

**OXIDATION PROCESSES IN BIOREFINERIES, FROM PRE-TREATMENT TO FINAL PRODUCTS****K.G. Kalogiannis<sup>1,2\*</sup>, Z. Frontistis<sup>1</sup>, S.D. Stefanidis<sup>2</sup>, M. Karakoulia<sup>2</sup>, A. Karnaouri<sup>3,4</sup>, E. Topakas<sup>4</sup>,  
A.A. Lappas<sup>2</sup>**<sup>1</sup> Department of Chemical Engineering, University of Western Macedonia, 50132 Kozani, Greece<sup>2</sup> Chemical Process and Energy Resources Institute (CPERI), Centre for Research and Technology Hellas (CERTH), 6th km Harilaou-Thermis, 57001 Thessaloniki, Greece<sup>3</sup> Laboratory of General and Agricultural Microbiology, Department of Crop Science, Agricultural University of Athens, Athens 11855, Greece<sup>4</sup> Industrial Biotechnology & Biocatalysis Group, School of Chemical Engineering, National Technical University of Athens, Zografou Campus, 15780, Greece(\*[kkalogiannis@uowm.gr](mailto:kkalogiannis@uowm.gr))**ABSTRACT**

The biorefinery technology aims to produce renewable fuels and chemicals from lignocellulosic non-edible biomass waste. To achieve sustainability, it must isolate and utilise all biomass fractions, i.e. cellulose, hemicellulose and lignin. In line with the refinery processes, the first and most costly stage in the utilisation of biomass is its fractionation. This is followed by the conversion of the biomass fractions into fuels and chemicals by chemical and biochemical methods. In recent years, oxidation processes for biomass utilisation have been developed; they are of particular interest as they can accelerate the individual steps and provide high value-added products<sup>1</sup>.

Oxidative delignification is an effective way to remove lignin and increase the hydrolysis of cellulose<sup>2</sup>. Furthermore, the development of oxidative processes for conversion of sugars and lignin is of particular interest and unique challenges as it requires the development of new selective catalytic systems that ensure high yields towards desired products and reduce side reactions.

In this work, we reviewed current research progress in the following oxidative processes: a) pre-treatment of biomass, b) upgrading of sugars and c) production of oxidants with Power to X technologies. We evaluated a pretreatment based on the replacement of commonly used inorganic acids, such as sulfuric acid, with O<sub>2</sub> gas; this resulted in low degradation by-product yields, high degrees of delignification (DD) and good quality biomass fractions. We investigated several process parameters such as solvent, temperature, O<sub>2</sub> addition and the use of polyoxometallic salts (POMs) that can enhance oxidative delignification.

The higher temperatures, and longer processing times were beneficial producing pulps with low lignin content (~1 % w/w), while maintaining high cellulose (100 %) and hemicellulose (40 %) recovery in the solid. The remaining hemicellulose was recovered as soluble oligosaccharides that were not degraded due to the absence of organic acids. Cellulose and hemicellulose sugars can be biochemically converted to different products such as ethanol<sup>2</sup>, lactic acid<sup>3</sup>, omega-3 fatty acids<sup>4</sup>. Alternatively, their oxidation to high value-added chemicals such as aldonic and aldaric acids<sup>5</sup> is of particular interest using photo-<sup>6</sup> and electro-<sup>7</sup> catalytic technologies and materials already developed in the context of hydrogen production and wastewater treatment<sup>8,9</sup>.

**KEYWORDS:** biorefinery, delignification, sugar oxidation, photoelectrocatalysis, aldonic and aldaric acids**REFERENCES**

[1] Junjiang et al. (2016). *ACS Sustainable Chem. Eng.* 4 (4): 2020-2026.

- [2] Katsimpouras C., Dedes G., Bistis P., Kekos D., Kalogiannis K.G., Topakas E. (2018). *Bioresource Technol.* 270: 208-215
- [3] Karnaouri, A., Asimakopoulou, G., Kalogiannis, K.G., Lappas, A., Topakas E. (2020). *Biomass and Bioenergy*, 140.
- [4] G. Asimakopoulou, A. Karnaouri, S. Staikos, S.D. Stefanidis, K.G. Kalogiannis, A.A. Lappas, E. Topakas (2021). *Fermentation*, 7 (4), 219.
- [5] O. Varela (2003). *Adv. Carbohydr. Chem. Biochem.*, 58, 307-369.
- [6] Ming Cheng, Quanquan Zhang, Changjun Yang, Bingguang Zhanga and Kejian Denga (2019). *Catalysis Science and Technology.*, 24.
- [7] Jay Pee Oña, Rose-Marie Latonen, Narendra Kumar, Markus Peurla, Ilari Angervo, Henrik Grénman (2023). *Electrochimica Acta*, 437, 141536.
- [8] Rebecca Dhawle, Zacharias Frontistis, Dionissios Mantzavinos, Panagiotis Lianos (2021). *Chemical Engineering Journal Advances*, 6, 100109.
- [9] Antoniadou M., Vaiano V., Sannino D., Lianos P. (2013). *Chemical Engineering Journal*, 224, 144-148.