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Steady State Analysis and Optimization of a Continuous Reactor for Acid Pretreatment of Lignocellulosic Biomass

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The problem of modelling, operation and optimization of a dilute acid pretreatment reactor for lignocellulosic biomass is addressed. A continuous reactor model is developed based on rigorous mass and energy balances, including a complete kinetic mechanism. The process design and operation are studied through steady state and dynamic analysis, together with an optimization problem that maximizes the reaction rates of the sugar production and of lignin elimination. The sugarcane bagasse as lignocellulosic biomass is considered as case study. The results are presented in terms of yields of fermentable sugars and reaction times, defining operating ranges for an efficient continuous process. The methodology also gives guidelines to: improve experimental design, optimize the operating conditions and control the pretreatment process; reducing costs and effort of research and development.

1. Introduction

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.

Moreover, the design and technologies of current pretreatment are still expensive in comparison with the subsequent steps. For instance in a bioethanol process production, the pretreatment requires around the 20% of the total process cost (Aden et al., 2002). Favourably the pretreatment could improve the global process efficiency and reduce the global costs through research and development, which will let increase the speed of commercial applications. Among various chemical techniques, dilute sulphuric acid hydrolysis is one of the most widely used and studied pretreatment process, due to its low cost, high effectiveness in removing the recalcitrant nature of native cellulose in short time, and the significantly enhancement of the enzymatic digestibility of many forms of lignocellulosic feedstocks (Mosier et al., 2005). Recently, the main research areas that have been address for this pretreatment process are: the kinetic characterization in experimental lab batch reactors (e.g.; Romero et al., 2010), the design and implementation of pilot-scale prototype reactors (e.g. Yan et al., 2009),

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and the technical-economic evaluation of an industrial conceptual design (e.g. Aden et al., 2002; Moiser et al, 2005). Nonetheless, little attention has been focused to the development of an integral process design, including modelling, design, optimization, and control.

In the present work, the problem of modelling, operation and optimization of a dilute acid pretreatment reactor for lignocellulosic biomass is addressed. A continuous reactor model is developed based on rigorous mass and energy balances, including a complete kinetic mechanism studied in a previous work (Lopez-Arenas et al., 2011). The non-isothermal process design and operation are studied through steady state analysis (including steady state multiplicity) and dynamic behaviour, together with an optimization problem that maximizes the reaction rates of the sugar production and of lignin elimination. The results are presented in terms of yields of fermentable sugars and reaction times, defining operating ranges and optimal conditions for an efficient continuous process.

2. Process Modelling

A non-isothermal continuous reactor for the lignocellulosic biomass pretreatment using dilute sulphuric acid and high temperature is considered, where hydrolysis reactions are carried out. The effect of the isothermal reactor modelling and the comparison of batch and continuous operation were studied in a previous work (Lopez-Arenas et al., 2010). Here the objective is to study the non-isothermal operation and the optimal operating conditions of a continuous reactor. So in this section, we recall briefly the reactor model to be used.

2.1 Kinetic model

Several kinetic models for acid hydrolysis of lignocellulosic biomass have been proposed in the literature (Romero et al., 2010; Lavarack et al., 2002; among others). The simplest and widely used model involves a series of pseudo-homogeneous irreversible reactions from solid polymer (i.e. A_i = xylan, glucan, arabinan, mannan, galactan, lignin) to aqueous monomer (i.e. B_i = xylose, glucose, arabinose, mannose, galactose, ASL: acid soluble lignin), and then onto decomposition products:

$$A_{j\ (polymer\ or\ biomass)} \xrightarrow{k_{1j}} B_{i\ (monomer\ or\ sugar)} \xrightarrow{k_{2j}} D_{i\ (Decomposition\ products)} \tag{1}$$

where the kinetic rate constants k_{ij} are given according next expression:

$$k_{ij} = C_{acid}^{n_{ij}} A_{ij} e^{-E_{ij}/RT} \tag{2}$$

where A_{ij} are the pre-exponential constants for the corresponding component j in the reaction i, C_{acid} is the sulphuric acid concentration (%w/w of liquid), E_{ij} are the activation energies, n_{ij} are the orders of reaction w.r.t. acid concentration, and T is the temperature.

All reactions of Eq. 1 are considered of first order, first reaction ($A_i \rightarrow B_i$) is given in solid phase and second reaction ($B_i \rightarrow D$) is given in liquid phase, so that

$$r_{1j}\left(a_i,T\right) = k_{1j}\left(T\right) a_i; \qquad r_{2j}\left(b_i,T\right) = k_{2j}\left(T\right) \phi b_i \tag{3}$$

Where a_i and b_i are the molar concentrations of A_i and B_i, respectively, and ϕ is the ratio of solid material to liquid (w/w).

2.2 Dynamic process model

The mass and energy balances for a non-isothermal continuous reactor with a jacket for heat transfer is given by

$$\frac{da_i}{dt} = \theta\left(a_{in,i} - a_i\right) - r_{1i}\left(a_i,T\right), \qquad a_i\left(0\right) = a_{i0} \tag{4}$$

$$\frac{db_i}{dt} = \theta\left(b_{in,i} - b_i\right) + r_{1i}\left(b_i,T\right) - r_{2i}\left(b_i,T\right), \qquad b_i\left(0\right) = b_{i0} \tag{5}$$

$$\frac{dT}{dt}=\sum_i\left[\Delta_{1i}r_{1i}\left(a_i,T\right)+\Delta_{2i}r_{2i}\left(b_i,T\right)\right]+\theta\left(T_{in}-T\right)-\eta\left(T-T_j\right),\qquad T\left(0\right)=T_0 \tag{6}$$

$$\theta=\frac{Q}{V};\qquad \Delta_{ij}=\frac{\left(-\Delta H_{ij}\right)}{\rho C_p},\qquad \eta=\frac{UA}{\rho C_p V} \tag{7}$$

Where sub-index *in* and *j* are referred to the inlet flowrate and the jacket, respectively; *Q* is the inlet and outlet volumetric flowrate, *V* is the reactor volume, ρ is the mixture density, C_p is the mixture heat capacity, ($-\Delta H_{ij}$) are the heats of reaction, *U* is the global heat transfer coefficient and *A* is the heat transfer area. In Eq. 5, commonly $b_{in,i}$ = 0 since there is no monomers in the lignocellulosic biomass.

3. Model Analysis Approach

3.1 Steady state analysis

Firstly, the reactor model (Eq. 4-7) was solved in steady state (SS) considering reference operating conditions, which correspond to an algebraic equation system:

$$\theta\left(a_{in,i}-a_i\right)-r_{1i}\left(a_i,T\right)=0 \tag{8}$$

$$\theta b_i+r_{1i}\left(b_i,T\right)-r_{2i}\left(b_i,T\right)=0 \tag{9}$$

$$\sum_i\left[\Delta_{1i}r_{1i}\left(a_i,T\right)+\Delta_{2i}r_{2i}\left(b_i,T\right)\right]+\theta\left(T_{in}-T\right)-\eta\left(T-T_j\right)=0 \tag{10}$$

Then bifurcation diagrams were constructed to analyze the possibility of finding multiplicity of steady states. By using this approach, it is possible to determine the feasible operation regions in terms of flowrates, temperatures, acid concentration, solid fraction, etc. In particular for (bio)chemical reactors, bifurcation parameters can be defined as the jacket temperature (T_j) and the dilution rate (θ).

3.2 Optimization problem

The optimization objective is to determine the optimal steady state where the maximum reaction rate of xylose production and of lignin elimination (equivalent to maximum reaction rate of ASL lignin) is achieved. It is important to mention that glucose production has not been included, because the remanent glucan can be converted into glucose in a next reaction step (i.e. enzymatic hydrolysis, second stage in the bioethanol production). The parameter to be optimized can be the jacket temperature, the solid fraction, the acid concentration, the inlet flowrate, etc. For instance defining the reactor temperature as the optimization parameter, the following objective function is defined:

$$\max_{T^*} J=\sum_{i=xilose,ALS}\left[r_{1i}\left(a_i^*,T^*\right)-\phi r_{2i}\left(b_i^*,T^*\right)\right] \tag{11}$$

Subject to the SS model (Eq. 8-10), and bounds $T_{\min}\le T^*\le T_b$ (T_b: mixture boiling point).

3.3 Dynamic analysis

The algebraic-differential equation system for the dynamic model (Eq. 4-7) can be solved to analyze the transient behaviour, determining residence times, phase diagrams, stability of the steady states, etc. Moreover the optimization results can be corroborated.

4. Results and Discussion

4.1 Case study

Sugarcane bagasse is selected as lignocellulosic biomass, whose composition is (%w/w): 38.9% glucan, 20.6% xylan, 23.9% Lignin, 5.6 % arabinan, and 11% others. The reactor design basis was taken according the proposal of Aden et al. (2002) and our previous work (Lopez-Arenas et al., 2010): C_{acid} = 5%, Q = 0.0536 m^3/min, V = 2 m^3, T = 190°C (at a pressure of 12 atm), ϕ = 0.42. Kinetic constants were taken from Lavarack et al. (2002). Aspen Plus simulator was used to evaluate the mixture boiling point, density and heat capacity, as well as the heats of reaction.

4.2 Simulation methodology

ICAS-MoT (Sales-Cruz and Gani, 2003; ICAS-Mot, 2012) has been used in this work to construct, analyse and solve the models. A generated model-code from ICAS-MoT can be easily changed from steady state to dynamic stated, and then to an optimization problem. The available futures of ICAS-MoT allow these calculations to be made by the model developer/user without the need for any programming. Consequently, the time saved in model implementation and programming is used in model-based process analysis. The results are next presented in terms of the main process variables: xylose (or xylan conversion), lignin (or ASL) and reactor temperature.

4.3 Steady state

The steady state model (Eq. 8-10) was solved using Newton-Powell method. As aforementioned, bifurcation diagrams were to determine the multiplicity of steady states. In particular, the results when the jacket temperature is used as bifurcation parameter are shown in Figure 1. The bifurcation diagram covers a wide range of numerical values for the jacket temperature, however physical only the grey region corresponds to the feasible operating range since the minimum temperature value should be around the environmental temperature and the maximum temperature value must be the mixture boiling point (T_b = 466 K). As it can be seen, there exist two possible steady states. According to the feasible temperature region is possible to define the maximum reachable xylose concentration (ignition state), where it can be seen that corresponds to T_j = 380 K, T = 358 K and C_{xylose} = 247.6 mol/m^3. But with T_j = 380 K, it is also possible to reach another undesired point (extinction state): T = 401.5 K and C_{xylose} = 30.8 mol/m^3. However to achieve the maximum ASL concentration (results do not shown due to limit of space) at C_{ASL} = 95.58 mol/m^3, it was obtained at a value of T_j = 340 K, corresponding to T = 530.27 K, which is not physically reachable since the boiling point is 466 K. From this analysis it is clear that the definition of the initial condition of a dynamic process will be important to determine the final steady state.

4.4 Optimization of the temperature

Several optimization problems (Eq. 8-11) were solved using SQP (Successive Quadratic Programming) based algorithm. First for the isothermal reactor, the reactor temperature was optimized to achieve a maximum objective function (Eq. 11). Results for this case are shown in Figure 2, where it can be observed that the optimal temperature is: T* = 460.68 K, corresponding to C^*_{xylose} = 246.96 mol/m^3 and C^*_{ASL} = 19.04 mol/m^3. Then for the non-isothermal reactor, two variables were optimized as shown in Figure 3. When the optimization variable is the jacket temperature, its optimal value is T_j^* = 379.37 K, corresponding to C^*_{xylose} = 245.45 mol/m^3 and C^*_{ASL} = 18.28 mol/m^3. When the optimization variable is the acid concentration (which bounds were $0 \leq C^*_{acid} \leq 5\%$, due to consequences in the undesired decomposition products), its optimal value is C_{acid} = 5% (upper bound), corresponding to C^*_{xylose} = 293.79 mol/m^3 and C^*_{ASL} = 21.21 mol/m^3. These results are in accordance with the previous steady state analysis.

4.5 Dynamic behaviour

Lastly, the dynamic model (Eq. 4-6) was solved using BDF (backward differential formula) method. In Figure 4 (a) shows the dynamic behaviour for the isothermal reactor to analyze the effect of the reactor temperature on the xylan conversion and the residence time. As it was expected at higher temperatures higher conversions are reached with faster time response. Figure 4 (b) shows the dynamic response when the optimal parameters are used. It is shown than the ignition point is achieved even when the initial condition is not so close to the desired point, meaning that it is stable.

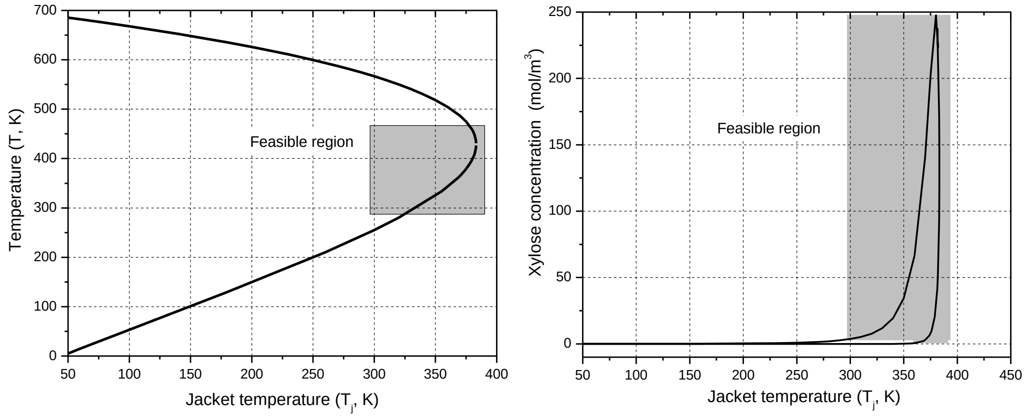

Figure 1: Multiplicity of SS and feasible operating region.

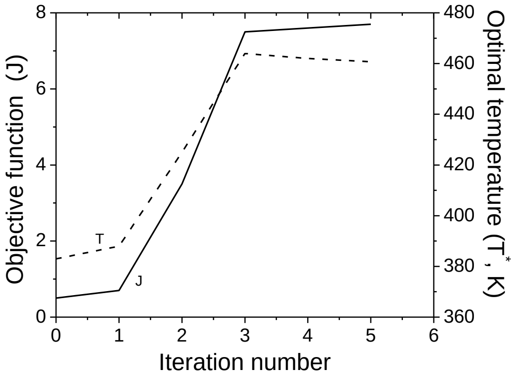

Figure 2: Optimized temperature for the isothermal reactor.

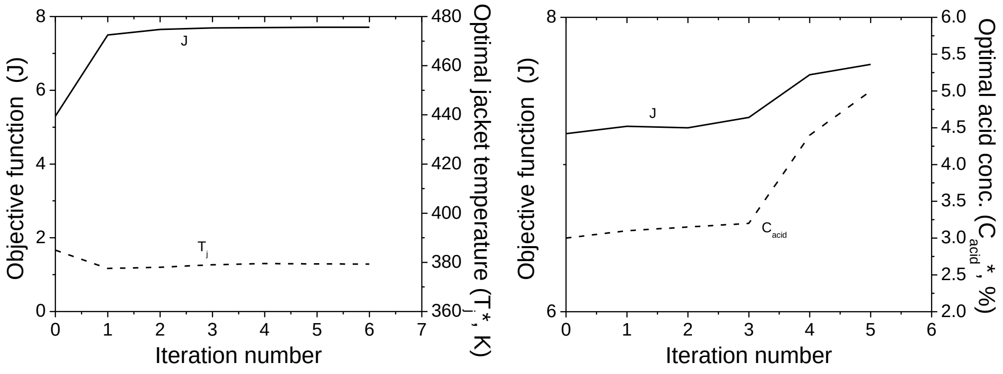

Figure 3: (a) Optimized jacket temperature and (b) optimized acid concentration for the non-isothermal reactor.

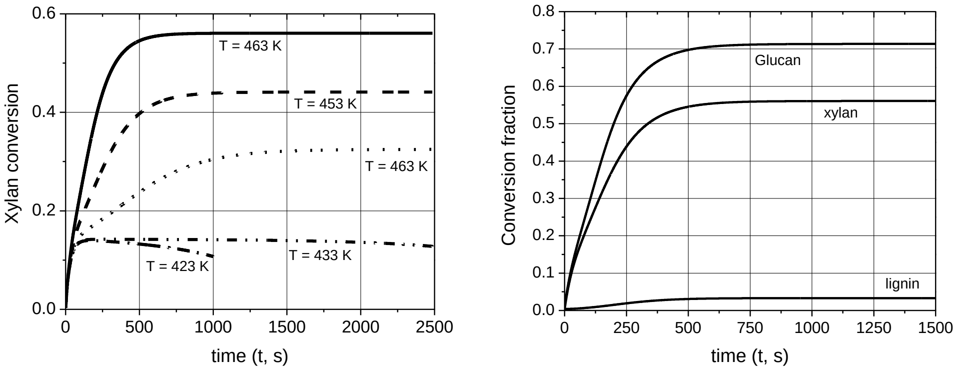

Figure 4: Dynamic behaviour of: (a) the xylan conversion at different reactor temperatures, (b) sugars and lignin conversions at optimal operating conditions.

5. Conclusions

The influence of several operating parameters has studied through rigorous modelling analysis. It can be concluded that efficient reaction conversions are strongly affected by jacket temperature, but slightly affected by acid concentration. The results for the non-isothermal reactor, in comparison with previous results of the isothermal reactor (Lopez-Arenas et al., 2010), demonstrate the importance of including the energy balance because: (a) steady state multiplicity appears, (b) optimization problems are more realistic, and (c) the dynamic response of all states are strongly dependent on the jacket and reactor temperatures. From an industrial point of view, the findings show that the well design and operation of the pretreatment reactor will be relevant for future monitoring and control projects.

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