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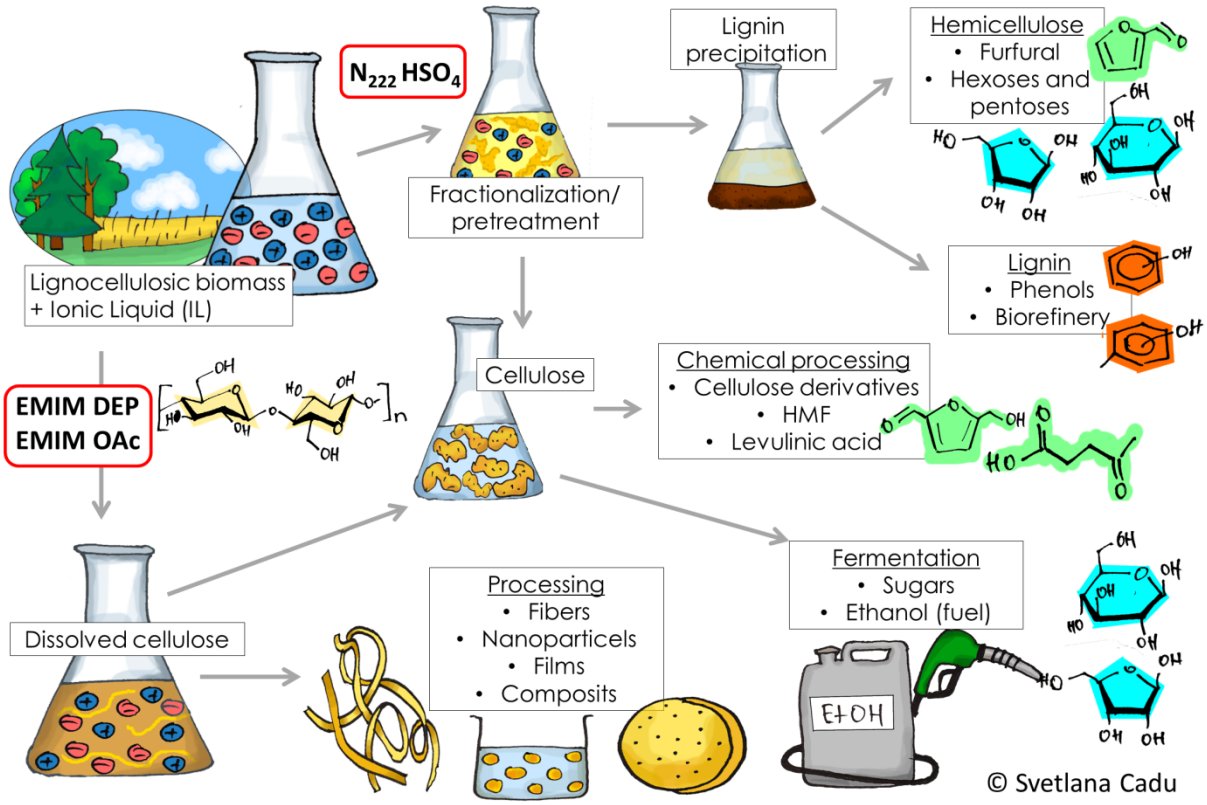
Ionic Liquids Technologies

Lignocellulosic biomass and ionic liquids

With the ever-growing demand for fuel and material and rapidly depleting fossil sources, a lot of attention has been paid to renewable materials, and lignocellulosic biomass as a main of them. Lignocellulosic biomass, as for example sawdust, nutshells, straw, corn stower and dedicated fast-growing energy crops, can be viewed as precursors to fuels, such as ethanol, platform chemicals, such as HMF – 5-hydroxymethylfurfural (HMF), as well as construction materials.

One main barrier on this way is a complicated structure of lignocellulosic feedstock, which brings about problems, like inefficient and costly (both in terms of money and environmental impact) pretreatment, low yields, high loadings of (bio)catalysts required. Lignocellulosic biomass consists mainly of cellulose, hemicellulose and lignin, which are all packed together in a compact structure. Therefore disturbing this structure and getting fractions of different compound types is the main challenge.

Ionic liquids have very high solubilizing ability and can dissolve cellulose and other wood components. This opens two main avenues.



Path one – fractional dissolution of lignicellulose, or pulping.

In principle, a couple of solvent systems exist, that allow dissolution of extractives, hemicellulose and lignin from wood, leaving cellulose behind. Examples include sulphite and kraft pulping, which break lignin and hemicellulose down to smaller water soluble molecules, that could be washed out and Organosolv, that uses

organic solvents to fraction the wood. Along the same lines, ionoSolv process helps to remove lignin and hemicellulose from wood, leaving behind the cellulose with quite porous structure, that can be cut down into sugars using conventional yeasts.[1] Ionic liquids are used as solvents in the process, owing to their good solubilizing power and ultralow vapour pressure and therefore negligible loss into environment. Moreover, used ILs, like N222 HSO4,[2] BuIm HSO4, BMIM Cl are quite cheap. High degree of lignin removal leaves behind the cellulose with quite porous structure, that can easily be transformed into hexoses in high yield. Further fermentation can afford bioethanol as fuels.[3] Alternatively, chemical treatment, that can also be done in ionic liquids,[4] can transform sugars into platform chemicals, such as HMF or levulinic acid[5].

Part two – dissolution and reconstruction of cellulose.

Some ionic liquids, e.g. EMIM OAc, EMIM DEP are good solvents for the dissolution of wood – dissolving all of the wood constituents: cellulose, hemisellulose, lignin. The dissolved cellulose[6] can be reconstructed in amorphous state by addition of water, spun into fibers, like in Ioncell-F[7] process, transformed into composites,[8] films,[9] nanoparticles[10] or chemically modified for further use[11].

Lignin and hemicellulose

Lignin can be quite easily obtained from IL solutions[12]. As ILs can be designed to have catalytic activity, it might be possible to make lignin digest in quite straightforward manner. It can be further used as a source of aromatics[13] or in biorefineries and for energy production.

Hemicellulose, being mostly constituted from sugars, can be further processed in ionic liquids and used for production of chemical building blocks, as furfural, or hydrolysed to pentoses and hexoses.

What are the perspectives?

The exploration of the potential of renewables, should relieve the environmental pressure from the use of fossils in terms of fuels and production of some chemicals. Furthermore, ability to efficiently use and modify lignocellulosic feedstocks opens up new possibilities, as more environmentally benign substitute for viscose as cellulose based fibre, new materials for modern engineering based solely on reconstructed renewables, medical application of nanocellulose, cellulose beads and nanoparticles as hosts for new catalytic systems to name just a few. It seems that ionic liquids have a big role to play in this scenario. Of course, there are still problems to solve, as recyclability of solvents, transformation into mature industrial processes, but for sure, there is a future to ionic liquids in the field of renewable biomass.

If you have an idea on the use of lignocellulose and need an ionic liquid for pretreatment of your starting material, feel free to contact us. We can provide

material and expert opinion on the choice of ionic liquid which fits right just your application.

Text and illustration: Dr. Svetlana Cadu, Iolitec 2019

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1 https://www.imperialinnovations.co.uk/media/uploads/files/ionoSolv_6555_WhitePaper_Imperial_Innovations.pdf

2 F. J. V. Gschwend, C. L. Chambon, M. Biedka, A. Brandt-Talbot, P. S. Fennell, J. P. Hallett, *Green Chem.*, **2019**, *21*, 692.

3 J. Sun, N. V. S. N. M. Konda, R. Parthasarathi, T. Dutta, M. Valiev, F. Xu, B. A. Simmons, S. Singh, *Green Chem*., **2017**, *19*, 3152.

4 X. Sun, Z. Liu, Z. Xue, Y. Zhang, T. Mu, *Green Chem*., **2015**, *17*, 2719; F. Tao, H. Song, L. Chou, *RSC Adv.*, **2017**, *7*, 47288; T. Okano, K. Qiao, Q. Bao, D. Tomida, H. Hagiwara, C. Yokoyama, *Appl. Cat A*, **2013**, 1.

5 K. C. Badgujara, L. D. Wilsonc, B. M. Bhanagea, *Renew. Sust. Energ. Rev.,* **2019**, *10*, 2266.

6 F. Hermanutz, M. P. Vocht, N. Panzier, M. R. Buchmeiser, *Macromol. Mater. Eng.,* **2018**, 1800450.

7 https://www.aalto.fi/department-of-bioproducts-and-biosystems/vtt-and-aalto-university-collaborate-to-develop-novel

8 Y. D. A. Freyburger, W. Kunz, C. Zollfranka, *Carbohydr. Polym*., **2018**, *192*, 159; M. B. Turner, S. K. Spear, J. D. Holbrey, D. T. Daly, R. D. Rogers, *Biomacromolecules*, **2005**, *6*, 2497.

9 B. J. C. Duchemin, A. P. Mathew, K. Oksman, *Compos. Part A Appl. Sci. Manuf.,* **2009**, *12*, 2031; J. Pang, X. Liu, X. Zhang, Y. Wu, R. Sun, *Mater.,* **2013**, *4*, 1270.

10 https://rua.ua.es/dspace/bitstream/10045/81249/1/2018_Montalban_etal_Biopolymeric-Nanoparticle-Synthesis-in-Ionic-Liquids.pdf; J. Hana, C. Zhou, A. D. French, G. Han, Q. Wua, *Carbohydr. Polym*., **2013**, *94*, 773.

11 S. Köhler, T. Liebert, T. Heinze, *J. Polym. Sci. A Polym. Chem*., **2008**, 4070; Z. Zhang, J. Song, B. Han, *Chem. Rev.* **2017**, *117*, 6834; M. Isik , H. Sardon , D. Mecerreyes, *Int. J. Mol. Sci.,* **2014**, *15*, 11922.

12 T. Akiba, A. Tsurumakia, H. Ohno, *Green Chem*., **2017**, *19*, 2260.

13 S. Gillet, M. Aguedo, L. Petitjean, A. R. C. Morais, A. M. da Costa Lopes, R. M. Łukasik , P. T. Anastas, *Green Chem*., **2017**, *19*, 4200.