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Biorefinery approach for lignocellulosic biomass valorisation with an acidic ionic liquid†

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The commercialisation of the biorefinery approach involving the integration of the multi-step valorisation of low value biomass feedstock into a variety of chemicals, fuels and bioproducts is still very limited. In this context, the present work proposes an advanced methodology that comprises a cascaded approach towards wheat straw valorisation. The studied concept lies in the employment of an aqueous solution of the acidic 1-ethyl-3-methylimidazolium hydrogen sulfate ionic liquid in a selective and efficient hydrolysis of the hemicellulose fraction of wheat straw into pentoses, namely xylose and arabinose. An experimental design was utilised to search for the optimisation parameters, resulting in a maximum 80.5 wt% pentose yield in the liquor. Furthermore, the remaining solid, which contained practically all of the initial cellulose and lignin, was processed by considering two scenarios: (i) a direct enzymatic hydrolysis of the reaction solid, which yielded 75.8 mol% glucose; or (ii) a preceding extraction of lignin followed by enzymatic saccharification of the cellulose pulp, which yielded 91.3 mol% glucose. For both scenarios, lignin-rich solid fractions were obtained with distinct purities and yields. Additionally, the second scenario allowed producing a stream of value-added aromatic (phenolic) compounds. This work also overcame the challenges in IL recycling and reuse, with a simultaneous recovery of the pentoses from the reaction liquor as high as 88.6 mol%.

1. Introduction

The low carbon economy is one of the main mid-century targets of the European Union.[1] Abundant lignocellulosic biomass is one from not many available sustainable carbon sources able to play a key role towards the achievement of this objective.[2] Hence, a more extensive valorisation of lignocellulosic biomass, where all the fractions are processed selectively towards a variety of products, is needed to accomplish the biorefinery concept. Efficient lignocellulosic biomass processing requires a selection of suitable technologies and strategies that underpin the maximum separation of the main polymeric fractions of biomass, namely cellulose, hemicellulose and lignin. On the other hand, the very complex inter- and intramolecular network existing between these components makes the fractionation of lignocellulosic biomass a very challenging task.[3] Various physical, chemical and thermal technologies have been widely studied to try to overcome the biomass recalcitrance.[4] Among the conventional treatments tried are processes involving acids (*e.g.* H_2SO_4) and alkaline reagents (*e.g.* ammonia and NaOH). In general, these can only achieve a partial biomass fractionation and further recovery of the catalysts (acid or base) is still challenging. Alternative solutions are water-based processes, *i.e.* steam explosion and the use of liquid hot water. Although an advantage of these processes is that there is no need for the addition of chemicals (catalysts), only hemicellulose can be extracted (often in an oligosaccharide form) and normally this takes place at elevated temperature, *e.g.* 220 °C.[5] Hence, to solve the bottlenecks of the current pre-treatment technologies, greener and more sustainable technologies for lignocellulosic biomass conversion are required. In this context, ionic liquids,[6] carbon dioxide[7,8] and bio-based solvents (*e.g.* ethanol, γ-valerolactone, tetrahydrofuran)[9–13] are often a first choice because they allow achieving selective biomass processing under less severe conditions, although concerns regarding the safety and the cost-efficient synthesis and recovery of these novel solvents/catalysts is still an issue.

Ionic liquids (ILs) are organic salts characterised by a low melting point. They are constituted by a large-sized organic cation with a low charge density that establishes weak electro-

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