós, S., Ariza, J., Garrote, G., López, F. and Díaz, M.J. Optimization of *Paulownia Fortunei* L. Autohydrolysis-Organosolv Pulping as a Source of Xylooligomers and Cellulose Pulp. *Ind. Eng. Chem. Res.* 2007, 46, 623-631.
- Carvalho, F., Duarte. L.C. and Gírio, F.M. (2008) Hemicellulose biorefineries: a review on biomass pretreatments. *Journal of Scientific & Industrial Research*. 67:849-864.
- Carvalho, F., Garrote, G., Parajó, J.C., Pereira, H., Gírio, F.M. 2005 Kinetic modeling of brewery's spent grain autohydrolysis. *Biotechnol Prog.* 21(1): 233-43.



- Chaibakhsh, N. and Abdul Rahman, M.B. 2011. Application of fuzzy modeling and optimization in enzymatic esterification process. *Int. J. Chem. Eng. App.*, 2 (6) 408-415.
- Chamy, R.; Illanes, A.; Aroca, G. and Nunes, I., 1994, Acid Hydrolysis of Sugarbeet Pulp as Pretreatment for Fermentation. *Biores Technol*, 50, 149-154
- Chandel, A.K., Chandrasekhar, G., Radhika, K., Ravinder, R. and Ravindra, P. (2011) Bioconversion of pentose sugars into ethanol: A review and future directions. *Biotechnology and Molecular Biology Review*. 6(1): 008-020.
- Chen, L.Z., Nguang, S.K., Chen, X.D. and Li, X.M. 2004. Modeling and optimization of fed-batch fermentation processes using dynamic neural networks and genetic algorithms, *Biochem. Eng. J.*, 22: 51-61.
- Cheng S. and Zhu, S., 2008. Use of lignocellulosic material for a sustainable chemical industry. *Bioresources* 3 (3) 666-667
- Dalin Yebo Trading, 2004. <http://www.dalinyebo.co.za/dyT/FurfuralMarket.htm>
- Díaz MJ, Alfaro A, García MM, Eugenio ME, Ariza J, López F, (2004) Ethanol pulping from tagasaste (*Chamaecytisus proliferus* L.F. ssp *palmensis*). A new promising source for cellulose pulp. *Ind. Eng. Chem. Res.* 43 (8): 1875-1881.
- Dutta, S. De, S., Saha, B. and Alam, M.I. (2012) Advances in conversion of hemicellulosic biomass to furfural and upgrading to biofuels. *Catal. Sci. Technol.* 2: 2025-2036.
- Eyles, A., Davies, N.W. and Mohammed, C.L. (2003) Wound wood formation in *Eucalyptus globulus* and *Eucalyptus nitens*: anatomy and chemistry. *Canad. J. Forest Res.*, 33 (12) 2331-2339.

- Garrote, G., Domínguez, H. and Parajó, J. C. (2004) Production of Substituted Oligosaccharides by Hydrolytic Processing of Barley Husks. *Industrial and Engineering Chemistry Research*, 43, 1608-1614.
- Garrote, G., Eugenio, M.E., Díaz, M.J., Ariza, J., López, F. 2003 Hydrothermal and pulp processing of Eucalyptus. *Bioresour. Technol.* 88(1):61-8.
- Jang JSR, (1993) ANFIS adaptive-network-based fuzzy inference system. *IEEE Transactions on Systems Man Cybernetics* 23 (3): 665-685.
- Jang JSR, Sun CT, (1995) Neuro-Fuzzy Modeling Control. *Proc. IEEE* 83 (3): 378-406.
- Klemola, A. (1976), Development and trends in industrial utilisation of fuller forest biomass (branch wood, foliage and stumps) in the wood chemical industry. Symposium on the harvesting of a larger part of the forest biomass. Geneva :Joint Committee on Forest Working Techniques and Training of Forest Workers. Vol. 1: 56-63.
- Kottke, R. H., in Kirk-Othmer Encyclopedia of Chemical Technology, Wiley Interscience, New York 2004; b) Biorefineries—Industrial Processes and Products (Ed. B. Kamm, P. R. Gruber, M. Kamm), Wiley-VCH, Weinheim 2006.
- Lee, J.M., Kim, Y.C., Y.C., Hwang, I.T., Park, N.J., Hwang, Y.K., Chang, J.S. *Biofuels, Bioprod. Biorefin.* 2008, 2, 438 –454.
- Lezchinsky, M., Sixta, H. and Patt, R. 2009. Detailed mass balances of the autohydrolysis of *Eucalyptus globulus* at 170°C. *Bioresources* 4 (2) 687-703.
- López, F.; Alfaro, A.; Caparrós, S. García, M.M. Pérez, A., Garrote, G. 2008. Aprovechamiento energético e integrado por fraccionamiento de biomasa lignocelulósica forestal y agroindustrial. *CIDEU*. 5: 17-29.

- Maloney, M. T., Chapman, T. W. and Baker, A. J. (1985) Dilute Acid hydrolysis of Paper Birch: Kinetics Studies of Xylane and Acetyl Group Hydrolysis. *Biotechnology and Bioengineering*, 27, 355-361.
- Palmqvist, E., Hahn-Hagerdal, B. (2000). Fermentation of lignocellulosic hydrolysates. Inhibition and detoxification. *Biores. Technol.*, 74: 17-24.
- Parajó, J. C., Alonso, J. L. and Santos, V. (1995) Kinetics of Catalyzed Organosolv Processing of Pine Wood. *Industrial and Engineering Chemistry Research*, 34, 4333-4342.
- Patt, R., Kordsachia, O., Fehr, J. 2006. European hardwoods versus *E. globulus* as a raw material for pulping. *Wood Sci. Technol.* 40: 39-46.

- Rencoret, J., Gutiérrez, A., Nieto, L., Jiménez-Barbero, J., Faulds, C.B., Kim, H. Ralph, J., Martínez, A.T. and del Río, J.C. 2011. Lignin Composition and Structure in Young versus Adult *Eucalyptus globulus* Plants. 155: 667-682.
- Rodriguez-Chong, A., Alberto Ramirez, J., Garrote, G. and Vazquez, M. (2004) Hydrolysis of sugar cane bagasse using nitric acid: a kinetic assessment. *Journal of Food Engineering*, 61, 143-152.
- Rong, C., Ding, X., Zhu, Y., Li, Y., Wang, L., Qu, Y., Ma, X., Wang, Z. 2012. Production of furfural from xylose at atmospheric pressure by dilute sulfuric acid and inorganic salts. *Carbohydr Res.* 1 (350) 377-380.
- Shen, J., Wyman, C.E. 2011 A novel mechanism and kinetic model to explain enhanced xylose yields from dilute sulfuric acid compared to hydrothermal pretreatment of corn stover. *Bioresour Technol.* 102(19): 9111-20.
- Sixta, H., (2006), *Handbook of Pulp*. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany. Vol 1: 189-191.
- Springer, E. L. and Harris, J. F. (1985) Procedures for Determining the Neutralising Capacity of Wood during Hydrolysis with Mineral Acid Solutions. *Industrial and Engineering Chemistry Product Research and Development*, 24, 485-489.
- Sproull, R. D., Bienkowski, P. R., Tsao, G.T., *Biotechnol. Bioeng. Symp.* 1985, 15, 561– 577
- Wang Z., Xu, J., Cheng J.J. 2011. Modelling biochemical conversion of lignocellulosic material for sugar production: A review. *Bioresources* 6 (4) 5282-5306.

- Wankasi, D. Tarawou, T.J. and Yabefa, J.A. 2011. Furfural production from the peels of ripe pawpaw (*carica papaya* l.) and pineapple (*ananas comosus*) fruits by acid catalyzed hydrolysis. *Am. J. Food Nutrit.*, 1(3): 136-140.
- Wiebren De Jong W. and Marcotullio, G. 2010. Overview of biorefineries based on co-production of furfural, existing concepts and novel developments. *International Journal of Chemical Reactor Engineering*. 8. Arti. A69.
- Yager RR, Filev DP, (1993) SLIDE A simple adaptive defuzzification method *IEEE Tram Fuzzy Syst* 1: 69-78.
- Yahyazadeh, A. 2011 Extraction and Investigation of Furfural in Tea leaves and comparing with furfural in rice hull. *J. Pharmacy Res.* 4(12), 4338-4339.
- Yang ST, (2006) *Bioprocessing for Value-Added Products from Renewable Resources*. Ed. Yang, S.T. Ohio.USA: Elsevier.
- Zadeh LA, (1965) Fuzzy sets. *Information and Control* 8: 338-353.

Table 1. Average chemical composition for *Eucalyptus Globulus* (EG) used and other bibliographic EG composition\*.

<b><i>Eucalyptus Globulus</i></b>						
	Present study	Garrote et al., 2002	Patt et al., 2006	López et al., 2008	Lezchynsky et al., 2009	Rencoret et al., 2011
1% NaOH sol. (%)	13.1	12.4	nd	nd	nd	nd
Ethanol extracts (%)	2.7	1.2	1.7	nd	1.7	0.6
Ash (%)	0.7	0.6	0.2	0.5	0.4	0.4
Glucan (%)	42.8	46.7	50.0	46.8	41.7	46.1
Klason lignin (%)	21.2	22.9	20.5	19.9	22.9	19.8
Xylan (%)	17.1	16.6	14.1	23.9	15.3	17.1
Arabinan (%)	0.4	0.5	nd	0.37	0.4	0.8
Acetyl groups (%)	3.5	3.5	nd	4.32	3.3	nd
Others (%)	7.2	10.1	nd	nd	nd	nd

\* Raw material percentages (100 kg dry matter).

Table 2: Solid phase composition (g/100 g raw material, dry basis)

t (min)	T (°C)	Xt <sup>a</sup>	XT <sup>a</sup>	H Factor	Glucan, %	Xylan, %	Araban, %	Acetyl Groups %	Yield, %
0	220	-1	-1	3111	67.7	1.4	0.0	0.0	63.9
0	235	-1	0	9386	68.5	0.9	0.0	0.0	61.2
30	220	0	-1	21494	58.4	0.0	0.0	0.0	60.4
0	250	-1	1	24370	62.9	0.0	0.0	0.0	59.4
60	220	1	-1	39878	53.1	0.0	0.0	0.0	57.8
30	235	0	0	57649	42.5	0.2	0.7	0.0	53.8
60	235	1	0	105911	28.5	0.9	0.2	0.0	50.0
30	250	0	1	144248	18.6	0.2	0.7	0.0	44.4
60	250	1	1	264127	1.9	0.0	0.0	0.0	45.2

<sup>a</sup>Xt and XT denotes normalized values for time and temperature respectively.

Table 3: Liquid phase composition (g/100 g raw material, dry basis)

t (min)	T (°C)	X <sub>t</sub> <sup>a</sup>	X <sub>T</sub> <sup>a</sup>	H Factor	Glucan, %	Xylan, %	Araban, %	Acetyl Groups, %	HMF <sup>b</sup> , %	Furfural, %
0	220	-1	-1	3111	1.13	3.79	0.12	2.89	0.51	3.17
0	235	-1	0	9386	0.99	0.94	0.14	4.28	1.56	4.05
30	220	0	-1	21494	0.31	1.07	0.28	4.10	2.84	3.93
0	250	-1	1	24370	0.99	0.61	3.26	4.32	2.23	4.42
60	220	1	-1	39878	0.47	0.23	1.51	4.11	2.81	3.01
30	235	0	0	57649	0.55	0.34	3.58	4.40	3.48	2.97
60	235	1	0	105911	0.27	0.96	0.34	4.40	3.05	1.81
30	250	0	1	144248	0.00	0.96	0.13	4.91	3.58	2.02
60	250	1	1	264127	0.05	0.69	4.72	4.95	1.72	0.96

<sup>a</sup>X<sub>t</sub> and X<sub>T</sub> denotes normalized values for isothermal residence time and temperature respectively.

<sup>b</sup>Hydroxymethylfurfural



Table 4. Rules and Parameters of the equations  $c_i$  ( $C_i = A \cdot t + B \cdot T + C$ ) in the neural fuzzy model for xylose, glucose, HMF and furfural respectively.

Rules			Parameters		
t	T		A	B	C
Xylose					
1	1	1			
2	1	2			
3	1	3			
4	2	1			
5	2	2			
6	2	3			
7	3	1			
8	3	2			
9	3	3			
Glucose					
1	1	1			
2	1	2			
3	1	3			
4	2	1			
5	2	2			
6	2	3			
7	3	1			
8	3	2			
9	3	3			
HMF					
1	1	1			
2	1	2			
3	1	3			
4	2	1			
5	2	2			
6	2	3			
7	3	1			
8	3	2			
9	3	3			
Furfural					
1	1	1			
2	1	2			
3	1	3			
4	2	1			
5	2	2			
6	2	3			
7	3	1			
8	3	2			
9	3	3			
Where t is isothermal residence time (min) and T is temperature (°C) <sup>1</sup> For time and temperature 1 is defined by low level in Table 5; 2 is defined by medium level in Table 5 3 is defined by high level in Table 5					

Table 5. Membership functions for variables in the neural fuzzy model for time and temperature.

			L
Membership function for isothermal residence time (t) (L is the width of the Gaussian membership function)	Low	$x_i = \exp(-0.5 \cdot (\frac{x - x_{low}}{L})^2)$	
	Medium	$x_i = \exp(-0.5 \cdot (\frac{x - x_{medium}}{L})^2)$	
	High	$x_i = \exp(-0.5 \cdot (\frac{x - x_{high}}{L})^2)$	
Membership function for temperature (T)	Low	$x_i = \exp(-0.5 \cdot (\frac{x - x_{low}}{L})^2)$	
	Medium	$x_i = \exp(-0.5 \cdot (\frac{x - x_{medium}}{L})^2)$	
	High	$x_i = \exp(-0.5 \cdot (\frac{x - x_{high}}{L})^2)$	

Where for isothermal residence time:  $X_{low}=0$ ;  $X_{med}= 30$ ;  $X_{high}= 60$   
 And for temperature:  $X_{low}= 220$  ;  $X_{med}= 235$ ;  $X_{high}= 260$ .

Figure 1. Operational time-temperature profile.

Figure 2. Liquid phase composition variation of sugars (g/100 g raw material) obtained under isothermal autohydrolysis for *Eucalyptus Globulus*.

Figure 3. Liquid phase composition variation of sugar degradation products (g/100 g raw material) obtained under isothermal autohydrolysis *Eucalyptus Globulus*.

Figure 4. Glucose (g/100 g raw material) evolution with respect to isothermal residence time and temperature.

Figure 5. Xylose (g/100 g raw material) evolution with respect to isothermal residence time and temperature.

Figure 6. 5-hydroxymethylfurfural (HMF, g/100 g raw material) evolution with respect to isothermal residence time and temperature.

Figure 7. Furfural (g/100 g raw material) evolution with respect to isothermal residence time and temperature.

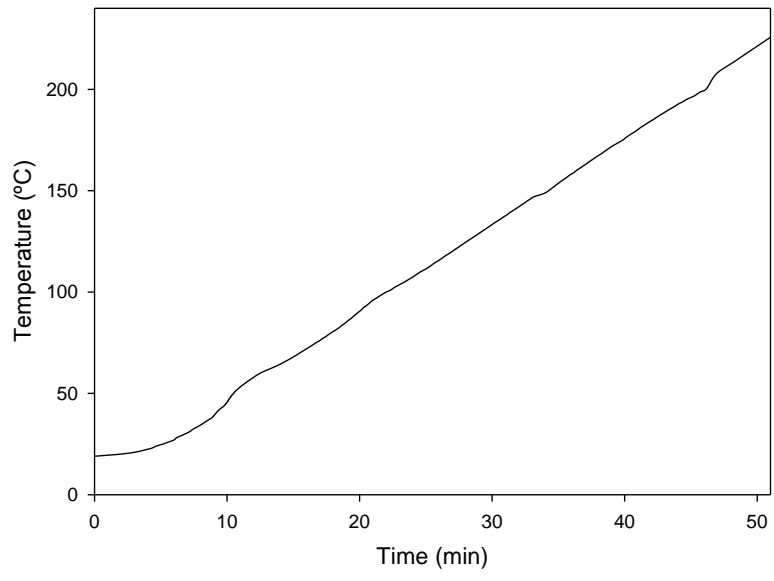


Figure 1

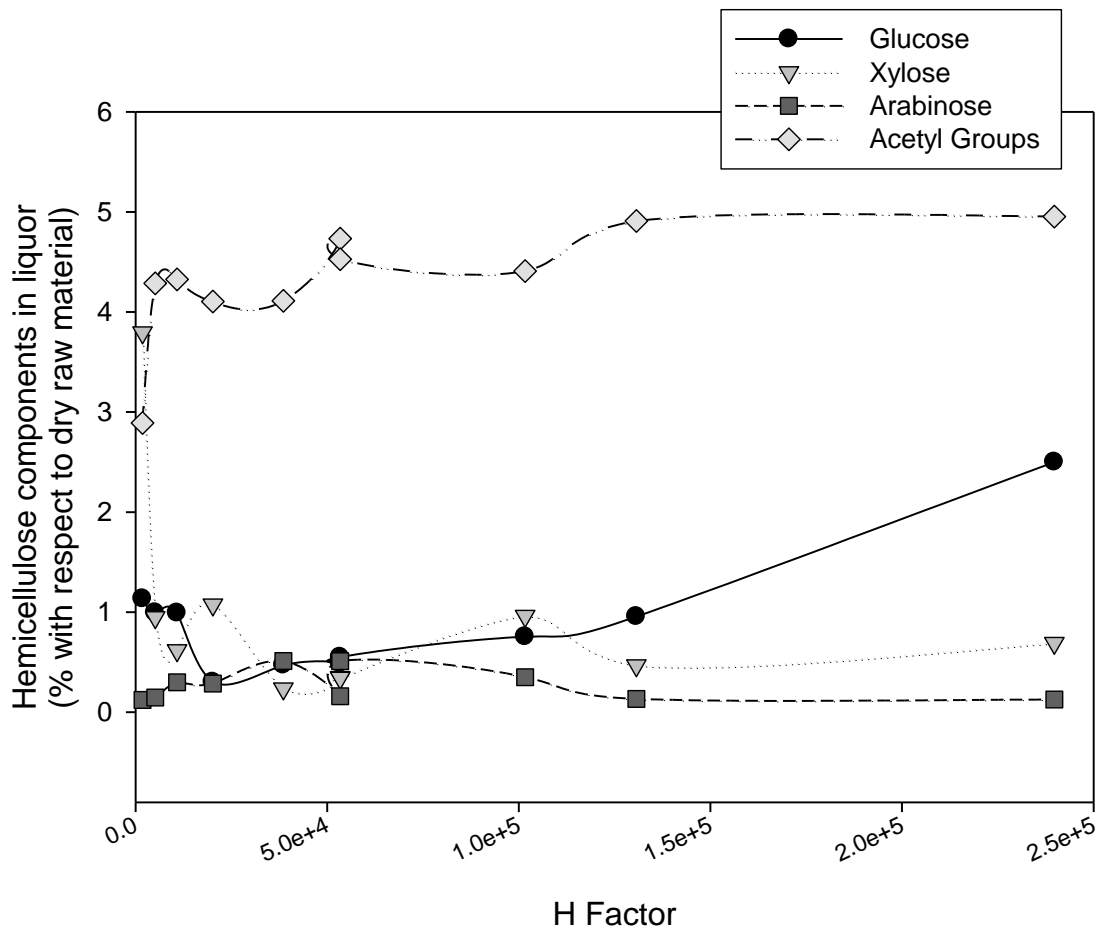


Figure 2

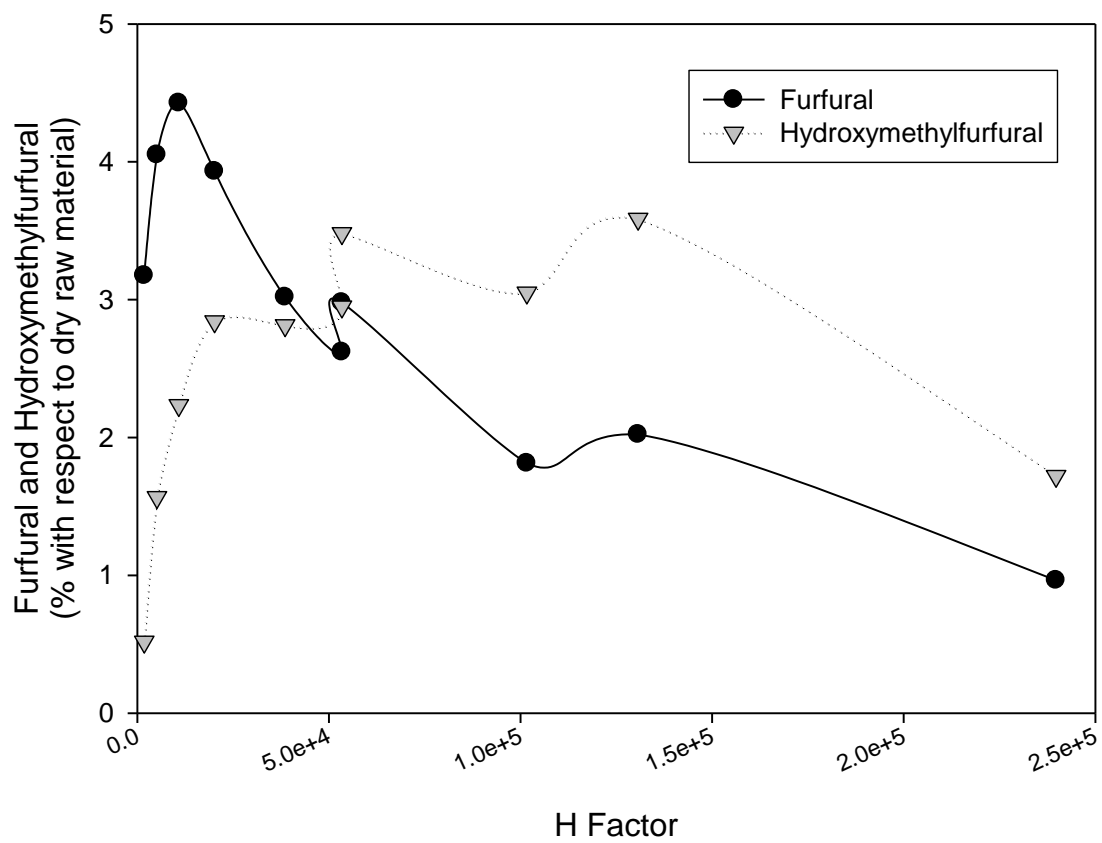


Figure 3

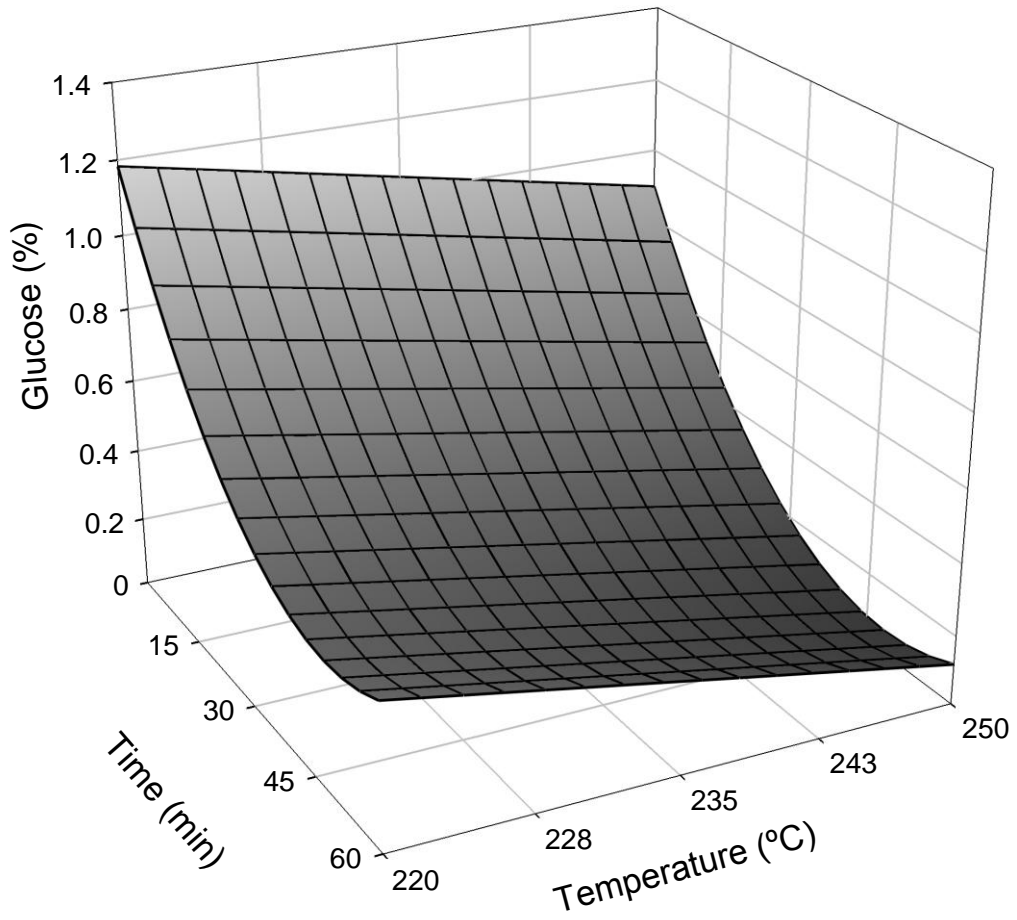


Figure 4

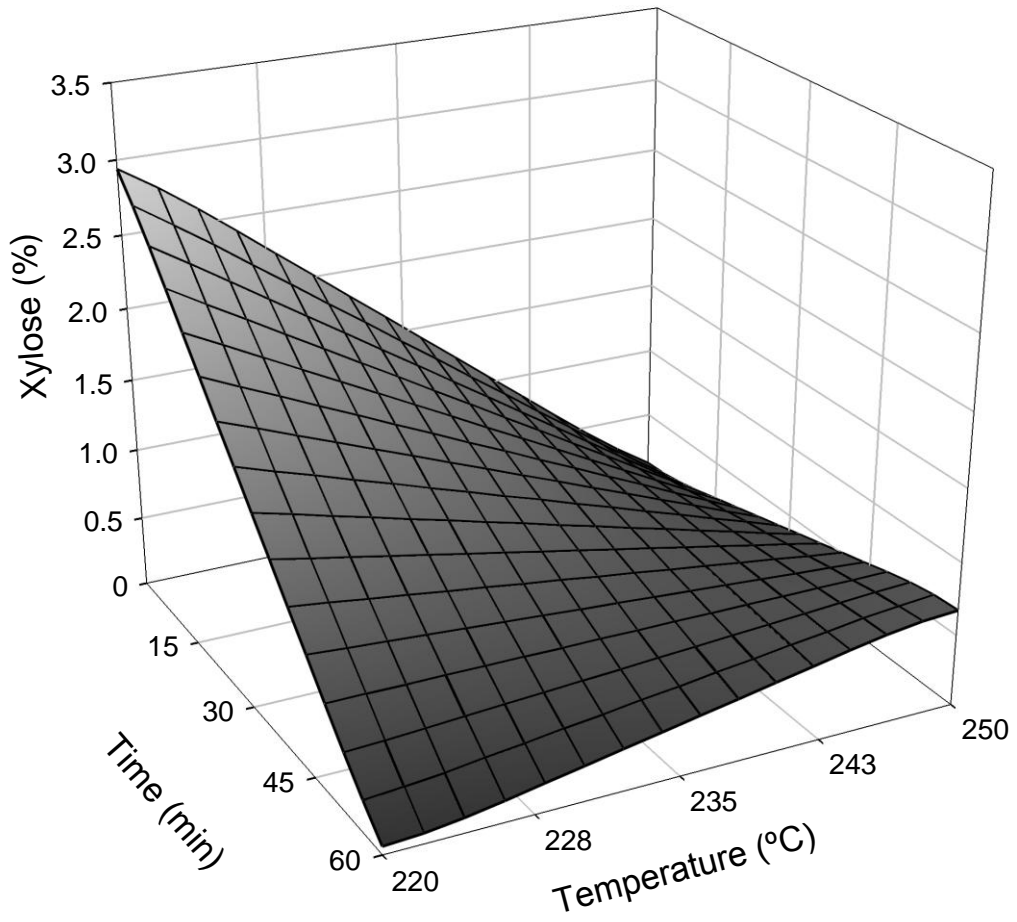


Figure 5



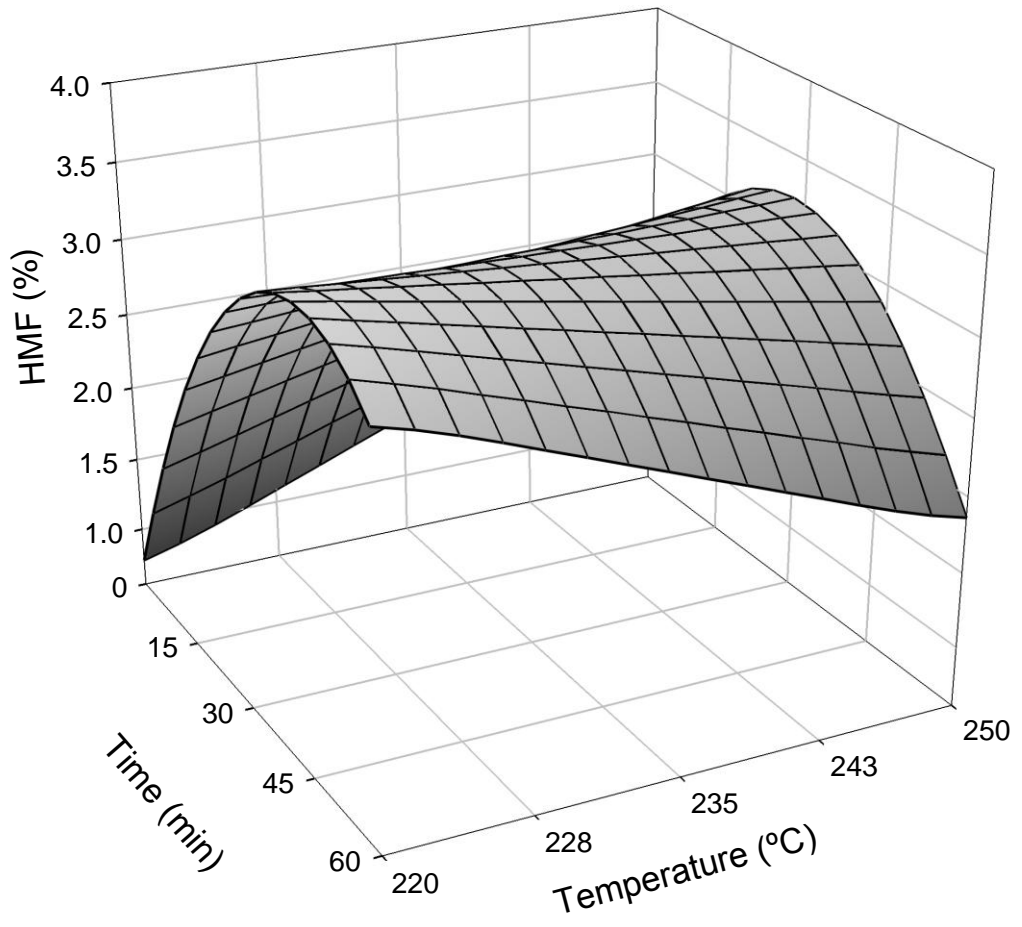


Figure 6

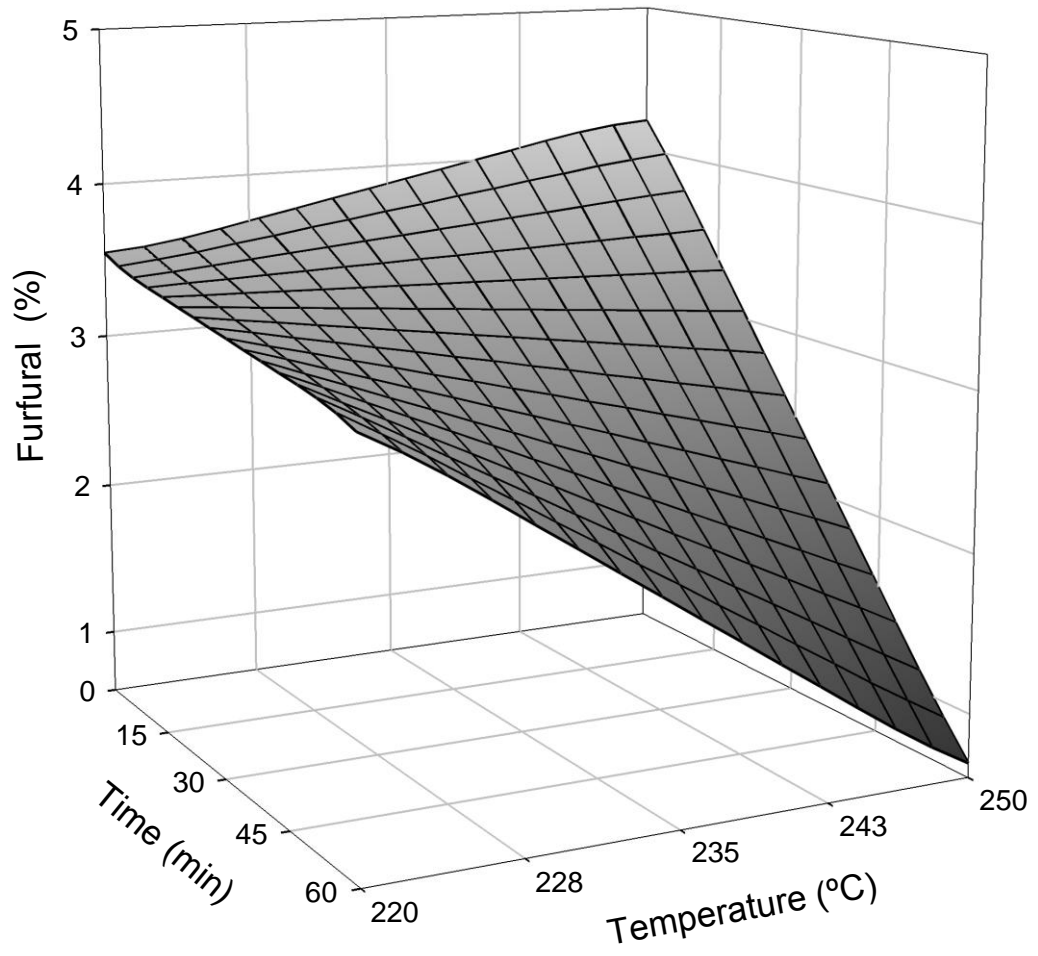


Figure 7