

Improving kinetic models of cellulose hydrolysis in supercritical water

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Processing real lignocellulosic biomass in biorefineries requires first the understanding of cellulose transformation fundamentals. This compound, which is the major component of lignocellulosic biomass (40-50%) and a polymer consisting on several glucose units, is a building block in the bio-based industry. The obtaining of glucose from cellulose requires cleaving the glycosidic bonds which connect the glucose molecules. In hydrolysis, the cleavage of these bonds is produced by the addition of a water molecule. Because of the cellulose insolubility in water at ambient temperature, cellulose hydrolysis requires the use of acids, enzymes or hot pressurized water from subcritical to supercritical state. Supercritical water hydrolysis of cellulose is a process characterized by its high selectivity (values over 98%), the reduced reaction times required (milliseconds) and the fact that no residual effluents are generated¹.

Although cellulose hydrolysis models by supercritical water have been already proposed²⁻⁴, they neglect the mass transfer effects. This simplification generates discrepancies between the theoretical and the experimental results when the cellulose concentration is increased.

This contribution proposes a kinetic model able to reproduce cellulose hydrolysis in supercritical conditions and at high concentrations. The model is based on the idea that the hydrolysis of the cellulose particles generates an oligosaccharides layer which creates a mass transfer resistance. Therefore, it considers both the diffusion of the water molecules from the bulk phase to the surfaces of the cellulose particles and the superficial hydrolysis kinetics. Experimental points were obtained working with two different cellulose types ($D_p = 75\mu\text{m}$, $\rho_p = 350\text{kg/m}^3$ and $D_p = 50\mu\text{m}$, $\rho_p = 600\text{kg/m}^3$) at 390°C and 25MPa, residence times between 50ms and 250ms and initial cellulose concentration from 3% to 7% w/w. The average deviation between the experimental points and the theoretical values is equal to 6.6% proving the applicability of the kinetic model.

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References

- 1 M. J. Cocero, Á. Cabeza, N. Abad, T. Adamovic, L. Vaquerizo, C. M. Martínez and M. V. Pazo-Cepeda, *J. Supercrit. Fluids*, , DOI:10.1016/j.supflu.2017.08.012.
- 2 M. Sasaki, T. Adschiri and K. Arai, *AIChE J.*, 2004, **50**, 192–202.
- 3 D. A. Cantero, M. D. Bermejo and M. J. Cocero, *J. Supercrit. Fluids*, 2013, **75**, 48–57.
- 4 C. M. Martínez, D. A. Cantero, M. D. Bermejo and M. J. Cocero, *Cellulose*, 2015, **22**, 2231–2243.

