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First insights into catalytic hydrolysis of hemicellulose in a continuous reactor

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PURPOSE OF THE ABSTRACT

Hemicellulose is one of the three main components of lignocellulose, representing 25-40 wt.%. It is a water-soluble polysaccharide containing pentoses (xylose, arabinose) and hexoses (glucose, mannose, galactose). However, the valorization of hemicelluloses into value-added bioproducts was often neglected in biorefineries design. Therefore, intensified catalytic processes for hemicellulose hydrolysis and valorization are needed. Process intensification is an essential key point to make next generation biorefineries viable: matter fluxes must be interconnected from the resource to the products and high concentration of substrates are required.

Hemicellulose hydrolysis is currently performed using mineral acids (H₂SO₄, HCl)[1] or organic acids. Some rare examples of catalysts for hemicellulose hydrolysis exist: zeolites, sulfonated carbons, etc. [2]. We recently demonstrated that TiO₂-WO_x catalyst could advantageously replace mineral acids for the hydrolysis of xylan [3]. Moreover, in the literature, hemicellulose hydrolysis was almost exclusively performed in batch reactors, where side-reactions leading to the degradation of sugars occurred. To avoid this drawback, most of the authors work with highly diluted feed.

We designed a continuous fixed bed reactor for the catalytic hydrolysis of concentrated streams of hemicelluloses. Using such a reactor gives an interesting insight of several phenomena occurring during the hydrolysis reaction: i) mass transfer limitations can be easily studied by varying the catalyst grain size and loading, evidencing the probability of a reaction between a solubilized polymer and a mesoporous catalyst; ii) catalytic and non catalytic reactions can be decoupled for a better understanding of hydrolysis and degradation reactions; iii) catalyst deactivation can be followed as a function of time on stream.

The first results showed that non-catalytic degradation of xylan can be avoided using suitable temperature and residence time (Figure 1). Indeed, in the absence of catalyst, the conversion of xylan was negligible until 160°C. The hydrolysis of each component of xylan, i.e. xylose, arabinose and glucose, can be followed using HPLC analysis. Degradation products such as furfural, hydroxymethylfurfural were also detected. Humins were analyzed by carbon quantification in aqueous solution using an innovative method developed at ISA laboratory. Temperature and residence time both have a strong impact on conversion and yields of each sugar (Figure 2). As expected, increasing the contact time led to increase monomers yield (e.g. xylose), whereas the temperature had a detrimental effect on sugars selectivity after 160°C, because of degradation reactions.

A detailed study of reactants and products will lead to a more comprehensive approach of the hemicellulose hydrolysis reaction. In a near future, an integrated catalytic process combining hemicellulose hydrolysis, sugars transformation, e.g. by hydrogenation or dehydration, and separation of the products will be designed.

FIGURES

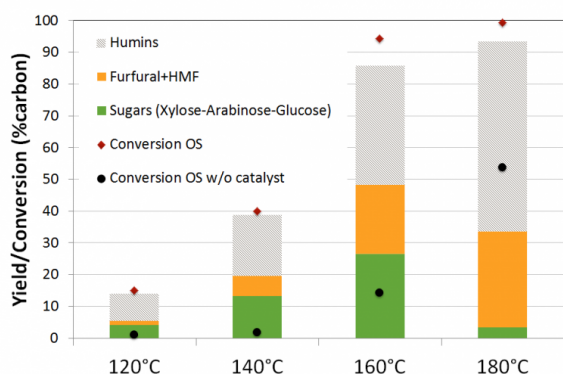


FIGURE 1

Conversion and yield obtained for the hydrolysis of corncob xylan.

Catalyst TiO₂-WO_x, temperature 120-180°C, pressure 25 bar, contact time 4 min.

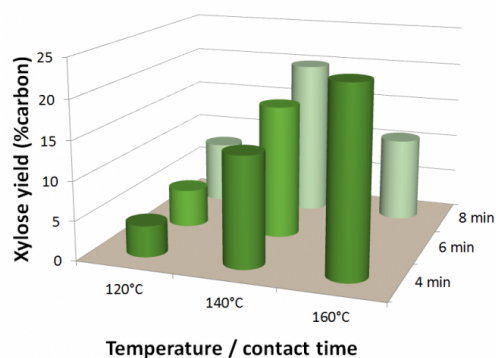


FIGURE 2

Xylose yield during corncob xylan hydrolysis as a function of temperature and contact time.

Catalyst TiO₂-WO_x, temperature 120-160°C, pressure 25 bar, contact time 4-8 min.

KEYWORDS

Hemicellulose | Continuous reactor | Hydrolysis | Solid acid catalysis

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