Valorization of olive stones to obtain furfural in the presence of γ-Al_2O_3 and $CaCl_2$

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Furfural is considered as one of the 12 platform molecules derived from biomass for the synthesis of high value-added chemicals [1]. It is mainly produced by acid-catalyzed dehydration of pentoses, such as xylose, which can be obtained from hemicellulose, one of the main components of lignocellulosic biomass. The aim of this work was to obtain furfural from lignocellulosic wastes from the agro-food industry, such as olive stones. For this purpose, the catalytic behavior of a mesoporous γ-Al_2O_3 as acid solid catalyst and the effect of the addition of $CaCl_2$ in order to improve the furfural yield were evaluated [2].

Firstly, the production of sugar-rich liquors from olive stones was optimized in a thermostated 2 L reactor under continuous stirring, by using water as solvent with a solid:liquid mass ratio of 1:10, at 160-200 °C for 30-75 minutes. The concentration of xylose was quantified by high performance liquid chromatography (HPLC) and the characterization of the liquid and solid fractions was carried out by different standarized techniques. The liquors H7 and H10 obtained at 180 °C and 60 minutes and 190 °C and 45 minutes, respectively, showed the highest xylose contents and they were chosen for furfural production. The catalytic dehydration of pentoses-containing liquors, mainly D-xylose, was studied in batch type glass reactors (Ace, 15 mL) in a thermostated aluminum block under magnetic stirring, at 150 °C for 50 minutes. In a typical test, 1.5 mL of liquor, 3.5 mL of toluene, 50 mg of γ-Al_2O_3 and 0.65 g $CaCl_2 \cdot g_{sol}^{-1}$ were added to the reaction medium. The reaction products were analyzed by HPLC. The presence of the catalyst, γ-Al_2O_3, hardly improves the performance of furfural with respect to the non-catalytic process (Figure 1). However, an increase in furfural yield is observed in the presence of $CaCl_2$, being maximum when γ-Al_2O_3 and $CaCl_2$ are used together (100% and 74% for H7 and H10, respectively). The lower yield attained from H10 could be due to the use of a higher temperature to obtain this liquor, since the formation of degradation products, such as formic acid, acetic acid and HMF, could promote secondary reactions of furfural, consequently decreasing the furfural yield.

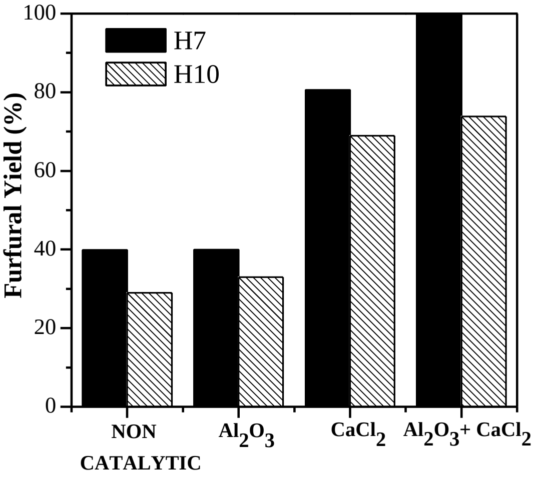

Figure 1. Furfural yield from liquors H7 and H10 in the presence of γ-Al_2O_3 and/or $CaCl_2$

References

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