

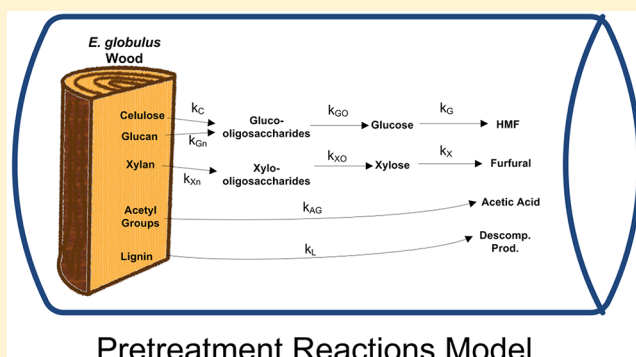
Modeling the Thermochemical Pretreatment of *Eucalyptus globulus* for Bioethanol Production

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Supporting Information

ABSTRACT: The production processes of second generation (2G) ethanol from lignocellulosic materials have been extensively studied in the last decades. In particular, the pretreatment of the raw material has received an important amount of research. This stage has the purpose of decomposing the hemicellulose and lignin walls to improve the yield of glucose on the next step (enzymatic hydrolysis). Among the raw materials studied, *Eucalyptus* wood has an important number of experimental works in the pretreatment, but few works propose a detailed model expressing the reaction kinetics of the compounds involved. In this work, we propose a mathematical model describing the reaction of the most relevant compounds involved in three pretreatments (diluted sulfuric acid, autohydrolysis, and steam explosion) taking *Eucalyptus globulus* as a raw material. The proposed model adequately adjusts the three thermochemical processes. The advantage, as compared to others in the bibliography, is that it contemplates a greater number of compounds in a wide range of process conditions. The model is simultaneously adjusted to contemplate the correlations among the parameters that describe the kinetics of each compound, using the complete set of available experimental data.



Pretreatment Reactions Model

1. INTRODUCTION

The forestry industry of Argentina is located in the northeast region of the country due to its climatic characteristics that favor the growth of the implanted forests. The local government policies aim to transform these resources into valuable products, because currently only 50% of this forestation is industrially used. The production of second generation ethanol (2G) is a viable alternative. For this purpose, the genus *Eucalyptus* is a good option, because it has a relatively rapid growth, and currently represents around one-third of the cultivated area of Argentina. On the other hand, according to FAO data, the portion of *Eucalyptus* forest area in South America represents 45% of the total.¹ The *Eucalyptus globulus* is one of the species studied for the production of 2G ethanol. Nowadays, this species is widely grown in Uruguay and other countries of South America to obtain cellulose pulp.² Recent studies³ reported that the production of ethanol from *E. globulus* in Brazil would be more profitable than the use of sugar cane bagasse. Also, there are studies about that material in Chile.⁴ *E. globulus* wood is a raw material with a great capability for the production of second-generation fuels in several countries of South America and the northeast region of Argentina, in particular.

The biochemical process is currently the most developed technology for the production of 2G ethanol. It is based on the biological fermentation of the glucose released by the decomposition of cellulose via an enzymatic hydrolysis. This process, as compared to the use of concentrated acid, offers a substantial improvement in the cost of the pieces of equipment, the

energy requirements, and the type of raw material to treat. These benefits are obtained because the process can be carried out at temperatures close to the environment. Also, the pieces of equipment use conventional materials, and, because of the action of the enzymes, the polysaccharides are hydrolyzed until they are monomers, without subsequent decompositions, obtaining a higher conversion efficiency.

However, the enzymatic hydrolysis of cellulose needs a pretreatment step to increase its efficiency. The reason is related to the chemical composition of the lignocellulosic material and its structure. It has been observed that hemicellulose and lignin partially enclose the cellulose microfibrils, which represents a physical barrier for the enzymes.⁵ Also, the structure of the material, under natural conditions, has low porosity, making difficult the diffusion of the enzymes.⁶ On the other hand, the cellulase enzymes decompose not only cellulose but also some constitutive hemicellulose polymers, such as xylan. This compound delays the decomposition of cellulose by competitive inhibition. Besides, lignins can bind to the enzymes, immobilizing and decreasing their effectiveness. Therefore, the pretreatment stage encompasses multiple functions, the main one being the solubilization of lignin and hemicellulose to increase the exposed surface of cellulose,⁷ and simultaneously

Received: June 19, 2018

Revised: August 23, 2018

Accepted: August 27, 2018

Published: August 27, 2018

decrease the magnitude of the enzymatic inhibition produced by said polymers. It also increases the porosity of the material, which facilitates the diffusion of the enzymes. One effect that was reported recently, and is actively studied, is the repolymerization of the solubilized lignin compounds. This repolymerized compound is named pseudolignin, and also contains residues of hemicellulosic origin, among others.^{8–10} Therefore, the pretreatment stage is essential to obtain 2G ethanol, because it allows a more efficient conversion from cellulose to glucose.

From a variety of pretreatment alternatives, the use of acid process, with or without acid catalyzer, has been reported to be more suitable for *E. globulus*. The reason is that the hemicellulose of these species is receptive to the hydrolysis via the catalytic action of the hydronium ion, and, unlike softwood species (gymnosperms), its lignin is less recalcitrant to the effect of acids.¹¹ The most studied acid pretreatments for *E. globulus* are the following: diluted sulfuric acid (DSA), autohydrolysis (AH), and steam explosion (SE). These last two are included in the group of the hydrothermal processes, so-called because the decomposition reactions occur because of the action of water under conditions of high pressures and temperatures, circumstances in which water presents acidic characteristics.⁸ Hydrothermal processes have the advantages in that they do not require the addition of the recovery of catalyst, they have low corrosion problem with the pieces of equipment, and its operation is more simple and economic.¹² An important disadvantage of AH and SE with respect to the DSA is that they need high temperatures and processing times to obtain the hemicellulosic monomers in the hydrolyzate phase, or, in its place, the process must include a second stage, commonly named posthydrolysis.¹³

The literature contains a large number of research works that directly or indirectly study the pretreatment process, reporting experimental data on different processing alternatives for lignocellulosic materials of *Eucalyptus* species. The autohydrolysis process is one of the most studied for this raw material, and in the literature can be found data of its application.^{14–19} In ref 20 can be seen a study of combined pretreatments of autohydrolysis and organic solvents;²¹ it presents a comparison between autohydrolysis and pretreatments with the addition of different acid catalysts. Also, there are several works related to the steam explosion for *E. globulus*^{22–25} and *E. vimialis*.²⁶

Also, there are some research works^{27–31} on pretreatments for *Eucalyptus* wood that adjust experimental data into simple empirical models. The goal is to estimate the mass of some compounds present in the reactor when changing the operating conditions of the process. It should be mentioned that in those works the duration of the process is fixed, neglecting the time variable that is an important one in thermochemical processes. Instead, this last aspect is included in the work of Marzialetti, Salazar, Ocampos, Chandra, Chung, Saddler, and Parra,⁴ which develop time polynomial equations of the pretreatment of *E. globulus* by autohydrolysis, adjusting the release of glucose and xylose in the aqueous medium.

Although simple empirical models may have some utility in specific cases, they have limitations. They do not present an adequate fit beyond the variable range used in the experimental work, and, because of that, their application is partial. For this reason, the use of semiempirical models is preferable, because they are more suitable to evaluate the behavior of the system under conditions that move away from the experimental data.³² Moreover, in general, to achieve a similar level of accuracy, a suitable semiempirical model requires fewer parameters than does a purely empirical model.³³

In the literature, few works deal with semiempirical modeling that includes time as an explicit variable. One of the most representative articles is the one of Garrote, Domínguez, and Parajó,³⁴ where the authors present a model for estimating the fraction of xylo-oligosaccharides obtained during an autohydrolysis pretreatment of *E. globulus*, under isothermal conditions. The approach consists of first-order kinetics to represent the decomposition reactions and an Arrhenius-type equation, to account for the variation of the reaction rate with temperature. In a later work of the same authors,³⁵ they introduce the study of the decomposition of the xylo-oligosaccharides in the liquid fraction obtained during isothermal autohydrolysis having posthydrolysis step. They formulate the variation of the reaction rates as a function of temperature and sulfuric acid concentration, using an Arrhenius-type equation and a logarithmic transformation. Moreover, the application of the previous modeling methodology is applied to nonisothermal autohydrolysis processes, obtaining similar results for the same material.³⁶ The research of Garrote, Domínguez, and Parajó is focused on the use of xylose and its oligosaccharides.

The composition of the lignocellulosic materials is complex. They have a high variability due to its biological origin; even with specimens of the same species, important differences may be found, and so the characterization of these materials is usually a difficult task. However, several works present a detailed quantitative and qualitative analysis of the polymers of wood of *E. globulus* and other species of *Eucalyptus*.^{37–39} It should be taken into account that during the pretreatment process a variety of compounds are released, and their relative fraction depends on the time and operating conditions. Garrote, Kabel, Schols, Falqué, Domínguez, and Parajó⁴⁰ performed a detailed analysis of the main compounds that have been identified during the pretreatment of *E. globulus* by autohydrolysis at 160 °C and processing times between 30 and 66 min. A complete material balance of autohydrolysis pretreatment of *E. globulus* can be found in the work of Leschinsky, Sixta, and Patt,¹⁴ where the authors describe the degradation reactions and their relationship with the pretreatment severity conditions. These works focused on the determination of the chemical species involved; they do not present models for the prediction of the concentrations of the compounds in other processing conditions. The number of experiments carried out is relatively small because, for each trial, a large number of analytical determinations must be made, which consumes a large number of resources. In turn, the difficulties to perform a large number of experimental runs affect the development of detailed mathematical models, because usually each reaction kinetic is adjusted separately, which requires many measurements of the reactant concentrations.

This problem can be partly solved by performing the model adjustment considering all of the reactions involved, employing the experimental measurements available. In this way, the search for the kinetics that best fit the data for a particular reaction is not only guided for the data of each reactant, but also with the interactions with other reactants in reactions that are linked among them. Although this methodology helps to minimize the problems associated with the number of experiments required, it introduces a new drawback, because, in the case of multicomponent systems, the parameters defining the kinetics are strongly correlated,⁴¹ and usually are nonlinear. The confidence region of the parameter set is nonconvex and often presents disconnected regions. For these cases, it is recommended to include the Arrhenius equation as part of the model together

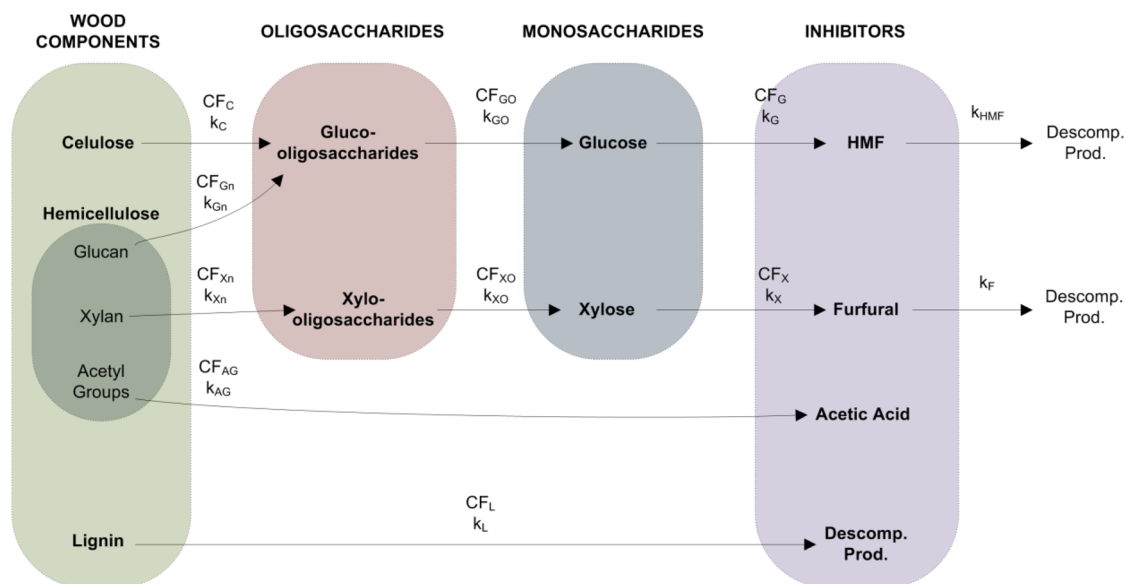


Figure 1. Decomposition reactions of *Eucalyptus globulus* wood in a thermochemical pretreatment.

with the parameters describing the reaction rate, by adjusting them simultaneously for all chemical species of interest.^{42,43}

This work deals with the development of a mathematical model to predict the behavior of three pretreatments for the production of 2G ethanol from *E. globulus*: diluted sulfuric acid, autohydrolysis, and steam explosion. A reaction scheme is proposed for these acidic pretreatments, taking into account the components that influence the subsequent stages of the process. For this purpose, a semiempirical mathematical model is developed, whose parameters are adjusted simultaneously, considering the data reported in the specialized bibliography.

2. MODELING METHODOLOGY

To adequately define a mathematical model for thermochemical pretreatments of lignocellulosic materials, the following points must be established: the scheme of reactions involved, the order of their kinetics, and the equation of the reaction rates as a function of the operating conditions. In the following paragraphs, each of these elements is described.

2.1. Reaction Scheme. The chemical species that are obtained during a pretreatment process depend on the polymers that compose the lignocellulosic material. In the case of *E. globulus*, it has been reported that the approximate constitution is as follows: cellulose 45% (C), lignin 20% (L), xylan 16–20% (Xn), glucan 4–6% (Gn), and acetyl groups 3.5% (AG).^{37–39} During the thermochemical treatments, the solids are depolymerized, releasing in the liquid phase a great variety of compounds, mainly xylo-oligosaccharides (XO), gluco-oligosaccharides (GO), xylose (X), glucose (G), and acetic acid (AA). At the same time, an important fraction of decomposition saccharides products is generated, such as furfural (F) and 5-hydroxymethyl-2-furfural (HMF). These last compounds, in conjunction with acetic acid, have been reported as strong inhibitors of alcoholic fermentation for several microorganisms.⁴⁴ In the case of the furfural and the HMF, their concentration depends on the operating conditions of the thermochemical treatments. In contrast, acetic acid is formed during the release of the acetyl group present in the hemicellulose, making the concentration of acetic acid directly related to the decomposition level of this compound. On the other hand, in the case

of *E. globulus*, the decomposition of the glucan must also be taken into account, because its fraction is not negligible in this species; it may introduce errors in the estimation of the degradation rate of cellulose because both polymers decompose into glycosides but with different speeds. However, this reaction has not been represented in other modeling works related to *E. globulus*.

In Figure 1 are shown the decomposition reactions considered in this work for the formulation of the mathematical models of the three mentioned thermochemical treatments for *E. globulus*.

2.2. Kinetics of Decomposition Reactions. According to previous works, first-order reactions are adequate to model the decomposition processes during the pretreatment stage of lignocellulosic materials.^{45–48} These reactions can be represented by a system of first-order differential equations, which are expressed in eq 1, where C_i and C_j are, respectively, the concentrations of the soluble compounds i and j , at a particular time (in $\text{g}_{\text{compound}}/\text{g}_{\text{water}}$). In the case of solid compounds, an equivalent concentration is calculated assuming that they are solubilized, while $K_{i,j}$ is an element of the matrix K containing the coefficients of decomposition and formation rates of compounds of interest. Each row and column correspond to a specific element of the ordered sets of reactants, i and j , respectively, where $i = j = \{C, \text{Gn}, \text{Xn}, \text{AG}, \text{GO}, \text{XO}, \text{G}, \text{X}, \text{HMF}, \text{F}, \text{AA}, \text{L}\}$. This matrix presents a correlation between the concentration of the different compounds present in the reactor at a certain instant against the variation of these concentrations concerning time. A positive element $K_{i,j}$ means that the compound of the j column is formed from the compound of the i row, and a negative value means that the j compound is decomposed.

$$\frac{dC_j}{dt} = \sum_{i \in \text{compounds}} K_{i,j} \cdot C_i \quad \forall j \in \text{compounds} \quad (1)$$

In many experimental works, the concentration of the compound is not reported in the reactor; instead, it is listed as the mass of compounds through the reaction or the relation between the mass of these compounds and the original raw material, this last commonly called mass fraction. Because of this, it is more convenient in an equation where the mass is

This SNLE can be observed in the complementary material (see Supporting Information part 1).

The SNLE and eqs 6 and 7 are an algebraic version of the original model, which is used to adjust the parameters Ea_j , k_j^{ref} , and n_j by the LSM. The parameters of the model are adjusted to data reported in the literature of the three pretreatment processes of *E. globulus* analyzed in this work: steam explosion,²⁵ autohydrolysis, and diluted sulfuric acid.²¹ For this purpose, a nonlinear programming model (NLP) is formulated, where its constraints correspond to the pretreatment algebraic model. The objective function is to minimize the sum of squares of residuals.

The optimization problem is solved using the NOMAD.⁵⁵ In each case, the reference temperature is fixed according to a trial and error procedure, selecting the values that show an improvement in the convergence rate of the solver. The temperatures selected are 443, 461, and 468 K for pretreatment of autohydrolysis, steam explosion, and diluted sulfuric acid, respectively.

The parameters Ea_j , k_j^{ref} , n_j , and T^{ref} , obtained by the previously described method, for the three pretreatments studied in this work, are shown in Tables 1, 2, and 3.

Table 1. Coefficient of Decomposition Rates for Different Compounds and Treatments, at the Corresponding Temperature of Reference

compound	k_{ref} [1/min]		
	AH	SE	DSA
cellulose	7.853×10^{-4}	1.978×10^{-3}	3.702×10^{-1}
glucan	2.967×10^{-2}	2.760×10^{-1}	2.251×10^2
xylan	1.889×10^{-2}	1.414×10^{-1}	1.051×10^{-1}
acetyl groups	3.898×10^{-3}	2.765×10^{-2}	1.594×10^{-1}
gluco-oligosaccharides	1.911×10^{-2}	2.113×10^{-2}	9.595×10^{-1}
xylo-oligosaccharides	8.574×10^{-03}	2.549×10^{-2}	5.957×10^{-1}
glucose	2.571×10^{-2}	3.218×10^{-3}	1.370×10^{-1}
xylose	1.625×10^{-2}	2.359×10^{-2}	3.580×10^{-1}
HMF	2.280×10^{-2}	1.458×10^{-1}	1.290×10^1
furfural	1.906×10^{-2}	2.200×10^{-1}	2.986×10^0
acetic acid	1.080×10^1	3.987×10^1	4.140×10^2
lignin	3.421×10^{-3}	1.146×10^{-2}	2.496×10^0
T_{ref} [K]	443	461	468

Table 2. Activation Energy for Different Compounds and Treatments

compound	Ea [J/mol]		
	AH	SE	DSA
cellulose	4.043×10^4	6.443×10^4	2.211×10^5
glucan	1.674×10^5	1.968×10^5	2.871×10^5
xylan	1.154×10^5	9.529×10^4	9.982×10^4
acetyl groups	1.668×10^5	5.761×10^4	1.209×10^5
gluco-oligosaccharides	5.844×10^4	1.214×10^5	1.389×10^5
xylo-oligosaccharides	7.810×10^4	8.562×10^4	1.046×10^5
glucose	2.491×10^4	2.022×10^5	5.300×10^5
xylose	9.789×10^4	8.712×10^4	2.543×10^5
HMF	4.949×10^4	2.301×10^4	5.480×10^5
furfural	4.181×10^3	2.261×10^4	1.703×10^5
acetic acid	9.987×10^4	5.529×10^4	1.297×10^5
lignin	1.277×10^4	2.090×10^4	2.560×10^5

3.1. Model Validation. The evaluation of the adequacy of the model is made by comparing the experimental values

Table 3. Catalyst Concentration Exponents of the Compounds (for DSA Pretreatment Only)

compound	n [dimensionless]
	DSA
cellulose	0.728
glucan	2.816
xylan	1.306
acetyl groups	1.134
gluco-oligosaccharides	2.743
xylo-oligosaccharides	1.474
glucose	0.066
xylose	1.950
HMF	0.146
furfural	0.825
acetic acid	1.394
lignin	0.942

against the predictions of the proposed kinetics at the same process conditions. In addition, the predictions are compared to the behavior reported in similar processes and materials by other authors. Because of the high number of compounds included in the model, the analysis of the behavior of the pretreatment models is focused on three compounds, xylan, xylose, and furfural. The reason for this selection is that it has a higher effect over the performance of the subsequent stages of the 2G ethanol production process. As was previously mentioned, it has been reported that xylan is one of the main compounds inhibiting the enzymatic hydrolysis of cellulose present in the solid phase of the lignocellulosic materials from angiosperm species.^{56,57} It produces a competitive inhibition of the hydrolysis process, so its separation is one of the main objectives of the pretreatment stage. Also, lignin has an important inhibitory effect, but its fraction is little affected during the acid pretreatments. Therefore, it can be ignored in an initial analysis, focusing on xylan as the main compound of interest, which remains in the solid phase. On the other hand, regarding the liquid phase, xylose and furfural can be mentioned as the most relevant compounds to analyze. The former is the main saccharide recovered in the process that can be converted into compounds of greater economic value, such as xylitol⁵⁸ or ethanol, through biological processes, while the second one has a strong growth inhibitor for several microorganisms involved in subsequent fermentative stages.^{59–62}

In the following sections, the behavior analysis of those three compounds is compared to the reports found in the bibliography. The comparison between predictions versus experimental data for the other compounds is presented in Supporting Information part 2.

3.1.1. Dilute Sulfuric Acid Pretreatment. Figures 2, 3, and 4 compare the experimental data reported of the mass fractions of xylan, xylose, and furfural,²¹ with the estimates obtained by the model presented in this work for DSA pretreatment. Because the evaluations are performed with three different concentrations of the acid catalyst (1.0, 5.0, and 10.0 cmol/L), in each figure the measured and estimated values are superimposed, for these concentrations, indicating the correspondence to each assays group. In these figures, it is observed that model predictions are adjusted with a good approximation to the reported data.

Figure 2 shows that, within the studied range of the processing variables, the concentration of catalyst is the most influential factor regarding the decomposition of xylan; the

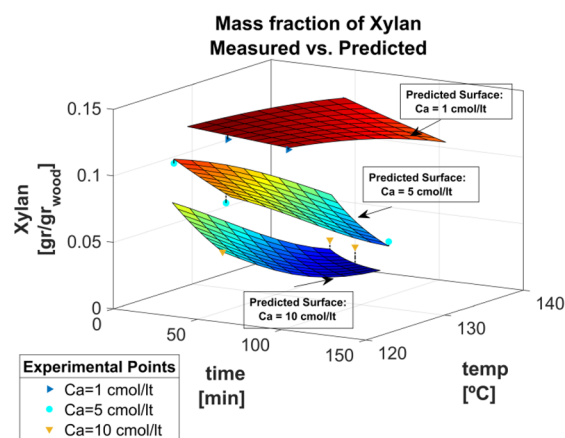


Figure 2. Graphical comparison between experimental data (dots) and model predictions (surfaces) of xylan mass fraction, for the diluted acid pretreatment with three acid concentrations: 1.0, 5.0, and 10.0 cmol/L.

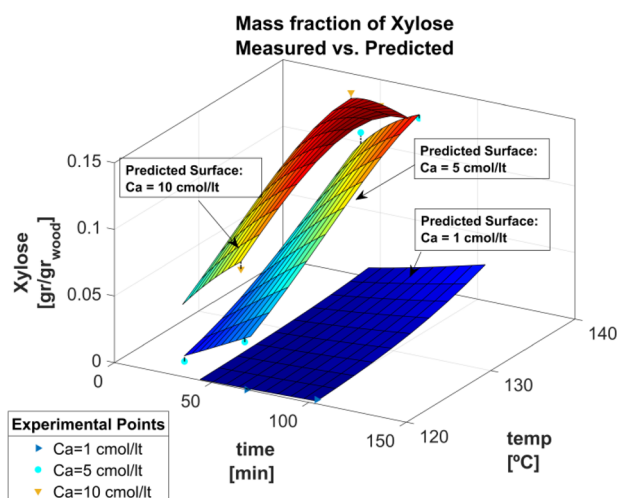


Figure 3. Graphical comparison between experimental data (dots) and model predictions (surfaces) of xylose mass fraction, for the diluted acid pretreatment with three acid concentrations: 1.0, 5.0, and 10.0 cmol/L.

higher concentrations favor this reaction. In turn, it is observed in Figure 3 that the highest xylose yields are obtained with relatively short processing times and maintaining high catalyst concentrations and process temperatures. This behavior has also been reported in works on DSA pretreatment from other materials from angiosperm species, such as corn stover.⁶³ Regarding the production of furfural, it can be observed in Figure 4 that its fraction increases with the severity of the pretreatment, which is in accordance with the report in ref 64, where the catalyst concentration is the factor of greater influence within the range studied.

3.1.2. Autohydrolysis Pretreatment. The AH pretreatment is easier to analyze than DSA because there are only two process variables, pretreatment time and temperature. Figures 5, 6, and 7 show graphical comparisons between the predicted values of the xylan, xylose, and furfural mass fractions, and the experimental values reported for these compounds in an AH pretreatment.²¹ In Figures 5, 6, and 7, it can be observed that the surfaces adequately describe most of the experimental data. In the particular case of Figure 6, which describes the mass fraction of xylose, a relatively greater difference is shown in the

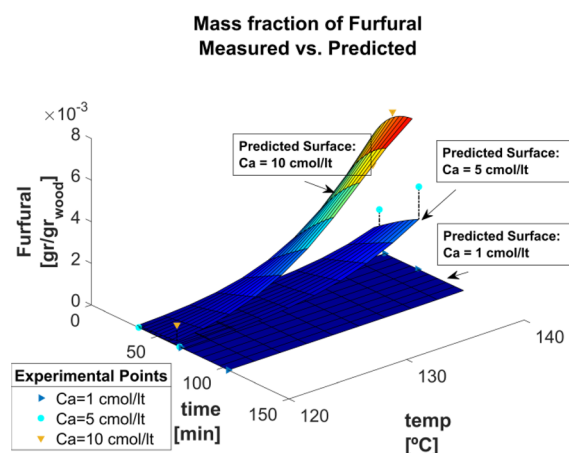


Figure 4. Graphical comparison between experimental data (dots) and model predictions (surfaces) of furfural mass fraction, for the diluted acid pretreatment with three acid concentrations: 1.0, 5.0, and 10.0 cmol/L.

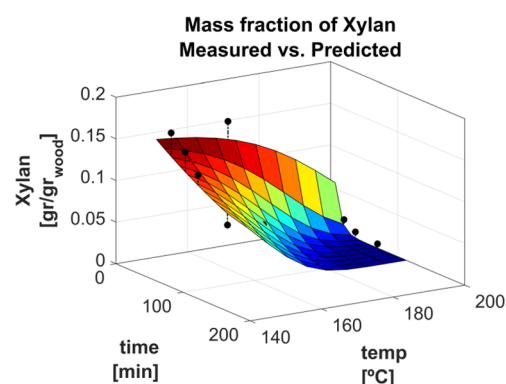


Figure 5. Graphical comparison between experimental data (dots) and model predictions (surfaces) of xylan mass fraction, for the autohydrolysis pretreatment.

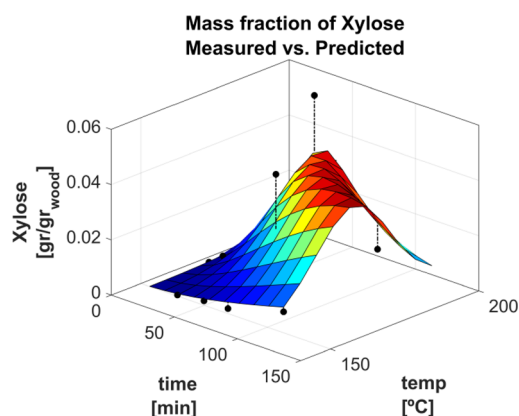


Figure 6. Graphical comparison between experimental data (dots) and model predictions (surfaces) of xylose mass fraction, for the autohydrolysis pretreatment.

process conditions that have a medium severity. However, the surface adjusts well enough the data trend, showing that under severe conditions, the fraction of xylose sharply decreases, so it is considered that the model adequately captures the behavior of the process.

3.1.3. Steam Explosion Pretreatment. In steam explosion pretreatment, similar to AH, there are only two variables of the

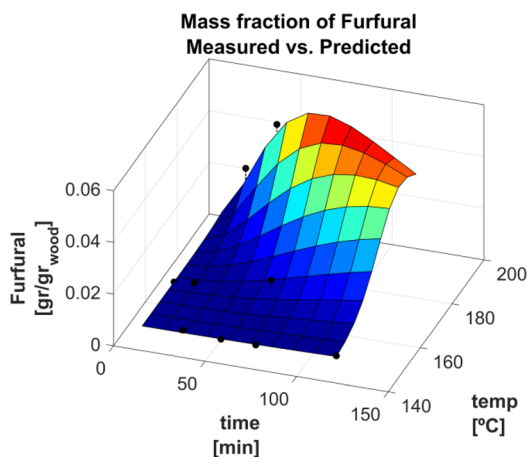


Figure 7. Graphical comparison between experimental data (dots) and model predictions (surfaces) of furfural mass fraction, for the autohydrolysis pretreatment.

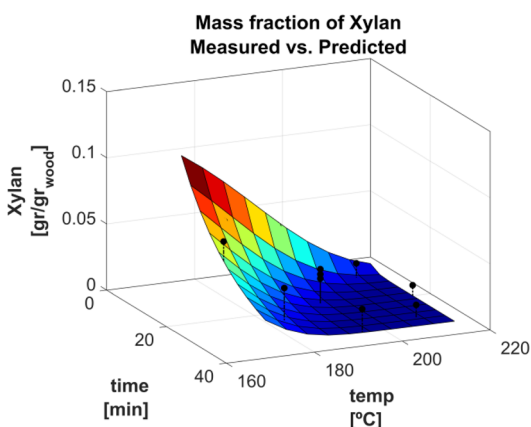


Figure 8. Graphical comparison between experimental data (dots) and model predictions (surfaces) of xylan mass fraction, for the steam explosion pretreatment.

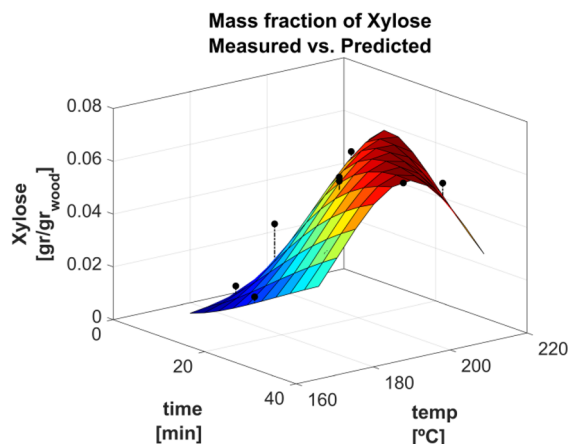


Figure 9. Graphical comparison between experimental data (dots) and model predictions (surfaces) of xylose mass fraction, for the steam explosion pretreatment.

process: temperature and duration. Figures 8, 9, and 10 show the adjustment of the predictions against experimental data for xylan, xylose, and furfural fractions, under different pretreatment conditions.²⁵ As observed in these figures, the proposed model predicts the behavior of the system with a reasonable approximation. The surfaces describe variations with process

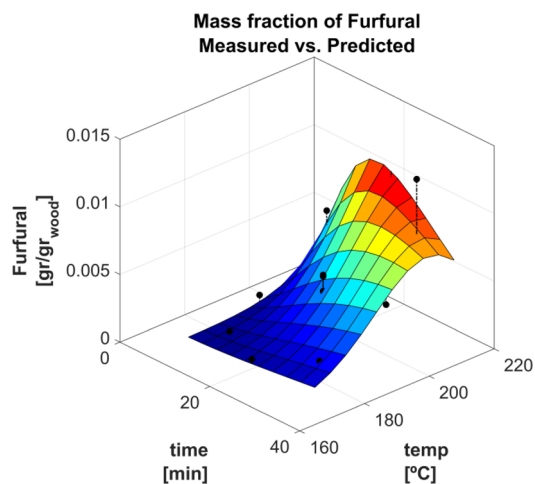


Figure 10. Graphical comparison between experimental data (dots) and model predictions (surfaces) of furfural mass fraction, for the steam explosion pretreatment.

conditions similar to those observed in the case of AH pretreatment.

3.2. Parameters' Correlation. The parameters presented in this work can adequately describe the pretreatments, because the set of corresponding factors has been obtained simultaneously. However, due to the existence of correlations between them, certain precautions must be taken when using these data in the modeling of processes using other bibliographic sources. To exemplify this issue, the case of autohydrolysis pretreatment is taken, and via bootstrapping⁶⁵ are obtained another 150 sets of experimental data, based on the original ones reported.²¹ For each new data set, the parameters are adjusted, obtaining 150 new values. The determination of the Pearson correlation matrix for the parameter set is then performed. In Table 4, a fraction of the matrix is observed, which includes the correlation coefficients of k^{ref} parameter for the different compounds. In the table, a correlation value that deviates significantly from zero indicates that it is probably to have a relationship between the parameters of the corresponding row and column. For example, in Table 4, the cellulose–xylan intersection is highlighted, where a coefficient of 0.38 is observed, so there could be a correlation. To verify this, the values obtained by bootstrapping for both parameters are represented in a scatter diagram of Figure 11.

By visual inspection of Figure 11, the presence of a positive correlation between the decomposition rate parameters of cellulose and xylan is confirmed. Because of this issue, modeling using parameters from different sources must be made with care because it could inadequately represent the desired pretreatment. For example, it could occur that a decomposition rate value of xylan taken from another source be much lower than that corresponding to a decomposition rate of cellulose. This would result in higher predictions of xylose/glucose ratio with respect to values reported experimentally.

A similar analysis is performed for other pretreatments, where it can be observed nonlinear correlations among the parameters in the DSA pretreatment. Some of them can be seen in Figures 12 and 13, where the scatter diagrams for the parameters n , k^{ref} , and Ea are represented, for cellulose and xylan, respectively.

4. CONCLUSIONS

In this study is proposed a mathematical model to describe the operation of acid pretreatment processes, applied to *E. globulus*

Table 4. Pearson Correlation Matrix between k^{ref} Parameters of the Model for AH Pretreatment

		k_ref											
		C	Gn	Xn	AG	GO	XO	G	X	HMF	F	AA	L
k_ref	C												
	Gn	-0.06											
	Xn	0.38	0.00										
	AG	0.08	-0.02	0.10									
	GO	-0.07	-0.15	-0.05	0.09								
	XO	-0.15	-0.01	-0.07	-0.07	0.08							
	G	-0.05	-0.15	-0.13	-0.10	0.71	0.03						
	X	-0.11	-0.01	-0.12	0.00	-0.07	0.29	-0.08					
	HMF	0.01	-0.12	-0.08	-0.04	-0.20	-0.09	-0.19	0.04				
	F	0.06	-0.03	0.01	-0.02	-0.03	0.04	0.00	0.02	0.47			
	AA	0.04	0.11	0.01	0.06	-0.02	-0.08	-0.01	0.15	0.35	0.41		
	L	-0.04	0.05	0.04	0.08	-0.57	-0.11	-0.51	0.08	0.43	0.47	0.22	

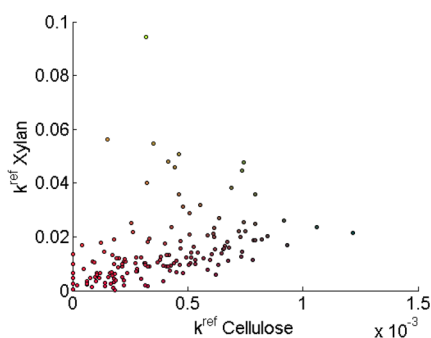
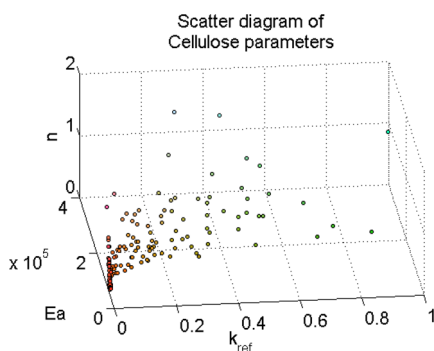
Figure 11. Scatter diagram of k^{ref} parameters for cellulose and xylan.

Figure 12. Scatter diagram of parameters for cellulose decomposition modeling.

wood, a raw material with high potential for the production of 2G ethanol.

The developed model considers the main compounds reported, as well as the decomposition products of greater relevance in the feasibility analysis of the process. Those compounds are a total of 12 (12): cellulose, glucan, xylan, acetyl groups, gluco-oligosaccharides, xylo-oligosaccharides, glucose, xylose, HMF, furfural, acetic acid, and lignin. Also, to find the solution, the system of algebraic and differential equations obtained in the first instance is solved into a system of nonlinear algebraic equations. The decomposition rate of each compound is represented by an Arrhenius equation, which is included in the model during the parameter fitting step. To the best of our

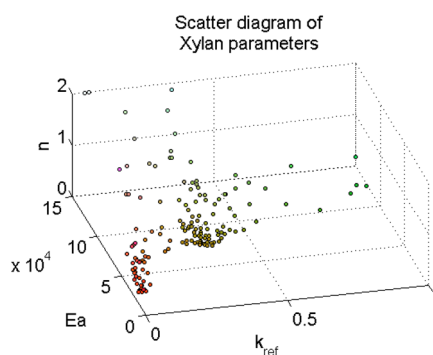


Figure 13. Scatter diagram of parameters for xylan decomposition modeling.

knowledge, this is the first approach reporting the reaction kinetic of 12 compounds that can be applied to three eucalyptus pretreatments: DSA, SE, and AH.

The adjustment of the parameters of the model is performed simultaneously to represent three processes of industrial interest: pretreatment by autohydrolysis (AH) with a process temperature between 150 and 200 °C, steam explosion (SE) with temperatures between 173 and 216 °C, and dilute sulfuric acid (DSA) with temperatures between 120 and 140 °C and catalyst concentrations between 0.1% and 1.0%. In turn, it has been shown that the proposed model adequately reproduces the behavior of the system under study, allowing one to include the variations of a wide variety of compounds involved in obtaining ethanol from *E. globulus* in future computational models.

Finally, using a bootstrapping methodology, the correlations that would exist between the parameters and the possible effects of using the models with other data sources are analyzed. This issue is often ignored when using parameters reported in the bibliography for the computational modeling of processes. However, knowing the possibility of the existence of correlations between these parameters and their possible influence is essential to perform a correct analysis of the results of the computational models of processes. Because, in this work, a simultaneous adjustment of the parameters of the kinetics of all of the relevant compounds has been made, the set of parameters found and the proposed model can be used to adequately predict the

behavior of the pretreatment stages of *E. globulus* by the processes ASD, AH, and SE, within the ranges of the aforementioned processing variables.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.8b02706.

Detailed analytical expressions for the temporal evolution of compounds; and graphical comparison of all compounds in the model for each pretreatment: AH, SE, and DSA (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge the financial support for this work presented to CONICET through Project PIP 688, ANPCYT, with grant PICT 2012 2484.

■ NOMENCLATURE

- i, j = ordered sets of compounds included in this work
 C_j = concentration of compound j in the reactor in a certain time [g/L]
 m_j = mass of compound j in the reactor in a certain time [g]
 K = matrix of decomposition and formation rate coefficients
 K_{ij} = element of K matrix, corresponding to the compounds i and j [min^{-1}]
 CF_j = conversion factor for the reaction that decomposes the j compound
 T = processing temperature of the pretreatment [K]
 T^{ref} = reference temperature for reparametrization
 t = time [min]
 Ca = catalyst acid concentration (sulfuric acid) [cmol L^{-1}]
 k_j = rate of decomposition of compound j [min^{-1}]
 k_j^0 = frequency coefficient of compound j , for the equations of original Arrhenius type [min^{-1}]
 k_j^{ref} = pre-exponential of reparametrized Arrhenius equation (decomposition rate of compound j for the T^{ref} temperature of pretreatment) [min^{-1}]
 Ea_j = activation energy of compound j [$\text{J mol}^{-1} \text{K}^{-1}$]
 n_j = exponential parameter for the acid catalyst concentration [dimensionless]
 R = gas constant [$\text{J mol}^{-1} \text{K}^{-1}$]

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