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Integrated conversion of agroindustrial residue with high pressure CO_2 within the biorefinery concept

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Sustainable production of energy and other added-value products from biomass-derived polysaccharides is a key challenge of an efficient biorefinery facility. Most technologies for biomass processing are energy demanding and use significant amounts of chemicals and catalysts. The need to develop a process which is devoid of all these shortcomings associated with conventional processes is emphasized. A new approach is demonstrated for an integrated wheat straw biorefinery using a green technology, high-pressure CO_2–H_2O, to produce oligosaccharides from hemicellulose fraction and to enhance the cellulose digestibility for the enzymatic hydrolysis. Over the range of reaction conditions (130, 215, 225 °C and 0 to 54 bar of CO_2), CO_2 adds value to the process by *in situ* formation of carbonic acid that leads to higher dissolution of hemicellulose into xylo-oligosaccharides and xylose and to the use of less energy in comparison with water-only technologies. Without an additional chemical catalyst, high-pressure CO_2–H_2O outperformed hydrothermal reactions and gave much higher total sugars yield for wheat straw (as high as 84% in comparison with 67.4% with auto-hydrolysis at a 10 °C higher temperature). Apart from the results obtained for valorisation of hemicellulose fraction, both chemical and physical effects of CO_2 coupled to enzymatic hydrolysis resulted in a glucan conversion to glucose yield of 82%, which consists of 26% improvement over those obtained during auto-hydrolysis. The influence of the high pressure reaction on the processed solid was examined by spectroscopic methods (namely Scanning Electron Microscopy and Fourier Transform Infrared Spectroscopy). The obtained results suggest that the high pressure CO_2-based method is a very promising alternative technology allowing integrated biomass processing within the biorefinery concept.

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Introduction

Global concern about the demand for fossil resources coupled with the quick reduction of readily and economically reachable fossil feedstock, as well as security of their supply and environmental impacts, has stimulated a global trend of mankind to seek alternative technologies and sustainable sources of energy, materials and chemicals.[1–3] One of the ways to provide a sustainable supply chain is the use of renewable lignocellulosic biomass as a source of energy, materials and chemicals. Biofuels and valuable products can be obtained by depolymerisation of biomass polysaccharides such as cellulose and hemicellulose. The selective depolymerisation typically involves a pre-treatment process, which is one of the most important steps in the development of biorefineries, since it has a significant influence on the efficiency and economy of the overall process.[4,5] Several biomass pre-treatment technologies such as dilute acid,[6] alkaline hydrolysis,[7] hydrothermal processes,[8–10] and high temperature solutions of various solvents including ammonia,[11] CO_2 [12–15] and ionic liquids[16–19] have been successfully developed in the last few years. However, the major drawbacks of these technologies are low selectivity and sugar yield or a still bench scale of processes. To avoid these limitations some additional steps must be taken, which on the other hand may lead to the production of undesirable products decreasing the efficiency of the process or may require high investments and elevated operational costs.[17,20]

The green reagents, such as CO_2 and water, used in the valorisation of lignocellulosic residues towards valuable products make the pre-treatment processes more environmentally acceptable. Recently, the CO_2–H_2O approach at high temperature (180–210 °C) and pressure of CO_2 (60 bar) was demonstrated to be an interesting alternative[13] to conventional technologies principally in comparison with dilute acid hydro-

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