Alternative Solvents in Green Processing of Biomass to Tailor-made Fuels and Platform Chemicals

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Alternative solvents is a term that includes supercritical fluids (scF) and ionic liquids (ILs), and both form a significant part of research in green chemistry.[1] ILs are an interesting class of compounds that are known for more than a century. However, they attracted major attention within the last two decades. ILs are salts with the melting point arbitrary determined to be below 100°C. They are composed by ions, thus, each IL possesses the unique properties that are the effect of a cation and an anion nature.[2] In general, ILs are characterised by low melting point, high thermal stability,[2] large electrochemical window, great solvent power,[3,4] non-flammability and negligible vapour pressure.[5-7] Density and viscosity as well as many other properties are in a very broad range that is characteristic for different types of fluids. The mentioned properties give the origin to the ample applications such as biotransformation,[8] chemical reactions (catalysis,[9] hydrogenation,[10-12] etc.), biorefinery concept,[13] extraction or separation.[14]

The second group of compounds considered as more sustainable are supercritical fluids. ScF is a compound above its critical temperature and critical pressure but below the pressure required to condense it into a solid. As the temperature increases, the liquid becomes less dense due to thermal expansion and as the pressure increases, the gas becomes denser. Once the densities become equal, the phase distinction between liquid and gas disappears and the critical point is reached. Above the critical point, there is only one gas phase. ScF properties take values that are somewhat in between the values usually taken by liquids and gases, leading many authors to claim important advantages for the use of scF in chemical processes. Additionally, scF show tunable properties as partition coefficients and solubility. Small changes in temperature or pressure close to critical point can result in up to 100-fold changes in solubility, thus, simplify separation.[15]

ScF are considered to be green solvents and have been employed in a diverse range of chemical reactions, including both homogeneous and heterogeneous catalytic processes.[16,17] Among scF, supercritical CO_2 ($scCO_2$) has received considerable attention as a useful replacement of organic solvents because it is inexpensive, non-toxic, non-flammable, recyclable, easily disposed, and capable of performing functions of a non-polar solvent while allowing manipulation of its solvent strength through a wide range of polarities. In addition, the solvent power of $scCO_2$ can be easily tuned by changes in both temperature and pressure, and reduction of the undesirable by-products yielding a higher end product quality can be achieved.[11]

This work will illustrate application of ILs and scF in divert areas of research with a special attention focused on processing of biomass to tailor-made fuels and platform chemicals.

Reference

1 F. M. Kerton, Alternative Solvents for Green Chemistry, RSC Publishing, Cambirdge, 2009.
2 U. Domanska and R. Bogel-Lukasik, *J. Phys. Chem. B*, 2005, **109**, 12124-12132.
3 M. E. Zakrzewska, E. Bogel-Lukasik, and R. Bogel-Lukasik, *Energ. Fuel.*, 2010, **24**, 737-745.
4 T. M. Letcher, D. Ramjugernath, K. Tumba, M. Krolikowski, and U. Domanska, *Fluid Phase Equilib.*, 2010, **294**, 89-97.
5 A. V. Blokhin, Y. U. Paulechka, A. A. Strechan, and G. J. Kabo, *J. Phys. Chem. B*, 2008, **112**, 4357-4364.
6 Y. U. Paulechka, G. J. Kabo, A. V. Blokhin, O. A. Vydrov, J. W. Magee, and M. Frenkel, *J. Chem. Eng. Data*, 2003, **48**, 457-462.
7 M. J. Earle, J. M. S. S. Esperanca, M. A. Gilea, J. N. C. Lopes, L. P. N. Rebelo, J. W. Magee, K. R. Seddon, and J. A. Widegren, *Nature*, 2006, **439**, 831-834.
8 R. Bogel-Lukasik, N. M. T. Lourenco, P. Vidinha, M. Gomes da Silva, C. A. M. Afonso, M. Nunes da Ponte, and S. Barreiros, *Green Chem.*, 2008, **10**, 243-248.
9 M. E. Zakrzewska, P. M. S. D. Cal, N. R. Condeias, R. Bogel-Lukasik, C. A. M. Afonso, M. Nunes da Ponte, and P. M. P. Gois, *Green Chem. Lett. Rev.*, 2012, **5**, 211-240.
10 J. M. Lopes, Z. Petrovski, R. Bogel-Lukasik, and E. Bogel-Lukasik, *Green Chem.*, 2011, **13**, 2013-2016.
11 E. Bogel-Lukasik, M. Gomes da Silva, I. D. Nogueira, R. Bogel-Lukasik, and M. Nunes da Ponte, *Green Chem.*, 2009, **11**, 1847-1856.
12 E. Bogel-Lukasik, I. Fonseca, R. Bogel-Lukasik, Y. A. Tarasenko, M. Nunes da Ponte, A. Paiva, and G. Brunner, *Green Chem.*, 2007, **9**, 427-430.
13 F. M. Gírio, C. Fonseca, F. Carvalheiro, L. C. Duarte, S. Marques, and R. Bogel-Lukasik, *Bioresource Technol.*, 2010, **101**, 4775-4800.
14 R. Bogel-Lukasik, V. Najdanovic-Visak, S. Barreiros, and M. Nunes da Ponte, *Ind. Eng. Chem. Res.*, 2008, **47**, 4473-4480.
15 C. I. Melo, R. Bogel-Lukasik, and E. Bogel-Lukasik, *J. Supercrit. Fluid.*, 2012, **61**, 191-198.
16 D. J. Cole-Hamilton, *Science*, 2003, **299**, 1702-1706.
17 P. G. Jessop, *Green Chem.*, 2011, **13**, 1391-1398.

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