J. of Supercritical Fluids 99 (2015) 95–102

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

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

Kinetic modeling of hemicellulose-derived biomass hydrolysis under high pressure CO_2–H_2O mixture technology

Frederico M. Relvas, Ana R.C. Morais, Rafal Bogel-Lukasik*

Laboratório Nacional de Energia e Geologia, I.P., Unidade de Bioenergy, Estrada do Paço do Lumiar 22, 1649-038 Lisboa, Portugal

ARTICLE INFO

Article history:
Received 8 October 2014
Received in revised form 25 January 2015
Accepted 26 January 2015
Available online 1 February 2015

Keywords:
Lignocellulosic biomass
Xylan
Hemicellulose
Kinetics
Oligosaccharides
Carbon dioxide

ABSTRACT

This work is focused on the development of kinetic models of hydrolysis of hemicellulose-derived wheat straw under high-pressure CO_2–H_2O technology. The experiments were performed at fixed temperature (180 °C), varying pressure from 0 (water-only reaction), 20, 35 to 50 bar of initial CO_2 pressure and reaction times varied from 0 to 45 min. The three accurate kinetic models allowed to describe the effect of reaction conditions mainly hitherto not studied CO_2 pressure and reaction time on the concentration of intermediate compounds such as xylose and arabinose in both oligomer and monomer form as well as final compounds e.g. acetic acid, furfural and other degradation products. Modeling demonstrated that addition of CO_2 plays an important role in kinetics study of hemicellulose fraction hydrolysis being the fastest step the polysaccharides' hydrolysis into sugars in oligomer form. Even negligible amount of CO_2 (20 bar of initial pressure) improves the initial kinetic constant of aforementioned reaction by almost 40% in comparison to water-only process. Depletion of oligosaccharides' concentration and counterbalanced production of monomer sugars were found for longer reaction times, achieving maximum faster for CO_2-assisted than CO_2-free processes. Moreover, the increase of initial CO_2 pressure demonstrated to be highly efficient in enhancement of the kinetic constants of all reactions occurring in the liquors. The developed models demonstrated a good fitting to the experimental data albeit the complex composition of raw material as well as the multistep analytical process.

1. Introduction

The annual production of lignocellulosic-derived biomass is estimated at the level of 10–50 billion metric tons per year on a dry matter basis [1–3]. Lignocellulosic residues have a vast potential as a source of a wide range of renewable, sustainable materials, chemicals and biofuels since they do not compete with food industry and animal feed [4–8]. The lignocellulosic biomass is comprised primarily by cellulose, hemicellulose and lignin [9]. Cellulose forms a skeleton surrounded by other components such as hemicellulose and lignin, which act as matrix and encrusting material, respectively. The presence of covalent cross-linkages between carbohydrates and lignin forms a lignin-carbohydrate complex, which provides a remarkable stability making it very challenging for direct conversion. Thus, the application of biomass pre-processing (pre-treatment) is essential to convert this feedstock into added-value products. In order to make biomass processing feasible, all components of biomass must be considered as a source of candidates for the production of co-products as described by the biorefinery concept [10,11]. The major aim of biomass pre-treatment is to process biomass to make it more subjectable for further processing [12,13]. The pre-treatment makes biomass fractions more subjectable biological and/or chemical treatments aiming further valorization toward particular products or pivot chemicals [14].

However, to achieve this goal various challenges must be addressed. Furthermore, depending on the expected results the most adequate pre-treatment method can be selected. In addition, the choice of pre-treatment should consider the overall compatibility of feedstocks, enzymes and organisms to be applied and overall economic assessment and environmental impact. Up to now several approaches have been used for developing low cost pre-treatments to generate sugar-rich liquors from cellulose and hemicellulose [15]. High-pressure CO_2–H_2O technology is a novel approach that is been demonstrated to be well suited in the hydrolysis of hemicellulose-derived biomass to produce predominantly xylooligossacharides and afterwards xylose and furfural. The benefits of this technology are highlighted by introducing of a known sustainable catalyst, such as CO_2, to water-only technology. Both CO_2 and water are considered green reagents that can be used in the valorization of lignocellulosic residues making

* Corresponding author. Tel.: +351 210924600x4224; fax: +351 217163636.
E-mail address: rafal.lukasik@lneg.pt (R. Bogel-Lukasik).

http://dx.doi.org/10.1016/j.supflu.2015.01.022
0896-8446/