

Heterogeneous vs Homogeneous Catalysis for Oxidative Organosolv

Fractionation of Biomass

AUTHORS

Konstantinos Kalogiannis / University of Western Macedonia - Department of Chemical Engineering

Stylianos Stefanidis / Chemical Process & Energy Resources Institute, Centre for Research and Technology-Hellas

Stamatia Karakoulia / Chemical Process & Energy Resources Institute, Centre for Research and Technology-Hellas

Anthi Karnaouri / Laboratory of General and Agricultural Microbiology, Department of Crop Science, Agricultural University of Athens

Angelos Lappas / Chemical Process & Energy Resources Institute, Centre for Research and Technology-Hellas

PURPOSE OF THE ABSTRACT

The key step to the successful valorization of lignocellulosic biomass lies in its fractionation towards its three main building blocks, cellulose, hemicellulose and lignin. In this work we present a novel organosolv pretreatment that replaces the commonly used inorganic acids, such as sulfuric acid, with O₂ gas (1); this leads to low yields of degradation byproducts while achieving high delignification degrees (DD) and good quality biomass fractions. To further optimize this process we introduce catalysis in the form of homogeneous and heterogeneous catalysts. In the case of homogeneous catalysis, we introduced polyoxometalates (POMs) that can enhance oxidative delignification by cleaving the lignin ether bonds, depolymerizing the lignin and thus making it more soluble in the organic solvent used. POMs had an additional catalytic effect; they conferred acidity to the water-organic solvent mixture that enhanced the hydrolysis of hemicellulose; this in turn liberated more lignin from the lignocellulosic biomass matrix as lignin and hemicellulose are strongly interconnected via covalent bonds. The pretreatment efficiently delignified hardwood (beech) and softwood (pine, up to 97% DD), a common weakness of organosolv processes. The addition of a POM, allowed the decrease of the processing temperature down to 150 °C while maintaining very high DD (up to 96%). Our oxidative organosolv process proved very efficient when treating agricultural residues (wheat straw) as well, making it a very flexible and efficient process.

We also investigated the effects of solid catalysts in our effort to efficiently delignify the biomass and achieve milder reaction conditions. We evaluated a variety of catalysts for the pretreatment of wheat straw, including Y, ZSM-5, Beta, and Mordenite zeolites. We found that the most crucial parameter to achieve efficient hemicellulose and lignin removal was high catalyst acidity. The catalyst-to-feed (C/F) ratio was optimized and it was observed that, at C/F ratios of 0.4-0.6, lignin and hemicellulose removal up to 70% and 62%, respectively, was achieved, significantly higher compared to non-catalytic OxiOrganosolv (42% and 15%, respectively). The catalyst mainly catalysed the acid hydrolysis and depolymerisation of hemicellulose, which secondarily exposed lignin and led to its depolymerisation via oxidation.

In both cases of catalytic fractionation, the pulps were recovered and their enzymatic hydrolysis was tested. We

found that the catalytic OxiOrganosolv pulps were highly digestible and the presence of the catalyst only marginally affected the hydrolysability and glucose yields. The obtained sugars were used as feedstock for their conversion to different types of products such as D-lactic acid by lactic acid bacteria of *Lactobacillus* species, docosahexaenoic acid (DHA) in the cells of heterotrophic marine microalga or ethanol; this proved the flexibility of the pretreatment method and the quality of the produced pulps.

Both homogeneous and heterogeneous catalysis proved to have their own advantages and challenges. POM enhanced delignification was very efficient and selective in the removal of lignin, the main challenge was the retrieval of the catalyst and its potential harmful effects in the downstream biochemical processes. Solid acid catalysis was efficient and removed the problem of acidic wastes commonly found in traditional organosolv. Its main challenges are the separation and retrieval of the solid catalyst and understanding how the solid catalysts may be affecting the organic solvent. Future research will focus on the recovery of the catalyst from the hydrolysis residue for reuse in the catalytic OxiOrganosolv process.

Acknowledgements

This project is carried out within the framework of the National Recovery and Resilience Plan Greece 2.0, funded by the European Union – NextGenerationEU (Implementation body: HFRI).

FIGURES

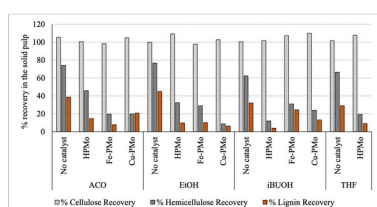


FIGURE 1

Figure 1. Lignin, cellulose and hemicellulose recovery yields in the solid pulp on a catalyst loading of 5% of the initial biomass.

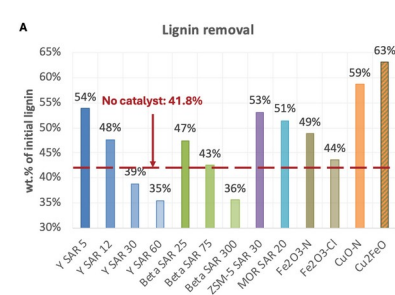


FIGURE 2

Figure 1. Lignin removal in the pulps produced from the OxiOrganosolv of wheat straw with different catalysts at 150 °C and C/F=0.1.

KEYWORDS

organosolv pretreatment | biorefinery | delignification | catalysis

BIBLIOGRAPHY

(1) Kalogiannis KG, Karnaouri A, Michailof C, et al. (2020), Bioresource Technol. 313, 123599.