CHEMICAL ENGINEERING TRANSACTIONS
VOL. 43, 2015
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet
Chief Editors: Sauro Pierucci, Jiří J. Klemeš

**ISBN** 978-88-95608-34-1; **ISSN** 2283-9216
DOI: 10.3303/CET1543105

# Kinetics of the Acid hydrolysis of Sugarcane Bagasse Using Different Milling Size, High Solid Load and Low Pretreatment Temperature

Pablo A. Alvarez*[a], Rubens Maciel Filho[a], Laura Plazas Tovar[a], Maria Regina Wolf Maciel[a]

[a]State University of Campinas UNICAMP Chemical Engennering School Av Albert Eintein 500, Campinas SP, Brazil.
palavarez@feq.unicamp.br

The aim of this work was to obtain experimental data in order to generate the kinetic model that showed the effect of the particle size on the performance of the pretreatment process. Data were obtained from the pretreatment kinetics process of sugarcane bagasse with dilute sulfuric acid in concentration of 1.0, 2.0 and 3.0% (w/v). The pretreatments were carried out at temperature of 121±1°C varying time and milling size, The studied times were 0, 15, 45, 60, 90 and 120 minutes and particle average diameter of 0.11, 0.25 and 0.50 mm. All the experiments were performed using a solid load of 15%.

## 1. Introduction

Sulfuric acid at low concentrations is commonly used as catalyst in physico-chemical pretreatment of sugarcane bagasse to increase the digestibility of cellulose in the subsequent enzymatic hydrolysis (Esteghlalian et al., 1997). Acids can break down the heterocyclic ether bonds between sugar monomers in the polymeric chains formed by hemicellulose and cellulose, thereby various compounds are released, which are mainly monomeric sugars such as xylose, glucose and arabinose and degradation products as acetic acid and furfural. After hydrolysis it is possible to obtain a solid waste without significant damage because the bonds are weaker than cellulose; this waste can be used in the production of butanol, ethanol, lactic acid or paper (Aguilar et al., 2002). The aim of this work was investigated the acid hydrolysis of sugarcane bagasse using high solid loads (15%) with different particle sizes of bagasse and diluted sulfuric acid. Kinetics models were developed to understand the variation in relation to time of the products generated. The results are showed taking into account the different milling size of sugarcane bagasse (0.11, 0.25 and 0.5 mm).

## 2. Material and Methods

### 2.1 The raw material

Sugarcane bagasse collected in a Sugar Mill (São João, Araras, Sao Paulo, Brazil) was used as raw material. The sugarcane bagasse was dried in environmental conditions during 3 days. After dried, it was milled and separated in sizes of 0.11, 0.25 and 0.50 mm of half diameter. The composition for sugarcane bagasse was determined by NREL laboratory analytical standard procedure.

### 2.2 Pretreatment experiments

Nine sets of experimental conditions were carried out; the temperature was kept constant (121±°C), the $H_2SO_4$ was ranged in concentrations of 1.0, 2.0 and 3.0% w/v and particles sizes of 0.11, 0.25 and 0.50 mm. These conditions were used in previous works by Tovar et al. 2014. The pretreatments were performed in glass flasks with a volume of 500 mL with high solid loading of 15%.All experiments were performed in an

Please cite this article as: Alvarez Gomez P.A., Maciel Filho R., Plazas Tovar L., Wolf Maciel M.R., 2015, Kinetics of the acid hydrolysis of sugarcane bagasse using different milling size, high solid load and low pretreatment temperature, Chemical Engineering Transactions, 43, 625-630 DOI: 10.3303/CET1543105

autoclave at several reaction times in the range 0-120 min. At the end of each experiment, the solid and liquid fraction were separated by manual compression of the material. The sugar analysis methods are based on a NREL laboratory analytical standard protocols.

### 2.3 HPLC methods

Samples filtered of 2 mL were loaded into HPLC (Agilent 1260 Infinity) for monomer sugar analysis. A Bio-Rad Aminex HPX87P column was used for the separation of sugar. For that, mobile phase of $H_2SO_4$ (5 mM), flow rate of 0.6 mL/min and oven temperature of 35°C and RID detector were adopted. For furfural analysis was used a C-18 column with 0.8 mL/min flux of mobile phase (Acetonitrile) (Gouveia et al 2009). All experiments were carried in duplicate, the fitting analyses of experimental data were performed with commercial software TableCurve 2D Systat Software Inc.

## 3. Results and Discussion

### 3.1 Concentrations of hydrolisates

The compositions of raw material is shown in the Table 1. These results shown the same behaviour when compared with those obtained with different herbaceous materials like straw (Sant'Ana da Silca et al 2010), indicating that different particle size lead to a small differences in their composition.

*Table 1: Sugarcane bagasse: composition in dry weight(%)*

| Components | Particle size (mm) | | |
|---|---|---|---|
| | 0.11 | 0.25 | 0.50 |
| Glucan | 26.9 ± 1.3 | 28.6 ± 1.4 | 31.8 ± 1.8 |
| Xylan | 15.7 ± 0.5 | 17.3 ± 1.5 | 20.2 ± 1.2 |
| Arabinan | 18.3 ± 0.8 | 17.9 ± 0.7 | 15.6 ± 2.0 |
| K-Soluble Lignin | 29.6 ± 2.1 | 22.3 ± 0.8 | 24.3 ± 0.3 |
| Others | 5.3 ± 0.9 | 7.1 ± 0.9 | 3.7 ± 0.1 |

The results of the nine sets of experiments were the solubilized fraction which showed an increase in the solubilisation when time and acid concentration raised. The hydrolysates were obtained using three particle sizes (0.11, 0.25, 0.50 mm of average diameter) combined with the three $H_2SO_4$ concentrations (1.0, 2.0 and 3.0% w/v) each combined sets was identified by PA1 to PA9. This results are showed in the Figures 1 - 4 exhibiting the concentrations of xylose, glucose, acetic acid and furfural released under different operational conditions.

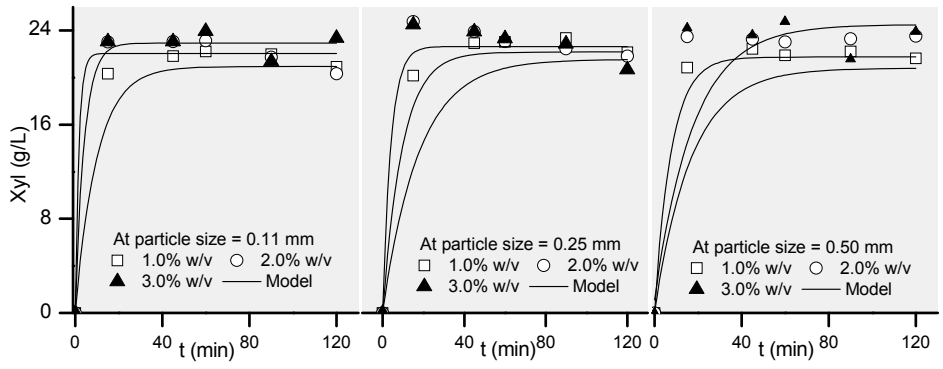


*Figure 1: Experimental data and predicted Saeman´s model data of the xylose (Xyl)*

It was observed in the Figure 1 a possible decomposition of the xylose to furfural by the decreased of xylose before reached the maximum value. The highest xylose concentration (26.6 g/L) was obtained at time 15 min in the conditions of particle size 0.25 mm average diameter, 2.0% $H_2SO_4$ and 121±1 °C. Is possible to find out a slight difference in the release of xylose when compared the size larger and smaller particle, where the

highest concentration of xylose for the particle size of 0.11 mm was 23.9 g/L and the highest concentration for 0.5 mm was 26.6 g/L The glucose concentration shows a quickly increment until about 15 min for all experiments, and from this time remained constant. Figure 2 shows the glucose concentration profile for each operational condition. As reported in the tests with sugarcane bagasse size of 0.5 mm at 2.0% $H_2SO_4$ for 120 min, there is no significant influence between the different particle sizes of sugarcane bagasse.

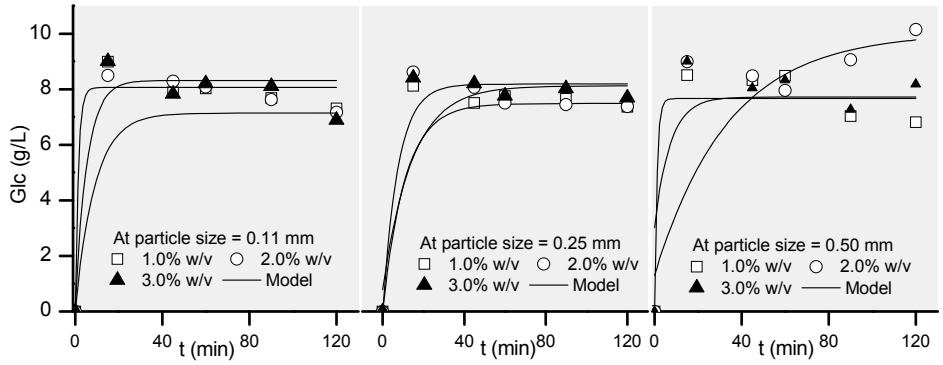


*Figure 2: Experimental data and predicted Saeman´s model data of the glucose concentration*

The acetic acid come to hydrolysis of acetyl group bound to the hemicellulosic monomers, in high concentrations it may inhibit the microorganism growth. This may lead to yield decrease in the subsequent fermentation step because acetic acid can go through the cellular membranes and decreases the intracellular pH (Aguilar et al., 2002). In this work the maximum of acetic acid released was into the extreme conditions (3% $H_2SO_4$ and 120 min) for the largest size of bagasse particles. It was observed, when taking into account the influence of particles sizes, that there is an increase in the acid release for time 120 min and the size 0.5 mm. Figure 3 shows the behavior of acetic acid. Furfural is derived from degradation of xylose and arabinose

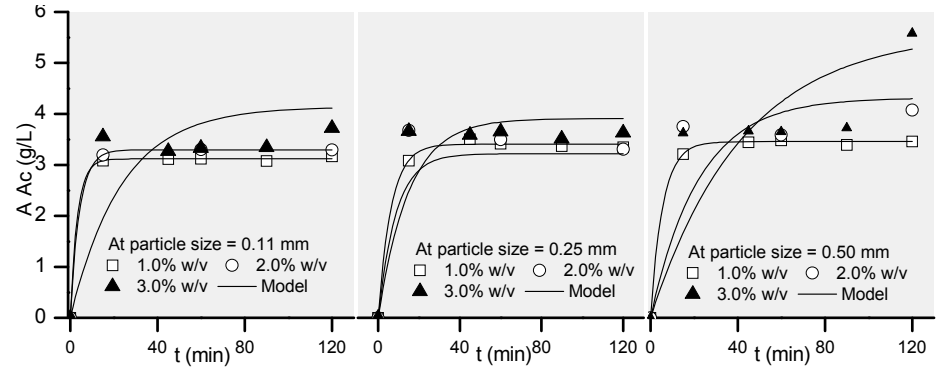


*Figure 3: Experimental data and predicted Saeman´s model data of the acetic acid concentration*

Figure 4 shows the behavior for the furfural, and it is possible to note that its concentration increases with acid sulphuric concentration and time. The highest concentration was achieved in the experimental conditions of 2.0% $H_2SO_4$ and 120 min, with no significant impact of the particle sizes. .

### 3.2 Kinetic Models

Usually the models in the literature are pseudo-homogeneous irreversible first-order reactions, This models are based on the model presented by Saeman (1945):

$$Cellulose \xrightarrow{k_1} Glucose \xrightarrow{k_2} Decomposition\ products \quad (1)$$

This model can be generalized to other polymers in Eq (2):

$$Polymers \xrightarrow{k_1} Monomers \xrightarrow{k_2} Decomposition\ products \quad (2)$$

where $k_1$ are the rate of generation reaction and $k_2$ is the rate of the decomposition reaction ($min^{-1}$). Resolving the differential equation for an isothermal reaction, the following model predicts the monomer concentration:

$$M = M_0 e^{-k_2 t} + P_0 \frac{k_1}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t}) \quad (3)$$

where $M$ and $P$ are the concentrations of monomer and polymer ($gL^{-1}$), respectively *t is the* time (min) and subscript 0 indicates initial conditions.

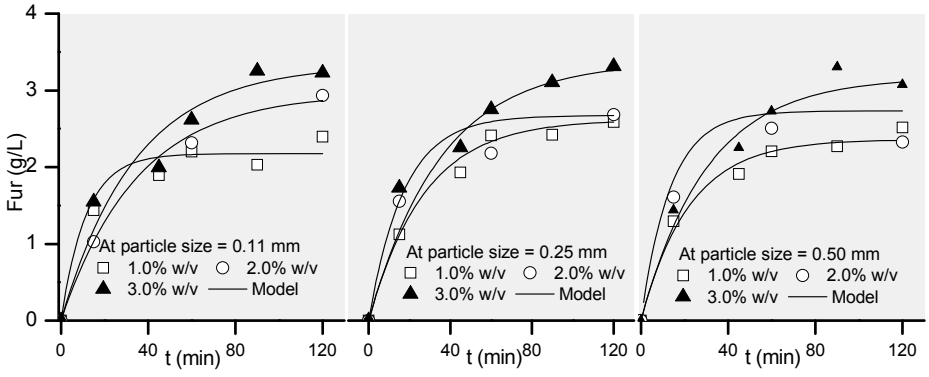


*Figure 4: Experimental data and predicted Saeman´s model data of the Furfural concentration*

### 3.3 kinetic modelling of xylose

Xylose is the main product of $H_2SO_4$ hydrolysis of the sugarcane bagasse. In previous works was demonstrated that experimental data were not enough successful for model of Eq (3) (Aguilar et al., 2002), A possible improvement is to include the parameter α which is the ratio between g of susceptible xylan/g of total xylan. This allows to take into account the existence of two fraction of hemicellulose, one easy to hydrolyze and the other difficult to hydrolyze, the Eq (3) was modified to include α as is show in Eq (4):

$$M = M_0 e^{-k_2 t} + \propto P_0 \frac{k_1}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t}) \quad (4)$$

where $M_0$is the initial xylose concentration (0 g/L), and α represent the ratio between the fractions g of susceptible xylan/g of total xylan. Table 2 shows the value of $\propto P_0$ .The data of the kinetic parameter of xylose release was shown in the Table 2. The experimental data was fitting applying the Eq (4), Figure. 1 shows the experimental and predicted data for xylose concentration. The statistical parameter $R^2$ shows good fit to low acid concentrations and an decreasing fit due the high concentration. The α values in the range of 0.55-1.00 (Aguilar et al., 2002), for the conditions of this work was found α values of 0.55-0.75.

*Table 2: Kinetics parameters of xylose released of sugarcane bagasse by sulphuric acid hydrolysis.*

| Particle Size (mm) | $H_2SO_4$ % | $P_0$ (g/L) | α (g/g) | $K_1$ ($min^{-1}$) | $K_2$ ($min^{-1}$) | $R^2$ |
|---|---|---|---|---|---|---|
| 0.11 | 1 | 31.52 | 0.664 | 0.0999 | 48143.58 | 0.95 |
| | 2 | 31.52 | 0.758 | 0.1041 | 17601.24 | 0.98 |
| | 3 | 31.52 | 0.743 | 0.1301 | 4.46E+27 | 0.99 |
| 0.25 | 1 | 34.73 | 0.635 | 0.5851 | 6.75E+34 | 0.99 |
| | 2 | 34.73 | 0.664 | 0.0560 | 5.37E+32 | 0.61 |
| | 3 | 34.73 | 0.726 | 0.0563 | 3.56E+59 | 0.81 |
| 0.50 | 1 | 40.54 | 0.556 | 0.0367 | 1.95E+19 | 0.91 |
| | 2 | 40.54 | 0.601 | 0.2456 | 1.46E+22 | 0.97 |
| | 3 | 40.54 | 0.551 | 0.0593 | 3.15E+41 | 0.59 |

### *3.4* kinetic modelling of glucose

Kinetics of glucose can be obtained similarly to xylose using the Eq (3):

$$M = G_0 e^{-k_2 t} + \propto Gn_0 \frac{k_1}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t}) \quad (5)$$

where $G_0$is the initial concentration of glucose (0 g/L) and $Gn_0$ is the glucan concentration corresponding to hypothetical quantitative conversion of glucan. Table 3 shows the kinetics parameters of glucose concentration and the Figure 2. depicts the experimental and predicted data. The α values are between 0.2-0.3, showing higher values for smaller particle size of bagasse.

*Table* 3*: Kinetics parameters of glucose released of sugarcane bagasse by sulphuric acid hydrolysis.*

| Particle Size (mm) | $H_2SO_4$ % | $G_0$ (g/L) | α (g/g) | $K_1$($min^{-1}$) | $K_2$($min^{-1}$) | $R^2$ |
|---|---|---|---|---|---|---|
| 0.11 | 1 | 54 | 0.151 | 0.6907 | 1.83E+85 | 0.97 |
| | 2 | 54 | 0.136 | 0.0922 | 9.44E+50 | 0.87 |
| | 3 | 54 | 0.142 | 0.8725 | 9.99E+22 | 0.95 |
| 0.25 | 1 | 57.4 | 0.124 | 0.1116 | 4.01E+12 | 0.82 |
| | 2 | 57.4 | 0.128 | 0.0698 | 8.99E+22 | 0.78 |
| | 3 | 57.4 | 0.152 | 0.0295 | 1.78E+24 | 0.66 |
| 0.50 | 1 | 43.8 | 0.186 | 0.1847 | 1.96E+33 | 0.93 |
| | 2 | 43.8 | 0.188 | 0.1337 | 1.38E+97 | 0.96 |
| | 3 | 43.8 | 0.107 | 0.1406 | 2.77E+82 | 0.76 |

### 3.5 kinetic modeling acetic acid concentrations

The acetic acid is generated by hydrolysis of the acetyl groups present in the lignocellulose. Therefore the model which describes the release of acetic acid is:

$$MActyl\ groups \xrightarrow{k_1} Acetic\ acid \quad (6)$$

based in the model the equation it would be:

$$Ac = Ac_0(1 - e^{k_1 t}) \quad (7)$$

where the $Ac_0$ is the potential concentration of acetyl groups and $k_1$ the rate of acetic acid formation ($min^{-1}$). Table 4 presents the kinetic parameters of the released of acetic acid, and Figure 3. shows the model fitting for the acetic acid. Through the values of $R^2$ it is possible to observe that the equations are well fitted for the smaller size of bagasse particles.

*Table* 4*: Kinetics parameters of acid acetic released of sugar cane bagasse by sulphuric acid hydrolysis.*

| Particle Size (mm) | $H_2SO_4$ % | $A_{C0}$(g/L) | $K_1$($min^{-1}$) | $R^2$ |
|---|---|---|---|---|
| 0.11 | 1 | 3.12 | 0.3001 | 0.99 |
| | 2 | 3.41 | 0.1577 | 0.99 |
| | 3 | 3.46 | 0.1766 | 0.99 |
| 0.25 | 1 | 3.30 | 0.2330 | 0.99 |
| | 2 | 3.22 | 0.1151 | 0.87 |
| | 3 | 4.32 | 0.0450 | 0.73 |
| 0.50 | 1 | 4.14 | 0.0424 | 0.65 |
| | 2 | 3.91 | 0.0670 | 0.85 |
| | 3 | 5.60 | 0.0236 | 0.65 |

### 2.6 kinetic modelling of furfural concentration

Furfural is generated from the degradation of the pentoses: xylose and arabinose. They are the main products of the hydrolysis of the hemicelulose (Zauter, 2011). A similar model to those used for acetic acid can be considerate, and the equation is:

$$Fc = F_0(1 - e^{k_1 t}) \quad (8)$$

where $F_0$ is the potential concentration of furfural and $k_1$the rate of furfural generation ($min^{-1}$), Table 5 shows the kinetic parameters for the generation of furfural and the Figure 4 shows the fitting of the experimental data. The statistical parameter $R^2$ indicates a good fit of the model. The kinetic parameters of the furfural released are given in Table 5.

*Table 5: Kinetics parameters of Furfural released of sugar cane bagasse by sulphuric acid hydrolysis.*

| Particle Size (mm) | H2SO4 % | $F_0$(g/L) | K1($min^{-1}$) | R2 |
|---|---|---|---|---|
| 0.11 | 1 | 2.18 | 0.0867 | 0.962 |
| | 2 | 2.62 | 0.0369 | 0.989 |
| | 3 | 2.36 | 0.0453 | 0.984 |
| 0.25 | 1 | 2.96 | 0.0284 | 0.997 |
| | 2 | 2.67 | 0.0581 | 0.958 |
| | 3 | 2.73 | 0.0740 | 0.936 |
| 0.50 | 1 | 3.33 | 0.0292 | 0.951 |
| | 2 | 3.37 | 0.0282 | 0.952 |
| | 3 | 3.17 | 0.0328 | 0.978 |

## 4. Conclusions

The acid hydrolysis in sugarcane bagasse, using low concentration of sulfuric acid, high load of solid and various particle size was investigated by kinetic model analysis. The Saeman' model was applied to the experimental data. It was found that *α* values do not show differences between different sizes of sugarcane bagasse, however α values of the xylose kinetics present differences, indicating a relationship between particle size and α value. It can be observed a variation between *k* values from the furfural and acetic acid released and the particle size of 0.11 mm led to higher *k* values when compared to particles of 0.50 mm.

**Acknowledgements**

The author are grateful to CNPEq (Grant N°161914/2011-0) and São Paulo Research Foundation-FAPESP (Grant N°. 2012/10857-3 and 2008/57873-8) for the financial support.

**References**

Aguilar R, Ramírez J.A., Garrote , Vázquez M, 2002. Kinetic study of acid hydrolysis of sugarcane bagasse. J. Food Eng. 55, 309–318,

Esteghlalian A, Hashimoto AG, Fenske JJ and PennerMH, 1997,Modeling and optimization of the dilute sulfuric acid pretreatment of corn stover, poplar and switchgrass. *Bioresource Technol* 59:129–136, 10.

Gouveia E.R., Nascimento R.T., Souto-Maior A.M., Rocha G.J.M. 2009. Methodology validation for chemical characterization of sugarcane bagasse. Quim. Nova 6, 1500-1504.

Sant'Ana da Silva A., Inoue H, Endo T, Yano S, Bon E, 2010, Milling pretreatment of sugarcane bagasse and straw for enzymatic hydrolysis and ethanol fermentation Biore source Technology 101 (2010) 7402–7409

Tovar, L. P., Maciel, M. R. W., Filho, R. M. 2014. Plug flow reactor model to analyse operating conditions on the dilute H2SO4-acid hydrolysis of sugarcane bagasse at high-solids loading. Chemical Engineering Transactions, 37**,** 325-300.

Zautsen R., 2011 Ethanol fermentation and simultaneous liquid-liquid extraction of ethanol and inhibitors present in the hydrolyzed lignocellulosic biomass, Thesis, 1977-Z19f , Brazil

Zhang R., Lu X., Sun Y., Wang X., Zhang S., 2010, Modeling and optimization of dilute nitric acid hydrolysis on corn stover, J Chem Technol Biotechnol, 86, 306-314.