

N°681 / OC

TOPIC(s) : Alternative solvents / Biomass conversion

## Modelling the physical chemistry of the interactions between organosolv mixed solvents and lignocellulose components

### AUTHORS

Francesco DI RENZO / INSTITUT CHARLES GERHARDT MONTPELLIER, 240 AVENUE JEANBRAU, MONTPELLIER

Tzonka MINEVA / INSTITUT CHARLES GERHARDT MONTPELLIER, 240 AVENUE JEANBRAU - ENSCM, MONTPELLIER

Corresponding author : Sonia Milena AGUILERA SEGURA / soni.aguileras@gmail.com

### PURPOSE OF THE ABSTRACT

The use of multicomponent solvents has provided remarkable results in biomass fractionation processes of several levels of severity. Present revival of organosolv pulping directed to the isolation of cellulose to produce bioethanol corresponds to new requirements of purity. Understanding the factors that drive to the interaction of lignocellulose components with different solvents is the key to successful optimization of organosolv processes. Moreover, comprehension of the mutual organization between organic solvents and water in multi-component systems and their specific interactions with the wood polymers can be achieved by means of computational methods, which can provide detailed information at the molecular level. Our results on the atomistic understanding of preferential interactions of water-organics solvent components with cellulose have been obtained from molecular dynamics simulations in conjunction with density functional theory (DFT) approaches, including ab-initio molecular dynamics. Structure and dynamics of cellulose-solvent interfaces were characterized by correlation functions (RDF), torsion angles of cellulose backbone and hydroxymethyl chains, H-bonding and H-bond lifetimes at several water-organosolv concentrations.

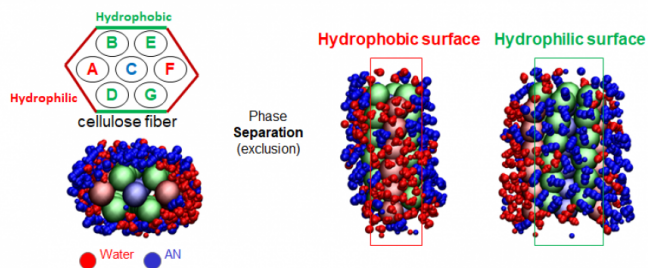
The analysis of the site-to-site RDFs shows a preferential orientation of solvent molecules toward specific oxygens of the glucose monomer. This preferential binding between solvent and oxygen of cellulose varies with the nature of the organic solvent and the water content. Moreover, the integration of the RDFs revealed a solvent phase separation at the cellulose interface, promoting the existence of water-rich and cosolvent-rich cellulose interfaces (Fig. 1). Furthermore, structure analysis shows that chain deformation of solvated cellulose by conformational transition of the hydroxymethyl chain obeys to the selective presence of solvents in the differences interfaces of cellulose. Consequently, intermolecular hydrogen bonds as well as their dynamics vary as a function of solvent concentration. Interestingly, it was found that the cellulose-water hydrogen bond lifetimes at the water-rich surface are shorter in comparison to those of the cosolvent-rich surface. Also, their lifetimes tend to increase with the cosolvent amount. Moreover, the non-linearity of interactions between mixed solvents and cellulose is in good agreement with experimental lignocellulose swelling data.

Similarly, we studied the solvation lignin- the main component of biomass to be extracted by organosolv pulping- in the form of lignin oligomers. In agreement with previous results, the phenol rings in water face each other by changing the configuration of the  $\beta$ -O-4 bonds, so reducing the exposition to the solvent. In contrast, the lignin conformer in ethanol displays a more linear disposition of the phenol rings, allowing better access of the solvent and increasing the solvent accessible surface area. This is in agreement with recent studies that show an increase lignin solubility in mixed water-ethanol mixtures.

In the pulping process, after hydrolysis or hydrogenation have cleaved lignin-polysaccharide links, easy separation of the products requires to minimize re-adsorption of dissolved lignin oligomers on the cellulose fibrils. Our simulation allowed to identify the most probable states of the cellulose-lignin complexes in different solvents. The distribution of H-bonds between models of cellulose fibrils and lignin oligomers (Fig. 2) is a good indicator of

the probability of interaction. In the presence of water, long-lasting H-bonds between lignin and cellulose are observed, promoted by the non favorable interactions with water with lignin and the hydrophobic surfaces of cellulose. The presence of mixed solvents decreased the probability of formation of cellulose-lignin H-bonds, a critical issue for the purity of ocelluloses issued from the pulping process.

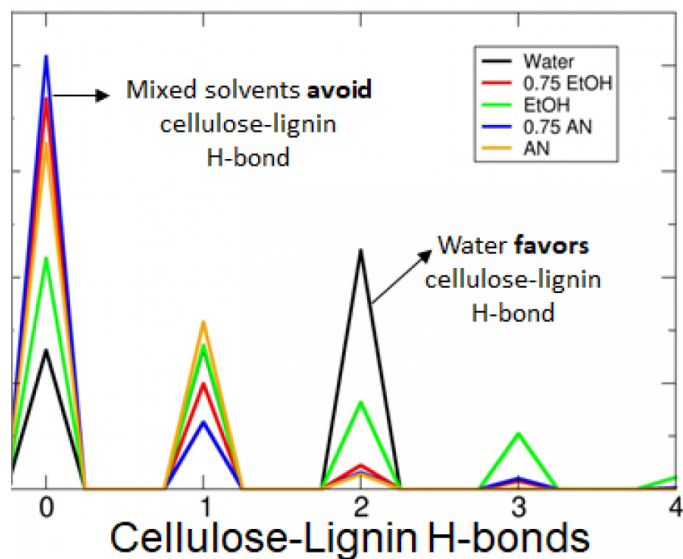
## FIGURES



**FIGURE 1**

Cellulose solvation in mixed solvents

Cellulose fiber in 75 wt% acetonitrile (AN). Water (red) and AN (blue) molecules in the first solvation shell of cellulose are shown. Water-acetonitrile mixtures spontaneously separate driven by the relative affinity with the hydrophilic and hydrophobic s



**FIGURE 2**

Cellulose-Lignin H-bond distribution

Cellulose-lignin H-bond probability distribution at the hydrophobic surface of cellulose

## KEYWORDS

theoretical chemistry | solvation | organosolv pulping | mixed solvents

## BIBLIOGRAPHY