

Oxidative Organosolv Fractionation of Lignocellulosic Biomass Assisted by Solid Catalysis and Biochemical Sugars Conversion

S.A. Karakoulia^{1*}, S.D. Stefanidis¹, A. Karnaouri², E. Topakas³, A.A. Lappas¹, K.G. Kalogiannis^{1,4},

¹Chemical Process and Energy Resources Institute (CPERI), Centre for Research and Technology Hellas (CERTH), 6th km Harilaou-Thermis, 57001 Thessaloniki, Greece

²Laboratory of General and Agricultural Microbiology, Department of Crop Science, Agricultural University of Athens, Athens 11855, Greece

³Industrial Biotechnology & Biocatalysis Group, School of Chemical Engineering, National Technical University of Athens, Zografou Campus, 15780, Greece

⁴Department of Chemical Engineering, University of Western Macedonia, 50132 Kozani, Greece *matoula@certh.gr

Keywords: Lignocellulosic biomass, organosolv fractionation, delignification, solid catalysis, zeolites

Organosolv fractionation (OS) is an efficient method employed for the pretreatment of lignocellulosic biomass, a renewable resource for the production of sustainable bioenergy and biobased products. OS fractionates biomass to lignin, hemicellulose and cellulose streams that can be valorized via biorefinery processes. We have previously developed an alternative oxidative organosolv process, named OxiOrganosolv (OOS), which was further optimized by using heteropolyacids (POMs) as soluble acid catalysts.

In the present work, OOS is further developed by using zeolites as solid catalysts with the aim to reduce the severity of the OOS conditions without affecting the efficiency of the fractionation and also enable catalyst recovery. Due to the acidity from the catalysts and oxidizing ability from the O_2 gas, efficient biomass fractionation is achieved at reduced temperature by the simultaneous catalysis of hemicellulose hydrolysis and the oxidation of the lignin ether bonds. Several zeolite types with variable silica-to-alumina ratios (SAR) were screened and compared to the OOS treatment without a catalyst. The catalyst-to-feed (C/F) ratio was then optimized with the most promising catalyst. Finally, a catalytic OOS-derived pulp was enzymatically hydrolyzed to assess its saccharification potential, and the hydrolysate was fermented towards omega-3 fatty acids.

Most catalysts facilitated the removal of hemicellulose and lignin and produced more cellulose-rich pulps compared to the non-catalytic OOS at the same temperature. The effectiveness of the different zeolite types was mainly correlated with their acidity. The most efficient fractionation and most cellulose-rich pulps were obtained at catalyst-to-feed ratios of about 0.4-0.5 with a Y zeolite with SAR 5. Evaluation of the enzymatic digestibility of the pulps revealed that a significantly higher portion of the cellulose in the catalytic OOS pulp could be converted to glucose compared to the corresponding pulp from the non-catalytic OOS. The presence of the zeolite particles had only a minimal effect on the glucose yield from the enzymatic hydrolysis of the pulp. This is an important step of the process as it allows pulps that are produced with the help of the solid catalysts to be processed biochemically. Finally, the catalyst was recovered from the hydrolysis residue by washing and calcination under air, and was characterized to study the impact of the process on its properties and its reusability.

Acknowledgments

The work was carried out in the framework of H.F.R.I's call "Basic research Financing (Horizontal support of all Sciences)" under the



National Recovery and Resilience Plan "Greece 2.0" funded by the European Union – NextGenerationEU (H.F.R.I. Project Number: 015795).