



# Loop vs. batch reactor setups in the fractionation of birch chips using switchable ionic liquids

Valerie Eta <sup>a,\*</sup>, Ikenna Anugwom <sup>a</sup>, Pasi Virtanen <sup>a</sup>, Kari Eränen <sup>a</sup>, P. Mäki-Arvela <sup>a</sup>, J.-P. Mikkola <sup>a,b</sup>

<sup>a</sup>Laboratory of Industrial Chemistry and Reaction Engineering, Process Chemistry Centre, Åbo Akademi University, Åbo-Turku FI-20500, Finland

<sup>b</sup>Technical Chemistry, Department of Chemistry, Chemical-Biological Center, Umeå University, SE-901 87 Umeå, Sweden

## HIGHLIGHTS

- Batch and loop reactors for efficient fractionation of wood.
- Partial fractionation of wood into cellulose, hemicellulose and lignin.
- Fractionation of birch chips using switchable ionic liquids.
- Effects of mass and heat transfer on wood fractionation.
- Dissolution and recovery of fractionated components.

## ARTICLE INFO

### Article history:

Available online 7 June 2013

### Keywords:

Switchable ionic liquids (SILs)  
Loop reactor  
Batch reactor  
Wood fractionation  
Birch chips

## ABSTRACT

The fractionation of lignocellulosic feedstock into its major components with high purity represents an important commercialization milestone in the transformation of lignocellulosic forest derived products into fuels and commodity chemicals. A comparison between the traditionally used batch reactor and loop reactor systems demonstrates that improved dissolution of hemicelluloses and lignin are obtained using switchable ionic liquids in a loop reactor system which facilitates decreased heat and mass transfer restrictions. The treatment of birch chips using switchable ionic liquid (SIL) based on 1,8-diazabicyclo-[5.4.0]-undec-7-ene, CO<sub>2</sub> and diethanolamine at 120 °C for 30 h in a loop reactor resulted in 24% loss of original weight of wood corresponding to dissolution of 52 wt.% of hemicelluloses and 42 wt.% of lignin, respectively, as opposed to 20% weight loss corresponding to 43 wt.% dissolution of hemicelluloses and 38 wt.% of lignin in the batch system. The non-dissolved material obtained from both reactors was efficiently fibrillated and softened cellulose fibres. The flow of switchable ionic liquid through the loop reactor and agitation of the chips enhanced the dissolution of hemicelluloses and lignin. The dissolved fractions recovered from spent SIL after treatment contained both hemicelluloses and lignin.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

The dependence on fossil fuels, diminishing petroleum resources, growing demand for energy, environmental degradation, etc. are important issues facing mankind. The increasing awareness of sustainable development and environmental protection has prompted the exploration of natural resources in environmentally-friendly ways. This has resulted in the utilization of alternative, carbon-neutral energy sources or renewable supplies for energy production or as platform chemicals and materials [1,2]. The conversion of abundant and widely available lignocellulosic feedstock to valuable chemicals, biomaterials, energy and fuels represent a major advancement in the transformation of biomass e.g. wood to new materials other than pulp and paper. Typically

biomass may be transformed to energy by combustion, or to fuels and chemicals via fermentation, gasification, pyrolysis, etc. [3].

The cell walls of lignocellulosic biomass are composed of cellulose, lignin, hemicelluloses, and small amounts of extractives, proteins and inorganic components (ash elements) present in different proportions in different wood types. Cellulose is composed of linear chains of D-glucose units linked by β-1,4-glycosidic bonds and forms the major component of the fibre wall contributing to 40–50 wt.% of the dry wood weight. The D-glucopyranosyl units form intra- and intermolecular hydrogen bonds which strengthen the linear cellulose chains and facilitate aggregation into a crystalline structure, thus limiting accessibility of water or chemicals during thermo-chemical treatments [4]. Hemicelluloses are mixtures of polysaccharides consisting of monomeric sugars, such as glucose, mannose, galactose, xylose, arabinose, 4-O-methylglucuronic acid, and galacturonic acid units. The main chains in the hemicelluloses backbone contain β-1,4-glycosidic linkages and may contain side

\* Corresponding author. Tel.: +358 408769993.

E-mail address: [valerie.eta@abo.fi](mailto:valerie.eta@abo.fi) (V. Eta).

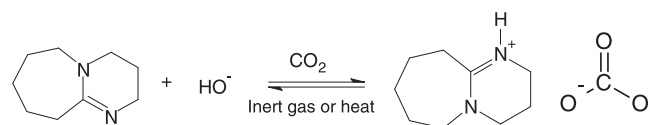
**Table 1**  
The major hemicelluloses in softwood and hardwoods [5].

Wood	Hemicellulose	Amount in wood (%)	Composition		
			Units	Molar ratio	Linkage ratio
Softwood	Glucomannan	14–20	$\beta$ -D-Manp	4	1 → 4
			$\beta$ -D-Glcp	1	1 → 4
			$\alpha$ -D-Galp-Acetyl	1	1 → 6
	Xylan	5–11	$\beta$ -D-Xylp	10	1 → 4
			4-O- $\mu$ e- $\alpha$ -D-GlcpA	2	1 → 2
Hardwood	Xylan	15–30	$\beta$ -D-Xylp	10	1 → 4
			4-O- $\mu$ e- $\alpha$ -DGlcpA-Acetyl	7	1 → 2
			$\beta$ -D-Manp	1–2	1 → 4
	Glucomannan	2–5	$\beta$ -D-Glcp	1	1 → 4

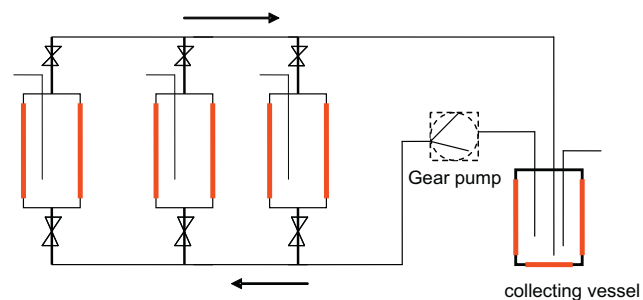
p: pyranosyl; f: furanosyl.

chains of  $\beta$ -1,3 or  $\beta$ -1,4-glucans making them essentially amorphous. Hemicelluloses include xyloglucans, xylans, mannans, arabinogalactans, gluronoxylans and glucomannans. The main structural features of hemicelluloses present in softwood and hardwood are summarised in Table 1 [5]. Lignin is a heterogeneous and highly cross-linked macromolecule consisting of polymers of phenylpropane units mainly coniferyl, sinapyl or *p*-coumaryl alcohols, linked via ester, ethers or carbon–carbon bonding during biosynthesis. The structure of lignin is complex and irregular, cross-linking to different polysaccharides in the cell wall. The chemical composition of the monomers and linkages constituting the polymer differ in the different morphological regions (middle lamella, secondary wall) and wood (or other lignocellulose) types (softwood, hardwood, reeds, grasses, etc.) [6]. The principal structure of natural lignin consists of units of aryl-glycerol- $\beta$ -O-aryl ether, phenylcoumaran ( $\beta$ -5), resinol ( $\beta$ - $\beta$ ), and dibenzodioxocins (5-5/ $\beta$ -O-4, R-O-4) [7,8]. Lignin is covalently bonded to carbohydrates forming a lignin–carbohydrate network made up of benzyl-ether, benzyl-ester, acetal and phenyl-glycoside bonds. The recalcitrance of lignin in the plant cell wall and the lignin–carbohydrate interaction reduces the surface area available to chemical penetration and activity towards delignification.

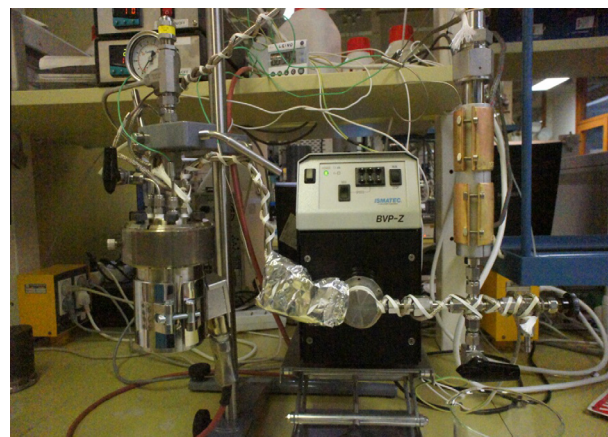
Novel processes capable of utilizing the wood components efficiently, not only as a fuel but also as materials for the production commodity and fine chemicals or constructs (i.e. templates for nanostructures, isolation or filtration materials, etc.) require selective fractionation and separation of the components into pure fractions. The separation and preparation of such lignocellulosic fractions has been a major technological challenge. In spite of the complex cross-linked matrix of lignin and other polysaccharides and the composite nature of wood, ionic liquids (ILs) have shown high efficiency for the disintegration of the crystalline lattice of native cellulose rendering it amorphous [9]. The dissolution of a large number of biomacromolecules e.g. cellulose, lignin, starch, chitin, etc. have been demonstrated in ionic liquids. Woody biomass may be solubilised completely or partially in ionic liquids at mild conditions, with hardwoods apparently dissolving faster than softwoods [10–15]. Chloride-based ILs partially dissolves fine-grained wood particles [16] and the dissolution kinetics is dependent on the size of particles or wood chips [10,11]. Improved cellulose dissolution has also been achieved using ILs based on acetate or phosphonate anions due to their low viscosity, water tolerance, the hydrogen bond interaction and the complex role played by the cation [17]. The water intolerance and challenging recycling procedures of some conventional ILs after wood fractionation make the overall process expensive.



**Fig. 1.** Switchable ionic liquid (SIL) formed from 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU), an alcohol and CO<sub>2</sub>.



**Fig. 2.** Simplified scheme of a loop reactor showing the basic operating principle.



**Fig. 3.** Picture of the loop reactor used in this work.

Recently, switchable ionic liquids (SILs) with higher thermal stability (Fig. 1) have demonstrated strong potential for the selective dissolution of hemicelluloses and lignin, resulting in enriched cellulose matrices [18–21]. SILs are salts formed from the exothermic reaction of an acid gas (CO<sub>2</sub>, SO<sub>2</sub> or other acid gases/gas mixtures) with a mixture of an organic superbases such as an amidine (e.g. 1,8-diazabicyclo-[5.4.0]-undec-7-ene, DBU) and alcohol (or other hydroxyl containing compounds) [22]. This class of ILs is capable of reversible compositional changes (polarity switch) upon the release of the acid gas facilitated by heating and/or passing an inert gas through the viscous ionic salt. The change in properties significantly affects the chemical processes involved during the reaction and separation steps.

Wood dissolution using different ionic liquids e.g. halide, acetate based, phosphonate based, switchable ionic liquids, etc. has resulted in incremental improvements in wood dissolution efficiencies; however, the effectiveness of the mass transport of dissolved species in solution has received less attention. The batch-wise operations often carried out during dissolution – and usually in the absence of mechanical agitation – result in hotspots and low transport of dissolved materials from the wood chips to the ionic liquid. Therefore, improved dissolution of components from wood chips may be achieved by decreasing the mass and heat

Download English Version:

<https://daneshyari.com/en/article/148059>

Download Persian Version:

<https://daneshyari.com/article/148059>

[Daneshyari.com](https://daneshyari.com)