

## **Aromatics compound from lignin by supercritical water ultrafast reactions: understanding the lignin re-polymerization.**

Tijana Adamovic, Emre Demirkaya, Eduardo Pérez , María José Cocero.

BioecoUva Research Institut. High Pressure Research Group. Chemical Engineering and Environmental Technology Department. University of Valladolid Spain

Lignin is an aromatic polymer with the potential to supply aromatics from an alternative source to the petrochemical industry. So far, the low selectivity has limited lignin depolymerization: it is possible to produce aromatic oils but with very low selectivity to produce monomers. Simultaneously, lignin re-polymerization has limited the hydrothermal depolymerization processes, producing a char with very low value.

Supercritical water (SCW) has demonstrated to be an excellent reaction media for the lignin depolymerization. At subcritical conditions, the ionic product is  $10^{-12}$ , what makes this reaction medium favor ionic reactions. At supercritical conditions, for example at 450°C and 25MPa, the density is 109.0 kg/m<sup>3</sup> and the ionic product  $10^{-18,1}$ [1]. Under these conditions, the reaction medium favors radical reactions, as we have demonstrated in previous works [2].

The reaction medium provides conditions to improve the processes intensification and the selectivity over other solvents, but, on the other hand, the reactions are very fast and, as soon as the products are formed, they are hydrolyzed and selectivity is lost. So, we have used our ultrafast SCW technology to control the selectivity of the lignin depolymerization [3]. Our SCW sudden expansion reactor allows to work with residence time well below 1s. Under this reaction time the lignin re-polymerization is minimized up-to concentrations of only 4% [3].

To understand the lignin re-polymerization under SCW conditions, a systematic study has been done. It follows the lignin reaction in SCW in the presence of the equimolar amount of different model compounds. Model compounds used were Vanillin, Vanillic acid, Vinyl alcohol, and Acetovanilon, all having guaiacol type of the ring and differ just in substituent in *p* position while lignin chosen for this propose was Alkali Lignin from Sigma Aldrich. Lignin to model compounds ration was varied as well as the concentration inside the reactor.

After the reaction, the sample was fractionated in solid and liquid fraction, and both fractions were extracted by ethyl acetate to optioned light and heavy oil. The result showed that in every experiment the total amount of solid fraction was higher when model compounds were used in the reaction mixture, compared to the blank experiment without model compounds, due to the re-polymerization between lignin and model compound presented. The reactivity of each model compound was measured by the conversion rate, and this conversion deepened on Lignin: Model compound ratio, but also on total concentration inside the reactor. Further analysis of the solid phase helps to understand the changes in the lignin structure as a result of the re-polymerization reaction with model compounds due to supercritical water treatment.

[1] Brunner G., Hydrothermal and supercritical water processes. Elsevier 2014.

[2] Cocero M. J. Supercritical water processes. Future prospects. J Supercritic. Fluids 2018, 134, 124-132.

[2] Abad-Fernandez N., Perez-Velilla E., Cocero M. J. Ultrafast lignin depolymerization processes. WO 2019/ 120956 A1.