

The CO₂-assisted autohydrolysis of wheat straw

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The CO₂-assisted autohydrolysis was used for wheat straw treatments at temperatures ranging from 180 to 210 °C and an initial CO₂ pressure of 60 bar. The study was performed using three different mixture loadings, such as 250 g of H₂O/25 g of wheat straw, 150 g of H₂O/15 g of wheat straw and 75 g of H₂O/7.5 g of wheat straw. The *in situ* formed carbonic acid was found to result in a higher dissolution of xylose as well as XOS (xylo-oligosaccharides) in comparison to CO₂-free pre-treatments under the same conditions (temperature and LSR). The effect of CO₂ concentration was also investigated to address the issue of CO₂ involved in the reaction that allows to significantly increase the XOS content. At 210 °C with a mixture loading of 75 g of H₂O/7.5 g of wheat straw, XOS were present in the liquor at a concentration of 15.75 g L⁻¹. However, with more severe conditions more degradation products (mainly furfural) were detected (in the liquor and the recovered gas phase from depressurization after the reaction). Glucan was mainly retained in the solid phase (containing up to 64%) together with Klason lignin (maximum dissolution of 18%). The dissolved XOS in the liquid phase are proposed to be used in other applications, either directly, such as prebiotic ingredients, or indirectly, after post-hydrolysis to biofuel production through C5 sugars' fermentation.

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1. Introduction

Lignocellulosic feedstock is mainly composed of cellulose (35–50%), hemicellulose (20–35%) and lignin (5–30%),¹ wherein the composition is dependent upon several parameters. Due to the complex macroscopic structure of lignocellulosic materials, several pre-treatment technologies are currently employed to overcome this resistance against chemical and microbial attacks. The pre-treatment methods can be categorised according to various criteria.^{2,3} Pre-treatments can be segregated between conventional (dilute acid hydrolysis, alkali⁴), hydrothermal (steam-explosion,⁵ wet oxidation,⁶ microwaves,⁷ and autohydrolysis⁸) and alternative methods (ionic liquids,^{9,10} sub- and supercritical fluids, mostly water and CO₂^{11–13}).

The autohydrolysis process uses compressed hot water (pressure above saturation point) with a general range of temperature between 150 and 230 °C and various reaction times from seconds to hours according to the operation mode applied.⁴ Hydronium ions generated *in situ* by water autoionization and acetic acid from dissolution of acetyl substituents of hemicelluloses have the capability to act as catalysts formed *in situ* in the autohydrolysis processes. A high recovery of

hemicellulose in the liquid-fraction (mainly in oligomeric form) and of cellulose and lignin in the solid fraction with negligible losses are generally reported. The hemicellulose-rich liquor can be a source of value-added products. Xylooligosaccharides (XOS) are one of these products and can be obtained directly from autohydrolysis pre-treatment.⁸ Xylitol, important due to its application in the food, pharmaceutical and cosmetic industries, can be produced after the bioconversion of hemicellulose liquor as well.¹⁴ Moreover, production of reducing sugars, organic acids (such as acetic acid or propionic acid), bio-composites, furfural and other miscellaneous compounds can be developed too.¹⁵ On the other hand, the solid fraction obtained is mainly converted to sugar monomers and further to bioethanol along with a possibility to produce value-added commodities.

SeCO₂ is a non-toxic, non-flammable and inexpensive reagent,¹⁶ and its employment generally lowers the temperature of the process leading to minor generation of degradation products and a higher yield of the reaction.^{4,17} Technologies involving the use of sub- (near its critical conditions) and supercritical treatments have been investigated for lignocellulosic material pre-treatments. In these processes sub- or supercritical water and/or supercritical CO₂ were commonly used. Considering economic efficiency supercritical water or liquid hot water (LHW) treatments seem to be superior due to the water facilitated feasibility of hydrolysis that provides an acidic environment at high temperatures.¹⁸ Particularly in the subcritical range of temperature and pressure ($P < 210$ bar,

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