

Optimization of the Pretreatment of the Mixture of Cassava Peelings and Pineapple Fibers Using Response Surface Methodology and a Process Simulator for the Bioethanol Production

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Abstract

The increase in oil prices and greenhouse gas emissions has led to the search for substitutes for fossil fuels. In Cameroon, the abundance of lignocellulosic resources is inherent to agricultural activity. Production of bioethanol remains a challenge given the crystallinity of cellulose and the presence of the complex. The pretreatment aimed to solubilize the lignin fraction and to make cellulose more accessible to the hydrolytic enzymes, was done using the organosolv process. A mathematical modeling was performed to point out the effect of the temperature on the kinetics of the release of the reducing sugars during the pretreatment. Two mathematical model was used, SAEMAN's model and Response surface methodology. The first show that the kinetic parameters of the hydrolysis of the cellulose and reducing sugar are: 0.05089 min⁻¹, 5358.1461 J·mol⁻¹, 1383.03691 min⁻¹, 51577.6100 J·mol⁻¹ respectively. The second model was used. Temperature is the factor having the most positive influence whereas, ethanol concentration is not an essential factor. To release the maximum, an organosolv pre-treatment of this substrate should be carried out at 209.08 °C for 47.60 min with an ethanol-water ratio of 24.02%. Organosolv pre-treatment is an effective process for delignification of the lignocellulosic structure.

Keywords

Bioethanol, Cassava Peeling, Pineapple Fibers, Organosolv Process and Optimization

1. Introduction

Energy is an engine of growth for any society. In Third World Countries, particularly in the Sub-Saharan zone, household energy coverage remains a luxury [1]. The biggest concern of households in our different municipalities remains access to stable, quality energy, respectful of the environment and above all at lower cost. To survive, many households in developing countries still rely on non-renewable sources of energy, the consumption of which increases over time. In Cameroon for example, it is estimated that wood consumption for energy supply will increase at a rate of around 3% per year. Most of the increase in wood is represented by firewood (91.2%) and charcoal (1%), the predominant energy sources in rural areas [2]. Overall, around 80% of Cameroonians and almost 100% of rural households depend on woody biomass as the main and only source of energy [3]. It's skyrocketing Deforestation. In Cameroonian communities where forests are rapidly disappearing, the use of firewood as a major energy source has become expensive. The Cameroonian economy is essentially based on agriculture, which produces nearly \$60 million in tons of different crops per year. This represents an enormous volume of agricultural residues which could be exploited to meet the country's energy challenges. Using fuelwood as a key energy source is time consuming and labor intensive and harmful to the environment [1] [3]. Biogas, which is a clean technology, has been considered in recent years as a promising source of alternative energy suitable for fuelwood, for in many other African countries in general and for rural households in Cameroon in particular. The world's stock of economically exploitable fossil Energy (oil, gas, and coal) are limited and the number of people in the world is estimated at 7.5 billion today and 10 billion in 2050. In these circumstances, it is essential to prepare the succession of the combustible fossil towards renewable forms of energy based on organic raw material. The development of second-generation biofuels based on the conversion of cellulosic biomass into bioethanol by enzymatic hydrolysis or into biodiesel by thermochemical gasification or liquefaction by catalytic conversion [2] [4]. Generally, agro food industries generate significant quantities of lignocellulosic waste which is poorly exploited. Also, the increase in the price of oil and the increase in greenhouse gas emissions justify the search for raw materials and alternative technologies capable of reducing dependence on these fossil fuels and protecting the environment. Bioethanol is already used to substitute a fraction of the volume of gasoline in many countries. Several authors have worked on the conversion of biomass into bioethanol using the organosolv processes. It emerges from this work that the

organosolv process is one of the best because it makes it possible to delignify the biomass without denaturing the other compounds, while ethanol and lignin can be recovered on the other hand [4] [5] [6]. But to the best of our knowledge, there is no work on the production of bioethanol from association of cassava waste and pineapple fibers waste pre-treated by the organosolv process.

The high cellulose and lignin contents are a hindrance to the biochemical conversion of lignocellulosic materials into liquid and gaseous bioenergy (bioethanol and biogas), due to the crystalline structure of cellulose, and the rigidity of lignin, which act as obstacles to the enzymatic hydrolysis of fermentable sugars [7]. A pretreatment is therefore necessary to separate the lignin from the polysaccharides, to increase the specific surface area and the porosity of the cellulose, to decrease the degree of polymerization of the cellulose [7]. There are several types of pretreatment: physical, chemical, biological and physico-chemical, but all of them release more or less inhibitory compounds for the subsequent biochemical steps [6] [7]. The organosolv process is the extraction of lignin using an organic solvent [8] [9] [10] [11] [12]. It gives the best yield of lignin solubilization [9]. Several works have focused on the non-mathematical modeling of pretreatments, in particular the organosolv process [13] [14] [15] [16], but very few have focused on mathematical modeling and optimization, hence the objective of our work which is to mathematically model and to optimize the pretreatment of cocoa shells by the organosolv process. More specifically, we will look at the influence of temperature on the kinetics of pretreatment and determine the optimal temperature profile as a function of time.

2. Materials and Methods

2.1. Substrate Sampling and Characterization

The cassava and pineapple skins used were collected at the Yaoundé market landfill, then they were transported to the laboratory, washed with distilled water, dried in an oven and ground until a fine consistency was obtained particle size of less than 80 microns. Once in the laboratory, the mixture 50:50 of raw material underwent a physico-chemical characterization through the determination of its dry matter (MS) and its mineral matter (MM) according to the calcination method. The lignin content was determined, the hemicellulose content and the cellulose content.

2.2. Substrate Pre-Treatments

Organosolv pre-treatment of sawdust is necessary to release the cellulose from the lignin-hemicellulose complex. It also makes it possible to reduce cellulosic crystallinity and makes the cellulose accessible to enzymes during the hydrolysis step. In order to better control this pre-treatment step, modelling by the response surface methodology was used. This is how the centred composite plan was used to determine the optimal levels of the various factors influencing treatment [6].

2.3. Choice of Factors and Operating Mode

The parameters of the organosolv treatment are the temperature, the treatment time, the liquid/solid ratio, the concentration of the solvent (ethanol) and this concentration is expressed in terms of the liquid/solid ratio generally fixed at 10:1 [7]. The optimization factors retained for the experimental device of the organosolv treatment are: the temperature (°C), the treatment time (min).

The organosolv pretreatment consists in introducing 3 g of shell into 60 ml of an ethanol solution at a concentration indicated by the experimental matrix, the whole is brought to the set temperature and for a period indicated by the experimental matrix. The warm-up time was between 15 - 20 minutes. The treatment was stopped by quenching and the liquid fraction was recovered using a filtration device. The content of total cellulose and phenolic compounds were determined in the liquid fraction.

The optimization carried out as part of this work will be carried out by two approaches. The first will consist of developing a mathematical model and the second an experimental model based on the experimental plans.

2.4. Mathematical Modeling and Optimization

➤ Mathematical modeling

The model chosen is that of SAEMAN which states that the hydrolysis reactions of cellulose and glucose are of first order and the rate constants are a function of the acid concentration and temperature [17].

$$\frac{dCi}{dt} = \begin{pmatrix} -1 & 0 \\ 1 & -1 \end{pmatrix} \cdot \begin{pmatrix} k_1 \cdot C_{cellulose} \\ k_2 \cdot C_{sucresred} \end{pmatrix} \quad (1)$$

With i the compound (cellulose, glucose, hydroxy-methyl furfural), k_1 and k_2 the hydrolysis constants of cellulose and glucose respectively.

The rate constants are related to the temperature by the Arrhenius relation:

$$k_1 = A_1 \times \exp\left(-\frac{E_1}{R \times T}\right) \quad (2)$$

$$k_2 = A_2 \times \exp\left(-\frac{E_2}{R \times T}\right) \quad (3)$$

• Parameter estimation

The parameters A_1 , A_2 , E_1 , E_2 are estimated by nonlinear regression with the experimental data using the Levenberg-Marquardt algorithm to solve the least squares problem.

• Model validation

The model goodness of fit was expressed by the correlation coefficient (R^2).

➤ Optimization

The chosen optimization technique used is optimal control which is an application of dynamic continuous-time optimization [18] [19] [20] [21].

The state variables are the cellulose and glucose concentrations, the control variable is the temperature of the reactor, the adjunct variables p_1 and p_2 . Thus,

we have the problem formulated as follows:

$$\text{Concentration rate: } \frac{dCi}{dt} = \begin{pmatrix} -1 & 0 \\ 1 & -1 \end{pmatrix} \times \begin{pmatrix} k_1 \times C_{\text{cellulose}} \\ k_2 \times C_{\text{sucresred}} \end{pmatrix}$$

$$\text{Objective function or cost: } \frac{dCi}{dt} = \begin{pmatrix} -1 & 0 \\ 1 & -1 \end{pmatrix} \times \begin{pmatrix} k_1 \times C_{\text{cellulose}} \\ k_2 \times C_{\text{sucresred}} \end{pmatrix}$$

$$\text{Hamiltonian: } H = k_2 \times C_s - k_1 \times C_c - p_1 \times k_1 \times C_c + p_2 \times (-k_2 \times C_s + k_1 \times C_c)$$

The model used in this work is similar to those used by [17] [18] [19] [20].

2.5. Choice of Factors and Experience Matrix

The temperature ranges during organosolv treatment are between 171 and 207°C for pretreatment Tchuidjjang *et al.* [7] and Carrasco [22]. The time range (15 - 45 min) was chosen based on the work of Kabir [17] and Kabel *et al.* [23]. The ethanol concentration between 30 and 70% v/v was set based on the work of Klason P [24] and N'Diaye [25]. **Table 1** presents the experimental matrix for the pretreatment of the organosolv method.

Table 1. Matrix of real and coded variables of the centred composite plane of organosolv pre-treatment.

Experience	Coded variables			Real variables		
	Temperature	Time	Concentration of ethanol	Temperature	Time	Concentration of ethanol
1	0	0	0	190	35	50
2	0	0	0	190	35	50
3	0	0	0	190	35	50
4	0	0	0	190	35	50
5	-1	-1	-1	190	20	30
6	1	-1	-1	210	20	30
7	-1	1	-1	170	50	30
8	1	1	-1	210	50	30
9	-1	-1	1	170	20	70
10	1	-1	1	210	20	70
11	-1	1	1	170	50	70
12	1	1	1	210	50	70
13	1.41	0	0	218.2	35	50
14	-1.41	0	0	161.8	35	50
15	0	1.41	0	161.8	56.15	50
16	0	-1.41	0	190	13.85	50
17	0	0	1.41	190	35	78.2
18	0	0	-1.41	190	35	21.8

The mathematical model postulated is of the second-degree polynomial type with interactions. Its expression is in the form of Equation (1).

$$Y = a_0 + \sum_{i=1}^k a_i x_i + \sum_{i^2=1}^k a_{ii} x_i^2 + \sum_{i=1}^k \sum_{j=1}^k a_{ij} x_i x_j + \mathcal{E} \quad (4)$$

Y = concentration of reducing sugars, pentoses, phenolic compounds, dependent variable (response)

x_i et x_j = dependent variable; a_0 = constante; \mathcal{E} = error

a_i = linear coefficient; a_{ii} = quadratic coefficient; a_{ij} = interaction coefficient

The quality of fit of the model was expressed by the coefficients of determination R^2 and adjusted R^2 which must be less than 80 [26]. As this mathematical tool was not sufficient to validate a model, other tools and methods were used to judge the adequate quality of the models. To this end, the absolute mean deviation analysis (AADM) between the calculated and observed values [27], the bias factor (Bf) [28] and the accuracy factor (Af) [29] were carried out. They were calculated from Equations (2)-(4).

➤ Bias Factor (Bf) $Bf = 10^B$ avec

$$B = \frac{1}{n} \sum \log \frac{Y_{the}}{Y_{obs}} \quad (5)$$

➤ Accuracy Factor (Af) $Af = 10^A$ avec

$$A = \frac{1}{n} \sum \left| \log \frac{Y_{the}}{Y_{obs}} \right| \quad (6)$$

➤ Absolute Mean Deviation Analysis (AADM)

$$AADM = \frac{\sum_{i=1}^n \left| \frac{Y_{obs} - Y_{the}}{Y_{obs}} \right|}{n} \quad (7)$$

Y_{the} and Y_{obs} are respectively the experimental response and calculated from the model for an experiment i ; n being the total number of experiments.

2.6. Pre-Treatment Operation

The organosolv a pretreatment consists of taking 3 g of mixture of pineapple fiber powder and cassava skin in a ratio of 50:50 and introducing into 75 ml of an ethanol solution as indicated in the test matrix. The assembly was brought to the set temperature and for the duration indicated by the methods described in **Table 1**. The duration of the pretreatment operation is taken when the temperature sensor displays the set point imposed by the matrix. Warm-up time is 10 - 15 minutes. The reaction ends by immersing the water at a temperature of 10°C and the filtrate will be recovered for subsequent analyses.

2.7. Characterization of the Pre-Treated Substrate

The concentration of reducing sugars was determined by the spectroscopic method of Godin B [28], Fisher and Stein [30]. Total phenolic compounds were determined by the Folin-Ciocalteu Hashimoto *et al.* [31] method with some

modifications. The pentose concentration of the pretreatment hydrolysates was determined by the method of Akpinar O. [32].

2.8. Optimization

The optimization which consisted in seeking the optimal conditions allowing to have the maximum of cellulose and glucose was carried out by the software Minitap 17.

3. Results and Discussion

3.1. Mathematical Modeling of the Pretreatment of Raw Material Mixture by Simulation

Modeling made it possible to study the influence of temperature on the kinetics of the pretreatment, for a powder with a particle size of 1 millimeter, a concentration of sulfuric acid of 1% or approximately 0.0914M and a pH = 1.039, a concentration of ethanol fixed at 75% (v/v) [31] [33]. **Figures 1-3** present the result of Pretreatment kinetics processing at 170°C, 185°C and 200°C.

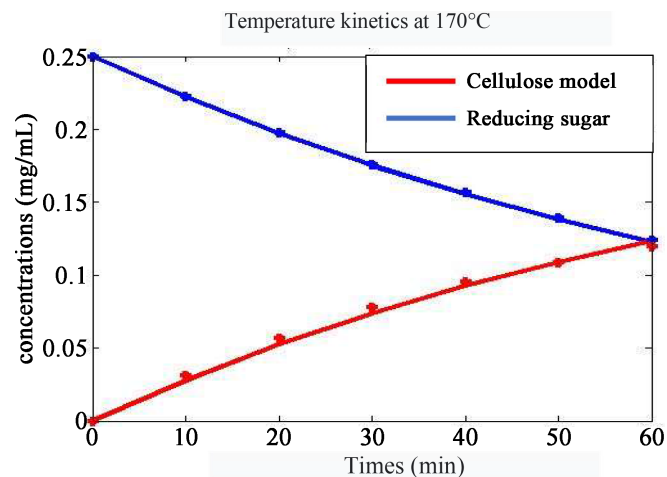


Figure 1. Pretreatment kinetics at 170°C.

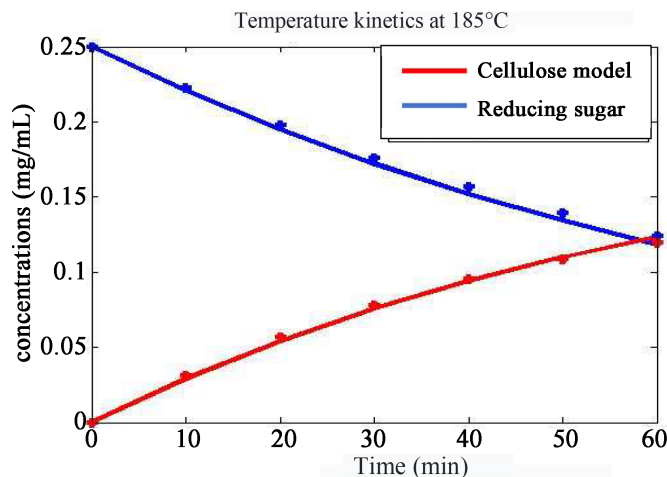


Figure 2. Pretreatment kinetics at 185°C.

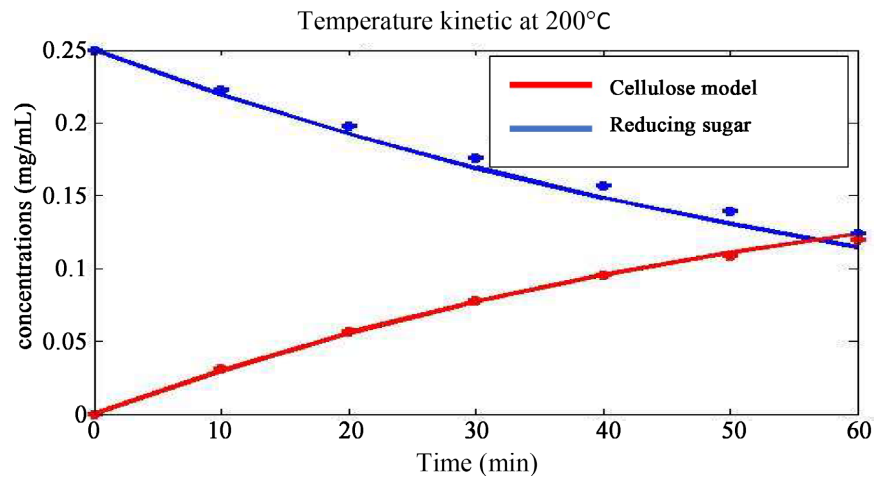


Figure 3. Kinetics of pretreatment at 200°C.

Table 2. Results of modeling and statistical validation criteria.

Compounds	Kinetic models	T = 170°C	T = 185°C	T = 200°C
Cellulose (C)	$\frac{dC}{dt} = -k_1 \times C$	$k_1 = 0.0119 \text{ min}^{-1}$ $R^2 \text{ adj} = 0.9992$ RMSE = 0.0025	$k_1 = 0.0125 \text{ min}^{-1}$ $R^2 \text{ adj} = 0.9988$ RMSE = 0.0013	$k_1 = 0.0130 \text{ min}^{-1}$ $R^2 \text{ adj} = 0.9965$ RMSE = 0.0002
Reducing sugars (G)	$\frac{dG}{dt} = k_1 \times C - k_2 \times G$	$k_2 = 0.0011 \text{ min}^{-1}$ $R^2 \text{ adj} = 0.9933$ RMSE = 0.0043	$k_2 = 0.0019 \text{ min}^{-1}$ $R^2 \text{ adj} = 0.9954$ RMSE = 0.0036	$k_2 = 0.0028 \text{ min}^{-1}$ $R^2 \text{ adj} = 0.9963$ RMSE = 0.0003

With RMSE and $R^2 \text{ adj}$: square root of the mean of the square of the error and Adjusted coefficient of determination respectively.

Table 3. Pre-exponential factors and activation energies.

Pre-Exponential Factor (min ⁻¹)	Activation Energy (J·mol ⁻¹)	Radj ²	P value
$A_1 = 0.05089$	$E_1 = 5358.1461$	1	0.000526
$A_2 = 1383.03691$	$E_2 = 51577.6100$	0.972	0.0403

The rate constants for the hydrolysis of cellulose and glucose are given in Table 2 above.

The results of the modeling show that the kinetics of the pre-treatment by the organosolv process are of order 1, the increase in temperature leads to that of the rate constants, which is in accordance with the work of Thierry Tchamba Tchuidjang, Eric Noubissié, Ahmed Ali [7].

The kinetic parameters of the kinetic constants, Equations (2) and (3) are presented in Table 3.

The results of the modeling show that the kinetics of the pretreatment by the organosolv process is of order 1, and that the influence of temperature on the kinetics obeys Arrhenius' law, which is in accordance with the results of Blaise

(2013) Kupiainen L *et al.*, and Kanchanalai P. *et al.* [18] [20] [33]. These results are consistent with those obtained by authors such as Park N. *et al.* and Fisher E.H., Stein E.A. [30] [34] in that the pre-exponential factors and the activation energies of the hydrolysis constant of reducing sugars are greater than those of the constant of hydrolysis of cellulose. However, Kanchanalai P. *et al.* [33] have found value pre-exponential factor and much higher activation energy for the constants of cellulose hydrolysis rates and reducing sugars for other agricultural residues lignocellulosic, these differences may be due to the absence of agitation in the pretreatment reactor, or to the nature of the lignocellulosic material. **Figure 4** presents the result of Simulation of the SAEMAN model of the pretreatment by the organosolv process.

3.1.1. Mathematical Simulation

According to **Figure 4**, the concentration of cellulose decreases with time and temperature while that of reducing sugar (glucose) first increases whatever the temperature this is due to the fact that the rate of formation of reducing sugar (glucose) is greater than that of its hydrolysis, then it reaches a maximum, which implies that the rates of formation and hydrolysis are equal, and finally it decreases with time and temperature, this may be due to Maillard reactions between proteins and glucose at high temperatures. The work of Kenmogne Yony Blaise [18] led to the same observations and attributed them to the increase in the rate of degradation of glucose by the increase in temperature. It should be noted that Hashimoto S. *et al.* [31] has found result diametrically opposite, it has been found that the activation energy and the pre-exponential factor of the hydrolysis of cellulose is higher than that of reducing sugars, and thus increasing the temperature increased the maximum concentration of reducing sugars.

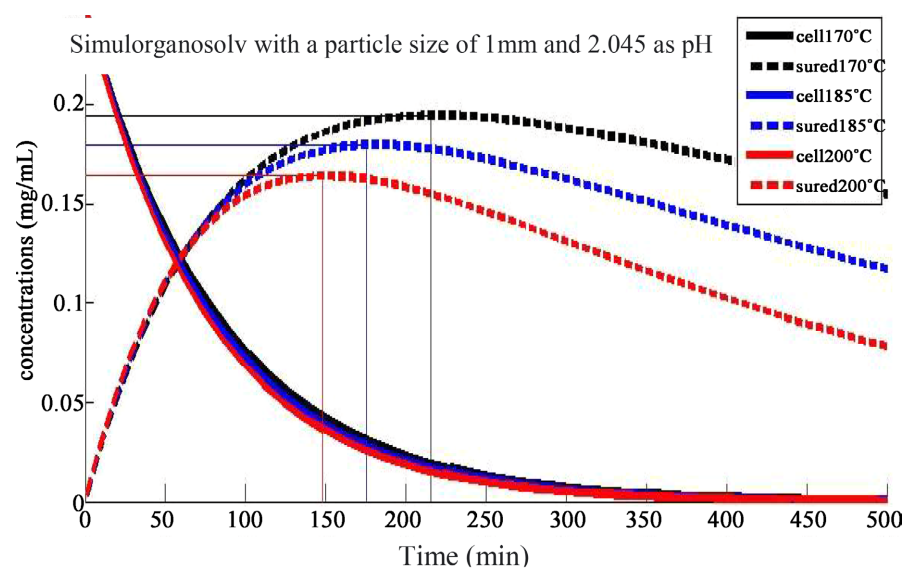


Figure 4. Simulation of the SAEMAN model of the pretreatment by the organosolv process.

3.1.2. Optimization of the Pretreatment of Raw Material

The optimization carried out with the optimal control, gave the following results:

This **Figure 5** shows that the optimal temperature drops as the reaction progresses and reaches a plateau after 200 minutes. **Figure 6** shows the evolution of cellulose model and reducing sugar during processing. This confirms the results obtained by numerical simulation which shows that the maximum glucose concentration decreases with temperature. This could be because the kinetic parameters of cellulose hydrolysis rate constant are much lower than those of glucose, so the rate of degradation of reducing sugars increases faster than that of hydrolysis of cellulose at high temperatures. The work of Hashimoto S. [31] led to the same observation.

Figure 7 below shows the evolution of the objective function as a function of the number of iterations. It appears that after each iteration, the objective function is improved, and this for decreasing temperatures, which validates the observations

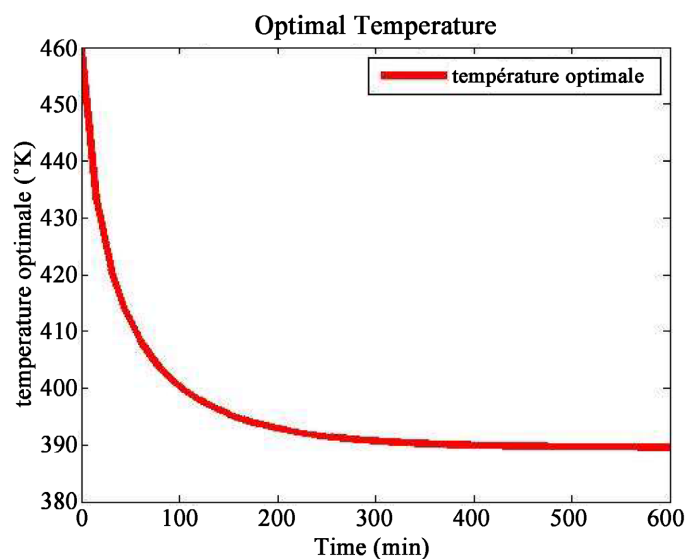


Figure 5. Optimal temperature profile.

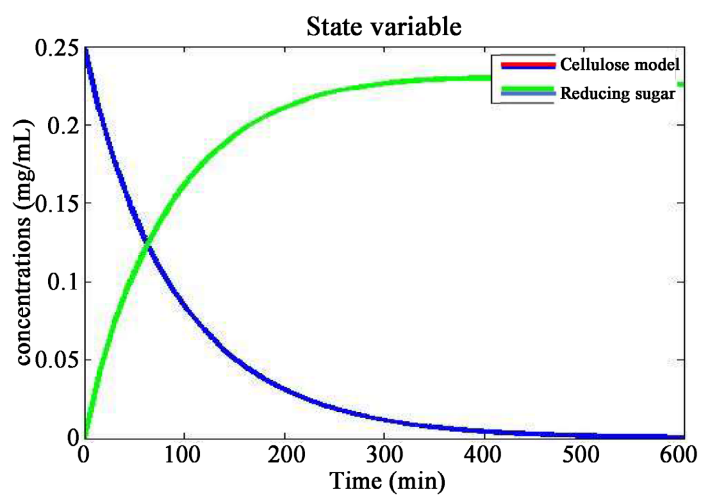


Figure 6. Optimal profiles of state variables.

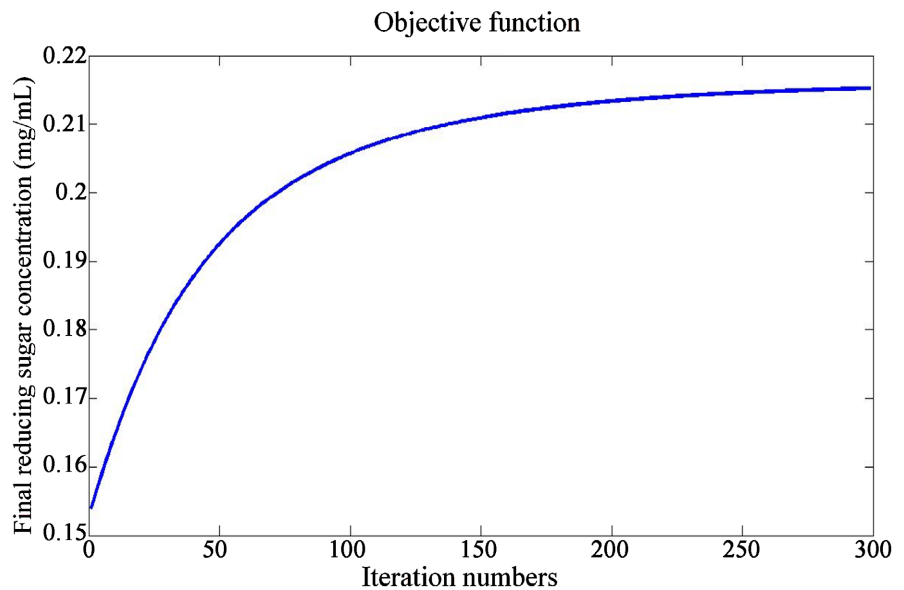


Figure 7. Final glucose concentration as a function of the number of iterations.

made during the simulation of the SAEMAN model with the estimated kinetic parameters.

3.2. Mathematical Models of the Different Experimental Responses

The experimental design responses are presented in **Table 4**.

Three second-degree polynomial mathematical models describing the extraction of the different responses during the organosolv pre-treatment of mixture raw material were generated by this centred composite plane. The content of Cellulose (Y_C) materialized by Equation (5) is a measure which reflects the solubilization rate of the hemi cellulosic fraction. The content of Reducing Sugars (Y_{RS}) materialized by Equation (6) reflects the solubilization of celluloses. The validation indicators for these three mathematical models are presented in **Table 5**.

Y_C = content of celluloses; Y_{RS} = content of reducing sugars;

$$Y_C = 2.925 + 0.338X_1 - 0.337X_2 - 0.227X_3 - 0.094X_1^2 - 0.248X_2^2 + 0.969X_3^2 + 0.263X_1X_2 - 0.564X_1X_3 + 0.270X_2X_3 \quad (8)$$

$$Y_{RS} = 2.049 + 0.2062X_1 + 0.4094X_2 + 0.1901X_3 - 0.1747X_1^2 + 0.4271X_2^2 - 0.1611X_3^2 + 0.0440X_1X_2 - 0.1546X_1X_3 - 0.1952X_2X_3 \quad (9)$$

The two mathematical models are valid under the basis of the intervals provided by the validation criteria presented in **Table 3**.

Figure 8 shows the response of the Cellulose extraction as a function of factors taken two by two.

It appears from this work that increasing the temperature favors the yield of cellulose while a long treatment time (36 minutes) will favor a low yield of obtaining cellulose (**Table 3**). The response surfaces perfectly illustrate these observations in **Figure 8(a)** and **Figure 8(b)**. It also appears that temperature is

Table 4. Experimental and calculated responses of the centred composite plan.

	Real variables			Cellulose (mg/mL)		Reducing Sugars (mg/mL)	
	X_1	X_2	X_3	Y_{Exp}	Y_{Cal}	Y_{ExpSR}	Y_{CalSR}
1	190	35	50	3.750	2.925	0.094	2.049
2	190	35	50	2.700	2.925	0.067	2.049
3	190	35	50	2.938	2.925	0.073	2.049
4	190	35	50	3.869	2.925	0.097	2.049
5	190	20	30	4.450	3.747	0.111	1.029
6	210	20	30	5.080	5.024	0.127	1.662
7	170	50	30	2.045	2.007	0.051	2.150
8	210	50	30	4.641	4.337	0.116	2.960
9	170	20	70	2.356	3.881	0.059	2.109
10	210	20	70	2.942	2.902	0.074	2.124
11	170	50	70	3.642	3.219	0.091	2.449
12	210	50	70	2.668	3.293	0.067	2.640
13	218.2	35	50	3.407	3.214	0.085	1.992
14	161.8	35	50	1.911	2.261	0.048	1.411
15	161.8	56.15	50	2.173	1.955	0.054	3.475
16	190	13.85	50	2.232	2.906	0.056	2.321
17	190	35	78.2	5.122	4.531	0.128	1.997
18	190	35	21.8	4.424	5.172	0.111	1.461

X_1 = temperature; X_2 = time; X_3 = ratio ethanol-water; Y_{exp} = experimental response; Y_{cal} = calculated response RS = Reducing Sugars.

Table 5. Validation indicators for mathematical models expressing pentoses, reducing sugars derived from the pre-treatment by the organosolv process.

Validation Indicator	Y_C	Y_{RS}
R ²	85.66%	93.74%
Adjusted R ²	74.56%	94.23%
AADM	0.11	0,09
Bias factor	1.00	1
Accuracy factor	1.03	1.05

a very important factor during cellulose extraction. This factor is followed by the preprocessing time and the E-W ratio, respectively. **Figure 8(c)** better illustrates this information where we clearly observe that it is easier to extract celluloses by neglecting the E-W factor ratio, rather than by neglecting the pretreatment time.

Reducing sugars

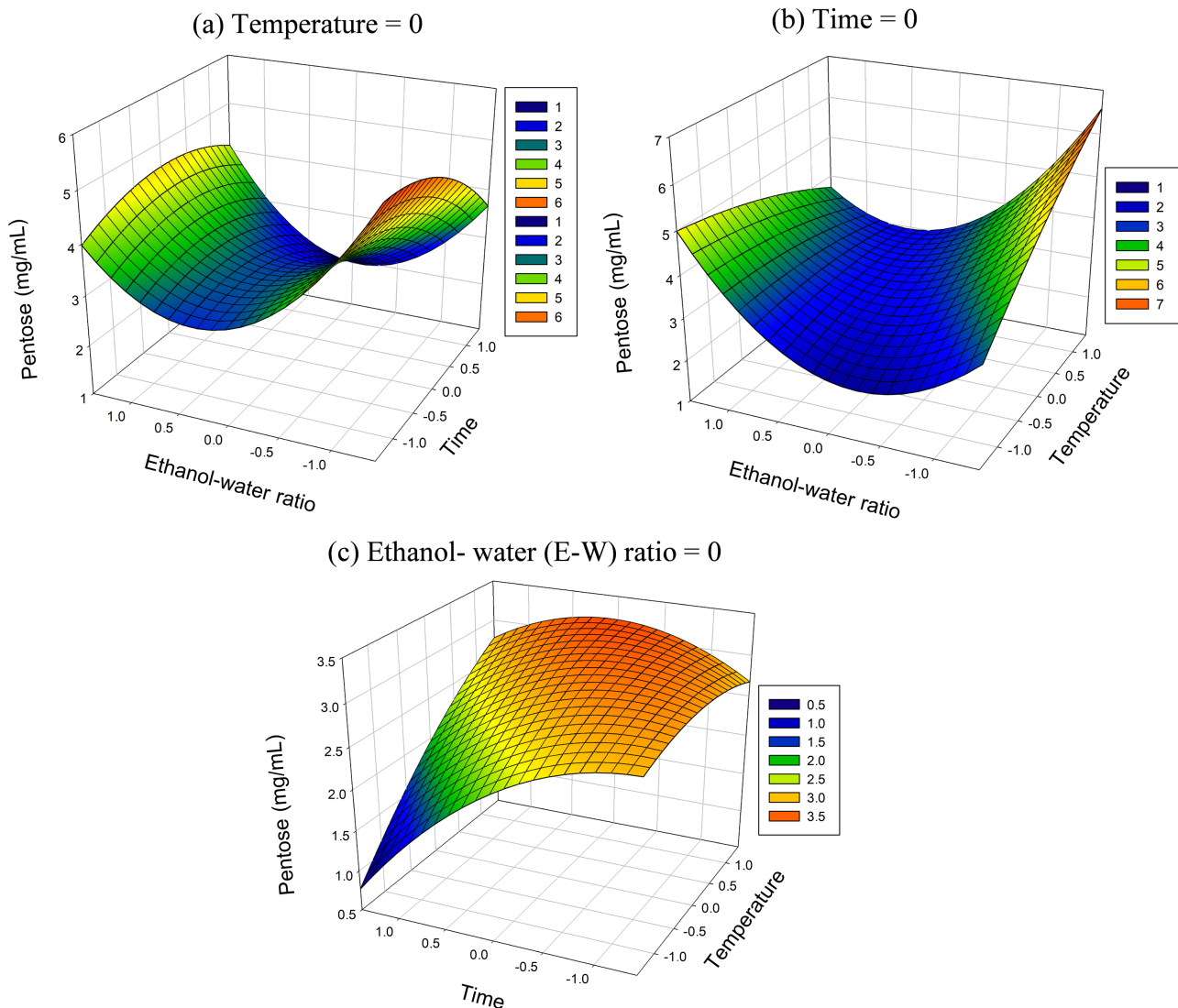


Figure 8. Areas of response of cellulose extraction as a function of time and E-W ratio (a), temperature and E-W ratio (b), time and temperature (c).

Figure 9 shows the response of the RS extraction as a function of factors taken two by two.

The increase in temperature contributes favorably and significantly to more than 95% during the extraction of reducing sugars. On the other hand, the time will contribute to reducing the yield beyond 35 minutes of treatment. The analysis of **Figure 9** illustrates that the E-W ratio will promote optimal extraction of RS in association with temperature (**Figure 9(a)**) and time (**Figure 9(b)**). Considering all these factors, temperature is the factor that has a great influence on extraction yield.

3.3. Optimal Points for the Extraction of Cellulose and Reducing Sugars

At a temperature of 218.2°C, a treatment time of 24.65 minutes and a concentration

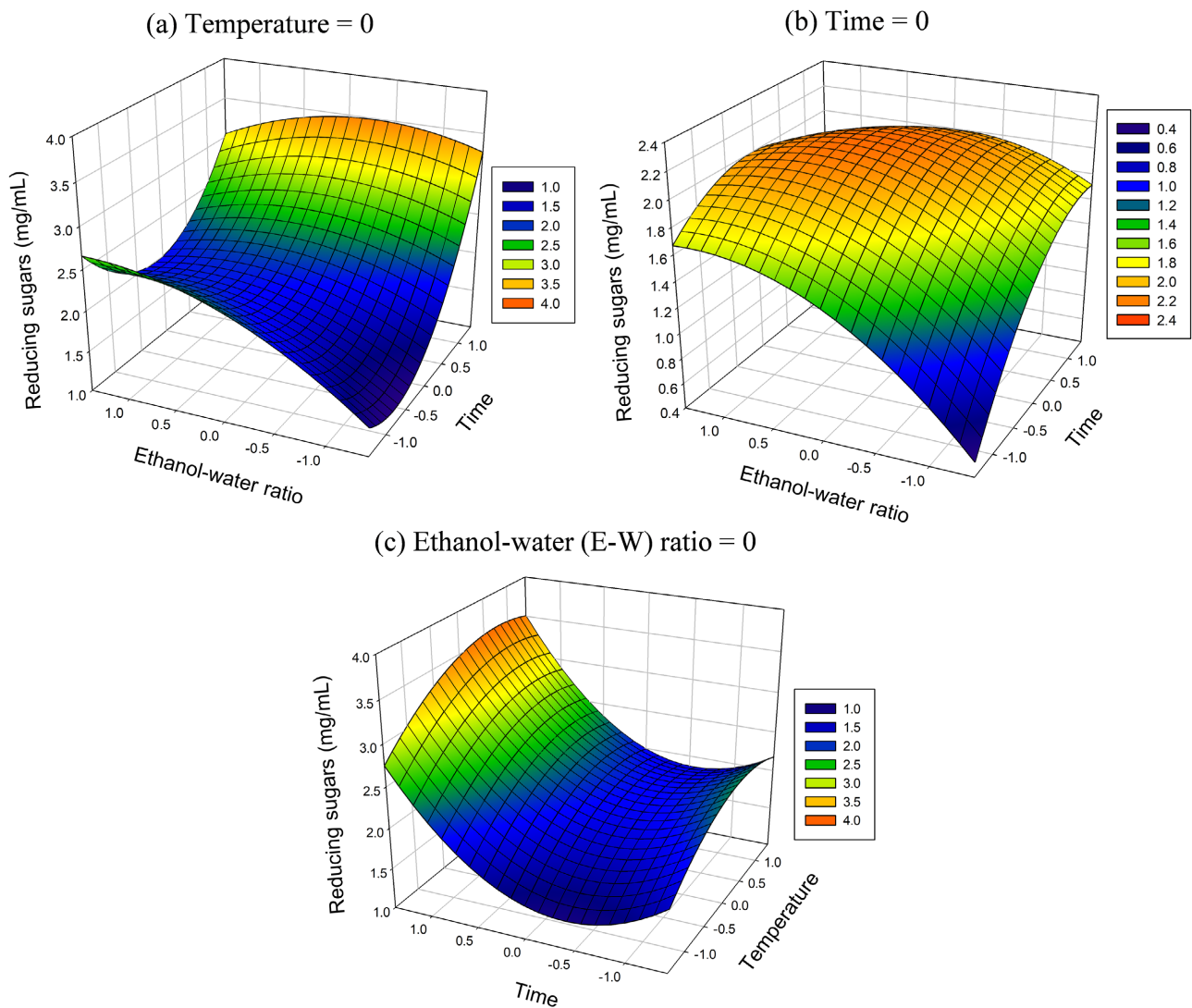


Figure 9. Response surfaces of the extraction of reducing sugars as a function of time and E-W ratio (a), temperature and E-W ratio (b), temperature and time (c).

of 21.8% ethanol, a yield of 6.70 mg/ml of cellulose is obtained using Minitab software Version 2017. The experimental verification in these conditions allowed us to obtain a value of 7.09 ± 0.8 mg/mL, which is not significantly different at the 95% threshold from the expected value (6.70 mg/mL) predicted by the simulator. As for the reducing sugars, the following conditions: 206.24 °C, 56.15 min and 33.19% ethanol, allowed us to obtain a concentration of 3.66 mg/mL. The experimental test gave 4.09 ± 0.8 mg/mL, which is very close to the expected theoretical optimal value (3.66 mg/mL).

Effect of factors on the extraction

The mathematical answers show that the extraction of Cellulose and reducing sugars illustrates that temperature is the most important factor during this pretreatment operation, which is in agreement with the work of Nanssou *et al.* [6]; Kanchanalai *et al.* [33] and Tchuidjang [7]. Indeed, temperature is the only one of the three factors whose increase contributes favorably to the extraction of RS

and cellulose. The model equation reveals that this positive contribution is significant on the RS and not significant on the cellulose. This could be explained by the fact that an increase in temperature would weaken the structure of the fiber contained in the mixture and then the lignocellulosic structure of the substrate, which would cause an increase in the kinetic energy of the water molecules which are the constituents. Under these conditions, the rise in temperature would favour diffusion phenomena and self-ionization releases the hydroxide ions. Time here is the second factor that affects extraction. After a certain value, the amount of cellulose and reducing sugar decreases in the pretreatment reactor. This decrease is due to the destruction of molecules due to an increase in temperature because these compounds are heat-sensitive. They will therefore be denatured when they are exposed for longer than expected to a temperature higher than the temperature necessary for the hydrolysis of their respective substrates.

The analysis of the two models studied shows that the second model using the experimental design method provides more precision on the results and the applicability of the theory compared to the second model. The continuation of this work will involve implementing this second model in order to size the bioethanol production units while having properties on the raw materials. It emerges from this work that knowledge of the characteristics of precursors is a good indicator for mastering simulation operations because the kinetics of sugar bio decomposition depends on the states and their bioavailability in the basic raw materials.

4. Conclusion

The objective of this work was to optimize the pretreatment of the mixture of pineapple fibers and cassava peels in a 50:50 ratio by the organosolv process in order to produce bioethanol. Two models were used. The SAEMAN model, which suggests two consecutive first-order reactions, with a dependence of rate constants on temperature; the kinetic parameters of cellulose and glucose hydrolysis are respectively $A_1 = 0.05089 \text{ min}^{-1}$; $A_2 = 1383.03691 \text{ min}^{-1}$; $E_1 = 5358.1461 \text{ J}\cdot\text{mol}^{-1}$; $E_2 = 51577.6100 \text{ J}\cdot\text{mol}^{-1}$. The other model uses an expert design MINITAB version 2017 by Methodology Response Surfaces was also used in order to compare the results of the numerical simulation and the experimental results. It appears from both models that the optimal pretreatment time and the maximum glucose concentration decrease with temperature, the optimal temperature profile decreases, which attests to the fact that the activation energy of the cellulose hydrolysis reaction is lower than that of glucose. The formation of the latter is therefore favored at low temperatures and limited at high temperatures. This work shows that organosolv pretreatment is an effective method for the delignification of the lignocellulosic structure of precursors. The optimization method developed will make it possible to properly control production performance. To improve this work, it would be wise to carry out a technic-

al-economic analysis of the process and make an energy assessment of the installation.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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