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Emília S. Lopes
Universidade Estadual de Campinas

Julio C.J. Gariboti
Universidade Federal de Sao Paulo

Luis H.Z. Feistel
Universidade Federal de Santa Maria

Elmer Ccopa Rivera
Andrews University, ccoparivera@andrews.edu

Rubens Mac Iel Filho
Universidade Estadual de Campinas

See next page for additional authors

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Acid Hydrolysis-based Sugarcane Bagasse Biorefining for Levulinic Acid Production: Dynamic Mechanistic Modeling Under Varying Operating Conditions

Emília S. Lopes[a*], Julio C. J. Gariboti[b], Luis H. Z. Feistel[c], Elmer C. Rivera[d], Rubens Maciel Filho[a], Laura P. Tovar[b]

[a]School of Chemical Engineering, University of Campinas, Zip code 13083-852, Campinas-SP, Brazil
[b]Department of Chemical Engineering, Federal University of São Paulo, Zip code 09913-030, Diadema–SP, Brazil
[c]Department of Chemical Engineering, Federal University of Santa Maria, Zip code 97105-900, Santa Maria-RS, Brazil
[d]Department of Engineering, Andrews University, Berrien Springs, MI, USA
emiliasavlopes@gmail.com

The study on the lignocellulosic material conversion into bio-based platform chemicals, such as levulinic acid (LA), is one of the most promising routes to promote the development of advanced biorefineries. In this work, a dynamic mechanistic model is developed to simulate the LA production from lignocellulosic material. A wide operating range is used to estimate the parameters of the reaction kinetics. Because multi-parameter estimation problem is complex, a genetic algorithm-based optimization procedure is used to determine the optimum parameters values. Measurements are obtained for various reaction times (0 - 45 min) temperatures (150 – 200 °C) and acid concentration of 7.0 % w/v H_2SO_4. The calculated reaction rates for the state variables, concentrations of LA, glucose, 5-hydroxymethylfurfural and humins are used to construct the dynamic mechanistic model. The prediction of measured state variables was particularly accurate, as determined by the root mean square error (RMSE) and correlation coefficient (R^2). Therefore, a satisfactory agreement between experimental LA yield of 57.2 mol% and computed LA yield of 56.4 mol% was achieved (at 200 °C, 7.0 % w/v H_2SO_4, 45 min). The proposed methodology drives the systematic development of an industrially reliable dynamic mechanistic model for LA production from sugarcane bagasse as a means to increase the LA yields in the biorefinery.

1. Introduction

The use of lignocellulosic materials in biorefineries to obtain value added products has being attained relevant space at the present time. Currently, Brazil is the world's largest sugarcane producer and is expected to produce about 602 million tons of sugarcane in the 2019 - 2020 harvest (Udop, 2019). This corresponds to a production of about 182 million tons of sugarcane bagasse (SCB).

In this sense, levulinic acid (LA) can be formed from lignocellulosic materials in acid conditions and relative high temperatures. Synthesis of LA occurs through serial acid hydrolysis reactions, including dehydration of hexoses formed in the decomposition of cellulose to 5-HMF, followed by a rehydration reaction for the production of levulinic acid and formic acid (Fleig et al., 2018). Formation of humins occurs mostly inside the hydrolysis reactor which operates in severe conditions (Leal Silva et al., 2018).

According to the U.S. Department of Energy (DOE) the LA stands out among the 12 most promising sugar-based building blocks selected as “Top Value Added Chemicals from Biomass”. LA is a versatile chemical platform with numerous potential applications for example textile dye, antifreezing agent, animal feed, coating material, solvent, food flavouring agent, pharmaceutical compounds, fuel additives, polymer and resin precursors. Besides that, LA has been employed as a precursor to produce a variety of chemicals, such as α-angelica lactone, benzodiazepines, butyl levulinate, ethyl levulinate, γ-valerolactone, 1,4-pentanediol, 2-methyl-tetrahydrofuran (MTHF), among others (Lopes et al., 2017).

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In this context, the genetic algorithm (GA) will be applied in this work by means of an optimization method inspired by the non-deterministic process of natural evolution (Hoffmann, 2019). Despite the natural ability of GAs to describe a highly complex reaction system, its application in the context of LA production has not yet been reported. Therefore, the consolidation of reliable kinetic mechanisms, including a wide range of conditions, will enable to find out high conversion of SCB to LA, achieving high yields.

2. Materials and methods

The sugarcane bagasse (SCB) was supplied by São José sugar-alcohol mill (Araras, São Paulo, Brazil). Its composition was calculated according to Sluiter et al. (2012) and Sluiter et al. (2008a) and is presented in Table 1.

Table 1: Chemical composition (on dry basis) of SCB, ISF-I after prehydrolysis and ISF-II after NaOH treatment. Data represent the mean ± standard deviation of three independent experiments

Component	Integral	ISF-I	ISF-II
	Content (w/w)		
Cellulose	40.5 ± 2.17	62.5±1.33	78.0± 0.51
Hemicelluloses	30.6 ± 4.04	12.5±1.70	6.4 ± 0.45
Lignin	19.1 ± 3.18	23.2±1.89	7.4 ± 0.45
Extractives	8.9 ± 0.06	0.0 ±0.00	0.0 ± 0.00
Ash	2,5 ± 0.12	1.8 ±0.03	2.1 ± 1.18
Total	101.6± 1.64	100 ±2.04	93.9± 1.47

The SCB was fractionated in 3 steps, as follow:
Step1: consisted of a prehydrolysis of the SCB in a solution of H_2SO_4 (1.0 % w/v) and temperature of 121 °C for 90 min. A liquid:solid ratio of 6.7 (with 15 g SCB on dry basis) was used. The suspension was then filtered and separated into a liquid fraction (AH-I) and a water insoluble solid fraction (ISF-I).
Step2: the hydrolyzed solid fraction was taken to the second process step (*step2*). At this stage, the solids were treated with NaOH (0.5 % w/v) and 121 °C for 90 min. The liquid:solid ratio used was the same as in the previous step. This step (*step2*) generated a black liquor (BL) and a water insoluble solid fraction (ISF-II).
Step3: consists of a catalytic depolymerization of cellulose. The experiments were performed in a bench system, with two 300 mL stainless steel vessels, that have 70 mm internal diameter and 5 mm wall thickness (Figure 1).

Figure 1: Scheme of the reaction system used in the step3. Mechanical strain and sprain profiles are presented

The system has 1 kW mica resistance heating, with temperature controller and pressure gauge. The reactor has operating limits of 200 °C and 20 bar. Certain amounts of FSI-II were weighed to achieve 12 % w/v solids loading. These samples were transferred to the reaction system with the 7.0 % w/v acid solution of H_2SO_4. Temperatures of 150, 175 and 200 °C were analyzed. After the reaction time (0, 15, 30 and 45 min) had elapsed the reactor was shut down and immediately immersed in an ice water bath for cooling and depressurization the system. In this step, the experiments were performed at different time intervals (0, 15, 30 and 45 min). Samples collected from acid hydrolysate (AH-II) for each experiment were filtered through

membranes (0.22 μm PVDF). The filtrates were transferred to clean flasks and kept in the freezer for further chromatographic analysis.
The AH-I, BL and AH-II fractions were analyzed based on standard procedures (Gouveia et al., 2009, Sluiter et al., 2008b).

3. Kinetic model

It is essential to have a detailed understanding of the reactions involved in AL producing from SCB in order to achieve a successful hydrolysis process. In addition, understanding the rate dependence of the temperature, a parameter that highly influence the process, is crucial. In Figure 2 is presented the proposed reaction scheme for the catalytic depolymerization of cellulose from SCB. It was considered the propositions that: batch reactor has no volume change; cellulose catalytic depolymerization from SCB was a function of temperature, reaction time, and concentration of acid solution; irreversible homogeneous reaction; temperature and concentration of acid solution are uniform in reactor and the effects of different particle sizes have been neglected. After two-step treatments of biomass, the particle size is uniform reducing the resistance against the diffusion process, resulting in uniform acid concentration inside the particle and leading to a uniform temperature distribution.

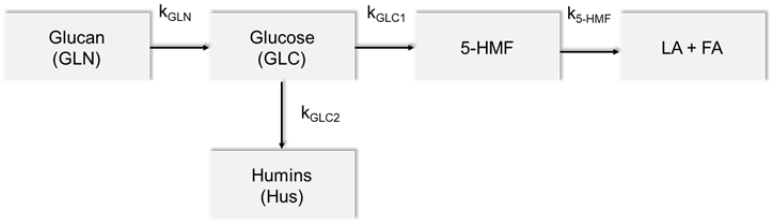

Figure 2: Proposed reaction scheme for the catalytic depolymerization of cellulose *from SCB*

The mechanistic model that describes the kinetics may be represented by the following ordinary differential equations Eq(1)-(5). These equations are macroscopic at maximum gradients; this means that no interphase resistances are considered.

$$\frac{d[GLN]}{dt} = -k_{GLN}[GLN] \tag{1}$$

$$\frac{d[GLC]}{dt} = k_{GLN}[GLN] - (k_{GLC1} + k_{GLC2})[GLC] \tag{2}$$

$$\frac{d[5-HMF]}{dt} = k_{GLC2}[GLC] - k_{5-HMF}[AL] \tag{3}$$

$$\frac{d[AL]}{dt} = k_{5-HMF}[5-HMF] \tag{4}$$

$$\frac{d[HUs]}{dt} = k_{GLC2}[GLC] \tag{5}$$

where [*GLN*] is the substrate concentration (glucan/cellulose) (g/L); [*GLC*] is the sugar (glucose) concentration (g/L); [*5-HMF*] is the concentration of 5-hydroxymethylfurfural (g/L); [*LA*] is the concentration of levulinic acid (g/L); [*HUs*] is the concentration of humins (g/L); k_{GLN} is the rate of glucan (GLN) to glucose (GLC) reaction; k_{GLC1} is the rate of glucose decomposition reaction (GLC) in 5-hydroxymethylfurfural (5-HMF); k_{GLC2} is the rate of glucose decomposition reaction (GLC) in decomposition products (HUs); k_{5-HMF} is the decomposition reaction rate of 5-hydroxymethylfurfural (5-HMF) in levulinic acid (LA); The velocity constants, k_{GLN}, k_{GLC1}, k_{GLC2} and k_{5-HMF} were expressed in min^{-1}; t is the reaction time (min). The reaction rate constants are represented by modified Arrhenius equation, including the effects of temperature (T) and acid concentration (*acid*), as in Eq(6).

$$k_i = A_i \exp\left(\frac{-E_{A_i}}{RT}\right)(acid)^{m_i} \tag{6}$$

where A_i is the frequency factor, m_i is the reaction order in acid, R is the ideal gas constant, and E_{Ai} is the activation energy.

The estimation of the optimal values of the parameters with the greatest effect on the responses was performed using a genetic algorithm (GA) based on the PIKAIA routine (Charbonneau and Knapp, 2002). This algorithm solved a nonlinear optimization problem where the objective function defined by Eq(8) is minimized.

$$FO(\theta) = \sum_{i}^{nep} \sum_{j}^{nsp} \left(\left(\frac{S_{j,i}^{\text{Predicted}} - S_{j,i}^{\text{Experimental}}}{S_i^{\text{Ult}}} \right)^2 \right) \quad (8)$$

where θ is the vector containing all parameters, *nep* is the number of experimental profiles; *nsp* is the number of experimental sampling points; $S_{j,i}^{\text{Experimental}}$ is the ith measured concentration, $S_{j,i}^{\text{Predicted}}$ and $S_{j,i}^{\text{Ult}}$ are the concentrations calculated by the kinetic model and the final measured concentration, respectively.

With GA configured, convergence is accelerated toward optimal values for the parameters that produce the best fit between the measured GLC, 5-HMF, and LA concentrations and their corresponding concentrations calculated by the kinetic model, minimizing FO(θ).

The FORTRAN-encoded kinetic model (Eq(1)-(5)) was integrated using the initial value problem, Runge-Kutta method (IVPRK) to obtain the profile of GLC, 5-HMF and LA concentrations. The estimation problem of the kinetic parameters using the GA coupled to the model was performed on an Intel (R) Core (TM) i7-4790 @ 3.60 GHz CPU.

4. Results and discussion

In the *step1*, prehydrolysis, the ISF had a solid recovery of 58.8 %. At this step, the solubilization of hemicelluloses occurred mainly, decreasing about 76 % in relation to the raw SCB. Cellulose and lignin were recovered mainly in solid fractions. At ISF, 91.0 % of the pulp was preserved in relation to the raw SCB.

In the *step2*, where solids (ISF) were treated with NaOH, the ISF-II had 80.0 % of the solids recovered for ISF-II. From the information presented in Table 2, it can be inferred that a significant solubilization of lignin occurred, corresponding to about 82 % of raw SCB. In addition, the ash removal in ISF-II was 7.0 % of raw SCB. In relation to cellulose, 91.0 % of the cellulose contained in the ISF was preserved in the ISF-II, favouring the production of LA that is performed in the *step3* (catalytic depolymerization of cellulose).

To understand the catalytic depolymerization of cellulose from SCB, the conditions studied were based on previous work (Lopes et al., 2017, Fleig et al., 2018). A total of 12 experiments (in triplicate) addressing the measurements of [*GLC*], [*5-HMF*] and [*LA*] was performed. Figure 3 shows the [*LA*] profile at 150 °C, 175 °C and 200 °C in relation to reaction time. It is possible to observe that [*LA*] behaves increasingly with the reaction time. It increased from 150 °C to 175 °C, reaching 31.9 g/L by the simulated value (31.5 g/L experimental) after 45 min of reaction and 200 °C. This fact proves the important positive influence that temperature exerts on the conversion of SCB to LA. Under the conditions studied was considering that GLC was almost fully consumed, with maximum residual contents of 2.2 g/L by simulated value (1.0 g/L experimental), and the same occurred to 5-HMF, with a maximum residual contents of 0.03 g/L by simulated value (0.1 g/L experimental). The highest [*LA*] represents a yield of 57.2 mol% by simulated value (56.4 mol% experimental). These results are in accordance with Zheng et al. (2017) when studying the conversion of corn stalk to LA using $FeCL_3$ as catalyst. The authors found a yield of 48.9 mol% under 180 °C, 0.5 mol/L $FeCL_3$ and 60 min of reaction. The higher yield achieved in this work, when compared to Zheng et al. (2017), may be due to the use of higher temperature.

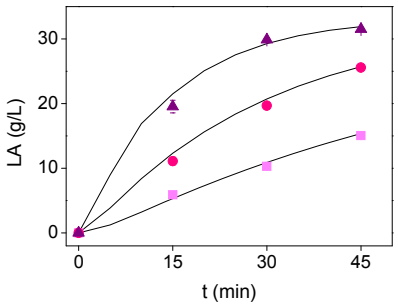

Figure 3: [LA] profile in function of time, where ■ correspond to 150 °C, ● correspond to 175 °C and ▲ correspond to 200 °C. Experimental data are expressed by symbols (bars represent the triplicate standard deviation) and simulated data by continuous lines

Each of the measurements of [GLC], [5-HMF] and [LA] were used to estimate the kinetic parameters, presented in Table 2, and consequently to determine the kinetic reaction rates (k_{GLN}, k_{GLC1}, k_{GLC2}, $k_{5\text{-}HMF}$).

Table 2: Kinetic parameters for the catalytic depolymerization of sugarcane bagasse for intermediate and side reactions to GLC, 5-HMF and HUs and the main reaction to LA

	Reaction	A_i (min^{-1})	E_{Ai} (kJ/mol)	m_i
k_{GLN}	*GLN → GLC*	1.12×10^5	57.50	0.31
k_{GLC1}	*GLC → 5-HMF*	4.50×10^5	32.54	2.30
k_{GLC2}	*GLC → HUs*	4.01×10^4	37.60	1.08
$k_{5\text{-}HMF}$	*5-HMF → AL*	3.18×10^5	24.42	1.94

The activation energy, E_A, of the *GLN → GLC* reaction (E_{AGLN} = 57.50 kJ/mol) is lower than the values reported in the literature, such as sugarcane bagasse reported by Girisuta et al. (2013) (E_A = 144.8 kJ/mol) and cellulose reported by Chang et al. (2006) (E_A = 86.3 kJ/mol). This difference in values can be explained by the number of steps involved in the process (*step1*, *step2*, *step3,* in specific case of this study), since the reported works only perform hydrolysis in a single step.

E_A indicates a higher temperature sensitivity for GLC formation, indicating that higher temperatures promote greater and faster GLC formation. At 150 °C and 175 °C after 15 minutes of reaction, GLC concentrations begin to decline due to their consumption to form other products, such as LA. Already at 200 °C this increase occurs only up to 5 min of reaction, from when the GLC begins to be consumed.

The reaction rate constant of *GLN → GLC* was lower when compared to the rate constants of the decomposition reactions of GLC. Consequently, the E_A of the GLN conversion (E_{AGLN} = 57.50 kJ/mol) was higher when compared to GLC decomposition reactions (E_{AGLC1} = 32.54 kJ/mol and E_{AGLC2} = 37.60 kJ/mol).

When evaluating the GLC decomposition, the E_A values (E_{AGLC1} *and* E_{AGLC2}) are similar. Therefore, the velocity constants values of k_{GLC1} (measuring the formation of 5-HMF) and k_{GLC2} (measuring the formation of degradation products, such as HUs) indicated the preferential formation of these latter products. In addition, these values also indicate that the use of higher temperatures gives preferential HUs formation over 5-HMF. It can be noted that decomposition of GLC at higher temperatures results in faster formation of HUs compared to formation of LA. In this case, using temperatures above 200 °C, GLC and 5-HMF are easily polymerized into HUs, resulting in a decrease in LA yield.

The velocity constants, analyzed by the different temperatures used in this study, show that the hydration reaction constants of 5-HMF ($k_{5\text{-}HMF}$) were up to 450 times faster than other reactions, which is in agreement with reported in previous studies (Girisuta et al. 2013, Girisuta et al. 2007). This indicates that the hydration of *5-HMF → AL* is not a limiting step during the catalytic depolymerization of cellulose from SCB. Once 5-HMF is formed, it is instantly converted to LA, and this explains the reason why the [*5-HMF*] in FSI-II that is always low. Thus, it is possible verify that the HUs are not formed from 5-HMF but from GLC, because the reaction of *GLC → 5-HMF* is very fast, as previously presented in other studies (Chang et al., 2006, Ren et al., 2015, Girisuta et al. 2013). These results lead us to believe that the *GLC → AL* reaction is the dominant reaction in catalytic depolymerization of cellulose from SCB.

The $k_{GLC1}/k_{5\text{-}HMF}$ values were 0.054, 0.061 and 0.068 under 150 °C, 175 °C and 200 °C, respectively, indicating that the temperature increase had a positive effect on the $k_{GLC1}/k_{5\text{-}HMF}$ values. This implies that higher temperatures are better suited to catalyze FSI-II to produce LA, as also found by Zhi et al. (2015).

Analyzing the experimental and the simulated values, was possible to determine the root mean square error (RMSE) and correlation coefficient (R^2). The values for RMSE were 0.440, 0.801 and 1.043, at 150 °C, 175 °C and 200 °C, respectively. Also, the values for R^2 were 0.998, 0.999, and 0.997, at 150 °C, 175 °C and 200 °C, respectively. These results show that the prediction of measured state variables was particularly accurate.

Thereby, the predictions made with the model and its parameters and the kinetic experiments showed us that the use of higher temperatures (200 °C) generates a promising process in the formation of AL from SCB. In relation to the overall yield as a function of the available initial pulp, 39.1 % were obtained by the simulation (38.6 % experimental). It is equivalent to a 15.0 kg LA production for SCB by simulation (14.8 kg experimental) on 100 kg of starting material (on dry basis).

These results are very promisors to improve the LA market. According to DSM (2019) the production estimates for using LA for polyamide intermediates, for example, is estimated in a market volume of 14,000 kton in 2029 with a market value of $ 25 billion (DSM, 2019). Knowing the high potential of the LA in the biorefinery, the proposed methodology drives a satisfactory dynamic mechanistic model for LA production from SCB. With this, is possible to increase the LA yields in the biorefinery, not only from SCB but also using different agroindustry residuals as feedstock.

5. Conclusions

In this work was developed a mechanistic model to simulate the kinetics of the production of levulinic acid (LA) from sugarcane bagasse (SCB) with initial cellulose content of 38.4 %. Sulfuric acid at 7.0 % w/v and temperatures ranging from 150-200 °C was used. The approach was developed by coupling the genetic algorithm (GA) with the differential equations of the deterministic model (calling a hybrid GA model) with the description of the main reaction to LA, and intermediate and side reactions to glucose, 5-HMF and humins. A good fit between the experimental data and the kinetic model was obtained. The yield gradually increased over the course of the reaction time, reaching 57.2 mol% when considering 200 °C and 45 min. In this way, the growth opportunity of the LA has been proven by integrating the use of three fractionation steps within the biorefineries.

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