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Continuous valorization of hemicelluloses into polyols in an innovative compartmented fixed-bed reactor

AUTHORS
Victoria DIAS DA SILVA FREITAS / CP2M, 43 BOULEVARD DU 11 NOVEMBRE 1918, VILLEURBANNE
Maxime PICHOU / CP2M, 43 BOULEVARD DU 1& NOVEMBRE 1918, VILLEURBANNE
Léa VILCOCQ / CP2M, 43 BOULEVARD DU 1& NOVEMBRE 1918, VILLEURBANNE
Régis PHILIPPE / CP2M, 43 BOULEVARD DU 1& NOVEMBRE 1918, VILLEURBANNE
Pascal FONGARLAND / CP2M, 43 BOULEVARD DU 1& NOVEMBRE 1918, VILLEURBANNE

PURPOSE OF THE ABSTRACT

Lignocellulosic biomass is the major renewable carbon source at human time scale, an interesting candidate to fossil resources substitution1. Even if it can represent almost 40% of lignocellulose structure, hemicelluloses remain under-exploited nowadays. One pathway to valorize hemicelluloses is the synthesis of polyols, value-added products mainly applied on food and pharmaceutical industries2. These carbohydrates can be obtained by hemicelluloses hydrolysis, followed by the ex-hemicellulosic sugar hydrogenation. Hemicellulose hydrolysis is susceptible to the formation of by-products (acetic acid, furfural, 5-HMF, for example) because of the fast degradation of xylose in acid media. It is therefore important to execute a rapid separation after the hydrolysis to avoid side reactions and to increase polyols yield at the end of hydrogenation step. For this reason, this project aim the coupling of the three steps in one compartmented reactor. The design of this compartmented reactor dedicated to hemicelluloses valorization could open access to the process industrialization through an only unitary operation, reducing production costs, space and enable value-added production from polymers under-exploited industrially.

In this work, the three steps were initially studied separately. TiO2-WOx were used to catalyze xylan hydrolysis into xylose in a fixed-bed reactor. The separation step was studied in continuous mode by tangential flow. Three ceramic membranes with different pores diameters were tested to separate xylan and xylose. Ruthenium supported by TiO2 prepared by incipient wetness impregnation was used to catalyze xylose hydrogenation to produce xylitol. This reaction was also studied in continuous mode at a fixed-bed reactor. The reaction was studied in continuous mode in a fixed bed reactor, and a kinetic model is being developed.

The three steps of polyols production were studied separately. First, the temperature effect was tested for the hemicellulose hydrolysis. Figure 1 shows the hydrolysis products yield and xylan conversion in function of the contact time for 140ºC and 180ºC. It is noticeable that the increase of the temperature favors the xylan conversion (a maximum of 100% at 180 ºC against 40% at 140 ºC). Besides that, the higher is the contact time between the reagents and the catalyst, the lower is the xylose selectivity. Three main by-products were identified: furfural, HMF and acetic acid. Furfural selectivity is the most favored by temperature increasing for both temperatures, represented by the increasing of the orange parts of Figure 1.

Then, ceramic membrane separation presented almost 30% of xylan mass retention, while xylose mass retention is up to 10%. It is probably due to the different polymerization degree of the studied xylan, smaller molecules might be able to pass through membrane pores.

Finally, in order to come closer to hemicelluloses hydrolysate, different sugars hydrogenation were tested. The C5 sugar (xylose) presented faster conversion when compared with C6 sugars (galactose, glucose and mannose). This effect suggests that the hydrogenation rate depends on sugars structure. As far as we know, it is the first time this behavior is described in literature.

The synthesis of sugar alcohols in continuous mode is an important pathway to valorise hemicelluloses. It is possible to produce sugars from hemicelluloses with high yield at mild temperatures. This yield could be improved with the fast separation of sugars from hydrolysis medium, which can be done by membrane separation. Thus, different sugar structures interfere on hydrogenation rate, highlighting the importance of study the interactions between ex-hemicellulosic sugars during the hydrogenation step. Individual kinetic models are being developed to provide enough information to establish the innovative reactor model, which will also be tested experimentally.

FIGURES

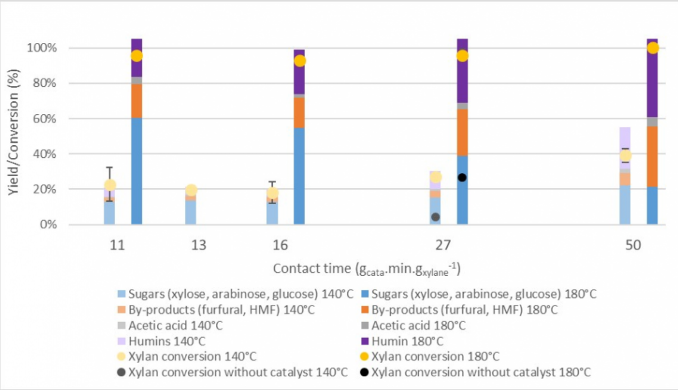

FIGURE 1

Figure 1

Temperature effect on hydrolysis products yield and xylan conversion.

FIGURE 2

KEYWORDS

Hemicellulose valorization | Reactor engineering | Flow chemistry | Heterogeneous catalysis

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