



Modeling of biomass fractionation in a lab-scale biorefinery: Solubilization of hemicellulose and cellulose from holm oak wood using subcritical water

A. Cabeza^a, C.M. Piqueras^b, F. Sobrón^a, J. García-Serna^{a,*}

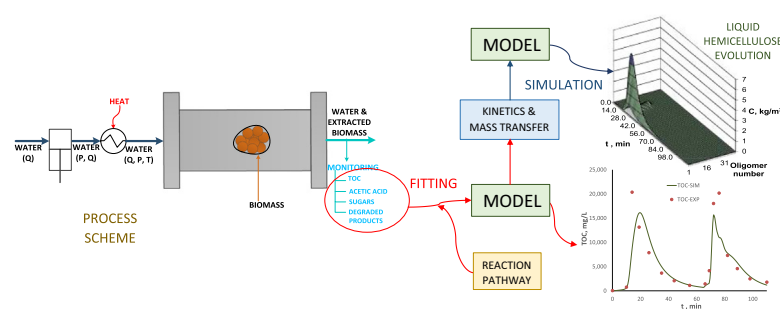
^aHigh Pressure Processes Group, Department of Chemical Engineering and Environmental Tech., University of Valladolid, 47011 Valladolid, Spain

^bPlanta Piloto de Ingeniería Química, PLAPIQUI-Universidad Nacional del Sur-CONICET, Camino La Carrindanga km 7, 8000 Bahía Blanca, Buenos Aires, Argentina

HIGHLIGHTS

- Hydrothermal fractionation of holm oak was studied in a packed bed reactor.
- Temperature has the main influence over the composition out flow stream.
- A kinetic model was developed which is able to reproduce the profile of TOC content.
- The model is capable to reproduce all the physical phenomena like porosity variation.
- A simulation of the whole process was done, checking its physical behavior.

GRAPHICAL ABSTRACT



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ABSTRACT

Lignocellulose fractionation is a key biorefinery process that need to be understood. In this work, a comprehensive study on hydrothermal-fractionation of holm oak in a semi-continuous system was conducted. The aim was to develop a physicochemical model in order to reproduce the role of temperature and water flow over the products composition. The experiments involved two sets: at constant flow (6 mL/min) and two different ranges of temperature (140–180 and 240–280 °C) and at a constant temperature range (180–260 °C) and different flows: 11.0, 15.0 and 27.9 mL/min. From the results, temperature has main influence and flow effect was observed only if soluble compounds were produced. The kinetic model was validated against experimental data, reproducing the total organic carbon profile (e.g. deviation of 33%) and the physicochemical phenomena observed in the process. In the model, it was also considered the variations of molecular weight of each biopolymer, successfully reproducing the biomass cleaving.

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1. Introduction

The concept of biorefinery is based on the definition of a conventional petroleum refinery. Therefore, it is an installation which transforms a raw material (biomass) into energy (heat, electricity

* Corresponding author. Tel.: +34 983184934.

E-mail address: jgserna@iq.uva.es (J. García-Serna).

and biofuels) and several products (chemicals and biomaterials) by fractionation or conversion processes. One of the most studied ways to perform this conversion is biomass pyrolysis, where heat is used to transform it into charcoal, gases and biofuels (Ranzi et al., 2008; Tanoue et al., 2007; Tock et al., 2010). On the other hand, hydrothermal fractionation is another promising option because it is capable to recover the cellulosic fraction of biomass, which corresponds between 38.3 and 81.3 wt% of woody biomass

Nomenclature

| | | | |
|---------------------------------|--|--|---|
| C_t | total concentration in the solid, mg/L | k_{Lj} | kinetic constant for compound “j” in liquid phase, $L^{n1} \cdot \text{mg}^{-1-n1} \cdot \text{min}^{-1}$ |
| ε and φ | porosity of the bed and the relation factor between it and C_t , dimensionless | r_{deg} | reaction rate for sugar degradation, mg/min · L |
| C_{Sj}, C_{Si} | concentration of the compound “j” or “i” in the solid phase, mg/L | $k_{\text{deg}1}, k_{\text{deg}2}$ | kinetic constant for C6 and C5 degradation, $L^{n2} \cdot \text{mg}^{-1-n2} \cdot \text{min}^{-1}$ |
| r_j | reaction rate of the compound “j”, mg/min · L | $C_{L_{\text{sugar-C6}}}, C_{L_{\text{sugar-C5}}}$ | concentration of the sugar “C6” or “C5” number “i”, mg/L |
| $k_j \cdot a$ | mass transfer coefficient multiplied by the specific exchange area, min^{-1} | r_{de} | reaction rate for sugar deacetylation, mg/min · L |
| C_{Lj}^* | equilibrium concentration of the compound “j” in liquid phase, mg/L | k_{de} | kinetic constant of r_{de} , $\text{mg}^{-1} \cdot \text{min}^{-1}$ |
| \bar{C}_{Lj} | average concentration of the compound “j” along the reactor in liquid phase, mg/L | $C_{L_{\text{sugar}}}$ | total sugar concentration in liquid phase, mg/L |
| H_j | equilibrium constant between the solid and the liquid, dimensionless | r_{rep} | reaction rate for the polymerization, mg/min · L |
| C_{Lj}, C_{Li} | concentration of the compound “j” or “i” in the liquid phase, mg/L | k_{rep} | kinetic constant of r_{rep} , $\text{mg}^{-1} \cdot \text{min}^{-1}$ |
| α_{ij} or $\alpha_{j,i}$ | stoichiometric coefficient of the compound “j” for the reaction “i”, mg | r_{acet} | reaction rate for the acetic acid dissociation, mg/min · L |
| k_{dj} | kinetic constant of the compound “j”, $\text{mg}^{-1} \cdot \text{min}^{-1}$ | k_{direct} | kinetic constant of acetic acid dissolution, $\text{mg}^{-1} \cdot \text{min}^{-1}$ |
| F_{auto} | auto catalytic factor for the solid kinetics, dimensionless | $k_{inverse}$ | kinetic constant of acetic acid recombination, $L \cdot \text{mg}^{-2} \cdot \text{min}^{-1}$ |
| β_{ij} or γ_{ij} | acceleration factor for the compound “j” in the reaction “i”, dimensionless | $C_{L_{acet}}$ | concentration of the acetate, mg/L |
| m_i, m_{i_0} | solid mass and its initial value of the compound “i”, mg | r_{prot} | proton consumption reaction rate, mg/min · L |
| r_{deaj} | deacetylation reaction rate for compound “j”, mg/min · L | k_{prot} | kinetic constant of r_{prot} , $\text{mg}^{-1} \cdot \text{min}^{-1}$ |
| r_{dead} | reaction rate of the direct deacetylation of HC ₁ , mg/min · L | $A(T)$ or A | Napierian logarithm of the kinetic preexponential factor, dimensionless |
| k_{dead} | kinetic constant of r_{dead} , $\text{mg}^{-1} \cdot \text{min}^{-1}$ | $H_0(T)$ | solubility constant, $^{\circ}\text{C}^{-1}$ |
| r_{deadi} | first reaction rate of the direct deacetylation of HC ₂ , mg/min · L | E_1, E_2 | base activation energy and correction factor of the base activation energy depending on the molecular weight, J/mol |
| k_{deadi} | kinetic constant of r_{deadi} , $\text{mg}^{-1} \cdot \text{min}^{-1}$ | PD_j | polymerization degree of compound “j”, dimensionless |
| r_{deadii} | second reaction rate of the direct deacetylation of HC ₂ , mg/min · L | PD_h | first correction factor of the PD_j for solubility calculations, dimensionless |
| k_{deadii} | kinetic constant of r_{deadii} , $\text{mg}^{-1} \cdot \text{min}^{-1}$ | h_p | second correction factor of the PD_j for solubility calculations, dimensionless |
| r_{cv} | C5 formation from HC ₁ reaction rate, mg/min · L | u | liquid velocity in the reactor, m/min |
| k_{cv} | kinetic constant of r_{cv} , $\text{mg}^{-1} \cdot \text{min}^{-1}$ | N | number of compounds, dimensionless |
| r_{lent} | C6 formation from HC ₁ reaction rate, mg/min · L | L | length of the reactor, m |
| k_{lent} | kinetic constant of r_{lent} , $\text{mg}^{-1} \cdot \text{min}^{-1}$ | z | dimensionless length of the reactor, dimensionless |
| C_{H^+} | proton concentration in liquid phase, mg/min · L | t | operating time, min |
| n_1, n_2 | reaction order for proton concentration in hydrolysis and sugar degradation, dimensionless | X_{exp}, X_{sim} | experimental and simulated value of the fitted variable |
| | | n | total number of experiments, dimensionless |

(Bobleter, 1994; Yedro et al., 2015), using only water as reactive. This technique has been highly studied and various articles can be found in literature (Charles et al., 2004; Mohan et al., 2015; Pronyk and Mazza, 2010; Rogalinski et al., 2008). However, the modelling of this process is an issue which still has not a final solution due to biomass complexity, which is formed by three main compounds: hemicellulose, cellulose and lignin. Cellulose and hemicellulose are polysaccharides composed by up to 10,000 and 200 monomers, respectively. The former is a linear biopolymer with a high degree of crystallinity formed by hexoses (C6) and the latter is amorphous and it is constituted by hexoses and pentoses (C5). On the other hand, lignin is an aromatic biopolymer formed by phenylpropane units (Bobleter, 1994; Harmsen et al., 2010). In addition, biomass diversity and the process monitoring also complicate the development and validation of a kinetic model. The first issue can be seen in Yedro et al., 2015 who studied the fractionation of several wood species in a semi-continuous reactor. They observed that the extraction yields were very different between the species, although the qualitative behavior of all of them were similar. Regarding monitoring, the problem would be that the analysis of the samples must be done at different conditions from which were used during the operation. The reason is

that the characterization requires wet chemical analysis followed by a separation of the different fractions by conventional analytical instruments at certain conditions (Carrier et al., 2011). Therefore, some measured values would be different from the real ones during the operation.

To sum up, it is not clear that a model with a single set of kinetic parameters could be used as a global solution for biomass solubilization. Nevertheless, several models for this process, with a reasonable success, can be found in literature (Haghighat Khajavi et al., 2005; Lin et al., 2015; Mohan et al., 2015; Rogalinski et al., 2008; Zhu et al., 2014). Zhu et al. (2014) studied the hydrolysis of peanut shell in subcritical water in a batch reactor. They proposed a kinetic model with a 1st reaction order respect to biomass concentration which was able to reproduce their experimental data. In the same way, Mohan et al. (2015) and Lin et al. (2015) assessed the hydrolysis of real biomass (bamboo and rice straw respectively) in a batch reactor and they also fitted their data applying a 1st order kinetic. Rogalinski et al. (2008) performed a successful kinetic analysis of the starch hydrolysis in a plug-flow reactor assuming a 1st reaction order. And Haghighat Khajavi et al. (2005) studied the hydrolysis of sucrose in a flow-type reactor but taking into account the effect

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