Chemical Engineering Science 138 (2015) 59–70

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Two-phase modelling and simulation of the hydrothermal fractionation of holm oak in a packed bed reactor with hot pressurized water

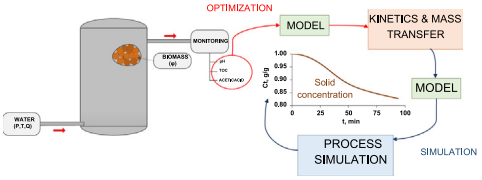
A. Cabeza, F. Sobrón, F.M. Yedro, J. García-Serna*

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

HIGHLIGHT

- The holm oak hydrothermal fractionation in a semibatch system was studied.
- An autocatalytic kinetic model could reproduce the cellulosic fraction cleavage.
- TOC and pH were fitted with an average deviation of 32.1% and 7.3% respectively.
- Acetic acid concentration was also adjusted with a greater deviation (56.0%).
- Mass transfer between solid and liquid was simulated with an error lower than 8.5%.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 3 March 2015
Received in revised form
14 July 2015
Accepted 16 July 2015
Available online 26 July 2015

Keywords:
Autocatalytic kinetic
Two-phase simulation
Holm oak
Hydrothermal fractionation
Packed bed reactor

ABSTRACT

Hydrothermal fractionation has been thoroughly studied in order to develop a sustainable process to recover the sugars and/or the biopolymers contained in biomass. However, a physico-chemical model which considers the main involved physical phenomena, like porosity variations, has not been fully developed yet. Thus, the objective of this work was to approach a more realistic model than other yet published, incorporating also a novel reaction pathway for biomass fractionation. It establishes that cellulose and hemicellulose begin their fractionation in the solid, breaking in water-soluble oligomers and sugar. Besides, deacetylation reactions and insoluble oligomer formation from cellulose were considered. Kinetics followed the Arrhenius' law and and it has been demonstrated that an autocatalytic kinetic model can be successfully used to simulate the biomass breaking in soluble oligomers. The process was carried out in a tubular reactor charged with 5 g of holm oak and continuously fed with hot pressurized water. To assess the mass transfer between the solid and liquid, 4 volumetric flows (5 mL/min, 10 mL/min, 20 mL/min and 40 mL/min) and two particle diameters (3 mm and 6 mm) were used. In the same way, temperature was set between 175 °C and 207 °C. The latter was the main variable due to its effect in biomass solubility and kinetics. The model was solved by the Runge-Kutta's method with 8th order of convergence and its discretization was performed by a new modification of the orthogonal collocation method on finite elements. It was validated by fitting total organic carbon (TOC) with Absolute Average Deviation (A.A.D. between 16.3% and 55.8%), acetic acid concentration (A.A.D. between 44.4% and 84.4%) and pH profiles (A.A.D. between 5.6% and 9.7%). Besides, the mass transfer between the solid and the liquid was checked and the deviations of the simulation were lower than 8.5%.

* Corresponding author. Tel.: +34 983184934.
E-mail address: jgserna@iq.uva.es (J. García-Serna).

http://dx.doi.org/10.1016/j.ces.2015.07.024
0009-2509/

Nomenclature

Acronyms

Co1	cellulose.
Co2	hemicellulose.
Co3	cellulose oligomer 1 (first oligomer soluble from cellulose).
Co4	hemicellulose oligomer 1 (first oligomer soluble from hemicellulose)
Co5	cellulose oligomer 2 (last oligomer from cellulose before sugar production)
Co6	hemicellulose oligomer 2 (last oligomer from hemicellulose before sugar production)
Co7	Sugars C6
Co8	Sugars C5
Co10	acetic acid
Co12	hemicellulose oligomer 3 (deacetylated oligomer from hemicellulose).
Co13	base (inorganic compound)
Co15	cellulose oligomer 3 (deacetylated oligomer from cellulose)
Co17	insoluble cellulose oligomer
TOC	total organic content.
A.A.D.	average absolute deviation.

Subindex and superindex

pH-SIM	simulated pH.
pH	experimental pH.
TOC-SIM	simulated TOC.
TOC	experimental TOC.
[Acetic acid]–SIM	simulated acetic acid concentration.
[Acetic acid]	experimental acetic acid concentration.

Greek letters and symbols

ε	porosity of the bed, dimensioless.
C_{Sj}	cocnetration of the compound "j" in the solid phase, mg/L.
r_j	reaction rate of the compound "j", mg/min L
$k_j \cdot a$	mass transfer coefficient multiplied by the specific exchange area, min^{-1}.
C^*_{Lj}	equilibrium concentration of the compound "j" in liquid phase, mg/L
$\overline{C}_{Lj}$	average concentration of the compound "j" along the reactor in liquid phase, mg/L
H_j	equilibrium constant between the solid and the liquid, dimensionless
C_t	total concentration in the solid, mg/L.
φ	relation factor between porosity and the total concentration in solid phase, dimensionless
C_{Lj}	concentration of the compound "j" in the liquid phase, mg/L
$\Phi_{i,j}$	stoichiometric coefficient of the compound "j" for the reaction "i", mg
r_i	reaction velocity "i", mg/min L
$\alpha_{i,j}$	initial velocity factor for the compound "j" in the reaction "i" dimensionless
$\alpha_{i,Cel}$	initial velocity factor for cellulose in the reaction "i", dimensionless
$\alpha_{i,Hcel}$	initial velocity factor for hemicellulose in the reaction "i", dimensionless
$\beta_{i,j}$	acceleration factor for the compound "j" in the reaction "i", dimensionless
$\beta_{i,Cel}$	acceleration factor for cellulose in the reaction "i", dimensionless
$\beta_{i,Hcel}$	acceleration factor for hemicellulose in the reaction "i", dimensionless
k_i	kinetic constant, $mg^{-1}\ min^{-1}$
C_{fj}	concentration of the compound "j" in the phase "f", mg/L
C_{Cel}	concentration of cellulose in the solid phase, mg/L
C_{Hcel}	concentration of hemicellulose in the solid phase, mg/L
C_{SLO}	concentration of the last oligomer before sugar production (from hemicellulose or cellulose) in the solid phase, mg/L
u	liquid velocity in the reactor, m/min
N	number of compounds, dimensionless
n_{rec}	number of reactions, dimensionless
L	length of the reactor, m
z	coordinate along the length of the reactor, dimensionless
t	operating time, min
$x_{i_{EXP}}$	experimental value of the fitted variable
$x_{i_{SIM}}$	simulated value of the fitted variable
o	total number of experiments, dimensionless
k	pre-exponential factor of the kinetic constant, $mg^{-1}\ min^{-1}$
Ea/R	activation energy, K
R^2	coefficient R^2, dimensionless
T	operating temperature, °C
m_{real}	final solid mass, g
m_{sim}	simulated final solid mass, g

1. Introduction

For several decades petrol has been used as the main source of energy and raw materials. Nevertheless, it is not a sustainable source and other option will be needed in a near future. One likely option would be biomass, and several international institutions, such as the European Union or the Organisation for Economic Co-operation and Development, have shown interest about it (King, 2009; OECD, 2009; Organisation, T.E.P.S, 2011). The general idea is to develop a hydrolysis process to obtain the sugars present in biomass, which will be converted into liquid fuels in a following process. In addition, the extraction of the biomass phenolic compounds would be interesting due to the fact that they would be used as raw material to chemical industry. Thus, biomass hydrolysis have been studied thoroughly and in different ways, such as, enzymatic hydrolysis, acid or alkaline hydrolysis (Alvarez-Vasco and Zhang, 2013; Charles et al., 2004; Feng et al., 2012; Gao et al., 2013; Yoon et al., 2014). One of the most promising options would be the biomass fractionation by hydrothermal processes at subcritical conditions because it can extract the main fraction of these sugars only using water as reactive (Cantero et al., 2013; Garrote et al., 2002; Sefik Tunc, 2008; Moniz et al., 2013; Parajó et al., 2004; Rissanen et al., 2014; Zakaria et al., 2015). Subcritical conditions refer to all temperature and pressure below the critical point and, supercritical conditions, when they are beyond it (Fig. 1). Focusing in water, subcritical water means a liquid at high pressure and