

**SOLID ACID CATALYSIS IN AGRICULTURAL RESIDUE FRACTIONATION**

**S.D. Stefanidis<sup>1\*</sup>, M. Karakoulia<sup>1</sup>, A.M. Tzika<sup>1</sup>, A. Karnaouri<sup>2,3</sup>, E. Topakas<sup>3</sup>, K.G. Kalogiannis<sup>1,4</sup>,  
A.A. Lappas<sup>1</sup>**

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

<sup>2</sup>Laboratory of General and Agricultural Microbiology, Department of Crop Science, Agricultural University of Athens, Athens 11855, Greece

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

<sup>4</sup>Department of Chemical Engineering, University of Western Macedonia, 50132 Kozani, Greece

([\\*s.stefanidis@certh.gr](mailto:*s.stefanidis@certh.gr))

**ABSTRACT**

Agricultural residues such as wheat straw are typically utilised as low-value animal feed. Because of their low selling price, they are often abandoned in the fields. However, cellulose, hemicellulose and lignin can be isolated and utilised to produce high-added value products. CERTH has developed a novel oxidative organosolv process (OxiOrganosolv) for the fractionation of lignocellulosic biomass feeds, such as wheat straw. It replaces the soluble acid catalysts typically used in organosolv with a pressurised oxygen atmosphere, resulting in a process that is more environmentally friendly, produces fewer byproducts, and high-purity cellulose-rich pulps that are more suitable for enzymatic and microbial processes.

The goal of this work was to improve the OxiOrganosolv process via the addition of solid acid catalysts to achieve the efficient fractionation of lignocellulosic feeds at lower reaction temperature (150 °C instead of 175 °C), aiming at the reduction of operating costs and the environmental footprint of the process. Several catalysts were screened at 150 °C, such as various zeolites (Y, ZSM-5, mordenite, beta), Cu and Fe metal oxides, and Cu-Fe mixed metal oxides. While all catalysts exhibited activity, one of the most effective catalysts was a Y zeolite with a low Si/Al ratio and high acidity. The delignification degree (DD) was increased from 42% to 54% with the addition of the solid catalyst. Y zeolites with higher Si/Al ratios and, hence, lower acidities led to lower DDs. The catalyst-to-feed (C/F) ratio was then optimised with the Y zeolite by changing the catalyst loading in the reactor to achieve C/F ratios from 0.1 to 1. The optimal C/F ratio was found to be 0.4, at which a DD of 67% was achieved. The cellulose content of the pulp increased from 56% at C/F=0 to 71% at C/F=0.4. Gas analysis showed that, despite the higher DDs achieved, oxygen consumption increased marginally. This indicated that the main effect of the catalyst was the hydrolysis of hemicellulose, catalysed by its acidity, while the impact of the catalyst on the oxidation of lignin was minimal. In the future, we will develop bifunctional acidic and redox solid catalysts to further optimise the process.

**KEYWORDS:** Lignocellulosic biomass, organosolv, fractionation, catalysis, zeolites