

## Direct hydrolysis of lignocellulosics on solid acid catalysts: an explorative screening

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### Introduction

Lignocellulosics are becoming of great importance as a source of key intermediates for production of biofuels (monosaccharides) and bioplatfrom molecules (HMF, furfural, levulinic acid). We report here about a screening of performances of different non-conventional solid acid catalysts in direct hydrolysis to obtain monosaccharides in aqueous phase. Catalysts were synthesized according to literature and compared with autohydrolysis and a commercial catalyst (Amberlyst15).

### Experimental

The biomass, dried at 80°C overnight, was loaded in a stainless-steel autoclave with water and the solid acid and kept at 150°C for 5h, under vigorous stirring. The reaction mixture was filtered and the residue was dried at 80°C overnight. Total dissolved biomass ( $X_{\text{lignocell}}$ ) was estimated by weighting the dry residue; monosaccharides yield was evaluated by means of HPAEC-PAD.

The total dissolved biomass ( $X_{\text{lignocell}}$ ) and the total yield in monosaccharides ( $Y_{\text{tot}}$ ) were expressed by means of the following equations:

$$X_{\text{lignocell}} = \frac{m_{\text{lignocell}} - m_{\text{residue}}}{m_{\text{lignocell}}} \quad Y_{\text{monosaccharides}} = \frac{m_{\text{monosaccharides}}}{m_{\text{lignocell}}}$$

Where  $m_{\text{lignocell}}$  is the amount of initial biomass,  $m_{\text{residue}}$  the mass of residue after reaction and  $m_{\text{monosaccharides}}$  the total sum of the masses of monosaccharides quantified by HPAEC-PAD. The catalysts, Tin-Tungsten mixed oxide [1] (SnW2800),  $\text{Zr}_7\text{Nb}_2\text{O}_{19}$  [2], and Iron-Zinc double metal cyanide (Fe-Zn-DMC) [3] were synthesized according to references.

Tin-Tungsten mixed oxide was synthesized by a co-precipitation method [1] starting from an aqueous solution of  $\text{NaWO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{SnCl}_5 \cdot 5\text{H}_2\text{O}$  to obtain the desired Sn/W ratio. After 1h under stirring at room temperature, a second amount was added and the colorless solution gradually became a white slurry, that was stirred for 24h. The precipitate Sn-W hydroxide was filtered, washed with water, dried at 100°C in vacuo and calcined at 800°C.

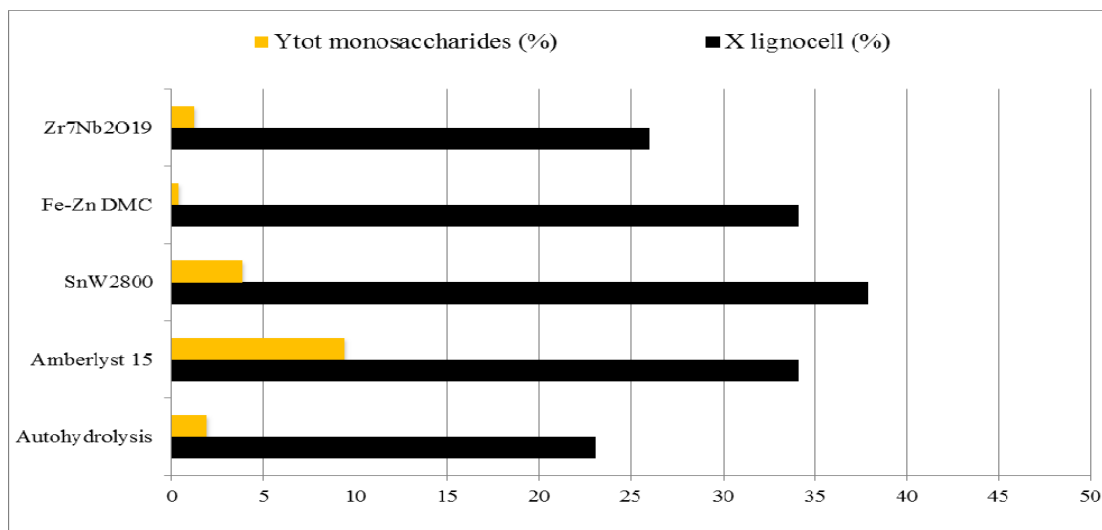
$\text{Zr}_7\text{Nb}_2\text{O}_{19}$  was synthesized by a sol-gel method [2].  $\text{ZrCl}_4$  and  $\text{NbCl}_5$  was added to an ethanolic solution of Pluronic-123 and stirred for 1h. A gel was obtained by solvent evaporation, while keeping the solution at 60°C for one week. The gel was calcined first at 350°C for 20h to remove the surfactant and then at 740°C for 10h to crystallize the phase.

Iron-Zinc double metal cyanide (Fe-Zn DMC) was synthesized as follows [3]: 0.01  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$  was dissolved in distilled water to prepare Solution 1. Solution 2 was prepared by dissolving 0.1  $\text{ZnCl}_2$  in 18 mL of distilled water and 20 mL Solution 3 was prepared by dissolving 15 g of P-123 in 2 ml of distilled water and 40 ml of tert-butanol. Solution 2 was added to solution 1 slowly over 1 h at 323 K under vigorous stirring. Precipitation of a solid occurred during the addition. To that mixture, solution 3 was added over 5–10 min and stirring continued for another 1 h.

The solid was filtered, washed thoroughly with distilled water (500 mL) to remove all the uncomplexed ions, and dried at 298 K for several hours. The material was used without any activation or after activating at 453 K for 4 h.

### Results and discussions

The purpose of the study to investigate brand new potential catalytic structures able to hydrolyze with high selectivity cellulose and hemicellulose into monosaccharides. Figure 1 reports the data of Yield and Total Dissolved Biomass versus the type of heterogeneous catalyst used. A comparison of the reactivity behavior of the catalysts synthesized is reported, and the performance obtained with both autohydrolysis and a commercial Amberlyst 15 catalyst. It is possible to notice that no catalyst is able to overtake the performance of sulfonic resin: just SnW2800 shows a moderate activity whereas Fe-Zn DMC and  $\text{Zr}_7\text{Nb}_2\text{O}_{19}$  does not present any significant activity even with respect to autohydrolysis.



**Figure 1:** Catalytic performance in direct hydrolysis of lignocellulose at 150°C for 5 hours

### Conclusions

In order to develop new catalytic technologies for future biorefinery operations it is necessary to explore and expand knowledge about heterogeneous acid-base catalysis. According to these criteria a screening of some non-conventional solid acid catalysts was carried out for direct hydrolysis of lignocellulosic material into monosaccharides in aqueous phase. A Sn-W mixed Oxide presents (but needs improvement) a moderate activity with respect to autohydrolysis.

### References

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### Acknowledgements

Eni S.p.A. is acknowledged for financial support.