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# The key role of pretreatment for the one-step and multi-step conversions of European lignocellulosic materials into furan compounds

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Nowadays, an increased interest from the chemical industry towards the furanic compounds production, renewable molecules alternatives to fossil molecules, which can be transformed into a wide range of chemicals and biopolymers. These molecules are produced following hexose and pentose dehydration. In this context, lignocellulosic biomass, owing to its richness in carbohydrates, notably cellulose and hemicellulose, can be the starting material for monosaccharide supply to be converted into bio-based products. Nevertheless, processing biomass is essential to overcome the recalcitrance of biomass, cellulose crystallinity, and lignin crosslinked structure. The previous reports describe only the furanic compound production from monosaccharides, without considering the starting raw material from which they would be extracted, and without paying attention to raw material pretreatment for the furan production pathway, nor the mass balance of the whole process. Taking account of these shortcomings, this review focuses, firstly, on the conversion potential of different European abundant lignocellulosic matrices into 5-hydroxymethyl furfural and 2-furfural based on their chemical composition. The second line of discussion is focused on the many technological approaches reported so far for the conversion of feedstocks into furan intermediates for polymer technology but highlighting those adopting the minimum possible steps and with the lowest possible environmental impact. The focus of this review is to providing an updated discussion of the important issues relevant to bringing chemically furan derivatives into a market context within a green European context.

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## 1. Introduction

The transition from petroleum-based refineries to novel bio-refineries is a key to maintaining sustainable global development and preserving the future of the planet. To adapt this context in an action plan, natural resources other than petrol should be involved as input to generate different value-added products, such as chemicals, materials, and fuels. Featured by guaranteed supply, large availability, constant production, and reasonable

cost, renewable sources constitute a key element in facing challenges reduce and fossil resource use. Vegetal biomass implication represents an advanced conception of the emerged existing model of food and paper biorefineries while producing a wide range of different platform molecules fulfilling the different societal requirements. Moreover, renewable biomass introduction has a beneficial impact on the balance of complex trade-offs among the socioeconomic and environmental points of view by promoting value-added product generation, creating new opportunities for employment, and reducing fossil resource use.<sup>1</sup> The furan compound-driven biorefinery approach, based on lignocellulosic biomass as a renewable resource, has lately evolved. The carbohydrate part of LCB (free sugars such as hexoses or pentoses, or from oligo- or polysaccharides) can be derived into versatile furan-based molecules, such as 5-HMF (5-hydroxymethylfurfural) or 2-F (2-furfural), which are promising bridges between biomass and a panel of possible chemicals and biopolymers.<sup>2</sup> In fact, 5-HMF and 2-F were identified as platform molecules since the early 2000s and both were obtained by the selective dehydration of C5 or C6 monosaccharides (including representative C5 sugars, such as D-xylose or C6 entities, such as D-glucose, D-fructose, or D-mannose).<sup>3</sup>

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Macromolecules in LCB have different susceptibilities to pretreatment, and the most common situation is hemicellulose removal as it consists of short side chains, and has a lower degree of polymerization, and inferior crystallinity compared to cellulose. During hydrothermal pretreatment, hemicellulose is easily extracted into oligo or polysaccharides or monomers as free sugars. In contrast, a low yield of cellulose is extracted into cellobiose and glucose.<sup>4-6</sup> The acid medium attacks hemicellulose and promotes its removal, and during LHW, autohydrolysis is induced through hydronium catalyzed reactions, leading to hemicellulose extraction.<sup>7,8</sup> Ionic liquids (IL) can dissolve both hemicellulose and cellulose by dint of the polarity of N–O bonds, which breaks cellulose hydrogen bond, forming new hydrogen bonds with the solute.<sup>9,10</sup> Cellulose has low solubility in deep eutectic solvents (DESs) compared to lignin and hemicellulose. DESs especially remove lignin and hemicellulose, due to their intrinsic ionic nature, which breaks the supramolecular H-bonds stabilizing the hemicellulose–lignin complex, allowing easily the breaking of the covalent bonds and leaving a cellulose rich-solid.<sup>11,12</sup> Supercritical fluids reduce cellulose crystallinity, promote its decomposition into  $\alpha$ - and  $\beta$ -glucosides and deal with direct carbohydrate hydrolysis.<sup>13</sup> The recovered sugars from cellulose and hemicellulose can be directly dehydrated to furanic compounds or undergo some added hydrolysis to be transformed. Their conversion depends on pretreatment parameters and their structural changes.

Many technical papers have been published on the only production routes involving “simple” monosaccharides such as xylose,<sup>14</sup> glucose,<sup>15</sup> and fructose.<sup>16</sup> However, this review pays excessive attention to the whole biorefinery schema starting from

raw materials from which carbohydrates would be extracted and the mass balance on the whole value chain. It is an unquestionable fact that from an industrial perspective, the issue of exploiting lignocellulosic resources, which are more strategic as sources of (C6 and C5) carbohydrates that can be converted into furan-based compounds of interest for the polymer materials sector.

Therefore, within a green European context, the present review intends to put forward two particular lines of thought. On the one hand, the choice of the most suitable lignocellulosic biomasses as the raw material to be converted into furan intermediates. Thirty-three European lignocellulosic biomasses emerging from agricultural residues, agri-food byproducts, energy crops, forest matrices, plant grasses, and non-food sectors are discussed.

On the other hand, this review describes in detail all the technological approaches allowing us to convert these matrices into furan compounds of interest. Focusing on the green processes, particularly under hydrothermal conditions and using neoteric solvents, potential carbohydrate extraction and furanic compound formation in the fewest possible steps and with the lowest possible environmental impact are investigated.

## 2. Furanic compounds' potential towards new bio-polymers

Furanic compounds, notably 5-HMF and 2-furfural, are promising “starting point” molecules derived from LCB, to form new platform molecules. Fig. 1 provides an overview of the molecular structures of the main furan entities under investigation to date. The economic and environmental stakes related to 5-HMF and 2-furfural are high and supported by multiple research

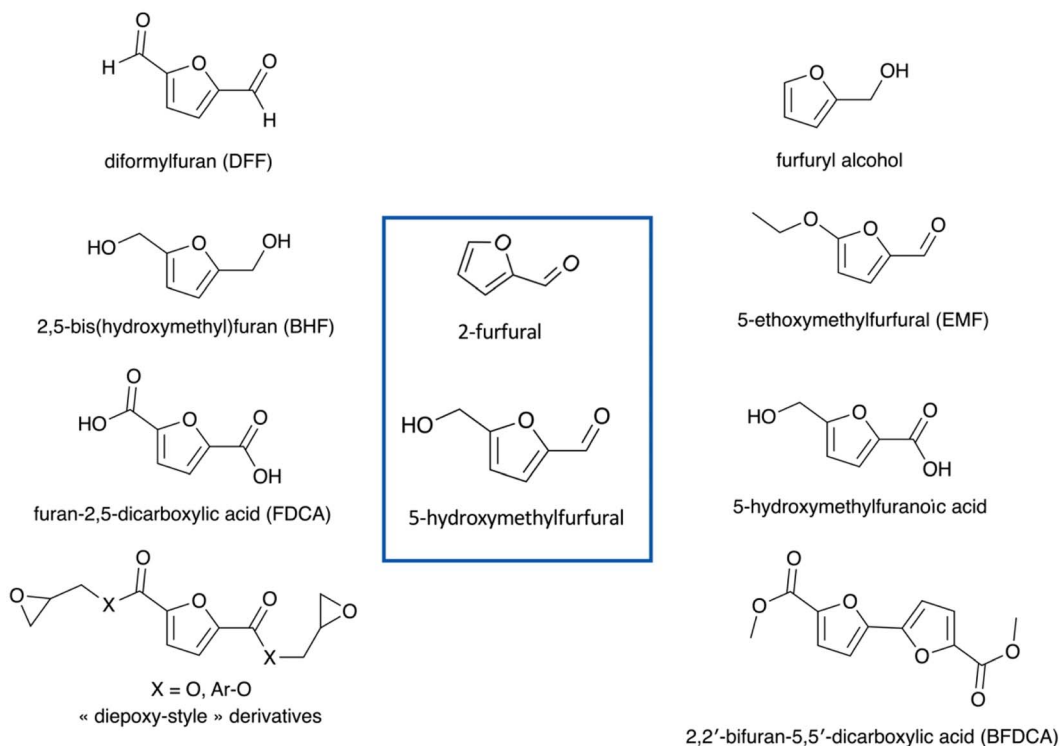


Fig. 1 Main molecules derived from 5-HMF or 2-F exploited for the design of new biobased polymers and additives (non-exhaustive list).<sup>17</sup>



initiatives on the subject, which results in abundant scientific literature.<sup>17</sup> The state of the art describes extensively the production of furans from hexoses and pentoses, which have often been considered as the “model case” studies (Fig. 2). A lot of fundamental knowledge has been gained on the role of the catalyst, the solvent (whether it is an aqueous solution, an organic solvent, or an ionic liquid),<sup>18</sup> and the reaction mechanism;<sup>19</sup> more specifically, D-glucose can be converted *via* isomerization to D-fructose, which is further dehydrated to 5-HMF, with homogeneous (inorganic acids and bases and metal chlorides) or heterogeneous (metal oxides, metal-doped zeolites, *etc.*) catalysts exhibiting basicity or Lewis acidity (for D-glucose isomerization) and Brønsted acidity (for D-fructose dehydration to 5-HMF).<sup>3,20–23</sup> Different organic solvents, mixtures of water-organic solvents, ionic liquids, and even pure water have been used as reaction media.<sup>24,25</sup> Attention should be paid to the selective production of 5-HMF instead of organic acids (levulinic acid and formic acid) and humin by-products,

stability of catalysts, and improvement of current separation methods of products, *e.g.*, use of biphasic systems.<sup>22,23,26</sup> Similarly, 2-furfural is produced from D-xylose *via* dehydration. Since the early 20s, the industrial production of 2-F is based on the acidic transformation of biomass derived C<sub>5</sub> sugars, but the low yield (50%) obtained, due to undesired side-reactions, led to further research on this process.<sup>27</sup> D-Xylose conversion to 2-furfural is catalyzed either by homogeneous organic and inorganic acids (HCl, H<sub>2</sub>SO<sub>4</sub>, metal chlorides, *etc.*) or heterogeneous catalysts, such as metal oxides and zeolites.<sup>28,29</sup> Regarding the solvents, water, organic solvents, or mixtures of water with organic solvents are frequently used.<sup>28–30</sup>

The most reported case study in the scientific literature, and the most studied by many private actors, is undoubtedly the case of 5-HMF-based furan-2,5-dicarboxylic acid (FDCA) allowing obtaining poly(ethylene 2,5-furanoate) (PEF), a possible alternative to the traditional poly(ethylene terephthalate) (PET),<sup>31</sup> but also suitable for a myriad of other biopolymers and

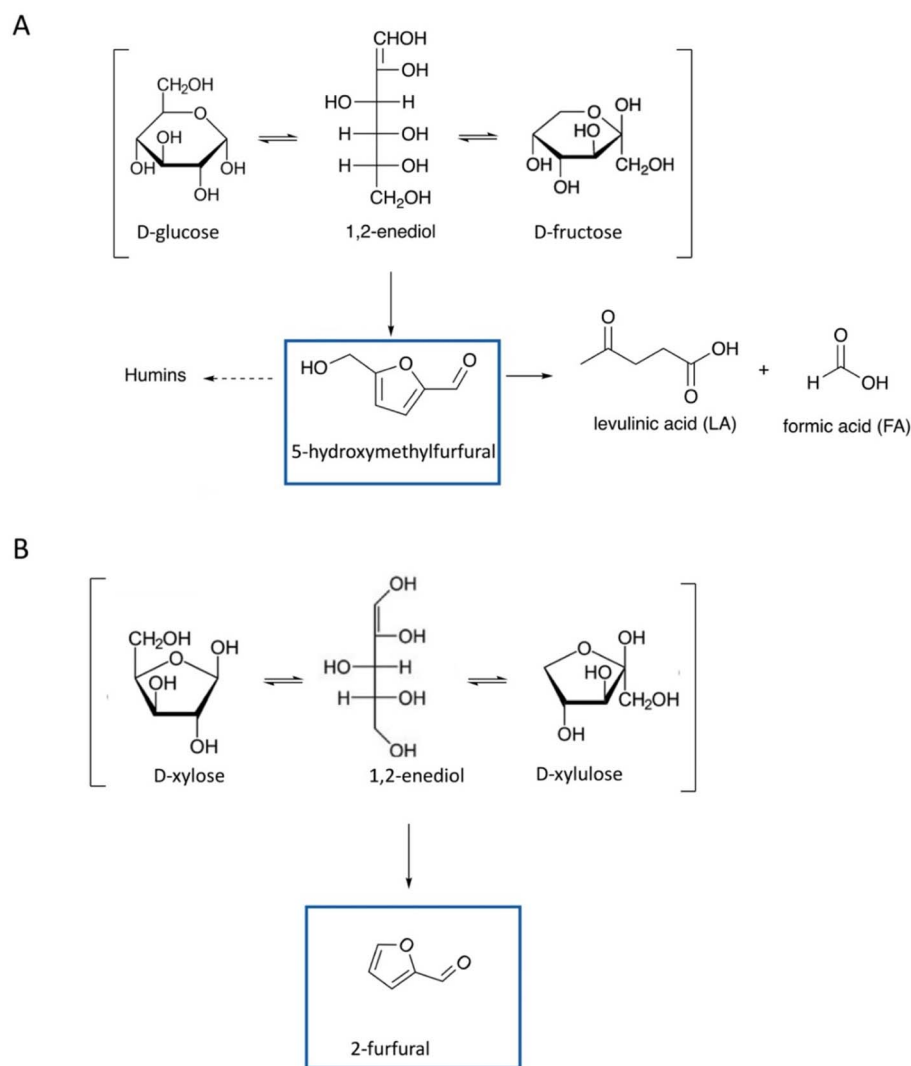


Fig. 2 Hydrothermal conversion of D-glucose (A) and D-fructose (B) into 5-HMF and derivatives. Reaction intermediates and/or subsequent decomposition (or rearrangement) products are not mentioned.<sup>18</sup>



technical additives.<sup>32</sup> Given the chemical reactivity of furan rings and the presence of C=O and C–O functional groups on whether 5-HMF or 2-F, numerous studies have been reported on the development of catalytic tools allowing their functionalization into a panel of derived molecules, among which we find 2,2'-bifuran-5,5'-dicarboxylic acid (BFDCA), which offers an alternative to bisphenol A for the design of dimethacrylate resins with thermomechanical properties comparable with those of traditional BisGMA (dimethacrylate derivative of bisphenol A).<sup>33,34</sup> The potential of 5-HMF among others is underlined through various works reported in the state of the art, with the alternative synthesis of “symmetrical” 2,5-functional derivatives such as 2,5-bis(hydroxymethyl)furan (BHF), or diformylfuran (DFF), and the “unsymmetrical” monomers such as 5-ethoxymethylfurfural (EMF), furfuryl alcohol (FA), 5-hydroxymethylfuranic acid, 5-(chloromethyl)furfural (CMF), and diamines and diepoxy analogs.<sup>35</sup> Nevertheless, the exploitation of specific chemical tools also allows obtaining other derivatives of interest for the plastics sector, with a loss of the typical furan ring structure, since it is possible to synthesize medium chain diols such as 1,6-hexanediol or even anhydrides (maleic anhydride).<sup>36</sup> It is commonly accepted that, in general, all aforementioned furan derivatives offer unique molecular architectures and notable physicochemical properties, opening new prospects in polymer science and technology. However, the great question is not on their value but rather on *how to prepare them*, starting from lignocellulosic matrices available to explore in the European context.

### 3. Lignocellulosic matrices as potential inflows for the production of furanic entities

Considering the natural composition of lignocellulosic biomass, highly enriched in carbohydrate polymers namely cellulose (source of D-glucose *via* hydrolysis) and hemicellulose (mostly rich in C5 and C6 carbohydrates),<sup>37</sup> and the attractive perspectives for 5-HMF or 2-F production therefrom, if suitable pretreatment steps are set up for its isolation, several authors' assessments for 2020–2030 have identified four strategic primary sources of lignocellulosic biomass that could support the development of biobased industrial activities, at the European level. These are (1) forest biomass, (2) agricultural residues, (3) non-food (or energy) crops, and (4) food or non-food side-products.<sup>38</sup>

However, one should have in consideration the fact that these four primary sources of lignocellulosic materials are heterogeneously distributed within the EU, both in terms of quantities and territorial repartition. This is due, among other things, to differences in climate (and soil type) between the EU member states, differences in “production tradition”, or differences in the management of the end of life of the by-products. Although it is rather complex to quantify rigorously the available biomass flows in Europe, it can be said that agricultural residues represent the most important sector with a (dry) mass of available lignocellulosic materials of 342 million tons (on an annual basis), followed by the forestry sector with

325 million tons and the forestry by-product sector accounting for 185 million tons. The food waste sector could contribute nearly 89 million tons. However, as already stated before these raw material flows are unevenly distributed in the European zone. Forestry production is massively concentrated in the Nordic countries such as Finland and Sweden, whereas France, Spain, and Slovenia are also producers but to a lesser extent. Agricultural production (mainly cereals) is strongly concentrated in France and Spain. The other European countries contribute in an equivalent way, with specificities of production. This is particularly true for sugar beet (which is produced mainly in Belgium, Germany and the Netherlands) in addition to northern France, and for olive (produced mainly in the southern countries such as Greece, Spain and Portugal).

Table 1 presents the four primary sectors of raw lignocellulosic materials as well as representative examples of interest for Europe. Table 1 also proposes the chemical composition of these lignocellulosic matrices, besides cellulose and hemicellulose previously mentioned, also the aromatic biopolymer lignin together with minor amounts of other organic components (proteins, secondary metabolites, *etc.*) and minerals.<sup>37</sup> As can be seen, this chemical composition is found specific, with cellulose contents fluctuating between 10 and 75% of the dry weight of the starting material, and hemicellulose contents oscillating between 5 and 35%. If we estimate (by simple calculation based on C6 contents) the theoretical yields of 5-hydroxymethylfurfural and 2-furfural that can be obtained, we deduce that all these raw materials are not equivalent in their strict potentiality to offer important yields of 5-HMF. The same conclusion can also be formulated if we consider the conversion of pentoses from hemicellulose to 2-F.

The analysis in Table 1 suggests that wood and its by-products as well as specific crops (such as hemp or miscanthus) or agricultural residues (cereal straws or sugarcane bagasse) offer timely potential to produce furan compounds in significant quantities. Either softwoods or hardwoods can offer (theoretically) up to one third of their weight in 5-HMF, while some by-products of the food industry seem, however, less suitable.

While the total hemicellulose content within a lignocellulosic material is a key factor to consider, it is worth mentioning that the very specific chemical nature of these hemicelluloses is also variable between the different materials presented in Table 1. The hemicellulose structure can be “homogeneous” or “heterogeneous” depending on the diversity (or not) of the “monomers” (oses) which constitute them. Amongst these “monomers”, the most representative are pentoses (xylose and arabinose), hexoses (glucose, mannose, and galactose), hexuronic acids (4-O-methyl-D-glucuronic acid, D-glucuronic acid, and D-galacturonic acid) and acetyl groups.<sup>39</sup> Based on the combination of the above building blocks, hemicellulose can be classified as xylan-based (homoxylans, glucuronoxylans, arabinoxylans, and glucuronarabinoxylans/arabinoglucuronoxylans), mannan-based (homomannans, galactomannans, glucomannan, and galactoglucomannan), xyloglucan and galactans.<sup>39</sup> As evidenced in Table 1, hemicellulose contents in wood could reach 18 to 30 wt%. Hardwoods are usually composed of xylans, while hemicelluloses in softwoods are mostly mannan and galactoglucomannan-type. Agricultural biomasses



Table 1 Chemical composition of several lignocellulosic matrices and theoretical yields for 5-HMF and 2-F productions

Matrices	Chemical composition (% referred to dry matter)					5-HMF yield <sup>a</sup> (kg)	2-F yield <sup>a</sup> (kg)
	Cellulose	Hemicelluloses	Lignin	Proteins	Inorganics		
<b>Forest biomass and grasses</b>							
Spruce	45.0	18.4	27.6	1.1	1.0	350.0	53.8
Beechwood	41.9	18.2	21.6	0.6	0.4	325.9	24.1
Hybrid poplar	39.0	17.0	25.0	3.3	2.0	303.3	103.9
Eucalyptus	46.7	17.3	28.0	0.6	0.6	363.2	65.4
Pine	38.6	20.5	29.2	0.6	4.7	300.2	36.8
Spruce barks	24.1	12.9	36.8	1.8	5.7	187.4	51.5
Willow	34.6	17.8	18.8	3.2	0.1	269.1	115.2
Birchwood	42.7	26.4	16.9	3.0	0.1	332.1	144.7
Black locust	45.0	19.0	29.0	3.6	0.8	350.0	119.7
Fresh grass	18.6	27.7	4.4	26.7	12.8	144.7	36.8
<b>Agricultural and agri-food residues</b>							
Wheat straw	40.8	35.3	8.2	2.9	7.4	317.3	152.8
Corn stovers	37.5	18.7	13.4	4.7	5.7	291.7	119.7
Sugarcane bagasse	42.1	21.5	24.0	0.9	1.6	327.4	124.2
Sugar beet pulp	28.5	28.1	9.7	9.4	5.7	221.7	135.0
Ryegrass	22.1	25.6	4.7	8.6	8.5	171.9	130.6
Olive kernels	37.7	22.8	29.1	4.4	2.7	293.2	129.9
Oat hulls	30.0	34.0	13.2	3.6	6.1	233.3	137.0
Oat straw	37.6	23.3	12.9	5.3	2.2	292.4	135.0
Fescue	31.3	15.2	19.4	7.3	11.5	243.4	97.3
Peach kernels	21.1	22.1	40.5	1.6	2.9	164.1	123.5
Apple pomace (cider industry)	23.3	24.9	15.4	3.5	1.6	181.2	51.8
Grape pomace (wine industry)	15.8	7.9	20.3	11.2	13.4	122.5	87.7
Orange peels (juice industry)	11.1	12.6	1.0	7.8	4.2	86.3	25.5
Destarched wheat bran	14.8	47.7	8.1	12.2	1.7	115.1	209.9
Spent coffee grounds	12.4	39.1	23.9	17.4	1.3	96.4	28
<b>Energy crops</b>							
Miscanthus	48.5	20.1	22.4	1.4	4.3	377.2	111
Hemp (woody core)	48.0	12.0	28.0	3.0	2.0	373.3	31.2
Switchgrass	33.5	26.5	18.1	5.3	6.4	260.6	90.2
<b>Residues from non-food sectors</b>							
Sawdust	45.1	28.1	24.2	1.3	1.2	350.8	45.2
Oak barks	24.0	13.0	25.0	1.1	9.0	186.7	55.1
Organic household waste	14.8	9.8	3.7	15.8	11.8	115.1	1.2
Garden waste	20.3	16.9	17.5	9.6	31.3	157.9	74.9
Mowing residues	38.3	31.0	6.4	4.7	7.7	297.9	36.2

<sup>a</sup> Theoretical yield (kg based on the conversion of 1 ton of dry biomass).

(cereal straws) and fresh grasses exhibit the highest amounts of hemicelluloses, mostly xylans and arabinoxylans.<sup>40</sup>

Based on these theoretical results, variable yields of 5-HMF were observed, ranging from 86 kg/ton dry raw biomass to more than 350 kg/ton dry raw biomass. These high yields were detected in rich cellulose matrices such as spruce, eucalyptus, miscanthus, and hemp sawdust. Concerning 2-F formation from hemicellulose, only pentoses were considered to calculate the theoretical yield, which oscillated between 1.2 and 209 kg/ton dry raw biomass. The most interesting lignocellulosic feedstocks to produce 2-F are pentose rich hemicellulose matrices such as destarched wheat bran, hybrid poplar, willow, birchwood, and black locust.

In addition to this purely quantitative perspective, two additional points are equally important. On the one hand, they

concern the availability of the lignocellulosic resource and its ability to be mobilized, and on the other hand the “technical” accessibility of the carbohydrate components within these lignocellulosic matrices. If the first point is related to economic, political and often territorial strategies, the second point is related to purely technical aspects linked to the efficiency of the pretreatment phases, which we will discuss below.

#### 4. Role of the pretreatment in the “lignocellulose-to-furan” pathway

In order to transform lignocellulosic matrices into 5-HMF and/or 2-F, the prerequisite remains the pretreatment step whose purpose is to separate and individualize the main lignocellulosic components. Once the structural polysaccharides are isolated,



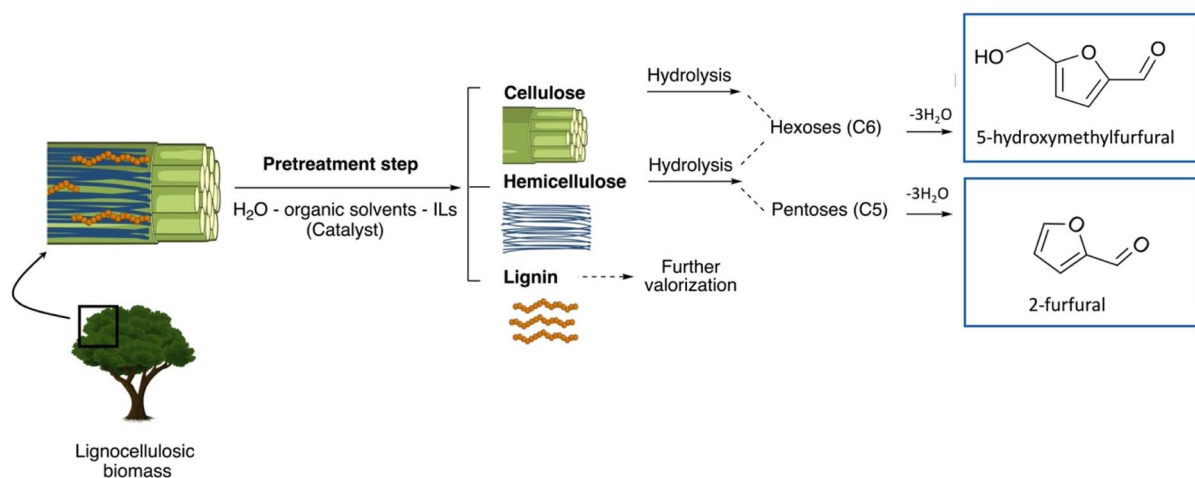


Fig. 3 Multi-step conversion of lignocellulosic resources into furanic compounds. ILs stands for ionic liquids.

subsequent hydrolysis steps (chemical or enzymatic) are then implemented to obtain the hexoses and/or pentoses that will be converted into furan derivatives (Fig. 3). Numerous pretreatment strategies are referenced in the state of the art and include chemical (acids or bases under aqueous conditions, and/or more or less innovative solvents including ionic liquids (ILs)), mechanical, and biological methods or a combination of several of these approaches. Each pretreatment method can be specific to the raw material and/or the targeted applications.<sup>41</sup> The formation of simple furanic compounds such as 5-HMF or 2-F during the pretreatment phases has been demonstrated for decades. This formation has often been avoided, especially because 5-HMF (and 2-F) is a known inhibitor of alcoholic fermentation and its presence decreases bioethanol yields.<sup>42</sup> It is recognized that pretreatment methods involving acids, whether solvent (or ionic liquid) methods with acid catalysts or hydrothermal methods, are the most likely to generate these furan species. Therefore, it is these particular pretreatment methods that are currently being used to produce specifically 5-HMF and 2-F.

#### 4.1. Hydrothermal pretreatments

Pretreatment methods that take place in the aqueous phase (with or without the addition of acid catalysts) are known under the scientific term of “hydrothermal pretreatments” (HT). They are classified as “physicochemical pretreatment” and encompass two distinct processes, namely, liquid hot water (LHW) and steam explosion (SE).<sup>43</sup> HT is recognized as a “green” process due to the absence (or minimum use) of toxic chemicals or added catalysts and was initially developed for the second-generation bioethanol production, with the aim to remove hemicellulose and partially degrade the robust lignocellulosic structure, leading ultimately to enhanced enzyme hydrolysis of cellulose to glucose. Considering the operational conditions of these processes, LHW utilizes water as the only solvent at elevated temperatures, in the range of 130–270 °C, for a time period of *ca.* 15 to 180 min depending on temperature.<sup>44–49</sup>

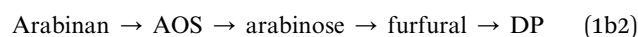
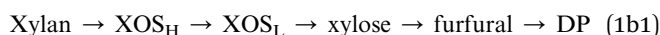
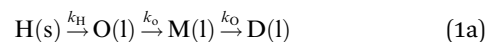
Similar to LHW, SE uses steam instead of water, under pressure (<50 bar) for relatively short reaction times (*ca.* up to 1–

10 min) in the temperature range 160–240 °C, followed by a fast explosive decompression of the high-pressure steam.<sup>43,50–52</sup>

HT pretreatment of lignocellulosic biomass has been applied on the pilot and industrial scale mainly for the production of second generation bioethanol considering also the “side” streams of hemicellulose and lignin, with Inbicon in Denmark and SEKAB in Sweden being two representative examples.<sup>53,54</sup>

**4.1.1. Hydrothermal pretreatment in neat water.** HT pretreatment has the great advantages, from a green perspective, of using only water and without addition of any acid catalyst, and hemicellulose is the main biomass component which is solubilized and partially hydrolyzed, and recovered in the liquid product stream. As discussed previously, hemicelluloses are heterogeneous polysaccharides and published results have evidenced that, generally, hardwoods are preferred for HT pretreatment due to their acetyl groups, which induce self-catalyzed mild acid hydrolysis of hemicellulose.<sup>47,55</sup> Cellulose and lignin are less affected during HT pretreatment and remain in the solid fraction, while small amounts of acid soluble lignin and extractives, such as non-structural sugars, proteins, terpenes, waxes and phenolic compounds, depending on the type of biomass, are removed to the liquid fraction.<sup>56</sup>

Hemicellulose deconstruction during LHW is carried out *via* first-order reactions, catalyzed by hydronium ions, produced due to the subcritical state of water ( $T < 374$  °C,  $P < 221$  bar).<sup>57</sup> Hemicellulose polymer (H) is initially depolymerised into oligomers (O), which with further breakdown are converted to monomers (M) and degradation products (DP). The reaction pathways and reaction steps for solubilization and hydrolysis of hemicellulose can be described by eqn (1a) and (1b).<sup>58</sup>



where  $XOS_H$  denotes the high molecular weight xylo-oligosaccharides,  $XOS_L$  the lower molecular weight xylo-oligosaccharides and AOS the arabino-oligosaccharides.

More specifically, hemicellulose in biomass is partially acetylated and, under hydrothermal conditions, acetic acid is formed *via* hydrolysis of ester bonds.<sup>59</sup> The *in situ* produced acetic acid promotes hydrolytic reactions of hemicellulose and to a lesser extent of cellulose into xylan and glucan oligomers, which can be further hydrolyzed to form xylose and glucose, respectively (Fig. 4, step 1). Under the mildly acidic hydrothermal conditions (notably for pH  $\sim$  2.5–3.5), C<sub>5</sub> sugars (xylose and arabinose) can be dehydrated towards furfural formation, which can be further converted to formic acid *via* hydrolytic

fission of the aldehyde group or to 2-furoic acid *via* oxidation (Fig. 4, step 2).<sup>47,60,61</sup>

Similarly, 5-HMF can be produced *via* dehydration of C<sub>6</sub> sugars (glucose, galactose, and arabinose) and can be further converted into levulinic and formic acids (Fig. 4, step 2).<sup>18</sup>

The extent of these reactions, as well as the biomass solubilization degree and hemicellulose removal, is controlled by the residence time and temperature of the pretreatment. Their combined effect can be expressed by the severity factor  $R_0$  (eqn (2)).<sup>62–64</sup> During HT pretreatment, water auto-ionizes into hydronium ions, leading to a pH drop, increasing the severity factor leading to promoting acetyl and uronic group cleavage, and thus improving hydrolysis reactions.<sup>65</sup>

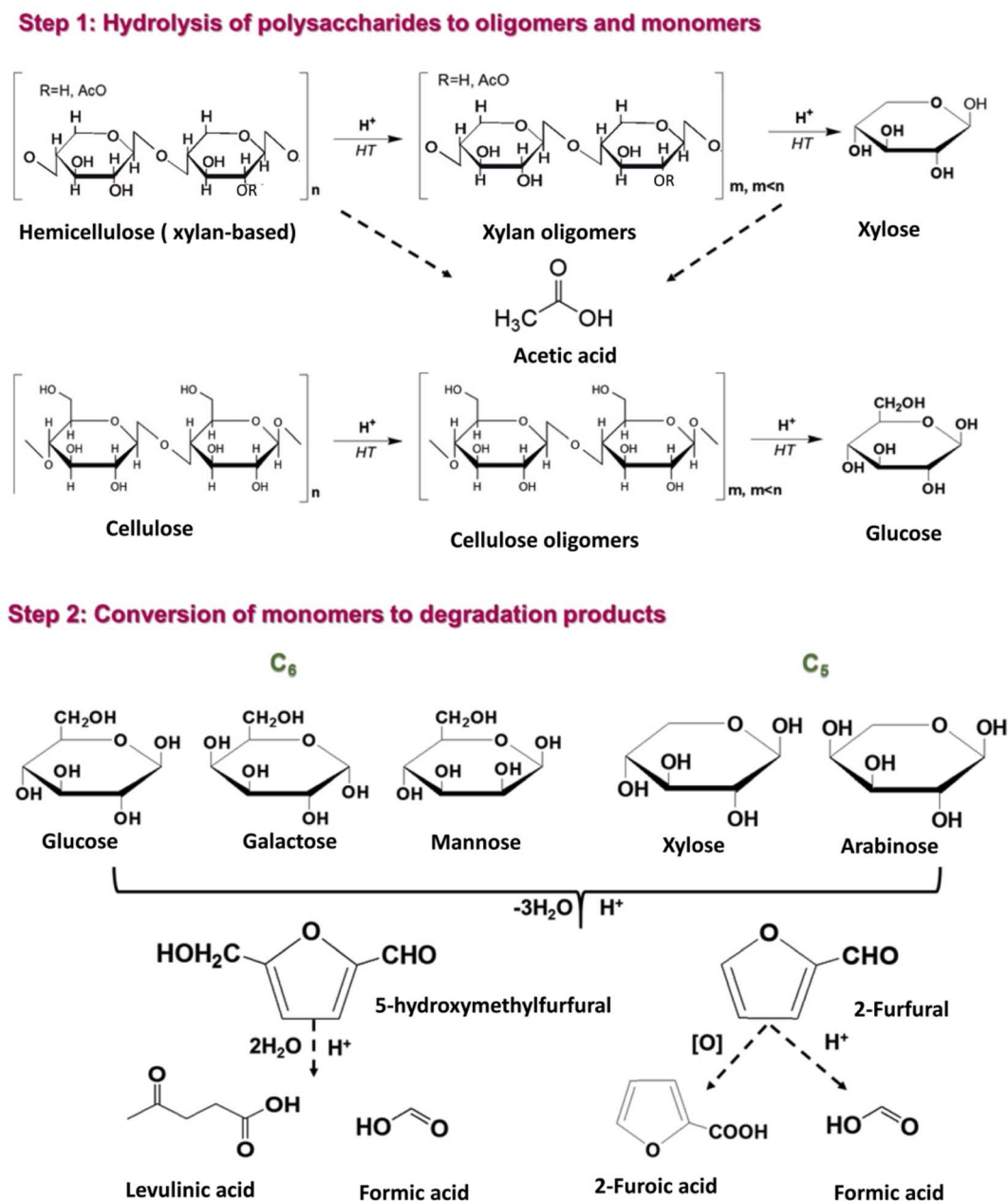


Fig. 4 Reaction pathways in the hydrothermal treatment of lignocellulosic biomass towards sugars and degradation products.



When small amounts of acid catalysts (*i.e.*, H<sub>2</sub>SO<sub>4</sub> and HCl) are used to facilitate hemicellulose hydrolysis, the modified severity factor is expressed by eqn (3), where *t* is the residence time (min) and *T* is the temperature (°C).<sup>66–68</sup>

$$R_o = t \cdot e^{(T-100)/14.75} \quad (2)$$

$$\log R'_o = \log R_o + |\text{pH} - 7| \quad (3)$$

In addition to temperature, time and use of small amounts of acids, the liquid-to-solid (biomass) ratio (LSR) may have a relatively small effect on biomass solubilization and a more pronounced impact on liquid product selectivity and yields, as discussed below.<sup>69,70</sup> Furthermore, considering the biomass particle size effects in LHW, they are correlated with heat and mass transfer limitations and it was shown that the particle size affects only sugar extraction and hemicellulose removal from biomass and not their thermal degradation in the liquid fraction.<sup>71,72</sup>

It should be highlighted that biomass particle size is a less important parameter than temperature and time and its effect is more profound in combination with that of LSR.

Considering the effect of temperature and time, under mild treatment conditions ( $\log R_o \leq 2.76$ , corresponding to  $\leq 150$  °C and short time of 15 min), low solubilization of beechwood sawdust was observed ( $\leq 6$  wt%), while under harsher conditions ( $\log R_o \geq 4.14$ , 170 °C, 120–180 min) the solubilization was increased substantially (to about 40 wt%) and complete removal of hemicellulose occurred at  $\log R_o = 4.69$ , corresponding to 220 °C and 15 min.<sup>47</sup> Regarding product yields, a maximum xylan recovery (60 wt%) in the liquid fraction was determined at 80 wt% hemicellulose removal, which was obtained at moderate severities ( $\log R_o = 3.8$ –4.1). Higher severities led to xylose degradation product formation, mainly furfural and formic acid.<sup>47</sup> Differentiations have been observed in the LHW pretreatment between softwood and hardwood biomass. More specifically, by increasing  $\log R_o$  from 3.3 to 4.7, the hardwoods, grapevine prunings and poplar branches, showed higher solubilization ranging from 28 to 48% and 23.5 to 40%, respectively, while the softwood pine sawdust was more resistant to hydrothermal pretreatment with solubilization ranging from 19 to 34%.<sup>59</sup> The recovery of xylan from poplar and grapevine and of mannan/galactan from pine in the liquid products showed a maximum of about 60% at moderate severities ( $\log R_o$  3.8–4.1), corresponding to 70–85% hemicellulose removal. By comparing the above results of the two relevant works, it can be suggested that the solubilization/removal of hemicellulose is similar for different types of hardwood biomass (forest and agricultural) and higher than that in softwood biomass (pine), while the recovery of hemicellulose in the liquids reaches a similar maximum and in the same severity region.<sup>47,59</sup>

A wide variety of forestry and agricultural residues have been hydrothermally treated in neat water: olive tree prunings with 37.6–45.3% biomass solubilization at  $\log R_o = 3.06$ –4.83 (ref. 73) and 34.4% solubilization at 3.79,<sup>68</sup> cotton stalks with 33% biomass solubilization and 82% xylan removal at 4.29 (ref. 74) bagasse with biomass solubilization of 14.8–27.6% at 2.8–4.8

(ref. 75) and xylan removal of 34.5% and 80% at 3.83 and 4.42,<sup>76</sup> eucalyptus sawdust with 0–48.2% biomass solubilization at 2.07–5.60 and 77.7% xylan removal at 3.3,<sup>77</sup> maple wood with 80% xylan removal at 4.25,<sup>78</sup> corn cobs with 10–40% biomass solubilization at 3.06–4.43 (ref. 79) and 74.1% xylan solubilization at 4.13,<sup>80</sup> poplar with 1.9–23% biomass solubilization and 6.8–62.8% xylan removal at 3.06–3.76 (ref. 81) and 50–77% xylan solubilization at 3.6–4.2,<sup>46</sup> hazelnut shells with 35.4% biomass solubilization at 4.44,<sup>82</sup> hazelnut tree prunings with 14–36% biomass solubilization and 43.2–98.5% hemicellulose removal at 3.24–4.89,<sup>83</sup> brewer's spent grains with 64.06% xylan solubilization at 4.13,<sup>80</sup> corn husks with 42% xylan solubilization at 4.13,<sup>80</sup> wheat straws with 16.5–45.7% biomass solubilization at 3.36–5.14 (ref. 84) and 39.26% xylan solubilization at 4.13 (ref. 80) and almond shells with 39.3% biomass solubilization at 3.79 (ref. 68). A correlation of pretreatment conditions (temperature and time) with biomass solubilization and hemicellulose/xylan removal, based on the above previously reported works, can be observed in Fig. 5.

Liquid to solid ratio (LSR) in LHW pretreatment can be varied in the range of 1–20 but usually is around 10.<sup>70</sup> An increase of solid concentration can raise acetic acid concentration and thus enhance the autohydrolysis mechanism. In general, biomass solubilization is slightly affected by LSR, while product distribution in the pretreatment liquor seems to exhibit differentiations. Under mild pretreatment conditions, at 160 °C for 45 min ( $\log R_o = 3.42$ ), an increase of LSR from 1 to 11 resulted in a decrease of xylose and xylan concentrations but an increase of xylose and acetic acid weight percentages (on biomass) in the liquor.<sup>70</sup> Garrote *et al.* studied the mild autohydrolysis of eucalyptus wood at 175 °C for 60 min ( $\log R_o = 3.99$ ) and found that an increase of LSR from 6 to 10 resulted in a decrease of xylose and xylan concentration, as well as a decrease of acetic acid, furfural and 5-HMF concentration in

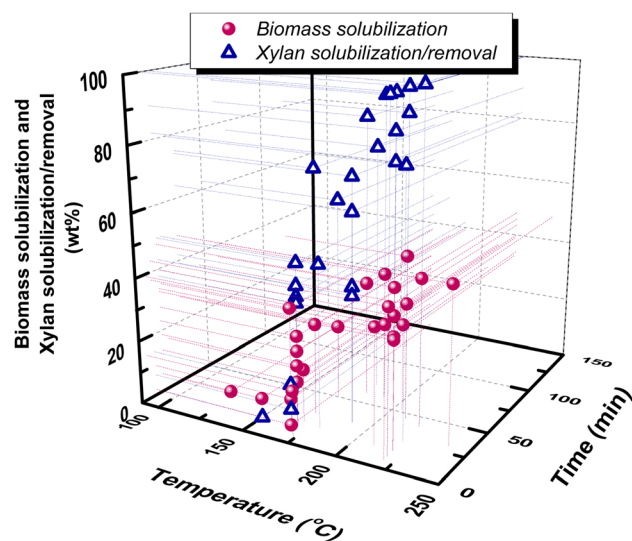


Fig. 5 Correlation of xylan solubilization/removal and biomass solubilization with hydrothermal (LHW) pretreatment temperature and time. Data are from ref. 46, 47, 59, 68, 73–75, 77–85.



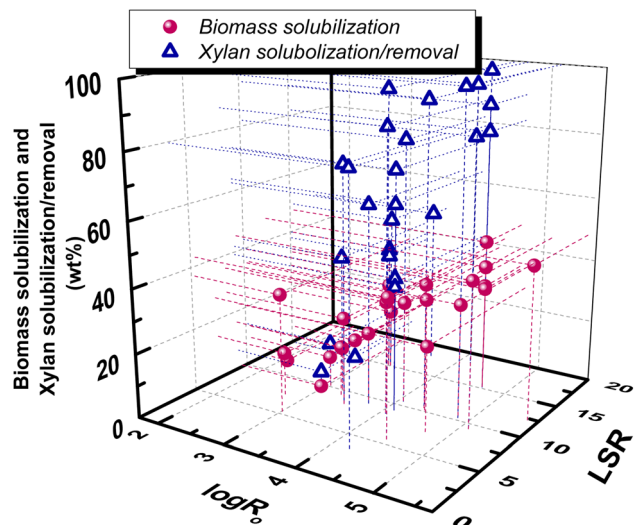


Fig. 6 Correlation of xylan solubilization/removal and biomass solubilization with hydrothermal pretreatment conditions, expressed by  $\log R_0$  and LSR. Data are from ref. 46, 47, 59, 68, 73–75, 77–85.

the liquors.<sup>69</sup> Fujimoto *et al.* studied the effect of solid concentration of the same wood under two pretreatment conditions.<sup>86</sup> At  $\log R_0 = 4.22$ , an increase of solid concentration (decrease of LSR) resulted in a decrease of xylose yield but an increase of acetic acid, furfural and 5-HMF, while at  $\log R_0 = 4.52$ , an increase of solid concentration resulted in a decrease of xylose and furfural yields but almost in similar acetic acid and 5-HMF.<sup>86</sup> A correlation of biomass solubilization and hemicellulose/xylan removal with  $\log R_0$  and LSR, based on the above previously reported works, can be observed in Fig. 6.

Steam explosion (SE) is also one of the most studied pretreatment processes of lignocellulosic biomass feedstocks. The parameters affecting the SE process are the biomass particle size, residence time and temperature. Although hemicellulose removal is indeed enhanced at elevated temperatures, it can simultaneously lead to sugar degradation.<sup>87</sup> Higher severities achieved at 270 °C for 1 min ( $\log R_0 = 5.01$ ) resulted in optimal hemicellulose solubilization towards degradation products, while lower temperature and longer residence time (190 °C, 10 min) avoided their formation.<sup>50</sup> Similar to LHW, the SE process has been applied to a vast variety of lignocellulosic feedstocks. In the SE pretreatment of banana rachis, an increase of the severity factor from 2.97 to 3.78 resulted in hemicellulose and amorphous cellulose solubilization towards monosaccharides.<sup>88</sup> Similar results were obtained for tall fescue grass, which was pretreated in a wide range of severities  $\log R_0 = 1.4$ –4.2. A gradual increase of hemicellulose removal was observed and at the highest severity, all the hemicellulose has been extracted in the liquid fraction.<sup>89</sup> SE of olive tree prunings led to 34–51% biomass solubilization at  $\log R_0 = 3.83$ –4.71, attributed to hemicellulose and extractives, while a higher hemicellulose sugar recovery of 35.6% was obtained at a severity of 4.12.<sup>90</sup>

**4.1.2. Dilute acid hydrothermal pretreatment.** The efficiency of hydrothermal pretreatment towards increased solubilization and hemicellulose removal in the liquor can be

enhanced by the use of dilute acid solutions. Alkaline conditions (NaOH or  $\text{NaCO}_3$ ) are not preferred due to the simultaneous lignin removal in the liquid fraction even under mild conditions.<sup>64</sup> Similar results were obtained in the HT pretreatment of sugarcane bagasse, where an increasing concentration of  $\text{NH}_3$  was used, which did not significantly affect hemicellulose removal but dramatically increased lignin removal.<sup>91</sup> Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) is the most widely used inorganic acid in the HT pretreatment, in various low concentrations, usually in the range of 0.1 to 2 wt%. Hydrochloric (HCl), phosphoric ( $\text{H}_3\text{PO}_4$ ) and acetic acids ( $\text{CH}_3\text{COOH}$ ) are less frequently used.<sup>92</sup> In a comparative study, HCl resulted in low lignin removal and high furanic formation, whereas  $\text{CH}_3\text{COOH}$  provided low furanic production but high lignin removal and  $\text{H}_2\text{SO}_4$  showed an intermediate performance.<sup>64</sup> Intense conditions (either high temperatures or prolonged pretreatment times) combined with relatively high acid concentrations (>2 wt%) led to higher solubilization but also induced partial degradation of sugars towards furanics and organic acids, as well as to the formation of low molecular weight phenolic compounds from lignin. Generally, addition of dilute sulfuric acid may increase the solubilization of lignocellulosic biomass feedstocks by more than 10 times, reaching 40.5 wt% solubilization, while hemicellulose removal can reach up to 100%,<sup>75,83,93</sup> as can be observed in Fig. 7. Hemicellulose sugar recovery reached 98% in HT pretreatment of brewer's spent grains at  $\log R_0 = 2.28$  combined with 1% w/v  $\text{H}_2\text{SO}_4$ .<sup>94</sup> Careful selection of pretreatment temperature, time and acid concentration can tune the composition of the liquid fraction. Indicatively, in sulfuric acid catalyzed HT pretreatment of poplar, an increase of temperature from 130 to 180 °C increased xylan degradation from 70 to 91%, initially towards xylose ( $T < 140$  °C) and further towards furanics ( $T > 140$  °C) and acids ( $T > 200$  °C).<sup>95</sup> Similarly, in acetic acid catalyzed HT pretreatment of the same wood, the higher acetic acid concentration (10% v/v) and the higher pretreatment time (50 min) resulted in 87.8% xylan removal in liquor, mainly

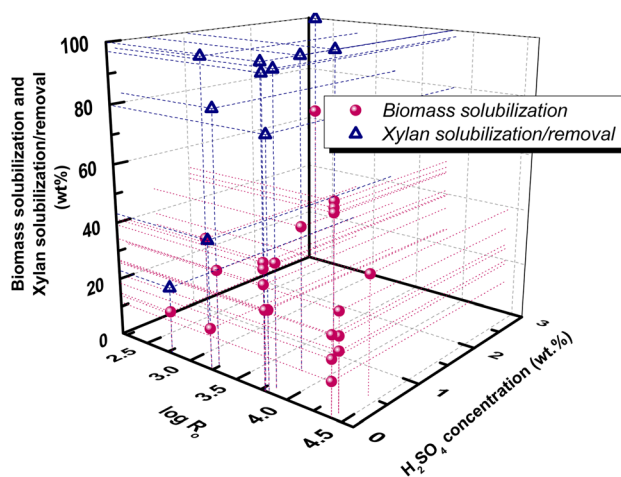


Fig. 7 Correlation of biomass solubilization with  $\log R_0$  in dilute acid ( $\text{H}_2\text{SO}_4$ , wt%) HT pretreatment. Data are collected from ref. 68, 75, 83, 93–95.



in the form of xylose (46.4%), while at lower acid concentration (5% v/v) and shorter time (30 min), xylan removal was equal to 71.3% toward xylo-oligosaccharides (55.8%) with lower xylose yield (32.9%).<sup>81</sup>

Redox environment was also pointed out as an important parameter in auto-hydrolysis and dilute-acid pretreatment of biomass. Addition of O<sub>2</sub> improved xylan removal in the liquid whose composition proved to be affected by the severity of the conditions. Under the most severe conditions in the presence of O<sub>2</sub>, xylan was removed towards the formation of furanics (furfural, 2-furoic acid, and 5-HMF) and organic acids (acetic acid, formic acid and levulinic acid), resulting also in lower glucan recovery in the solid fraction.<sup>75</sup> Alternatively to the classic heating, microwave heating has been applied in the acetic acid catalyzed corn stover leading to higher heating rate and high glucose yield in the solid fraction.<sup>96</sup>

In SE pretreatment the addition of acid catalysts or the impregnation of wood chips with acids prior to pretreatment is more often, allowing for significantly decreased residence temperature and time, and inducing improved hydrolysis rate, decreased degradation products and increased removal of hemicellulose and lignin.<sup>87</sup> Addition of 1 wt% H<sub>2</sub>SO<sub>4</sub> in the pretreatment of almond shells, olive tree prunings and grapevine prunings resulted in similar biomass solubilization (53.5%, 50.4% and 49.9%, respectively) but with different hemicellulose recovery percentages (14.19%, 27.68% and 43.31%, respectively) in the liquid fraction.<sup>68</sup> Immersion of wheat straw in 0.2% H<sub>2</sub>SO<sub>4</sub> prior to SE resulted in 36–48% biomass solubilization at log R<sub>0</sub> = 2.95–4.24 with increased recovery of hemicellulose in the liquid fraction, while glucose remains in the solid.<sup>97</sup> Apart from sulfuric acid, other inorganic acids have been also utilized in the catalyzed SE pretreatment and H<sub>3</sub>PO<sub>4</sub> resulted in slightly higher sugarcane bagasse solubilization compared to H<sub>2</sub>SO<sub>4</sub>.<sup>66</sup>

**4.1.3. Effect of HT pretreatment on biomass/cellulose enzymatic digestibility.** The majority of pretreatment studies target the efficient removal of hemicellulose and/or part of lignin, in order to limit the inhibition phenomena in the subsequent biochemical processes towards 2G-bioethanol production, *i.e.*, the enzymatic hydrolysis of cellulose and hemicellulose into monomeric sugars and their subsequent fermentation. The pretreated solids are more susceptible to glucose production by hydrolysis with cellulases (*exo/endo*-glucanases, *etc.*) and in the last years, to xylose production in the presence of xylanases.<sup>98</sup> In a following step, the produced sugars are converted to ethanol *via* microbial fermentation. The above processes can be combined in one step and the process is known as simultaneous saccharification and fermentation (SSF) or simultaneous saccharification and co-fermentation (SSCF).<sup>99</sup> As a consequence, optimization of biomass pretreatment is crucial for the efficient valorization towards ethanol production. Both LHW and SE may induce structural and physicochemical alterations in biomass particles, such as the disruption of the lignocellulose complex and rigid structure, increase of particle external surface area and accessibility of enzymes, hydration and crystallinity decrease of cellulose, as well as removal of hemicellulose and part of lignin *via*

depolymerization into low molecular weight fragments.<sup>48,100,101</sup> Generally, HT pretreatment enhances biochemical processes with moderate to intense HT conditions, resulting in maximum yields of glucose or ethanol.<sup>47,73,86</sup> HT pretreatment also proved to facilitate microbial activity during anaerobic digestion for methane production.<sup>102</sup> Furthermore, delignification of HT solids may further facilitate enzymatic hydrolysis. Removal of “surface” lignin, *i.e.*, partially solubilized lignin during HT pretreatment that has been recondensed on the biomass surface, can be achieved by mild extraction with “green” and easily recoverable solvents, *e.g.*, acetone or ethanol, resulting in a 25% increase in enzymatic digestibility.<sup>103</sup> The complete delignification of HT solids showed controversial effects on enzymatic hydrolysis. Alkaline post-treatment of HT-hazelnut shells, with NaOH either in water or in ethanol/aqueous solutions, as well as through organosolv and acid-catalyzed organosolv post-treatments did not improve the enzymatic hydrolysis of cellulose to glucose compared to the direct acid catalyzed organosolv pretreatment of raw biomass.<sup>82</sup> On the other hand, sequential organosolv-hydrothermal pretreatment of cotton stalks resulted in higher ethanol production.<sup>74</sup> Similarly, delignification of HT vine shoots with NaClO<sub>2</sub> in aqueous solution of acetic acid led to enhanced ethanol production.<sup>104</sup> Ball milling of HT solids prior to the hydrolysis was proved to enhance the enzymatic digestibility of cellulose to glucose.<sup>77,105</sup>

**4.1.4. Production of furanics (furfural and 5-HMF): cascade (two-step) and *in situ* (one-step) processes during HT pretreatment.** Instead of studying the conversion of “purified” monosaccharides into furanics as described in Fig. 1, process modelling and optimization studies have been performed utilizing “real” streams of hydrothermally pretreated biomass and down-stream catalytic hydrolysis and dehydration steps, in order to evaluate the potential industrial scale production of 5-HMF where heat integration, and mass and energy balance are also critical.<sup>106</sup>

The one-step (*in situ*) aimed production of furanics from raw biomass feedstocks during HT pretreatment in neat water is rarely referred in the literature, despite its evident usefulness. The HT pretreatment of lignocellulosic feedstocks results in relatively low yields of furfural and 5-HMF, in the range of 0.05–2 wt% on initial biomass, which are usually not considered as the primary target but as degradation by-products.<sup>64,73,107</sup>

As can be observed in Fig. 8, the concentration of furfural in the pretreatment liquor may reach up to 5 mg ml<sup>-1</sup> in a wide range of log R<sub>0</sub> = 2.5–4.7, thus indicating that other parameters in addition to temperature and time, such as biomass type, may have an important effect. The concentration of 5-HMF is even lower, not exceeding 1 mg ml<sup>-1</sup> in most cases. The addition of homogeneous catalysts in the hydrothermal pretreatment process can improve the *in situ* production of furanics. Dilute inorganic acids under severe conditions of LHW pretreatment resulted in higher furanic production.<sup>94,95,108</sup>

However, intense hydrothermal conditions in the presence or absence of dilute acids, at *ca.* log R<sub>0</sub> > 4, usually lead to enhanced “loss” of biomass carbon as humins or even gaseous products.<sup>47,48,109</sup>



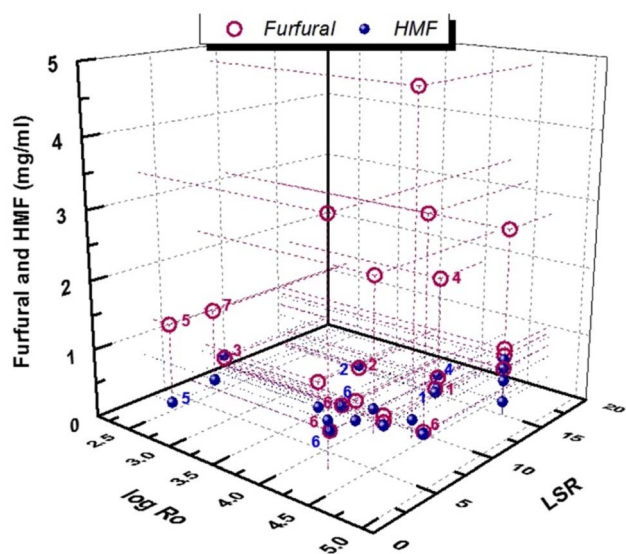


Fig. 8 Furanic production via LHW pretreatment. Numbers correspond to acid concentrations: 1: 0.5% v/v  $\text{H}_2\text{SO}_4$ , 2: 1% v/v  $\text{H}_2\text{SO}_4$ , 3: 1.6 w/v  $\text{H}_2\text{SO}_4$ , 4: 400 g  $\text{kg}^{-1}$   $\text{CH}_3\text{COOH}$ , 5: 3 wt%  $\text{H}_2\text{SO}_4$ , 6: 0.5 wt%  $\text{H}_2\text{SO}_4$ , and 7: 3% w/v  $\text{H}_2\text{SO}_4$ . Purple numbers correspond to furfural and blue numbers to 5-HMF. Data are from ref. 47, 59, 75, 76, 78–80, 85, 92, 94, 95, 108, 114 and 115.

Aiming to avoid mineral acids, metal chlorides can be utilized as catalysts in the HT pretreatment, which under optimal reaction conditions can convert almost 98% of corn stover hemicellulose towards furfural production (25% wt% of liquid product) without significantly affecting cellulose and lignin.<sup>110</sup> In broader research, poppy stalk carbohydrates were converted to furfural and 5-HMF in neat water over a wide range of metal chlorides and among them,  $\text{CuCl}_2$  was the most active, resulting in 79.9% furfural and 12.2% 5-HMF production yields (based on xylose and glucose of raw biomass) under optimized conditions.<sup>111</sup> In general, hydrothermal pretreatment under intense conditions, low LSR and addition of inorganic acids may enhance the production of furfural and 5-HMF, but care of biomass degradation to humins should be taken. To this end, direct furfural and 5-HMF production from lignocellulosic biomass can be further enhanced using co-solvents, which can also minimize the humin formation. The most promising co-solvents are  $\gamma$ -valerolactone (GVL), tetrahydrofuran (THF) and dioxane, which can partially replace water in the hydrothermal pretreatment and enhance the furanic production in the presence or absence of catalysts.<sup>25,29,112,113</sup>

Another important parameter considering the viable production of furanic compounds from lignocellulosic biomass is their separation and recovery from aqueous pretreatment solutions. Generally, adsorption, distillation, precipitation or solid/liquid phase extraction is applied to selectively recover 5-HMF and furfural. High costs derived by large amounts of solvent consumption and scaling issues led to most suitable processes. 5-HMF recovery from aqueous solutions via extraction has been studied with many solvents, but methyl isobutyl ketone (MIBK) and 2-methyltetrahydrofuran (2-MTHF) gained great interest due to the high recovery yields of 5-HMF.<sup>116,117</sup>

Similarly, furfural can also be recovered from aqueous solutions either via classic extraction separation or  $\text{CO}_2$  assisted phase separation.<sup>118–120</sup> Considering a low cost and environmentally friendly solvent, 2-pentanone is an alternative for furfural separation, providing low separation load in case of downstream conversion of furfural to fuels, because 2-pentanone can also be converted to hydrocarbon fuels.<sup>121</sup> Another interesting approach is the recovery of both furfural, 5-HMF and acetic acid from aqueous solutions with polyethylenimine, a soluble polyelectrolyte, which was successfully applied in biomass pretreatment slurries to remove the fermentation inhibitors.<sup>122</sup> Similarly, furanics and acetic acid can be removed from the hydrolysate via sorption on activated charcoal and anion exchange resins.<sup>108</sup>

#### 4.2. Neoteric solvents as reaction media for pretreatment and conversion of lignocellulosic matrices

Neoteric solvents have gained interest in the last decade and have been deeply investigated as alternative media for the pretreatment and the conversion of the lignocellulosic feedstock into furanic derivatives. In particular, the use of ionic liquids (ILs), deep eutectic solvents (DES) and supercritical fluids is discussed, highlighting the advantages, strengths, and opportunities of their use in this field. These neoteric solvents present unique properties in comparison with traditional solvents, allowing not only the development of more efficient processes in terms of diversity of materials and catalytic efficiency but also the reduction of the environmental impact for the key treatments and synthetic transformation required to transform lignocellulose materials into high-added value products.

**4.2.1. Pretreatment of biomass feedstock in ILs.** Ionic liquids (ILs), which are very particular solvents composed exclusively of ions and generally having negligible vapour pressure, high thermal and chemical stability, and outstanding solvation potential,<sup>123,124</sup> have emerged as an attractive alternative for the production of furan-derived compounds from biomass.<sup>125</sup> The specific properties of the ILs can be fine-tuned by the right design and combination of anion and cation components. It is estimated that combination of the possible cations and anions would result in the formulation of more than ( $10^{12}$ ) potential ILs,<sup>126</sup> so one can infer the huge flexibility of this class of solvents. Importantly, the structure of the ILs can be adjusted to be used not only as a solvent for an efficient biomass pretreatment, but also to enable its catalytic transformation into valuable chemicals and biofuel.<sup>127–133</sup>

The pretreatment of the biomass is a key step for its further conversion into chemical products. In this regard, ILs are among the most efficient solvents for the dissolution of lignocellulosic biomass (*i.e.*, wood chips, straw, cornhusks, *etc.*).<sup>134</sup> Hence, ILs offer a simple alternative to conventional pretreatment methods. Imidazolium based ILs represent the most common type of ILs but pyridinium, phosphonium, morpholinium and ammonium derived ILs have also been evaluated for biomass pretreatment.<sup>135,136</sup> While they are generally considered to be ecofriendly compounds due to their non-volatility and non-flammability, the green calcification of the ILs should be



carefully considered as some of them present potential toxicity and biodegradability issues.<sup>137</sup>

Nevertheless, ILs are efficient media for the fractionation of biomass into its components, some of them being a suitable feedstock (*i.e.*, polysaccharides and sugars) for the production of 5-HMF. The typical initial step is the heating of the biomass in the presence of the ILs. The generated non-covalent interactions with the structural elements of the involved biomass help to disrupt the non-covalent interactions between lignocellulose components, leading to its dissolution without significant degradation.<sup>138</sup> Different solvents (*i.e.*, acetone-water mixtures, alcohol, or dilute acid) are added to the mixture or removed from it (*i.e.*, by evaporation) in order to induce the precipitation of the different components of the lignocellulosic biomass.<sup>139</sup> This type of process requires, for every step, a well-designed separation and purification of the product from the IL-phase, as well as an energy-efficient recycling of the IL, if

a potential industrial application of ILs for biomass pretreatment is envisaged (Fig. 9) as well as in the perspective of a green chemistry approach.

The initial reports of biomass dissolution dealt with cellulose. Although the first report on the dissolution of cellulose in a mixture of 1-ethylpyridinium chloride and a nitrogen-containing base dates back to 1934,<sup>140</sup> it was not until the seminal work of Rogers *et al.* that the potential of room temperature ILs for cellulose dissolution was fully revealed.<sup>141</sup> The IL-dissolved cellulose could be regenerated without severe degradation by addition of water or other precipitating solvents (*e.g.*, ethanol or acetone). In general, regarding the structure of the cation, decreasing the length of the alkyl chains (decreasing their hydrophobic character) or introducing allyl chains improved the dissolution power of the ILs.<sup>142</sup> On the other hand, anions like  $\text{Cl}^-$ ,  $\text{HCOO}^-$  and  $\text{OAc}^-$  provided good dissolution capacity. These anions are relatively small and good hydrogen

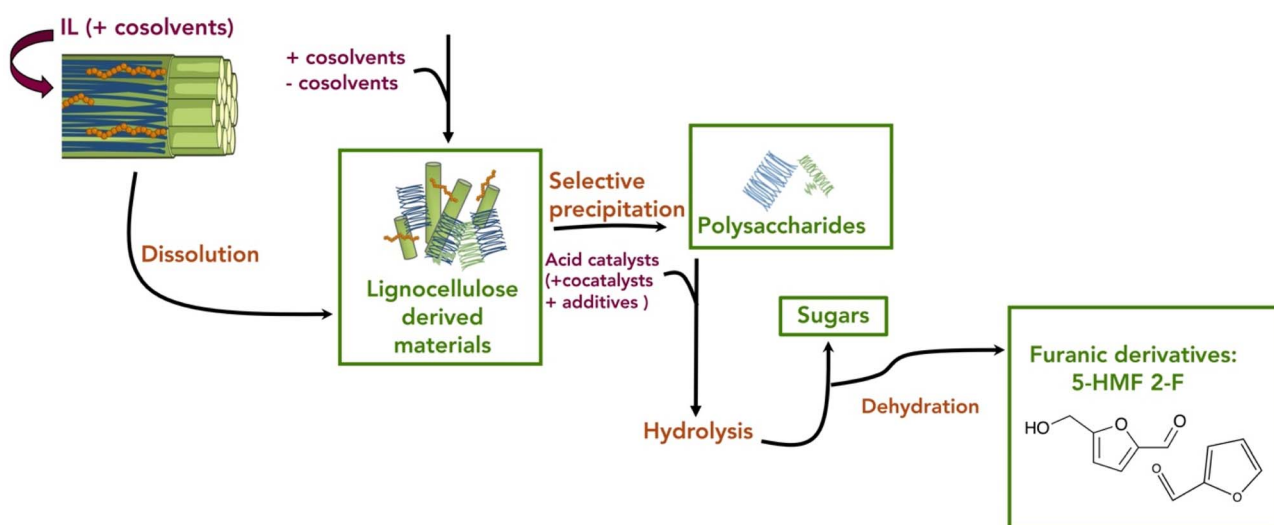


Fig. 9 General scheme for the preparation of furanic derivatives in IL-based processes.

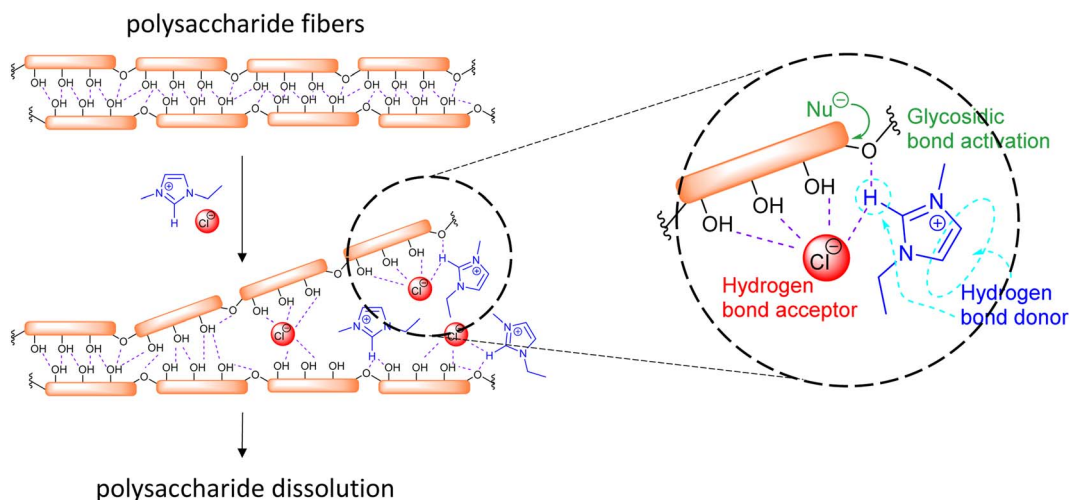


Fig. 10 Schematic representation of the main interactions involved in the dissolution and activation for hydrolysis of polysaccharide fiber in ILs.



bond acceptors, favouring the formation of hydrogen bonds with the acidic hydrogen atoms of the hydroxyl groups of the polysaccharides. In imidazolium cations, the proton on the C2 position of the ring is relatively acidic and can also form hydrogen bonds with the oxygen atoms in cellulose (Fig. 10).<sup>143,144</sup> Possible additional interactions (*i.e.*, van der Waals interactions and hydrophobic effects) have been also claimed to occur between the cation and the cellulose.<sup>145,146</sup> The use of an additional organic solvent with the ILs can induce co-solvency and anti-solvency effects.<sup>35</sup>

Later studies have demonstrated that ILs can be used to process different types of lignocellulosic biomass, such as agricultural residues, dedicated energy crops and forest biomass.<sup>147,148</sup> As for cellulose, ILs' structure and properties can be fine-tuned to improve the capacity for dissolving lignocellulosic biomass from different sources (Fig. 11).<sup>32,149,150</sup> The most commonly used ILs for lignocellulosic pretreatment are [EMIM][OAc] (1-ethyl-3-methylimidazolium acetate), [AMIM][Cl] (1-allyl-3-methylimidazolium chloride) and [BMIM][Cl] (1-butyl-3-methylimidazolium chloride).<sup>10</sup> The appropriate design of the IL can lead to a reduction of the required dissolution temperature, price, ecotoxicological profile and viscosity, which are key factors to enable their industrial implementation. A simple to prepare, biocompatible and low cost (~\$1 per kg) protic IL such as ethanolamine acetate has been reported for the direct production of biofuels *via* one-pot synthesis.<sup>151</sup> Protic ionic liquids are a subset of ILs produced through the combination of a Brønsted acid and a Brønsted base.<sup>152</sup> In this example, after pretreatment of switch grass, the whole slurry is directly used for simultaneous saccharification and fermentation with commercial enzyme cocktails and wild type yeast strains, generating 70% of the theoretical ethanol yield. On the other hand, the so called *ionoSolv* process based on the use of triethylammonium hydrogen sulfate ([TEA][HSO<sub>4</sub>]) as a protic ionic liquid has been implemented for the fractionation of even highly recalcitrant feedstocks and for separation of cellulose-rich pulp and lignin fractions.<sup>153,154</sup> In addition, the easy recycling, high yields, and low pretreatment times facilitate potential commercialization of this process.<sup>155</sup>

Apart from the fractionation of the biomass, ILs can also be used as solvents for the depolymerisation of polysaccharides like cellulose, hemicellulose, inulin or starch into the

corresponding sugars.<sup>32</sup> As mentioned above, the basic anion from the IL disrupts the crystallinity of the polysaccharide that is transformed into an amorphous structure by interfering with the hydrogen bonding network, enhancing its dissolution but also facilitating its modification. On the other hand, the interaction between the cation and the glycosidic moieties of the polysaccharide makes the carbohydrates more susceptible to hydrolysis. Thus, the addition of an acid catalyst, either homogeneous (*i.e.*, sulfuric, acetic, oxalic acids, *etc.*) or heterogeneous (Amberlyst, zeolite, MOF, *etc.*), to the polysaccharide dissolved in the IL facilitates the catalytic hydrolysis of the glycosidic bonds linking the sugar monomers in the polysaccharide, leading to its depolymerisation into the corresponding monosaccharide.<sup>156</sup> Alternatively, different task-specific ILs displaying a built-in acid function in the cation (*e.g.*, -SO<sub>3</sub>H and -COOH) or/and in the anion (*e.g.*, HSO<sub>4</sub><sup>-</sup>) have been designed to play a dual role as a solvent for the dissolution of the polysaccharide and as an acid catalyst for its hydrolysis into sugars.<sup>128,157</sup>

**4.2.2. Converting biomass feedstock into 5-HMF.** ILs in the presence of an additional catalyst or playing by themselves a catalytic role can also provide a pathway for the transformation of monosaccharides into 5-HMF.<sup>16,158</sup> It has been observed that ILs minimise decomposition of the produced HMF in comparison with other conventional solvents, which is a step forward within the green chemistry principle of waste-prevention. This stabilization of 5-HMF from decomposition provides a great potential for the use of imidazolium ILs in highly selective and efficient biomass-derived 5-HMF synthesis, even though imidazolium-based ILs are associated with toxicity issues. Lansalot-Matras *et al.* demonstrated that the presence of ILs in IL/DMSO mixtures had a positive effect for the acid-catalyzed dehydration of fructose to 5-HMF.<sup>159</sup> Thus, under catalyst-free conditions a 27% 5-HMF yield was reported after 15 h by adding 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF<sub>4</sub>]) to DMSO, while in pure DMSO only trace amounts of 5-HMF were obtained. The yield could be further improved using a polymer-supported acid (Amberlyst-15) as a co-catalyst, reaching an 87% yield in 24 h. These results indicate the non-innocent nature of the ILs in the conversion of fructose to 5-HMF.

Lewis acidic cations such as those in metal chlorides are also suitable catalysts for the dehydration of fructose to 5-HMF.<sup>160</sup>

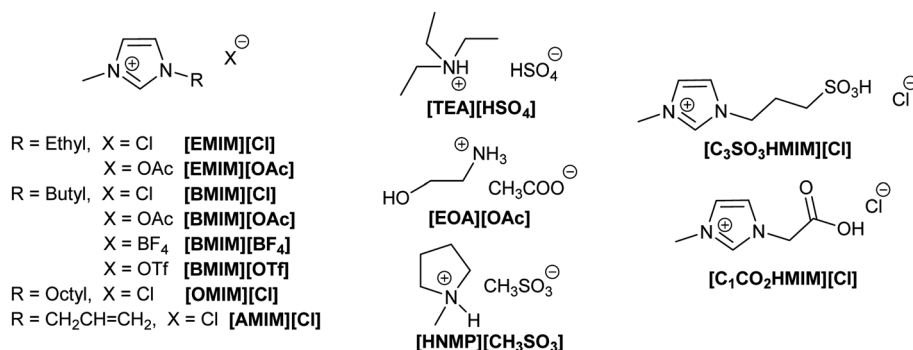


Fig. 11 Some examples of ILs used for the processing and transformation of lignocellulose.



Zhang and co-workers demonstrated that metal chlorides (*i.e.*, CrCl<sub>2</sub>) dissolved in 1-alkyl-3-methylimidazolium chloride can efficiently catalyse the synthesis of 5-HMF from fructose, while other less potentially harmful metal chlorides in [EMim]Cl showed poor activity or very low selectivity to 5-HMF.<sup>161</sup> From the tested imidazolium ILs displaying different *N*-alkyl chain lengths (octyl, butyl and ethyl) the one with the shorter chain ([EMIM][Cl]) provided the higher yield (73% 5-HMF yield at 120 °C).

5-HMF can also be obtained from other sugars, although the efficiency of the reaction is significantly affected by the nature of the feedstock. When sucrose is used (a disaccharide of glucose and fructose) the sugar is nearly quantitatively transformed into 5-HMF and unreacted glucose.<sup>87</sup> Indeed, to convert glucose to 5-HMF, longer reaction times and higher reaction temperatures are required. Two different reactions are needed to convert glucose into 5-HMF: (i) isomerization of glucose into fructose, and (ii) dehydration of fructose to 5-HMF. The coordination of the ILs with a metal salt enables the proton transfer at the isomerization required to convert glucose into fructose.<sup>162</sup> The nature of the ILs defines again the reaction conditions (temperature and time) and the yield obtained. In general, ILs containing imidazolium cations combined with nucleophilic anions such as halides (*e.g.*, Cl<sup>-</sup> or Br<sup>-</sup>) led to more efficient conversions of sugars into 5-HMF.<sup>32</sup>

Zhao and co-workers achieved a significant conversion of cellulose and glucose, with *ca.* 60% and 90% isolated yields, respectively, mediated by CrCl<sub>3</sub>/[BMIM][Cl] under microwave irradiation (MW).<sup>163</sup> Microwave heating allowed for a remarkable reduction in the time required (from hours to minutes). Thus, the combined use of MW and ILs can lead to a fast and more cost-effective process for the conversion to 5-HMF in comparison with conventional heating.<sup>164,165</sup> Because of the high dielectric constant and the ionic nature of the ILs, the reaction is heated up quickly, volumetrically and simultaneously leading to a more efficient heating.<sup>166</sup> For instance, up to 97% yield of 5-HMF can be obtained from fructose in [BMIM][Cl], in the absence of catalyst, in only three minutes under microwave irradiation.<sup>167</sup> The combination of [BMIM][Cl]/CrCl<sub>3</sub> yielded *ca.* 70% of 5-HMF from glucose in only thirty seconds, which represents a yield significantly higher than the one obtained under conventional heating (*ca.* 48% 5-HMF yield). With this system, a 5-HMF yield of 54% was obtained for cellulose conversion at 150 °C during 10 min of reaction time, with the [BMIM][Cl]/CrCl<sub>3</sub> being recyclable for six cycles of use.<sup>168</sup>

J. P. Hallett and co-workers have reported the efficient use of [BMIM][OTf] for the synthesis of 5-HMF from fructose. The water content plays an important role in stabilising the obtained 5-HMF and in suppressing side reactions. Thus, high yields (>80% 5-HMF yield) from high substrate loadings (14% w) can be obtained in a short reaction time (<10 min), even with the use of non-coordinative ILs and halide anion free ILs.<sup>169</sup>

The use of ILs as reaction media can also decrease the operational temperature required for the dehydration of sugars to 5-HMF with a reduction in the energy requirements and operational costs. In general, under conventional conditions temperatures as high as 100 to 300 °C are needed. However, when ILs are used, much lower temperatures, in the range of

80–140 °C or lower, can be usually applied, which constitutes a major advantage from the energetic point of view. Indeed, Smith, Qi and co-workers have reported an efficient catalytic system for the conversion of fructose into 5-hydroxymethylfurfural at room temperature.<sup>170</sup> Reactions proceeded smoothly and efficiently with 78–82% 5-HMF yields at 25 °C after pre-dissolving the fructose into [BMIM][Cl] and subsequently adding a small amount of a co-solvent (*i.e.*, acetone, DMSO, ethanol, *etc.*) and using Amberlyst-15 as the catalyst. The transformation of fructose to 5-HMF can also be achieved with a high yield (>90% HMF yield) at room temperature using multicatalytic systems such as [BMIM][Cl]/WCl<sub>6</sub>,<sup>171</sup> or a mixture of [BMIM][Cl] and an acid IL like [HNMP][CH<sub>3</sub>SO<sub>3</sub>] (*N*-methyl-2-pyrrolidonium methyl sulfonate).<sup>172</sup> This reduction of the temperature can allow for the continuous extraction of 5-HMF by using organic solvents with low boiling points. This can simplify the implementation of large-scale biphasic continuous systems enabling the 5-HMF separation and recovery by solvent distillation and the recycling of the catalytic IL-phase for subsequent catalytic cycles.

Despite being more challenging than the conversion of fructose, other complex carbohydrates such disaccharides (*i.e.*, sucrose, maltose, lactose and cellobiose)<sup>173</sup> and polysaccharides (*i.e.*, inulin, cellulose, chitosan and starch)<sup>87</sup> can also be transformed to 5-HMF using ILs. The nature of the ILs, the co-catalyst and the reaction conditions should be properly adjusted depending on the feedstock, as the increase in the degree of polymerization of the feedstock gradually decreases the efficiency of the catalytic system. ILs, being compatible with different catalytic units, also open the possibility to integrate different steps required for the synthesis of furanic derivatives (*i.e.*, dissolution, hydrolysis, isomerization, dehydration, *etc.*) in a multistep cascade process, where the product from one step becomes the feedstock of the next one without any need of purification processes between them. This integration can save time and energy in pretreatment and isolation steps, increasing profitability and enabling its industrial implementation. For instance, the combination of two metal chlorides (CuCl<sub>2</sub>/CrCl<sub>2</sub>) dissolved in [EMIM][Cl] (1-ethyl-3-methylimidazolium chloride) catalyzes the single-step conversion of cellulose to 5-HMF with an unrefined 96% purity among recoverable products (at 55% 5-HMF yield at 80–120 °C).<sup>174</sup> The catalytic performance of the CuCl<sub>2</sub>/CrCl<sub>2</sub>/[EMIM][Cl] catalytic system can be preserved after the isolation of 5-HMF, keeping the activity for at least three consecutive runs. Some other paired metal catalytic systems have been studied, such as CrCl<sub>2</sub>/CuCl<sub>2</sub>, CrCl<sub>2</sub>/CrCl<sub>3</sub>, CrCl<sub>3</sub>/FeCl<sub>3</sub>, CrCl<sub>3</sub>/FeCl<sub>2</sub>, CrCl<sub>3</sub>/AlCl<sub>3</sub>, CrCl<sub>3</sub>/SnCl<sub>4</sub>, CrCl<sub>3</sub>/MnCl<sub>4</sub>, and CrCl<sub>3</sub>/CuCl<sub>2</sub>, in this context.<sup>175,176</sup>

In the search of low-temperature, one-pot processes, Raines and co-workers used *ortho*-carboxyl-substituted phenylboronic acids as organocatalysts, together with MgCl<sub>2</sub>·6H<sub>2</sub>O/H<sub>2</sub>SO<sub>4</sub>, to convert cellulose and cellulose-rich municipal waste (*i.e.*, cotton, paper towels, and newspaper) to 5-HMF in [EMIM][Cl] at 105 °C. 5-HMF yields as high as 41% could be achieved with a catalytic system that is devoid of heavy metals.<sup>177</sup>

A variety of related catalytic systems have been exploited for lignocellulosic biomass conversion to 5-HMF. In these systems,



the ILs assist the dissolution and fractionation of the biomass, and as a source of active sites for subsequent transformation of sugars to 5-HMF.<sup>17,32,53,72,75</sup> For instance, corn stalk, rice straw and pine wood treated with  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}/[\text{BMIM}][\text{Cl}]$  produced 5-HMF and furfural in 45–52% and 23–31% yields, respectively, after 3 min.<sup>178</sup>

In summary, IL solvent systems have shown a huge potential for the preparation of 5-HMF from biomass. They can be used for the pretreatment and conditioning of different lignocellulosic materials and for the saccharification of the polysaccharides into the sugars needed for the synthesis of furanic compounds. They also allow the integration of the pretreatment and transformation of different types of natural feedstocks into 5-HMF in a single process. However, there are still some challenges for the acceptance of this technology as a feasible alternative to conventional processes. Among them, we can highlight the reduction of the IL price, the decrease in viscosity, which is an important technical parameter, the improvement in cellulose dissolving capacity, the selection of ILs not providing additional environmental concerns, and the reduction of the conditions required to carry out the corresponding processes at ambient temperature. There is also a need to develop simple strategies for an efficient separation/recovery of all the elements (*i.e.*, products, catalysts, ILs, and co-solvents) used in the process. A simple and efficient separation and reuse of the IL-phase can mitigate the concerns on their cost.<sup>179</sup> Although different approaches have been proposed for the isolation of 5-HMF and the recovery of ILs, such as the use of supercritical  $\text{CO}_2$  or high-vacuum entrained distillation, or the use of membranes, these approaches are still far away from being suitable for large scale 5-HMF production.

**4.2.3. Use of deep eutectic solvents (DESS).** Deep eutectic solvents can also be used for the pretreatment of biomass (*i.e.*, delignification and solubilization of cellulose) and as reaction media for its further conversion to 5-HMF.<sup>180,181</sup> Deep eutectic solvents (DESS) are special liquid solvents resulting from the mixture of two components: a hydrogen-bond donor (HBD) and a hydrogen-bond acceptor (HBA) (Fig. 12).<sup>182,183</sup> The mixture of these components, forming strong hydrogen-bonding interactions, presents an eutectic point temperature below that of an ideal liquid mixture. DESS share some of the properties of ILs (*i.e.*, low volatility and nonflammability) but they are often easier to prepare, and typically display low cost, low toxicity for

properly selected components, and can be prepared from highly biodegradable raw materials.<sup>184</sup> Research into the use of DESS is still in the early stages of development especially compared to IL-based technologies, but they have already been successfully applied for biomass pretreatment, carbohydrate conversion, and lignin valorization. For instance, the pretreatment of eucalyptus wood with the DES prepared from choline chloride and lactic acid (ChCl–lactic acid) afforded >80% of delignification and 94% yield of glucose.<sup>185</sup> The ChCl–citric acid DES was proposed as both a solvent and catalyst for the dehydration of fructose to 5-HMF and resulted in 78% yield of 5-HMF at 80 °C after 1 h.<sup>186</sup>

Su and co-workers have developed the dehydration of glucose to 5-HMF under continuous flow conditions using  $\text{CrCl}_3 \cdot [\text{N}_{2222}][\text{Cl}]/\text{EG}$  as the catalytic system. A 42% 5-HMF yield was obtained at 150 °C using 10% glucose in only 3.64 min residence time, while under batch conditions only a 10% yield was reached in a much longer period (30 min).<sup>187</sup> After the reaction, the products were extracted with ethyl acetate as the solubility of the DES and  $\text{CrCl}_3$  in ethyl acetate was negligible. The treated catalytic system could be efficiently recycled for four runs.

Catalytic valorization of native biomass has been systematically evaluated in the choline chloride/oxalic acid DES system.<sup>188</sup> This acidic DES promotes transformations of structurally branched glucans, fructans, or xylans into glucose (yields up to 68%), fructose (yields up to 60%), xylose (yields up to 73%), 5-HMF (yields up to 14%), or furfural (yields up to 72%). A choline chloride–formic acid– $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  (ChCl–Fa– $\text{SnCl}_4$ ) catalytic system has been reported for the transformation of herbal residues into furanic derivatives.<sup>189</sup> Up to 67% total furfural and xylose yield from herbal residues of *Heteropogon contortus* (L.) Beauv was reached at 140 °C in 10 min. The same catalytic mixture led to a total yield of 93.8% of 5-HMF and glucose from herbal residues of *Anemarrhena asphodeloides* Bunge at 120 °C.

A better understanding of the mechanistic aspects for both pretreatment and conversion of the biomass in DES media is required to be able to design more efficient systems. There is also a need to increase the thermal stability of the DES as well as developing efficient ways to isolate/recover the products and for the recycling of the DES-based systems.

**4.2.4. Application of supercritical fluids.** The use of supercritical fluids (scFs) constitutes another promising

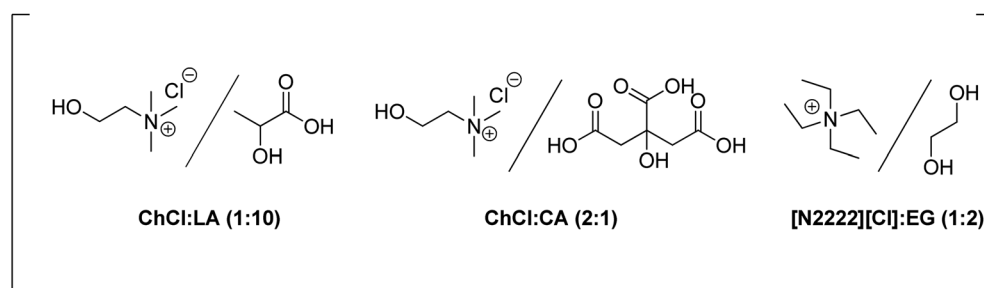


Fig. 12 Some examples of DESSs used for the processing and transformation of lignocellulose. ChCl: choline chloride, LA: lactic acid, CA: citric acid,  $\text{N}_{2222}$ : tetraethylammonium, and EG: ethylene glycol.



alternative for the pretreatment, fractionation and conversion of biomass into furanic derivatives. ScFs present a series of properties (*i.e.*, gas-like mass transfer with liquid-like solvation), which can be exploited to achieve a simpler fractionation/pretreatment, depolymerisation and conversion of the reducing saccharides into furanic derivatives. The use of high temperatures and pressures is an economic bottleneck for the widespread utilization of supercritical pretreatment techniques on a large scale. However, supercritical fluids are a mature technology currently industrially applied for a wide range of processes dealing with biomass (*i.e.*, supercritical extraction). In the same cases, the additional cost can be compensated by not requiring the addition of any catalyst or solvent and the high quality of the building blocks obtained free of impurities that may hamper further valorization of the biomass (*i.e.*, fermentation). In this context, sub- and supercritical CO<sub>2</sub> have been evaluated to develop the concept of green biorefineries.<sup>190</sup>

Supercritical CO<sub>2</sub> (scCO<sub>2</sub>) presents a low critical pressure and temperature (7.4 MPa and 31.0 °C) in comparison with other supercritical fluids (*i.e.*, 22.1 MPa and 374.2 °C for scH<sub>2</sub>O). Furthermore, CO<sub>2</sub> can be considered as a low cost, nontoxic, non-flammable, readily available solvent and can be easily removed from the final product by simple de-pressurisation.<sup>191</sup>

scCO<sub>2</sub> has proved as a suitable tool to perform the treatment of lignocellulosic biomass prior to biological processing.<sup>192,193</sup> Thus, scCO<sub>2</sub> has been used for cellulose pretreatment, reducing its crystallinity by *ca.* 50% and enabling its enzymatic hydrolysis to glucose.<sup>194</sup> An enhancement of up to 18–51% in the yield of reducing sugars can be achieved from dilute acid hydrolysis of scCO<sub>2</sub>-pretreated corncob, cornstalk, and rice straw.<sup>195</sup> Other systems included H<sub>2</sub>SO<sub>4</sub>-catalyzed cascade hydrolysis–dehydration of rice husk enabled by CO<sub>2</sub> extraction, which directly gave furfural in a high yield of around 90%.<sup>196</sup>

High-pressure CO<sub>2</sub> in contact with water produces, in a reversible way, carbonic acid.<sup>197–199</sup> This has opened the way to the direct use of this carbonic acid as an environmental friendly catalytic system for the dehydration of carbohydrates to 5-HMF.<sup>200</sup> Yields of 5-HMF from fructose, glucose, sucrose, and inulin of *ca.* 67%, 36%, 50%, and 47%, respectively, at 190 °C and 2 MPa of CO<sub>2</sub> in a mixture of 2-propanol/water have been reported.<sup>201,202</sup> This evidences the capacity of CO<sub>2</sub> to provide an acid catalyst for an environmentally friendly synthesis of 5-HMF from carbohydrates, achieving efficiencies comparable to those obtained with a typical homogeneous or heterogeneous acid catalyst.

Supercritical water (scH<sub>2</sub>O) is another scF used for processing and transforming lignocellulosic materials.<sup>203</sup> Subcritical and supercritical water exhibit unique characteristics, including increased diffusivity and decreased hydrogen bonding and dielectric constant. By varying the temperature and pressure of the water, its dielectric constant ( $\epsilon$ ) decreases, from  $\epsilon \sim 78$  under room conditions to  $\sim 6$  at the vapor–liquid critical point, increasing dramatically, at this point, the solubility of organic compounds.<sup>204</sup> On the other hand, the ion product of supercritical water is two orders of magnitude higher than that at ambient temperature. High concentrations of H<sup>+</sup> and OH<sup>-</sup> can be obtained in SCW, and it is possible to provide a perfect

environment for acid- or base-catalysed reactions.<sup>205,206</sup> These properties can be exploited to develop hydrothermal pretreatment processes, under sub-critical and supercritical conditions, in the absence or presence of an additional acid catalyst, for the selective production of reducing sugars. A novel technology for the continuous and selective hydrolysis of cellulose and biomass to sugars has been reported based on the use of scH<sub>2</sub>O in a fast heating and fast cooling reactor. This reactor set-up together with the unique properties of the scH<sub>2</sub>O allows for the dissolution and hydrolysis of cellulose in a very short reaction time.<sup>207,208</sup> At 400 °C and 25 MPa, a total recovery of C-5 sugars was achieved in 0.19 s, while the highest yield of C-6 sugars (65% w/w) was achieved at 0.22 s reaction time. The main hydrolysis product of C-6 and C-5 sugars was glycolaldehyde (20% w/w), while 5-HMF production was highly inhibited (yields lower than 0.5% w/w). The process for the hydrolysis of biomass in scH<sub>2</sub>O has been scaled-up from laboratory to pilot plant scale. Sugar beet pulp and wheat bran were used to validate the scaling up. The larger particle size (250  $\mu$ m vs.  $\leq 150$   $\mu$ m) used for the pilot plant scale slows down the hydrolysis. This reduction increased the selectivity and reduced sugar degradation (degradation yield < 15%). For sugar beet pulp, the yields for sugars were 55% and 66%, respectively for pilot plant and lab experiments, respectively. However, the selectivity reached values around 90% for both sugar beet pulp and wheat bran in the pilot plant.<sup>209</sup>

Low yields of 5-HMF have been reported for the treatment of fructose in supercritical water in the presence of 10 mM H<sub>2</sub>SO<sub>4</sub> (35% selectivity, 80% conversion, 25 MPa, 180 °C, 600 s residence time). The substitution of scH<sub>2</sub>O by supercritical acetone in the presence of water (acetone : water 90 : 10) resulted in higher yields of 5-HMF (77% selectivity, 98% conversion, 20 MPa, 180 °C, 120 s residence time).<sup>210</sup> Alternatively, when the reaction was carried out in scMeOH, the corresponding furfural ether was obtained (methoxymethylfurfural, MMF, 79% selectivity, 99% conversion, 20 MPa, 240 °C, 2 s residence time), while the reaction in subcritical acetic acid (scAcOH) afforded the corresponding furfural-ester although in lower yields (5-acetoxymethylfurfural, AMF, 38% selectivity, 98% conversion, 20 MPa, 180 °C, 120 s residence time).<sup>211</sup>

#### 4.3. Critical assessment of potential of pretreatment technologies for carbohydrate extraction and furanic compound formation

A comparison between the different pretreatment approaches based on the carbohydrate recovery and furan yield is summarized in Table 2. The hydrothermal pretreatment is cheap and effective for hemicellulose extraction by selective hydrolysis of ether bonds, resulting in a high sugar recovery. LHW and steam explosion do not require any chemical recovery after the process, but low product concentrations are recuperated without catalysts. Regulating different parameters (temperature, time, LSR, and dilute acid catalyst), the formation of 2-furfural can be promoted. This treatment can be applied in a wide range of biomass types, such as hardwood and softwood forestry and agricultural residues as well as food industries and food wastes.



Table 2 Main effects of lignocellulosic structure and furanic compound yield related to pretreatment technology

Pretreatment	Main effects on biomass structure	Carbohydrate removal/recovery	Key furanic compounds yields
Hydrothermal	LHW	-Complete hemicellulose removal -Structural changes on cellulose	-Low yield of 5-HMF and furfural in catalyst-free conditions (0.05–2 wt%) <sup>64,72</sup> -With catalysts conditions, CuCl <sub>2</sub> , up to 79.9% furfural and 12.2% 5-HMF production yields <sup>111</sup> Furfural yield up to (11.09%) <sup>212</sup>
	Steam	-Fiber separation -Auto-hydrolysis and partial. Solubilization of the hemicelluloses	
	Dilute acid	-Reduction of cellulose crystallinity -High recovery of sugars from hemicellulose -Low recovery of sugar from cellulose	
	-Enhance cellulose accessibility to enzymes -Conversion of soluble hemicelluloses into fermentable sugars	-Hemicellulose recovery up to (98%) <sup>94</sup> -Xylan removal up to (87.8%) <sup>81</sup>	
Neoteric	Ionic liquids	-Dissolution of cellulose and hemicellulose	-Catalyst-free conditions: 27% 5-HMF yield <sup>159</sup> -With catalyst conditions: 54–80% 5-HMF yields <sup>159,161,168,169</sup> -5-HMF yields (42–78%) <sup>187,214</sup>
	DES	-Liquid phase is rich in hemicellulose sugar -Cellulose is in pretreated solid phase	-Glucose yields (32–94%) <sup>185,213</sup> -Xylose yield up to (73%) <sup>188</sup>
	Supercritical fluids	-Promote hemicellulose decomposition and decrease cellulose crystallinity	-Glucose yields (14–51%) <sup>192</sup> -Furfural yield up to (70%) <sup>188,189</sup> -5-HMF yields (18–67%) <sup>201,202</sup>

Supercritical fluid pretreatment is attractive because it is non-toxic and nonflammable to extract carbohydrates and transform them into furanic compounds. This method is effective for high cellulose and hemicellulose content biomass such as wheat straw, sugar beet pulp, oat hulls, apple pomace, and garden waste. However, similarly to hydrothermal treatment, it requires high temperature and pressure.

In ionic liquid media, depending on the based solvent, complex polysaccharides can be solubilized by breaking  $\beta$ -O 4-bonds, thus enabling their application to a wide range of lignocellulosic biomass feedstocks, by fine tuning the treatment parameters and catalysis to achieve optimum lignocellulosic fractionation and conversion. One major advantage of ILs is the fact that they do not require high pressure, can be recyclable, and when adequately selected they can have low toxicity. However, this solvent has severe drawbacks that may hamper upscaling, the fact that they are not easy to prepare and some of them are considered toxic.

With a similar mechanism, deep eutectic solvents have the same advantages over ILs since they tend to be cheaper and easier to formulate. Furthermore, DESs can degrade the physical structure of the biomass with minimal energy consumption during pretreatment, comparable with the chemical and physical methods in terms of energy consumption and conversion efficiency. This treatment type can be applied on biomass enriched in cellulose, such as spruce, beechwood, hybrid poplar, birchwood, black locust, fescue, miscanthus, hemp, and sawdust. The drawback of their high viscosity requires a high consideration on a pilot scale together with cost effective strategies for the recovery and reuse of the DESs in multiple cycles without compromising their performance.

## 5. Circular biorefinery as a transitional object of the bioeconomy

Integrating lignocellulosic biomass as an alternative non-fossil resource is an incentive for developing a bio-based economy. Biorefineries are based on renewable feedstocks that can be assembled from several supply categories, available at low cost in a short time throughout the year.

From an environmental point of view, the oil refinery is a main contributor to carbon dioxide and air pollution. Conversely, biomass-based biorefineries utilize a wide range of feedstocks: (i) cultivated biomass, whose growth contributes to carbon capture from the atmosphere and storage for varying periods of time,<sup>215,216</sup> and (ii) exploited biomass which was earlier left untouched or burned for energy needs, causing a significant amount of greenhouse emission, and therefore its exploitation contributes to waste management and reduction in polluting gas emissions.<sup>217</sup>

Unlike petroleum-based refineries, where the process is costly due to the needed oxidation step to synthesize hydrocarbons, in biorefineries, renewable feedstocks are naturally rich in oxygen and converted into functional intermediates with lower energy.<sup>217</sup>

Shifting toward green and sustainable biorefineries is a prospect for the future circular bioeconomy. It can start with integrating biomass-based refineries with current petrochemical refineries by exploiting the current infrastructure, thus minimizing the startup cost of the biorefinery. In addition to that, several processes, notably chemically catalyzed reactions already used in petroleum refineries, can be adapted for biorefineries.



Technoeconomic assessment is a needed tool to design novel circular biorefinery schemes. This analysis starts with an economic analysis of process scalability from the laboratory to pilot and industrial scales. Based on the laboratory study, the equipment cost can be estimated with the scaling exponent for each equipment (eqn (4))<sup>218</sup> and adjusted to the base year using the Chemical Engineering Plant Cost Index (CEPCI) expressed by (eqn (5)).<sup>219</sup>

$$CAE = CBE \times \left( \frac{EC}{EBC} \right)^f \quad (4)$$

where CAE: calculated actual equipment, CBE: base cost equipment, EC: equipment capacity, EBC: equipment base capacity, and  $f$ : empirical scaling exponent.

$$AC = C_o \times \frac{CEPCI}{CEPCI_o} \quad (5)$$

where AC = adjusted cost,  $C_o$ : reference cost, CEPCI: studied equipment price, and  $CEPCI_o$ : equipment base price.

The pretreatment method cost is directly associated with capital expenditure (CAPEX) and operational expenditures (OPEX). CAPEX consists of start-up and fixed costs (FC), which englobes equipment. Regarding hydrothermal and supercritical fluid treatment, the reactor vessel is the most expensive in capital cost.<sup>220</sup> For example, in LHW pretreatment ( $14.33 \times 10^6$  L, at 180 °C, 10 min, and 20% solid:water ratio), a fixed capital investment of (US\$  $102 \times 10^6$ ) represents 28.17%.<sup>219,221</sup> In subcritical conditions, the pretreatment of lignocellulosic biomass for industrial processes of the order of 310 tons of feedstock daily represents US\$  $27.4 \times 10^6$  of the FC, and 35% (US\$  $9.6 \times 10^6$ ) is associated with the reactor.<sup>219,222</sup> However, in the case of the ILs and DESs, the capital cost of the reactor is expected to be lower than that of supercritical fluids and hydrothermal treatment, which require special instrumentation for high temperatures and excessive pressure.<sup>155</sup>

OPEX are subcategorized into direct production costs, including raw material, waste steam charges, and fixed operating costs, including labor and general expenses.<sup>223</sup> In the case of supercritical fluid and hydrothermal pretreatment, the energy demand dominates as the major operating cost and represents around 70% of OPEX.<sup>224</sup> For example, the needed heat required for lignocellulosic biomass treatment under these conditions varied between  $610 \text{ kJ kg}^{-1}$ <sup>225</sup> and  $1096 \times 10^6 \text{ kcal day}^{-1}$ .<sup>222</sup> However, the hydrothermal process is carried out without using chemicals or catalysts.<sup>219</sup> And among supercritical fluids,  $\text{scCO}_2$  presents the lowest cost compared to other supercritical fluids.<sup>139</sup>

Unlike HT and ScFs, OPEX in IL and DES-based biorefineries concerns mainly chemicals. ILs suffer from high costs ranging from \$20 to  $101 \text{ kg}^{-1}$ . A bulk-scale of 1-methylimidazolium hydrogen sulfate was studied in order to decrease the cost index ratio to 1.47 and an exchange rate of  $1.1 \text{ \$ } \text{€}^{-1}$ .<sup>155</sup> However, DESs are cheaper than ILs and easily recyclable, where operating costs dropped significantly from \$1573.56 million to \$1060.03 million when DES recycling time increased from 5 to 20.<sup>226</sup>

Optimizing the total cost in biorefineries is recommended depending on the base treatment type. For example, in

hydrothermal conditions using higher solid loading can improve energy efficiency,<sup>221</sup> and implementation of renewable energy, like wind farms, can contribute to achieving lower prices of electricity.<sup>227</sup> Concerning DES and IL-based pretreatment, some improvements can be made by reducing costs and loading, and increasing recycling.<sup>226,228</sup>

## 6. Conclusions and outlook

It is an unquestionable fact that fossil resources available for the world population are facing environmental, economic, and social challenges. As an alternative, biomass constitutes an inexhaustive source for platform molecules such as 5-hydroxymethylfurfural and 2-furfural. Both of them can be derived from lignocellulosic carbohydrates to form new chemicals and bio-based polymers. Therefore, a screening of chemical identification and quantification of major molecules of four categories of LCB, including forest biomass and grass, agricultural and agri-food residue, energy crops, and residues from non-food sectors, showed that these renewable resources revealed a considerable potential within the European context to be exploited for furanic compound formation aiming at their use in the bioplastic industry.

In a green chemistry context, an updated overview of eco-friendly pretreatment technologies was comparatively reported to efficiently convert them into furans. Regarding the hydrothermal pretreatment in neat water, hemicellulose is completely solubilized and recovered in the liquid fraction. Solubility of biomass, hemicellulose removal and liquid fraction composition are strongly related to the severity and the process parameters, mainly temperature and time. Furfural and 5-HMF yields are increased under more severe conditions, but attention should be paid to avoid carbon loss due to humin formation. Alternatively, the formed humins can be upgraded by recovering them followed by added-value material production. Aiming to increase the isolation of hemicellulose as xylose monomers in the liquid fraction, dilute acid pretreatment at relatively lower temperature is preferred, coupled with controlled downstream dehydration of xylose to furfural. Contrarily, neoteric solvents solubilize carbohydrates and result in high furanic compound yield.

Lignocellulosic biomass is an attractive renewable source to be exploited for bio-based molecule production for new polymers and additives. However, there are challenges for the wide-scale commercialization of these value-added products to satisfy the community demands.

As a starting premise, it is recommended that future investigations for further industrial development take into account the following gaps:

- Tackle the whole value chain system including (i) feedstock cultivation, harvesting, collection, transport, and storage; (ii) processes concerning biomass pretreatment technologies and monosaccharide extraction; (iii) intermediate molecule production notably 5HMF and 2-F, (iv) and finally desired products such as chemicals, biomaterials, and biofuels.
- Ensure sustainable biomass supply regarding geolocation, storage, and transport logistics.



- Manage development practices of standardized process techniques to achieve the most adequate process conversion.
- Establish different combined approaches using efficient green processes to fulfil sustainable production.
- Provide an action plan to adapt commercialization and eventually application of produced furanic products.

## Abbreviations

2-F	2-Furfural
2-MTHF	2-Methyltetrahydrofuran
5-HMF	5-Hydroxymethylfurfural
AOS	Arabino-oligosaccharides
BFDCA	2,2'-Bifuran-5,5'-dicarboxylic acid
BHF	2,5-Bis(hydroxymethyl)furan
ChCl	Choline chloride
CMF	5-(Chloromethyl)furfural
DES	Deep eutectic solvents
DFF	Diformylfuran
EMF	5-Ethoxymethylfurfural
FA	Furfuryl alcohol
FDCA	Furan-2,5-dicarboxylic acid
GVL	$\gamma$ -Valerolactone
HBA	Hydrogen-bond acceptor
HBD	Hydrogen-bond donor
HT	Hydrothermal pretreatments
ILs	Ionic liquids
LCB	Lignocellulosic biomass
LHW	Liquid hot water
LSR	Liquid-to-solid ratio
MIBK	Methyl isobutyl ketone
PEF	Poly(ethylene 2,5-furanoate)
PET	Poly(ethylene terephthalate)
scCO <sub>2</sub>	Supercritical CO <sub>2</sub>
ScFs	Supercritical fluids
SE	Steam explosion
THF	Tetrahydrofuran
XOS <sub>H</sub>	Xylo-oligosaccharides
XOS <sub>L</sub>	Xylo-oligosaccharides

## Conflicts of interest

There are no conflicts to declare.

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