

Acid pretreatment of lignocellulosic biomass: Steady state and dynamic analysis

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In this work, a systematic study of the reactor design and of the selection of the operating conditions for the dilute acid pretreatment of lignocellulosic biomass is presented, using modeling and simulation tools to improve the process efficiency. As case study, the acid pretreatment of corn stover in a continuous process is considered. Static and dynamic simulations were performed using Aspen Plus. The results are presented in terms of yields of fermentable sugars, reaction times and bioethanol production. The results show the potential of the methodology for improving the process efficiency (i.e. high conversions and short reaction times).

1. Introduction

The growing industrialization has derived in an increasing demand of fuels attempting to satisfy both the industrial and domestic demands. Nevertheless, not only the production but its use also affects the environment leading to modifications in the weather conditions (at a local and worldwide level). Hence, the need to search for biofuels as an alternative to fossil fuels that are major responsible for the greenhouse effect. The bioethanol comes as an alternative for this quest.

In particular, lignocellulosic biomass, such as corn stover and sugarcane bagasse, is a domestic feedstock that has potential to produce considerable quantities of bioethanol and other bioenergy and biobased products. Processing of lignocellulosic biomass to ethanol consists of four major operations: pretreatment, enzymatic hydrolysis, fermentation and ethanol separation/purification. To implement successfully the bioethanol production process, the first drawback that must be solved is the efficient removal of lignin and hemicellulose through a pretreatment process, but considering a low cost. Recently it has been demonstrated that the dilute acid pre-hydrolysis can achieve high reactions rates in short time and significantly improve cellulose hydrolysis (Eggeman and Elander, 2005). However, pretreatment operating conditions must be tailored to the specific chemical and structural composition of the various sources of biomass.

Despite continuing interest in the kinetic mechanism of solid-phase acid-catalyzed hydrolysis for several type of biomass, little attention has been given to the static and dynamic studies of the continuous process. For the one side, most of the techno-economic studies based on steady-state process simulations for bioethanol production from lignocellulosic biomass (e.g. Aden et al., 2002; Kwiatkowski et al., 2006; Cardona and Sanchez, 2006) take into account the hydrolysis reactions of hemicellulose (polymers) to produce mainly sugar monomers (glucose, xylose, arabinose, mannose) and acid-soluble lignin (ASL), but using conversion fractions at fixed operating conditions. On the other side, from recent batch kinetic studies (Romero et al., 2010; Morinelly et al, 2009; Jensen et al., 2008; Lavarack and Rodman, 2002; Aguilar et al., 2002) it has been revealed that the main factors affecting the acid pretreatment are the type of biomass, the type of acid, the feed acid concentration and the reaction temperature. So that kinetic modeling and the operating conditions of the pretreatment unit play an important role in the design, development, and operation of the complete process of bioethanol production.

In this work, a systematic study of the reactor design and of the selection of the operating conditions for the dilute acid pretreatment of lignocellulosic biomass is presented, studying its influence in the final bioethanol production. As case study, the bioethanol production from corn stover in dilute sulfuric acid is considered. First the complete continuous process is simulated in Aspen Plus, then simulations are performed to analyze the influence of several factors: (a) the pretreatment reactor temperature, (b) the feed concentration of the dilute sulfuric acid, (c) the fraction of solids in the feed stream, and (d) the kinetic model. The results are presented in terms of yields of fermentable sugars, reaction times and bioethanol production.

2. Bioethanol production from lignocellulosic Biomass

A simplified flowsheet of the process is shown in Figure 1, which was implemented in Aspen Plus. Processing of lignocellulosic biomass to ethanol has three main sections: pretreatment, simultaneous enzymatic saccharification and fermentation, and ethanol separation/purification; and includes subsections for solid separation and enzyme production. Figure 2 shows the flowsheet for the specific section of the biomass conditioning and the dilute acid pretreatment (or prehydrolysis), which is the subject of this work. Our intention was not to implement a detailed bioethanol plant, but rather a generic plant design containing equipment and unit operations necessary to convert biomass into bioethanol. So that this plant flowsheet will be helpful for the study of the pretreatment effect on the bioethanol production.

3. Lignocellulosic Biomass Pretreatment

3.1 Process description

A continuous reactor for the lignocellulosic biomass pretreatment using dilute sulfuric acid and high temperature is considered where hydrolysis reactions are carried out. Corn stover is selected as lignocellulosic biomass, whose composition is (%w/w): 37.4 % glucan, 21.1 % xylan, 18 % Lignin, 2.9 % arabinan, 2.0 % galactan, 1.6 % mannan, 15 % moisture, 5.2 % ash, 2.9 % acetate, 3.1 % protein, 4.7 % extractives, and 1.1 %

unknown soluble solids. The reactor design basis was taken according the proposal of Aden et al. (2002): acid concentration = 1.1 %, residence time = 2 min, temperature = 190 °C, solids concentration = 42 %.

3.2 Kinetic modeling

The main reactions (Aden et al., 2002) are given in Table 1, where mannan and galactan have not included but they are assumed to have the same reactions and conversions as arabinan. Most of the hemicellulose portion is hydrolyzed to soluble sugars (primarily xylose, mannose, arabinose, and galactose). Glucan in the hemicellulose and a small portion of the cellulose are converted to glucose. Moreover, the reactor operating conditions also solubilize some of the lignin in the feedstock. Degradation products of pentose sugars and hexose sugars (primarily furfural) are also formed.

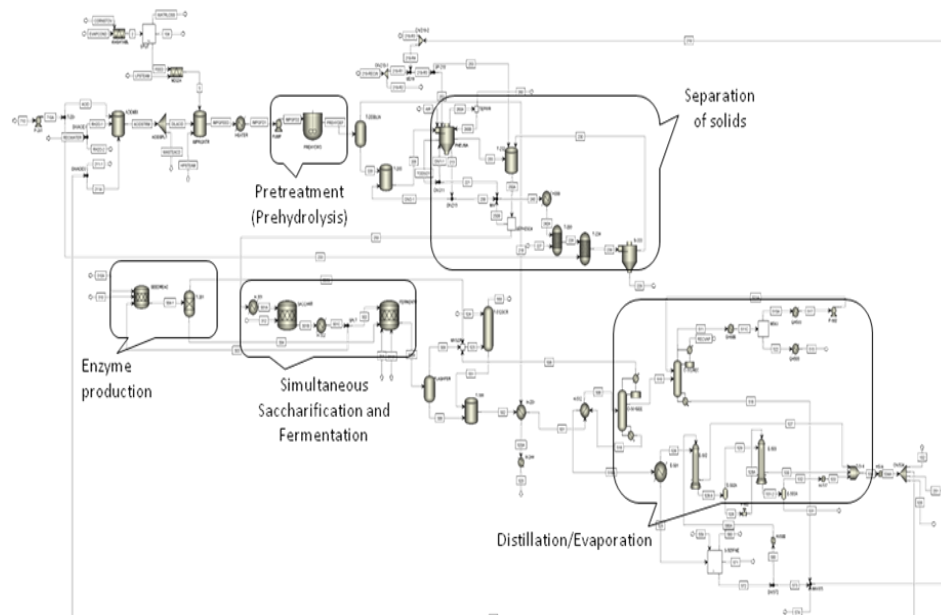


Figure 1: Flowsheet for bioethanol production from lignocellulosic biomass.

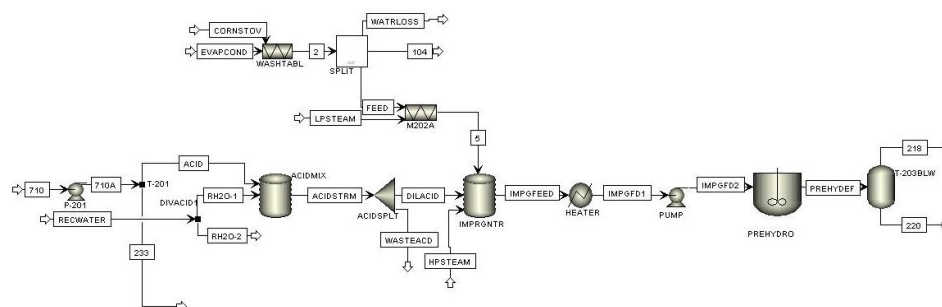
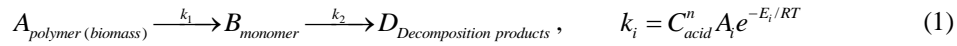


Figure 2: Flowsheet for the section of biomass conditioning and pretreatment.

Several models for acid hydrolysis in batch reactors have been proposed in the literature (Romero et al., 2010; Morinelly et al., 2009; Jensen et al., 2008; Lavarack et al., 2002; Rahman et al., 2006; Aguilar et al., 2002). The simplest and widely used model involves a series of pseudo-homogeneous irreversible first-order reactions from solid polymer (i.e. A = xylan, glucan, arabinan, mannan, galactan, lignin) to aqueous monomer (i.e. B = xylose, glucose, arabinose, mannose, galactose, ASL), and then onto decomposition products:



Here k_i , A_i and E_i ($i = 1, 2$) are the kinetic rate constants, the pre-exponential constants and the activation energies for i -th reaction, respectively; C_{acid} is the sulfuric acid concentration (% w/w of liquid), n is the order of reaction w.r.t. acid concentration, T is the temperature, and ϕ is the ratio of solid material to liquid (w/w).

For reactions reported in Table 1, kinetic parameters are taken from Lavarack et al. (2002). It is important to note that there are other reactions with conversion fractions less than 0.025, but they are not considered in this work, since their contribution do not affect meaningfully the general results.

4. Numerical Simulations: Results and Discussion

The influence of four factors on the design and operability of the process was studied: (a) the reactor temperature (from 100 °C to 190 °C, this latter in close proximity to the calculated boiling point), (b) the feed concentration of the dilute sulfuric acid - from 1.1 to 6% w/w, (c) the fraction of solids in the feed stream - from 0.23 to 0.5, and (d) the kinetic model. Regarding this one, two scenarios are compared: model *A* that considers only the generation reactions i.e., $k_2 = 0$ in Eq. (1), and model *B* that considers both generation and decomposition reactions i.e., series reaction in Eq. (1).

Table 1: Pre-hydrolysis reactions and conversion fractions (X)

Reaction	X
$(\text{Xylan})_n + n \text{ H}_2\text{O} \rightarrow n \text{ Xylose}$	0.90
$(\text{Xylan})_n \rightarrow n \text{ Furfural} + 2n \text{ H}_2\text{O}$	0.05
$(\text{Glucan})_n + n \text{ H}_2\text{O} \rightarrow n \text{ Glucose}$	0.07
$(\text{Glucan})_n + \frac{1}{2} n \text{ H}_2\text{O} \rightarrow \frac{1}{2} n \text{ Cellobiose}$	0.007
$(\text{Arabinan})_n + n \text{ H}_2\text{O} \rightarrow n \text{ Arabinose}$	0.90
$(\text{Arabinan})_n \rightarrow n \text{ Furfural} + 2n \text{ H}_2\text{O}$	0.05
$(\text{Lignin})_n \rightarrow n \text{ Acid soluble lignin (ASL)}$	0.05

4.1 Static simulations

Figure 3 shows the simulation results for xylose at the exit of the pretreatment reactor (see Figure 2), where the main highlights are: (a) Model *B* gives a non-monotonic behavior with lower conversions in comparison with Model *A*, (b) monomer concentration increases as the temperature is increased, and (c) higher conversions are

obtained when C_{acid} is reduced. Figure 4 shows the simulation results (using Model B) for xylose, glucose and ASL at the exit of the pretreatment reactor (see Figure 2) and for bioethanol production at the exit of the production plant (see Figure 1). The main highlight is that sugar concentrations and bioethanol production increase as solid fraction is increased. However, there is a tradeoff between production and operation, because high solid fraction involves high bioethanol production but the energy consumption for pumping and heating is higher too.

4.2 Dynamic simulations

For the dynamic behavior, it was corroborated the influence of Model A and B, as shown in Figure 5. Finally the dynamic response of all monomers is presented in Figure 6, where the specific operating conditions where define to keep a trade-off between high conversion and low reaction times: $T = 160$ °C, $C_{acid} = 4\%$, and $\phi = 0.42$.

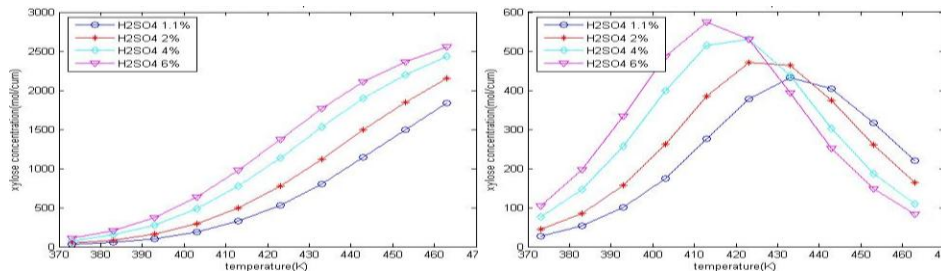


Figure 3: Influence of temperature and acid concentration ($\phi = 0.42$): (a) model A; (b) model B.

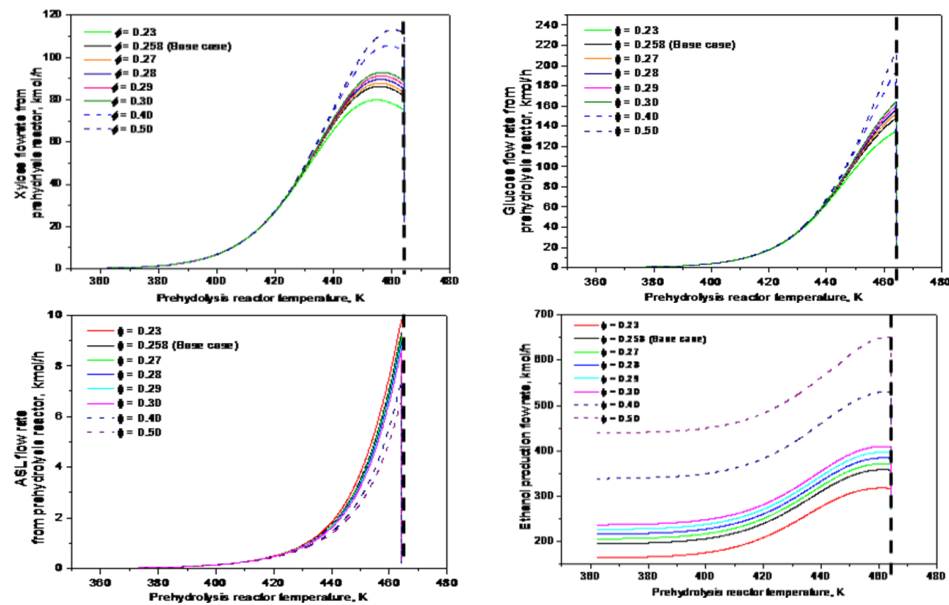


Figure 4: Influence of solid fraction (ϕ) and temperature in a static reactor (model B).

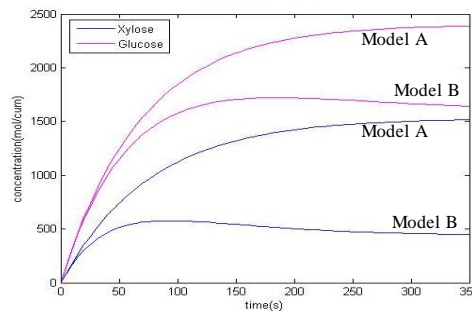


Figure 5: Influence of the kinetic model.

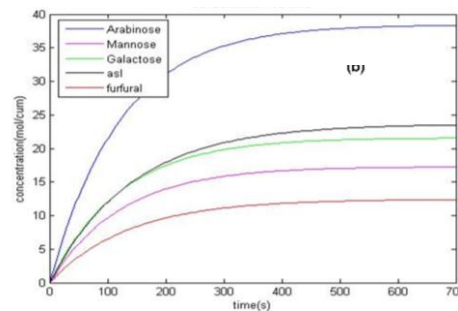


Figure 6: Dynamic response for Model B.

5. Conclusions

The influence of several operation parameters has been shown through rigorous modeling and numerical simulations. It can be concluded that efficient reaction conversions are strongly affected mainly by pretreatment temperature and solid fraction of fed biomass, and there is slight dependency on the acid concentration. From an industrial point of view, the results show that the well design of the pretreatment reactor is relevant for the design, operation and control of the bioethanol production process.

References

- Aden, A., Ruth, M., Ibsen, K., Jechura, J., Neeves, K., Sheehan, J. and Wallace, B., 2002, Lignocellulosic biomass to ethanol process design and economics for corn stover, National Renewable Energy Laboratory, NREL/TP-510-32438.
- Aguilar, R., Ramírez, J.A., Garrote, G. and Vázquez, M., 2002, Kinetic study of the acid hydrolysis of sugar cane bagasse, *J. Food Engng.* 55, 309-318.
- Cardona, C.A. and Sanchez, O.J., 2006, Energy consumption analysis of integrated flowsheets for prod. of fuel ethanol from lignocell. biomass, *Energy* 31, 2447-2459.
- Eggeman, T. and Elander, R.T., 2005, Process and economic analysis of pretreatment technologies, *Bioresource Technology* 96, 2019-2025.
- Jensen J., Morinelly, J., Aglan, A., Mix, A., and Shonnard, D.R., 2008, Kinetic charact. of biomass dilute sulphuric acid hydrolysis, *AIChE J.* 54, 1637-1645.
- Kwiatkowski, J.R., McAloon, A.J., Taylor, F. and Johnstone, D.B., 2006, Modeling the process and costs of fuel ethanol production, *Ind. Crops & Prod.* 23, 288-296.
- Lavarack, B.P., Griffin, G.J., Rodman, D., 2002, The acid hydrolysis of sugarcane bagasse hemicellulose, *Biomass and Bioenergy* 23, 367-380.
- Morinelly, J.E., Jensen, J.R., Browne, M., Co, T.B. and Shonnard, D.R., 2009, Kinetic characterization of xylose monomer and oligomer concentrations during dilute pretreatment of lignocellulosic biomass, *Ind. Eng. Chem. Res.* 48, 9877-9884.
- Rahman, S.H.A., Choudhury, J.P. and Ahmad, A.L., 2006, Production of xylose from oil palm empty fruit bunch fiber using sulfuric acid, *Biochem. Engng.* 30, 97-103.
- Romero, I., Ruiz, E., Castro, E. and Maya, M., 2010, Acid hydrolysis of olive tree biomass, *Chem. Eng. Res. and Des.* 88, 633-640.