RSC Advances

PAPER

Cite this: *RSC Adv.*, 2015, **5**, 73935

Selective hydrolysis of wheat straw hemicellulose using high-pressure CO_2 as catalyst

Frederico M. Relvas,†[a] Ana Rita C. Morais†[ab] and Rafal Bogel-Lukasik*[a]

Received 23rd July 2015
Accepted 24th August 2015

DOI: 10.1039/c5ra14632a

www.rsc.org/advances

The processing of wheat straw using high-pressure CO_2–H_2O technology was studied with the objective to evaluate the effect of CO_2 as catalyst on the hydrothermal production of hemicellulose-derived sugars either as oligomers or as monomers. Also, the reduction of the crystallinity of the cellulose-rich fraction was assessed. Over a range of reaction conditions (0 to 50 bar of initial CO_2 pressure and 0 to 45 minutes of holding time, at $T = 180$ °C), the addition of CO_2 to water-based processes led to the *in situ* formation of carbonic acid, which allowed us to obtain a higher dissolution of wheat straw hemicellulose. Furthermore, this approach led to a xylo-oligosaccharide (XOS) rich fraction, yielding 79.6 g of XOS per 100 g of the initial xylan content (at 50 bar of initial CO_2 pressure and 12 min of residence time) while the water-only process gave only 70.8 g of XOS per 100 g of initial xylan content. Furthermore, for higher pressures of CO_2, a decrease in oligosaccharide content was found and was counterbalanced by production of monomer sugars, achieving a maximum of 5.7 g L^{-1} at the severest condition.

1. Introduction

Worldwide energy demands coupled with a reduction of readily and economically available fossil feedstock and their environmental impacts have resulted in an extensive need for novel and sustainable sources of energy. Lignocellulosic biomass is the unique economic and environmentally acceptable alternative since it is abundant, renewable and low-cost, and does not compete with food and feed applications.[1,2] Nowadays, lignocellulosic biomass is one of the most important energy sources, having an estimated annual production of 10–50 billion metric tons worldwide.[3] One great example of the importance of lignocellulosic biomass is wheat straw, which is produced throughout the world as a residue of wheat cultivation. Wheat straw has drawn special attention due to its many interesting features that facilitate its valorization.[4] For instances, it is produced in high amounts and it does not present an excessive commercial value.[5] Presently, it is employed in low added-value applications such as animal-feed and bedding,[6] mulch[7] and pulp production.[8] Furthermore, it is considered the agro-industrial residue that represents the uppermost potential for the production of second generation of bioethanol in Europe since its annual production is around 170 million tons per year.[9,10]

Lignocellulosic biomass has a very heterogeneous composition as it is generally composed of three main fractions: cellulose, hemicelluloses and lignin.[11] Cellulose and hemicelluloses are constituted by polymers of hexosans and pentosans representing 35–50% and 20–40% of biomass, respectively. Lignin is a complex polymer matrix of aromatic alcohols constituting between 10 and 25% of the weight of entire biomass. The aforementioned complex composition and recalcitrant structure of lignocellulosic biomass creates a great challenge for its valorization in the biorefinery framework. In an effort to obtain all benefits of each biomass component, specific technologies are needed to deconstruct them and to make biomass available for further conversion to value-added products.[12] Various physical, chemical, physico-chemical and biological pretreatment technologies have demonstrated to be efficient in deconstruction of recalcitrant structure of biomass increasing its susceptibility to enzymatic-based processes.[13] On the other hand, most of these pretreatments are characterized by low selectivity influencing negatively the production of diverse value commodities at competitive costs. Thus, beyond the need to find alternative sources of energy, the development of novel and more environmentally benign technologies for lignocellulosic biomass processing is still strongly required.

Recently, green technologies such as high-pressure CO_2–H_2O approach have been used in the valorization of lignocellulosic and starch-based biomass to produce a wide-range of chemicals and others value-added products.[14–20] Recently, Morais *et al.* published a review where the applicability and effectiveness of high-pressure CO_2 and CO_2–H_2O technology for biomass pretreatment and its potential as alternative to conventional methods such as acid-catalyzed and water-only reactions were

[a]*Unidade de Bioenergia, Laboratório Nacional de Energia e Geologia, I.P., Estrada do Paço do Lumiar 22, 1649-038, Lisboa, Portugal. E-mail: rafal.lukasik@lneg.pt; Fax: +351 217163636; Tel: +351 210924600 ext. 4224*

[b]*LAQV/REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal*

† The authors wish it to be known that the first two authors should be regarded as joint first authors.