**The production of furfural directly from hemicellulose in lignocellulosic biomass: A review**

Yiping Luoa,b, Zheng Lia, Xiaoling Lia, Xiaofeng Liub, Jiajun Fanc\*,

James H. Clarkc, Changwei Hua\*

a Key Laboratory of Green Chemistry and Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu, Sichuan 610064, P. R. China.

b Chengdu Institute of Biology, Chinese Academy of Sciences, Chengdu, Sichuan 610041, P. R. China.

c Green Chemistry Centre of Excellence, Department of Chemistry, University of York, York, YO10 5DD, U.K.

**Abstract：**As one main component of lignocellulosic biomass, hemicellulose is a promising alternative for the replacement of limited fossil resources to produce furfural, thus preserving a high atom efficiency. However, the complex structure of hemicellulose and the interaction between the other two components in lignocellulosic biomass (cellulose and lignin) make the effective utilization of naturally formed structure of hemicellulose challenging. This review presents an overview of the production of furfural directly from hemicellulose in lignocellulosic biomass with special emphasis on achieving the effective utilization of hemicellulose, which includes the selective dissolution of hemicellulose from lignocellulosic biomass and the selective formation of furfural from hemicellulose derivatives. Whereas the cellulose and lignin structures are retained, which can be utilized separately. Solvents and catalysts are considered as two main factors in this valorization process of hemicellulose.

**Keywords:** Biomass; Hemicellulose; Furfural; Catalysts; Solvents.

1. **Introduction**

The challenges faced by the over-dependence of petroleum-based resources are increasing due to diminishing fossil fuel reserves and environmental concerns. [1-5] Lignocellulosic biomass is viewed as a sustainable feedstock because of its renewability, abundance and wide distribution in nature, which is mainly composed of the three components, hemicellulose, cellulose, and lignin.[2,6-9] This composition holds significant challenges for the effective utilization of biomass due to the rigid structure of polymeric composite and complicated interactions connecting the three main components. [10,11] Successfully replacing petroleum based fuels and chemicals by lignocellulosic biomass-based products will require high-yield, low-cost and energetically efficient targeted upgrading processes. [1] Therefore, the development of green and sustainable technologies is required for the conversion of lignocellulosic biomass to value-added chemicals and biofuels.

Hemicellulose is the second most abundant polysaccharide after cellulose in plant cell walls, accounting for 15-30% of lignocellulosic biomass by weight. [8] In general, the amounts of hemicellulose in wood and woody biomass are greater than those in herbaceous and agricultural biomass. [12] Among the three main components in biomass, hemicellulose is a promising material to produce value-added chemicals. Unlike cellulose, hemicellulose consists of short, highly branched polymer of five- and six-carbon polysaccharide units, such as xylan, mannan, β-glucans and xyloglucans. [2,13,14] The highly branched and amorphous nature of hemicellulose enables it to be easily converted. Noteworthy is that hemicellulose has a much lower degree of polymerization (100-200 U) compared with that of cellulose and lignin. Hemicellulose is more unstable than cellulose and therefore, degrades more easily when subjected to heat treatment. [15] Hemicellulose shows many excellent properties, including biodegradability, biocompatibility, bioactivity, and so on, which enable it be applied in a variety of areas such as food, medicine, energy, chemical industry and polymeric materials. [16-21] At present, there are many researches about the conversion of cellulose and lignin, however, the reports about hemicellulose conversion are limited.



**Figure 1** The pathways for the conversion of furfural into chemicals and fuels.

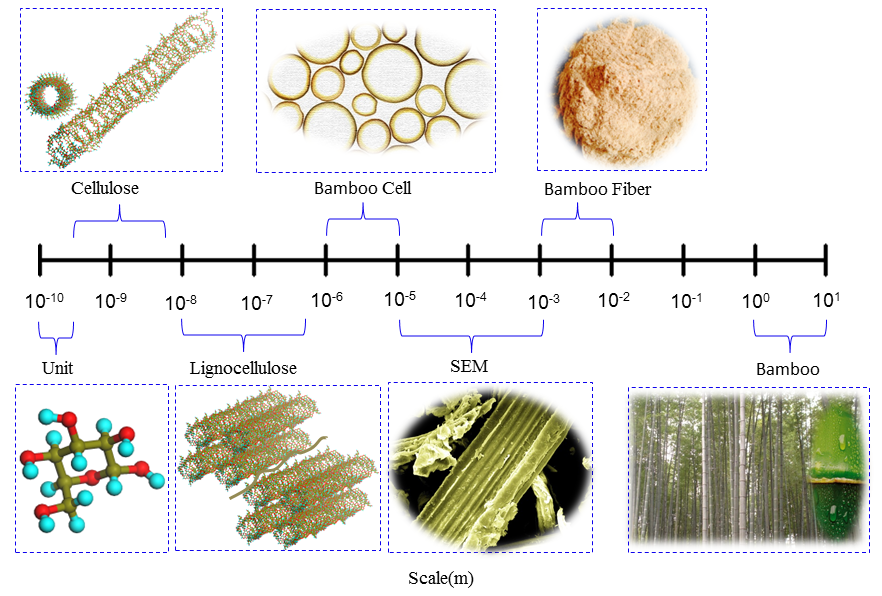
The effective utilization of hemicellulose in lignocellulosic biomass includes the selective dissolution of hemicellulose from raw biomass and the selective formation of target products from hemicellulose derivatives. In the plant cell walls, hemicellulose is thought to adhere to cellulose through hydrogen bonds and Van der Waal’s interactions, which enable hemicellulose to form highly resistant networks with cellulose. [22,23] Ferulic acid forms covalent feruloyl ester-ether bridges between hemicellulose and lignin, resulting in the formation of hemicellulose-lignin linkages. The extraction of hemicellulose is restricted by the physical and /or covalent interactions with other cell-wall components. So, the development of effective methods toward the selective conversion of hemicellulose to target products with high yield and selectivity is crucial in facilitating the effective utilization of hemicellulose, avoiding significant decomposition of cellulose and lignin. [24-26]

Furfural, identified by the US Department of Energy (DOE) as one of the top 12 value-added products, is a valuable product with a word market of around 300.000 tons per year. [27-28] Furfural is a typical product which could be obtained from hemicellulose in raw biomass and is also a key platform chemical produced in lignocellulosic biorefineries that could further be transformed to fuels and useful chemicals, which is widely used in oil refining, plastics, pharmaceutical and agrochemical industries (Figure 1). [29] With the aim to obtain furfural with high yield and selectivity from the selective dissolution and conversion of hemicellulose, solvent and catalyst were considered as two main crucial factors. In this paper, different techniques investigated in the selective dissolution of hemicellulose from raw biomass using solvents or catalysts have been reviewed. Additionally, a potential bio-refinery aim is to produce furfural with high yield and selectivity via the further depolymerization and conversion of dissolved hemicellulose derivatives obtained directly from raw biomass materials (Figure 2).



**Figure 2** The roles of solvents and catalysts on the selective dissolution and conversion of hemicellulose in actual biomass to produce furfural.

1. **Solvent-thermal conversion of hemicellulose in biomass**



**Figure 3** The multi-scale complexity from molecular levels to macro raw biomass level in biomass conversion.

Lignocellulosic biomass has proved to be difficult to degrade, with its complex composition and interactions among the three main components, requiring additional energy inputs for their dissolution. [11,30] The conversion of biomass involves multi-scale complexity from molecular to macro raw biomass level (Figure 3), which limits the conversion of biomass into valuable products. [30-32] Among the three main components in biomass, hemicellulose is a promising resource to produce furfural. Therefore, the development of efficient pre-treatment methodsis of great significance for the effective utilization of hemicellulose in lignocellulosic biomass to produce furfural with high yield and selectivity.



**Figure 4** (A) Categories of pre-treatment methods in biomass conversion; (B) Categories of catalysts and roles of catalysts in biomass conversion.

Typically, as shown in Figure 4(A), pre-treatment methods can be divided into three categories: physical, chemical and biological methods. [33,34] Physical pre-treatment methods use mechanical force and/or heat to open the biomass structure and reduce its particle size by grinding, milling or fibre steam-explosion. [35] Biological pre-treatment methods use microbes or fungal enzymes for the digestion of plant biomass. [36,37] Chemical pre-treatment methods use ionic liquids or dilute acids, bases, or other reagents to dissociate the biomass fractions and alter its composition. [38,39] In past decades, biochemical and thermal-chemical conversion technologies and processes have been investigated to produce chemicals and biofuels from biomass. [37,40] Thermal liquefaction was identified as the most promising method to obtain low molecular weight liquid products, gas fuel and solid residue. Among thermal liquefaction, pyrolysis and solvolysis were the two main methods used for the conversion of biomass to chemicals and fuels. [40] The pyrolysis of biomass relied on high temperature for the degradation of lignocellulosic biomass. The high operating temperature of pyrolysis (400–1000 oC) could lead to cross-linking reactions between hydrocarbons and aromatics, resulting in tar, which was difficult to be decomposed further. [40] Moreover, the liquid products obtained (bio-oil) was a mixture of compounds, which made separations difficult prior to upgrading to targeted chemicals and fuels, and additional costs were required in the process. [41] Solvent-thermal reactions, generally in the presence of aqueous solvents, organic solvents or ionic liquids, have been proposed as one of the most efficient approaches to improve selectivity of chemicals from biomass. [42] Compared with pyrolysis methods, solvolysis exhibited many advantages, such as (1) The presence of solvents diluted the concentration of the products, thus preventing the cross-linked reactions and reverse reactions. (2) The heat and mass transfer become easier in the fluid system. (3) Relatively low temperature (less energy consumption) was needed. [40] Li *et al*.reported that solvents have significant effects in biomass conversion, through reaction rate, reaction pathways, product distributions, and yields. [43] So reaction rates and product selectivity can be controlled to a certain degree by simply changing the solvent medium. Furthermore, because the three main components in biomass showed different solubility in different solvents, fractional conversion of biomass could be achieved in solvent-thermal processes. Therefore, the utilization of solvents in biomass conversion might be benefit for the selective dissolution and conversion of hemicellulose in biomass to furfural.

1. **The role of catalyst in hemicellulose conversion to furfural**

Breaking down the complex lignocellulose to dissolve and convert hemicellulose selectively requires pre-treatment under harsh conditions such as high temperature, high pressure and long reaction time. [44-48] These processes of achieving the selective dissolution and conversion of hemicellulose were complex, and chemically-energy intensive. Therefore, it required additional upgrading and separation steps, leaving a distinct negative environmental footprint. Holm *et al.* reported that catalysis could improve process efficiently, resulting in higher productivity and reduced costs. [49] The addition of catalysts promoted the cleavage of inter- and intra-bonds in the reaction process, which enhanced the selective dissolution of hemicellulose in biomass and facilitate its conversion to furfural. The addition of catalysts also promoted the formation of furfural via the following effects:(1) Enhancing the chemical bond cracking of xylose and/or xylose oligomers to form furfural; (2) Enhancing the rearrangement of different species to form furfural; (3) Enhancing the selectivity to furfural. Therefore, catalysts play important roles in hemicellulose conversion to furfural (Figure 4(B)). Catalysts can be divided into homogeneous and heterogeneous. Homogeneous catalysts were dissolved in the reaction medium, facilitating the interaction with the solid biomass. However, homogeneous catalysts have difficulties for the recovery of catalysts from reaction media. Heterogeneous catalysts, with easy separation and recovery, would be beneficial in view of the principles of green chemistry. [50] However, heterogeneous catalysts, such as solid acids faced the problem of their easy deactivation in aqueous solution or biphasic systems containing salt.[17,51] To achieve the effective utilization of hemicellulose in biomass to produce furfural with high yield and selectivity, the design of effective catalyst capable of being used in the solvent system was required.

1. **Dissolution and conversion of hemicellulose in raw biomass to furfural**
   1. **Conversion of xylose and pure hemicellulose to furfural**

**Table 1** The conversion of xylose as model compound to furfural

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Starting materials** | **Solvent** | **Catalyst** | **Conditions** | **Yield/mol/%a** | **Reference** |
| Xylose | GVL | H2SO4 | 175 oC | 75 | [57] |
| Xylose | GVL-10% H2O | H2SO4 | 170 oC, | >80 | [58] |
| Xylose | GVL-10%H2O | H-Mordenite | 175 oC | 80 | [59] |
| Xylose | H2O | HCl, NaCl | 200 oC | 81.3 | [60] |
| Xylose | GVL-10%H2O | H-Beta | 160 oC | 71 | [61] |
| Xylose | SBP-H2O-DMSO | NaCl-Sn-MMT | 180 oC | 76.8 | [62] |

a mole yield of furfural from the conversion of xylose

As an abundant and non-edible component of biomass, hemicellulose possessed the potential to serve as a sustainable feedstock for bio-based energy and value-added chemical products. [52-55] Furfural can be derived from hemicellulose in raw biomass, generally from C5 sugars, mainly xylose, the monomer unit contained in hemicellulose of lignocellulosic materials. [27,56] Much attention has been paid to use xylose as model compound to produce furfural (Table 1). Solvent-thermal conversion of xylose was one of efficient methods to improve the yield of furfural. Concern about what was considered to be a “green solvent” has arisen in the scientific community, and more attention has been given to this concept as efforts to replace petroleum-derived solvents with those from biomass were undertaken. [41] Various solvents such as H2O, GVL, 2-MTHF and DMSO were used for the conversion of xylose. [56-62] Among these solvents, GVL was considered as a biomass-derived green solvent and it was identified as an effective solvent in hemicellulose conversion compared to H2O. Mellmer *et al.* studied the effects of polar aprotic organic solvents on the acid-catalyzed conversion of xylose into furfural by reaction kinetics. [57] Significant increases in reaction rates as well as increased product selectivity were observed using GVL as solvent. The work also showed that the use of GVL as the solvent changed the activation energies for the probe reaction, that is, the dehydration of xylose to furfural. Gallo *et al.* reported that xylose dehydration reactions occurred faster in GVL than in water, which minimized the degradation products, and furfural was thus obtained in higher yields (70 %). [58] Furthermore, some researchers used GVL with a small amount of water for the conversion of xylose to furfural with high yield and confirmed that GVL/H2O co-solvent systems could further improve hemicellulose conversion to furfural.[58-59] Besides GVL/H2O co-solvent, other organic solvents such as SBP and DMSO were also added into water to form a biphasic system for hemicellulose conversion,[62] and a high yield of furfural was obtained.

In the solvent-thermal conversion of pure hemicellulose process, some homogeneous catalysts were added to improve furfural yield. [58-60] For example, with the addition of 0.05 mol L-1 sulfuric acid, furfural could be produced from xylose in higher yields (80 %) with short reaction times (15 min) using a mixture of 10 wt% water in GVL as solvent. [58] Marcotullio *et al.* obtained 81.3 mol% furfural with 90% selectivity from the conversion of xylose in 50 mM HCl aqueous solution with the addition of NaCl.[60] It indicated that the Cl-- as catalyst promote the formation of the 1,2-enediol from the acyclic form of xylose, and thus the subsequent acid catalyzed dehydration to furfural. In order to further improve furfural yield, heterogeneous catalysts were used. Gurbuz *et al.* presented a processing strategy for the conversion of xylose into furfural with high yield (80%) in GVL-10 wt% H2O solvent using H-M catalysts. [59] When xylose was reacted at 180 oC for 30 min using Sn-MMT catalyst, 76.8% furfural yield with 82.5% furfural selectivity was obtained in SBP/NaCl-DMSO-H2O biphasic system with saturated NaCl.[62]

**Table 2** The conversion of pure hemicellulose to furfural

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Starting materials** | **Solvent** | **Catalyst** | **Conditions** | **Yield /%** | **Reference** |
| Xylan | H2O | HCl | 180 oC | 36.5b | [63] |
| Xylan | MIBK-H2O | HCl | 177 oC | 45.79a | [64] |
| Xylan | GVL-10% H2O | FeCl3·6H2O | 170 oC | 68.6a | [65] |
| Xylan | 2-MTHF-H2O | SnCl4 | 150 oC | 78.1a | [66] |
| Xylan | H2O-THF | AlCl3·6H2O-NaCl | 140 oC | 64 a | [67] |
| Xylan | GVL-H2O | Al2(SO4)3 | 130 oC | 87.8a | [68] |
| Xylan | 2-MTHF-H2O | NaCl-SO42-/Sn-MMT | 160 oC | 77.35a | [69] |

a yield of furfural based on the moles of C5 fraction in pure hemicellulose

b yield of furfural was based on the weight of the starting materials

Excepting xylose as model compounds to produce furfural, many researchers use pure hemicellulose such as xylan as starting materials for the production of furfural (Table 2). Yemis *et al.* studied the acid-catalyzed conversion of xylan to furfural by microwave-assisted reaction, and obtained 36.5 wt% furfural using 0.1 M HCl at 180 oC for 30 min.[63] The effect of different Brønsted acids on the conversion efficiency of xylan was evaluated, and it was found that HCl was the most effective catalyst. Several organic solvents such as GVL, THF and 2-MTHF, and homogeneous catalysts such as FeCl3·6H2O, SnCl4, AlCl3·6H2O and Al2(SO4)3 were added to promote the conversion of xylan to furfural. [64-69] For example, Wang *et al.* found that a bio-based 2-MTHF/H2O biphasic system, was more conducive for the conversion of xylan-type hemicellulose to produce furfural with highest yield of 78.1% using SnCl4 catalyst at 150 oC for 120 min. [66] Yang *et al.* obtained 64% yield of furfural using xylan as the starting material in H2O-THF medium containing AlCl3·6H2O and NaCl under microwave heating at 140 oC.[67] Yang *et al.* tested a variety of metal salt for the conversion of xylan under microwave conditions in GVL/H2O solvent system, and 87.8% furfural was obtained at 130 oC using Al2(SO4)3 catalyst.[68] Their results showed that the Brønsted acidity and Lewis acidic species were key factors for the high conversion of xylan in GVL/H2O system. In the same reaction system, other organic solvents such as MIBK, THF and 2-MTHF were also used to compare the solvent effects on the conversion of xylan. It was found that the other three organic solvents provided lower yields of furfural compared with GVL. This suggested that organic solvent with a specific catalyst was benefit for the production of furfural from xylan.[68] Lin *et al.* prepared SO42*-*/Sn-MMT as a solid acid catalyst for the heterogeneous catalytic transformation of xylan.[69] The highest furfural yields were achieved up to 77.35% from xylan at 160 oC in 2-MTHF/NaCl-H2O biphasic system. The results also suggested that SO42*-*/Sn-MMT contained both Brønsted acid and Lewis acid sites, which could improve the reaction conditions.

The conversion of xylose and pure hemicellulose to furfural gave valuable ideas for the understanding of the furfural formation mechanism, which will be beneficial to the better utilization of hemicellulose. A high yield of furfural was also obtained from xylose and pure hemicellulose by the use of co-solvent or biphasic system with the addition of catalysts, which opened the possibility of using more complex carbohydrate, such as raw biomass, as a starting material. However, the use of xylose and pure hemicellulose as a substrate in the production of furfural was not an economically viable option, as they needed to be obtained in pure form from biomass. Besides, there remained a large gap between the structure or state of xylose or pure hemicellulose and the actual lignocellulosic biomass. Compared with pure hemicellulose, the intermolecular bonds linking hemicellulose, cellulose and lignin existed in actual biomass. Moreover, the intramolecular bonds of hemicellulose in actual biomass were more complex. These inter- and intra-molecular bonds in actual biomass would inhibit the conversion of hemicellulose. Therefore, the production of furfural with high yield and selectivity from hemicellulose in actual biomass was more challenging than from xylose and pure hemicellulose.

* 1. **“One-pot” method for the dissolution and conversion of hemicellulose in actual biomass to furfural**

Industrially, furfural was produced from pentosane sugars present in lignocellulosic materials using homogeneous mineral acid catalysts (H2SO4 catalyst) in aqueous solutions. The C5 polysaccharides were first hydrolyzed to monosaccharides (mainly xylose), which were subsequently dehydrated to furfural (Figure 5 A). Furfural was then recovered from the liquid phase by steam stripping to avoid further degradation and purified by double distillation. However, a yield of only 40%-50% furfural was obtained. [59,70] Furthermore, conventional furfural production required high energy and generated acidic waste streams. [71] Therefore, research on more economic and environmentally benign furfural production strategies from hemicellulose in biomass has attracted worldwide interests.

Because the three main components in biomass have complicated interactions, the dissolution of hemicellulose was always accompanied with the dissolution of cellulose and lignin. In order to study the dissolution and conversion of hemicellulose in actual biomass for the production of furfural, many researchers used “one-pot” methods (Table 2), including the simultaneous conversion of hemicellulose and lignin, simultaneous conversion of all the three main components firstly and then recovered dissolved lignin, and the simultaneous conversion of all three main components in raw biomass.



**Figure 5** Reaction scheme for the acid-catalyzed conversion of hemicellulose into furfural (A), atwo-step method in H2O/organic solvent to achieve the selective dissolution of hemicellulose in biomass(B), and a biphasic system to produce furfural from lignocellulosic biomass(C).

Most lignocellulosic fractionations involved delignification, which was often accompanied with hemicellulose conversion, leaving a rather pure cellulose as solid residue that could be further used to produce value-added chemicals by fermentation. [72] This is because the dissolution of highly structured cellulose usually needed harsher conditions. [73] Moreover, the conversion of pure cellulose to value-added chemicals (e.g. sugars, levulinic acid) have attracted many researchers’ attention. [74-76] Therefore, some researches focus on the simultaneous removal of hemicellulose and lignin in biomass to obtain furfural and high purity cellulose. For example, Sasaki *et al.* [77] reported that hemicellulose and lignin were removed as a water-soluble fraction at 200–230 °C by hydrothermal treatment of sugarcane bagasse to obtain low yields of furfural, while the cellulose fraction was hydrolyzed at higher temperatures (230–280 °C) or recovered as solid residue from this treatment. A GVL-H2O co-solvent system was developed for the conversion of *pubescens*. At 160 oC for 4 h, H2O promoted the cleavage of chemical bonds linking hemicellulose, lignin and cellulose, and GVL further helped the co-dissolution of hemicellulose- (93.6 wt%) and lignin- derivatives (80.2 wt%), leaving a high purity cellulose (83.3 wt%). The maximum furfural yield from hemicellulose conversion reached 33.6 wt% (based on the weight of hemicellulose in *pubescens*). [78]

**Table 3** “one-pot” method for the dissolution and conversion of hemicellulose in raw biomass to furfural

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Starting materials** | **Solvent** | **Catalyst** | **Conditions** | **Yield/%** | **Reference** |
| Sugarcane bagasse | H2O | - | 200-230 oC | low | [77] |
| *Pubescens* | 25% GVL/H2O | - | 160 oC | 33.6a | [78] |
| Corn stover | 90% GVL-H2O | 0.025 M H2SO4 | 170 oC | 96a | [79] |
| Bagasse | THF-H2O (2:1) | 0.4 M HCl | 200 oC | 66.3b | [80] |
| Birch wood | H2O | H2SO4 | 147 oC | 11.09c | [81] |
| Corn stover | GVL-SBP | 0.05wt% H2SO4, AlCl3 | 170 oC | 70a | [82] |
| Corncob | H2O | 0.9 mmol H2SO4 | 160 oC | 71b | [83] |
| Corncob | H2O | 0.10 wt% H2SO4 | 190 oC | 99.5b | [84] |
| Bagasse | H2O, | HUSY | 170 oC | 18b | [17] |
| Bagasse | H2O/*p*-xylene, | HUSY | 170 oC | 56b | [17] |
| Bagasse/ rice husk /wheat straw | H2O/toluene | SAPO-44, | 170 oC | 93b | [85] |
| Corn stover | GVL | SC-CaCt-700 | 200 oC | 93b | [86] |
| Corncob | GVL | SPTPA | 175 oC | 73.9b | [87] |

a yield of furfural was based on the weight of C5 fraction in biomass

b yield of furfural was based on the moles of C5 fraction in biomass

c yield of furfural was based on the weight of the starting materials

One strategy for the simultaneous conversion of the three main components firstly and then recovery of the dissolved lignin in co-solvent with the addition of mineral acid, was used to obtain furfural from hemicellulose. Alonso *et al.* reported a process for obtaining hemicellulose and cellulose mixture in 90% GVL-H2O solvent using 0.025 M H2SO4, while the dissolved lignin was precipitated upon addition of water and removed by filtration. The cellulosic fraction of corn stover could be converted into levulinic acid (LA, 66%, yield based on C6 fraction), while under the same conditions the hemicellulose fraction could be converted into furfural (96%, yield based on C5 fraction).[79] A biphasic system consisting of THF and water (2:1) was studied to achieve the integrated conversion of cellulose and hemicellulose in bagasse to 66.3 mol% furfural and 44.3 mol% levulinic acid using 0.4 M HCl at 200 oC, while lignin was precipitated as a solid residue. [80] As compared to GVL solvent, the utilization of a lower boiling point solvent, THF, also achieved the simultaneous hydrolysis of C6 and C5 carbohydrates in lignocellulosic biomass.

The conversion of all the three components in raw biomass was also adapted to study the dissolution and conversion of hemicellulose in raw biomass to furfural. For instance, a new dilute sulphuric acid hydrolysis method was used for the conversion of hemicellulose in birch wood, and 11.09 wt% furfural was obtained based on the weight of birch wood at 147 oC for 90 min. [81] Luterbacher *et al.* reported a laboratory-scale production of soluble carbohydrates from corn stover, hardwood, and softwood at high yields (70 to 90%) in a solvent mixture of GVL, H2O, and 0.05 wt% H2SO4. The separated aqueous phase from GVL/water solvent systems with addition of NaCl, was further treated with AlCl3 and SBP, and 70% furfural based on the weight of C5 fraction in biomass was obtained at 170 oC. [82] Furfural with the yield of 71 mol% could be produced by acid hydrolysis of raw corncob. [83] Li *et al.* studied the conversion of corn cob to furfural using GVL as the solvent with a dilute sulfuric acid catalyst. A maximum furfural yield of 99.50% was obtained at 190 °C for 20 min with 0.10% sulfuric acid. [84] Current methods for production of furfural from hemicellulose used mineral acid catalysts, which were corrosive, difficult to recover, and posed environmental and health risks. [1,59]

To overcome the drawbacks posed by mineral acid methods in converting hemicelllulose, Sahu *et al.* presented a solid-acid catalyzed one-pot method for the selective conversion of solid hemicellulose in crop waste without its separation from other lignocellulosic components. [17] When bagasse was reacted at 170 oC for 6 h in the presence of only water and HUSY catalyst, 30% xylose+ arabinose and 18 mol% furfural were obtained. While in a biphasic reaction system (water +*p*-xylene, 170 oC, 6 h) with HUSY catalyst, 56 mol% yields of furfural with 17% xylose+arabinose was obtained. Their work also showed that the addition of organic solvents increased the furfural yield from 18 to 56%. If furfural was formed near the catalytically active acidic sites, it may easy degrade. In contrast, furfural was extracted into the organic phase in the biphasic system, it could be protected from further degradation. However, the catalysts recycling study revealed a 20% drop in activity for each subsequent run. In an efficient one-pot methodology using SAPO-44 as catalysts, a high yield of furfural of about 93 mol% was obtained by the conversion of hemicellulose from raw biomass (bagasse, rice husk and wheat straw) at 170 oC in H2O/toluene (1:2) biphasic solvent system. [85] Recently, Li *et al.* used a novel heterogeneous strong acid catalyst (SC-CaCt-700) for the conversion of corn stover, and 93% furfural was obtained at 200 oC in GVL. In comparison, there was almost no furfural obtained in GVL without the addition of catalyst, while only 51.5% furfural yield was achieved in aqueous media under the same conditions. [86] Zhang *et al.* found that a new porous polytriphenylamine–SO3H (SPTPA) had better catalytic performance on the conversion of corncob in GVL solvent. Under the optimum reaction conditions, 73.9% furfural was obtained at 175 oC.[87] These results suggested that solvent and catalyst were important for the production of furfural.

Although high yield of furfural was obtained by a “one-pot” method for the dissolution and conversion of hemicellulose in actual biomass, the products obtained were a mixture that composed of many kinds of carboxylic acids, furans, phenols and some oligomers, causing the difficulty in product separation and the further use of the products. [88] Hence, the selectivity to furfural was low. Therefore, the development of new technologies to produce furfural with high yield and selectivity from raw biomass in environmentally sustainable manners deserves further study.

* 1. **Selective dissolution and conversion of hemicellulose in actual biomass to furfural**

**4.3.1 One-step method to produce furfural from hemicellulose in raw biomass**

Most lignocellulosic fractionations involved the conversion of hemicellulose, which needed to be upgraded, however generally accompanied by the conversion of lignin and cellulose, because the structure of hemicellulose–lignin linkages coating on cellulose was destroyed and then made the degradation of lignin and cellulose easy. [89] Efficient conversion of hemicellulose from raw biomass prior to fermentation was crucial, because the cellulase enzyme was significantly inhibited by xylose, xylan and especially xylo-oligosaccharides. [90-92] Demartini *et al.* found that the subsets of hemicellulose were the key recalcitrance-causing factors in switchgrass, and the conversion of hemicellulose could achieve nearly 100% glucose yields at high enzymatic loading in subsequent enzymatic hydrolysis. [93] Dussan *et al.* reported that the amount of soluble lignin in the liquor solutions could significantly affect the selectivity of the pentose dehydration reaction to form furfural. [94] Therefore, the selective dissolution and conversion of hemicellulose to furfural with high yields and selectivity avoiding significant influence on other components (cellulose and lignin) was very important for the effective utilization of biomass to its fullest.

The One-step method to produce furfural from the selective dissolution and conversion of hemicellulose in raw biomass was studied (Table 4). Ionic liquids have received increasing attention as environmentally preferable solvents for the selective conversion of hemicellulose in biomass. Carvalho and co-workers achieved the selective catalytic conversion of hemicellulose fraction in wheat straw to produce 36.2 wt% furfural based on the weight of C5 sugars in [bmim][HSO4] ionic liquids at 160 oC. [94] Fractionation of corn stover into cellulose, hemicellulose and lignin was successfully performed in ultrasound-assisted ionic liquids at low reaction temperature of 70 oC for 3 h followed by alkaline extraction. [95] A high yield of reducing sugars was obtained (97.77%), while the yield of furfural was quite low in this process. However, it has proved challenging using ionic liquids in the fractionation of biomass. Apart from the expense and chemical waste of losing some of the ionic liquid, it could prevent the enzymes from functioning in the subsequent fermentation step. [11]

Water was considered as an efficient reaction medium, since it is environmental friendly. Besides, water has good hydrogen bonds accepting ability, which could disrupt the inter- molecular linkages (e.g. hydrogen bonds, ether bonds) connecting hemicellulose, cellulose and lignin, and then promote the dissolution of hemicellulose. Some researchers studied the dissolution of hemicellulose in biomass using traditional autoclave heating method in water. For example, Nitsos *et al.* discovered that 80% hemicellulose from beech wood and various

**Table 4** One-step method to produce furfural from the selective conversion of hemicellulose in raw biomass

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Starting materials** | **Solvent** | **Catalyst** | **Conditions** | **Yield/%** | **Hd** | **Ce** | **Lf** | **Reference** |
| Wheat straw | [bmim][HSO4] | - | 160 oC | 36.2a | 24.8/0.0g | 38.5/52.4 | 17.7/36.7 | [95] |
| Corn stover | ionic liquid | - | 70 oC | low | 19.3/0.4-2.6 | 43.2/31.2-40.0 | 22.5/21.1-20.7 | [96] |
| Hard- and softwood | H2O | - | 170-220 oC | low | 25.4/5.1 | 42.1/37.9 | 26.1/20.9 | [97] |
| *Pubescens* | H2O | - | 160 oC | 1.2b | 19.7/8.0 | 44.7/41.3 | 21.1/16.7 | [99] |
| Eucalyptus globulus | H2O | - | 196 oC | low | Most dissolved | remained | remained | [100] |
| *Pubescens* | H2O | - | 180 oC | <1b | 17.9/3.0 | 46.5/41.1 | 25.4/16.7 | [88] |
| *Pubescens* | H2O, microwave | - | 200 oC | ~1b | 20.6/1.0 | 42.8/remained | 24.7/remained | [101] |
| *Pubescens* | H2O-cyclohexane | - | 160 oC | ~1b | 17.9/1.8 | 51.9/46.6 | 24.0/17.9 | [102] |
| olive tree pruning | H2O | 0.025 M H2SO4 | 180-230 oC | low | 20.8/8.23-0 | 16.5/11.6-10.6 | 21.3/remained | [104] |
| Corn stover | H2O | AlCl3 | 140 oC | 26a | 18.8/2.6 | 46.1/33.4 | 17.3/10.9 | [105] |
| *Pubescens* | H2O | AlCl3 | 120 oC | 0.91b | 17.9/4.9 | 46.5/41.7 | 25.4/22.0 | [88] |
| Wheat straw | H2O | SO42-/Fe2O3 | 141.97 oC | low | 27.5/17.5 | 45.6/remained | 19.4/remained | [106] |
| Cardoon | CPME/H2O | 1wt% H2SO4 | 170 oC | ~100c | 21.0/unknow | 37.0/unknow | unknow | [109] |
| Maple wood | THF/H2O (3:1) | 1wt% H2SO4 | 170 oC | 87c | 15.5/0.0 | 40.9/38.9 | 24.4/22.0 | [110] |
| Poplar | THF/H2O | AlCl3-NaCl | 160 oC | 64c | unknow | unknow | unknow | [67] |

a yield of furfural was based on the weight of C5 fraction in biomass; b yield of furfural was based on the weight of the starting materials;c yield of furfural was based on the moles of C5 fraction in biomass;d Hemicellulose percent before and after reaction; e Cellulose percent before and after reaction; f Lignin percent before and after reaction. g The percent of composition before reaction/ the percent of composition after reaction.

other hard- and softwoods was removed in hydrothermal pre-treatment using hot compressed water, with about 60% C5 monomers and oligomers obtained. [97,98] In these researches, an optimization study of the pre-treatment conditions led also to maximization of one-pot furfural yield, using water as sole solvent. Luo *et al.* proposed that the liquid product with high furan content could be obtained at a moderate temperature for a shorter time, while phenol compounds could be obtained at a higher temperature for a comparatively longer time. [99] Thus, the selective dissolution and conversion of hemicellulose to furfural from raw biomass was possible. Eucalyptus globulus wood samples were treated with hot, compressed water at 196 oC to separate hemicellulose as soluble saccharides, leaving a solid phase mainly made up of cellulose and lignin. [100] Luo *et al.* found that more than 80 % hemicellulose was dissolved from *pubescens*, accompanied with 30% lignin and 10% cellulose at 180 oC for 0.5 h. [88] It could be seen that traditional heating method was not very efficient for the selective dissolution and conversion of hemicellulose to furfural in raw biomass, because a large amount of lignin and cellulose were also dissolved. In order to improve the selective dissolution of hemicellulose, a green process for the microwave-assisted hydrothermal selective dissolution and utilisation of hemicellulose in *pubescens* was developed. The process facilitated the efficient dissolution of hemicellulose at 200 oC (>95%), while obtaining hemicellulose-free residue that could be further used as starting materials within many industrial processes. [101]

The mixed solvent played an important role in reducing the degradation of hemicellulose, cellulose and lignin, compared with water solvent, and the reduction of conversion rate of cellulose and lignin was more significant that benefited the selective conversion of hemicellulose. [102] The simultaneous separation and selective conversion of hemicellulose in *pubescens* samples was achieved in water-cyclohexane solvent at 160 oC. [102]

Some catalysts were also added in the solvent system to enhance the selective dissolution of hemicellulose in raw biomass. Dilute acid hydrolysis was also used to remove hemicellulose selectively as sugars. [103] Mateo *et al.* reported that acid hydrolysis of hemicellulose fractions of olive tree pruning can also lead to a valuable solid residue mainly composed of cellulose and lignin. [104] Yi *et al.* achieved the selective dissolution of hemicellulose from corn stover in water using AlCl3 catalyst. [105] Luo *et al.* investigated the selective dissolution of hemicellulose from *pubescens* promoted by AlCl3 under solvent-thermal conditions. In the AlCl3 promoted dissociation of hemicellulose from *pubescens*, the conversion of hemicellulose reached 72.6 wt% without significant degradation of cellulose and lignin (only 10.4 wt% and 13.3 wt%, respectively) after hydrothermal treatment at a low temperature of 120 oC for 4 h. [88] The above investigation showed that the addition of homogeneous catalysts such as mineral acid and metal salts in water improved the selective dissolution of hemicellulose in biomass. The utilization of heterogeneous catalysts has recently gained more attention because they can recycle compared with homogeneous catalysts. A nanoscale heterogeneous catalyst, solid acid SO42-/Fe2O3, with both lewis and Brønsted acidity, was found to effectively hydrolyze 63.5 % hemicellulose in wheat straw while keeping cellulose and lignin inactive. [106]

The simultaneous dissolution of hemicellulose and lignin was generally used first, then the dissolved lignin was separated from dissolved hemicellulose by precipitation by the addition of water (Figure 5(B)). For example, in the absence of acid, 79.4 % of the lignin and 79.6 % of the hemicellulose in birch sawdust, could be removed using GVL/H2O (1:1) from cellulose, and 33.3 % lignin could be subsequently recovered by precipitation. [107] The addition of an acid catalyst (H2SO4) can improve the efficiency of the organosolv fractionation process. He *et al.* used an ethanol/H2O (1/1, v/v) co-solvent system with 0.050 M oxalic acid, to simultaneously fractionate 88.0 wt% of hemicellulose and 89.2 wt% of lignin in corn stover at 140 oC for 1 h, while cellulose was not obviously degraded. [108] After evaporation of ethanol from the liquid, a yield of 83 wt% lignin (a rufous powder) could be recovered.

The investigations above have achieved the selective dissolution of hemicellulose from biomass by changing the solvent medium or using catalysts to control the reaction. However, most researchers still used mineral acid catalysts. The utilization of green solvent, alleviating the need to purchase and transport petroleum-derived solvents to biomass conversion, was a benefit for the development of sustainability in biomass conversion. Therefore, the development of effective catalytic and solvent systems was still needed to achieve the selective dissolution and conversion of hemicellulose in biomass. Furthermore, the yield of furfural obtained from the selective dissolution and conversion of hemicellulose in biomass was low.

To improve the yield of furfural, some organic solvents were added with water and mineral acids for the simultaneous dissolution and conversion of hemicellulose in biomass. Molina *et al.* studied the conversion of cynara cardunculus (cardoon) lignocellulose with 1 wt% H2SO4 catalyst in a cyclopentyl methyl ether(CPME)/H2O system, obtaining a higher yield of furfural (near 100 mol%) at 170 oC, however, the yield of furfural was only about 60 mol% in water under the same reaction conditions. [109] Furthermore, they also found that the addition of NaCl notably accelerated the reaction rate of furfural formation from hemicellulosic pentoses and required a much shorter reaction time to produce furfural at such high yields. Cai *et al.* obtained 87 mol% furfural from the conversion of maple wood in the THF/H2O (3:1) biphasic system at 170 oC with 1 wt% H2SO4, however, the yield of furfural was only 39 mol% in water under the same reaction conditions. [110] Due to the extraction of furfural to the organic phase in THF/H2O (3:1) biphasic medium, the side reactions to produce undesirable intermediates were suppressed, while the equilibrium of the reaction system shifted to furfural production, so improved yield of furfural was achieved. Although high yield of furfural was achieved from the conversion of biomass, the problems associated with the need for mineral acid made the process inefficent. Yang *et al.* obtained furfural yield of 55%, 38%, 56% and 64%, respectively, from corn stover, pinewood, switch grass and poplar at 160 oC in NaCl-THF/H2O systems using AlCl3 catalyst. The aqueous phase containing AlCl3·6H2O and NaCl could be recycled multiple times (>5) without any loss of activity or selectivity for furfural. [67]

Catalysts and organic solvent can be added to improve the selective dissolution of hemicellulose, and the simultaneous conversion of hemicellulose to furfural by using a one-step method. However, the yield and selectivity of furfural needed to be improved. Therefore, the simultaneous selective dissolution and conversion of hemicellulose to furfural needs to be investigated further.

**4.3.2 Two-step methods to improve furfural yield from hemicellulose in raw biomass**

Hemicellulose in biomass can be selectively dissolved in solvent. However, the dissolved hemicellulose as water-soluble carbohydrates were mainly in the form of oligomers. [94,103,111] Bai and co-workers obtained a high xylo-oligosaccharides (XOS) yield of 54.7 wt% based on xylan content from the catalytic conversion of bamboo hemicellulose at 150 oC for 45 min using novel solid acid catalysts of sulfonated bamboo-based carbon materials. [112] Therefore, the production of furfural from lignocellulosic biomass with high yields imposed high demands on the development of depolymerization processes for the effective utilization of hemicellulose in raw biomass. Two-step methods for the conversion of hemicellulose in raw biomass has been proposed as one of the efficient approaches to obtain furfural with high yield and selectivity. This included the selective dissolution of hemicellulose from other two components and then further depolymerization and conversion of the dissolved hemicellulose. Therefore, many researchers focus on the production of furfural from raw biomass via a two-step method.

Kim *et al.* performed microwave conversion of biomass (corn stover, switch grass, and poplar) to furfural using maleic acid in a two-step procedure. [113] In the first step at the reasonably mild temperature of 160 oC, the efficient conversion of hemicellulose in biomass to xylose with high yields was achieved. In the second step at higher temperatures of 200 oC, higher selectivity of furfural (67%) was obtained by the further reaction of xylose derived from corn stover. Heterogeneous catalysts were often added to improve the furfural yield instead of using homogeneous catalysts in the second step. A microwave-assisted, two-stage cascade process, using only corn stover and water in the presence of niobium phosphate (NbP) as a catalyst, lead to good furfural yields. [51] In the first stage of the process, corn stover was hydrothermally fractionated to obtain soluble hemicellulosic sugars (mostly oligomers) and a solid residue containing cellulose and lignin. In the second step of the process, the obtained hemicellulosic sugars (mostly oligomers) were hydrolyzed and dehydrated over NbP catalysts to yield furfural at moderate temperature (<200 oC), with both steps being performed in water. Furfural yield was only up to 23 mol% with respect to the starting raw biomass.

The addition of only organic solvents in water to form biphasic system was also an effective method to improve furfural yield in the second step. Mittal *et al.* demonstrated that a MIBK-H2O (2:1) biphasic reaction system could be used to convert biomass-derived pentose hydrolyzates to furfural with the yield of 80%. [114] Gurbuz *et al.* achieved a high yield of furfural by using biphasic reactors and alkylphenol solvents. Firstly, corn stover was treated for 5 h at 90 oC in an aqueous solution containing 0.1 M HCl and saturated NaCl. This corn stover feed (1.1 wt% xylose) resulted in the maximum yield of 70% to produce furfural with the addition of SBP. [53] Morais *et al.* developed a novel approach to produce furfural from lignocellulosic biomass via two reaction stages. The first consisted of an extraction of hemicellulose from wheat straw using high-pressure CO2 and H2O to produce a water-soluble fraction containing pentoses in oligomeric and monomeric form. The second step was performed at 180 °C for 60 min in a water/THF/MIBK biphasic system with 50 bar of initial CO2 pressure, which favored the production of furfural and allowed to obtain furfural at a yield and selectivity of 43 mol% and 44 mol%, respectively. [115] Therefore, it could be seen that the addition of catalysts or organic solvents both benefitted the production of furfural for the further depolymerization and conversion of dissolved hemicellulose.

To obtain furfural with high yields, catalysts and organic solvents were simultaneously added for the further depolymerization and conversion of the dissolved hemicellulose in the second step. For example, Xing *et al.* presented a new process to produce furfural (89.8 %) with the addition of THF and NaCl by the further depolymerization and conversion of waste aqueous hemicellulose solutions (mainly xylose oligomers) using a continuous two zone biphasic reactor. [116] With the addition of NaCl and THF, a liquid system containing hemicellulose derived monomers and oligomers was further heated to 200 °C, achieving the maximum yield of 76.9 mol % with 82.2% selectivity to furfural based on the moles of converted hemicellulose using a 5 wt % *pubescens* to solvent ratio. Some organic solvents and heterogenous catalysts instead of homogenous catalysts were added for the further conversion of dissolved hemicellulose. Li *et al.* studied the further hydrolysis and dehydration of hydrolysates (C5 monosaccharide and oligosaccharides) obtained from corncob using Sn-MMT as a solid catalyst in a biphasic system (SBP/NaCl-DMSO). [117] Furthermore, Sn-MMT catalyst also demonstrated excellent catalytic performance in the conversion of water-insoluble hemicelluloses (WIH, average molecular weight(Mw)=64700) and water-soluble fraction (WSF, average molecular weight(Mw)=10770) in the SBP/NaCl-DMSO system. [62] Gao *et al.* produced a high yield of furfural (82.4%) from waste aqueous hemicellulose solution of a hardwood kraft-based dissolving pulp production processing (mainly oligomers), when carried out in Toluene/H2O (30:15) solvent with the addition of ZSM-15 and NaCl catalyst at 190 oC for 3 h. [118] Luo *et al.* obtained 72.6 wt% dissolved hemicellulose without significant degradation of cellulose and lignin after hydrothermal treatment at a low temperature of 120 oC for 4 h for the first step. [88] The extracted hemicellulose could be divided mainly into two parts, that is, small molecular products such as xylose, furfural and acetic acid (about 36.1%) and oligomers (about 63.9%). Therefore, the further conversion of the oligomers and monomers derived from hemicellulose was carried out at 160 oC for 2 h with the addition of THF and SiO2 by forming a SiO2–AlCl3–H2O/THF system, and 33.1 wt% furfural based on the weight of hemicellulose in *pubescens* was obtained. It was demonstrated that the co-contribution of NaCl and co-solvent depolymerized the oligomers to small molecular products (Mw < 150 Da) and improved the selectivity to furfural. [78] The synergetic effects of specific catalysts with certain solvents may be one reason to produce furfural with high yield and high selectivity (Scheme 1).

C:\Users\luoyiping\AppData\Local\Microsoft\Windows\INetCache\Content.Word\2.tif

**Scheme 1.** (A) The conversion of *pubescens* to furfural with high yield and lower molecular weight lignin derivatives in H2O/GVL/THF system; (B) Proposed reaction network for the NaCl promoted depolymerization and conversion of hemicellulose in *pubescens* to furfural with high yield in H2O/GVL/ THF system. Dimer is as a representative for oligomers. [78]

Lê *et al.* reported that water exhibited better performance on the hydrolysis of hemicellulose while GVL was benefit for the dissolution of lignin in GVL/H2O co-solvent system, leaving cellulose intact. [119] Based on the above literature, it was found that H2O played important roles in the selective dissolution of hemicellulose. Besides, in our previous work, it was observed that little hemicellulose dissolved in pure GVL. [78] Water was an obvious choice

as green solvent and hydrolysis was the key reaction to degrade biomass especially hemicellulose. [120] Furthermore, because H2O acted as nucleophile agent with higher hydrogen bonds accepting ability, so it could be speculated that H2O might form hydrogen bonds with intermolecular linkages connecting hemicellulose, cellulose and lignin, which contributed to the cleavage of these linkages. The addition of catalysts, such as mineral acid or solid acid catalysts, might also form hydrogen bonds with intermolecular linkages, which enhanced the cleavage of intermolecular bonds and then promoted hemicellulose dissolution. In the further reaction of dissolved hemicellulose-derivatives, H2O promoted the cleavage of intramolecular linkages (such as β-1,4 glucosidic bond) in hemicellulose with the help of catalysts and organic solvents, which was benefit to produce furfural.

Therefore, an environmentally benign two-step method was proposed to improve the yield and selectivity of furfural as follows: (1) Adding acid catalysts, especially replacing the homogeneous catalyst by heterogenous catalysts, may be helpful for the dissolution and conversion of hemicellulose to oligo- and mono-saccharides under acid catalytic systems. The addition of organic solvent, such as biomass derived green solvent (GVL), helped H2O break down the intermolecular linkages and dissolved hemicellulose selectively. (2) Using a biphasic system by the addition of organic solvent (Figure 5(C)). In biphasic system, because furfural produced was continuous extracted into the organic phase, so the side reactions producing undesirable intermediates were suppressed and the equilibrium of reaction system was shifted to furfural production, which improved the yield of furfural. [78] (3) NaCl showed not only salt effects but also as promoter effects to enhance the reacction of xylose to furfural in biphasic system. In contrast with homogenous catalytic processes, it was desirable for the development of heterogeneous catalysts to promote the depolymerization of hemicellulose derivatives to furfural.

1. **Conclusions and future perspectives**

Today, there is a need to rapidly develop new technologies that allow us to convert biomass to value-added chemicals. In the domain of value-added chemicals, furfural possesses significant advantages using biomass as a starting material, which could alleviate the utilization of petroleum-derived chemicals. However, the production of furfural with high yield and selectivity from raw biomass is challenging. A large volume of work has investigated the conversion of hemicellulose to furfural. However, the use of pure hemicellulose model components as starting materials is not an economically viable option as separation and purification of hemicellulose from biomass is not easy. Furthermore, the performance of pure hemicellulose and the actual lignocellulosic biomass is quite different. Here, two strategies to produce furfural directly from raw biomass are discussed in detail. One is the conversion of hemicellulose in biomass to furfural by using the one-pot method. Although high yields of furfural are obtained, the selectivity to furfural is still low because of the products obtained are a mixture including those from the conversion of both cellulose and lignin. Another one is the selective dissolution and conversion of hemicellulose in actual biomass to furfural. One-step and two- step methods for the selective dissolution and conversion of hemicellulose in actual biomass to furfural are usually used. The selective dissolution of hemicellulose in biomass is achieved using a one-step method, which could simply the reaction processes, but the yield of furfural needs to be improved. In contrast, a two-step method for the conversion of hemicellulose in raw biomass is identified as one of the efficient approaches to obtain furfural with high yield and selectivity. The effective utilization of hemicellulose in lignocellulosic biomass to furfural includes the selective dissolution of hemicellulose from raw biomass and the selective formation of furfural from dissolved hemicellulose-derivatives. For the sake of the production of furfural with high yield and selectivity, catalysts and organic solvents are the most commonly required for the further depolymerization and conversion of dissolved hemicellulose. Especially, the biphasic system formed by the addition of organic solvents and NaCl is benefit to produce furfural. Because furfural produced in biomass conversion could be continuously extracted into the organic phase in biphasic system, so the side reactions producing undesirable intermediates are suppressed and the equilibrium of reaction system are shifted to furfural production, which improve the yield of furfural.



**Scheme 2.** The role of solvents and catalysts in the hemicellulose selective dissolution, depolymerization and conversion to furfural needs more further attention.

The production of furfural with high yields and selectivity directly from hemicellulose in raw biomass is challenging but crucial. In order to obtain furfural with high yield and selectivity from hemicellulose, two strategies are highly considered (Scheme 2): The selective dissolution of hemicellulose in biomass, and simultaneous selective conversion of hemicellulose to produce furfural with high yield and selectivity directly via one-step method are recommended. The one-step method to achieve furfural with high yield and selectivity, appeals the development of multifunctional catalytic systems. By adjusting and controlling the function of the catalysts and solvents, the selectivity of hemicellulose dissolution and of the production of furfural is controlled. The use of biomass-derived green solvent such as GVL, 2-MTHF and so on, is highly expected in the reaction system. Alternatively, considering the selective dissolution of hemicellulose, as well as the production of furfural with high efficiency, two-step conversion of biomass is highly recommended. In the two-step reaction, it is expected to achieve the selective dissolution of hemicellulose while cellulose and lignin retained firstly, and then the further depolymerization and conversion of hemicellulose derivatives to furfural. For the selective dissolution of hemicellulose, the main challenges are to inhibit the dissolution of cellulose and lignin, which improve the selectivity of hemicellulose dissolution that simplifying the complexity of the starting materials. Simultaneously, the inhibition of the formation of side products, which are not benefit to produce furfural, is needed. Furthermore, the further valorization of hemicellulose derivatives to furfural with high yield and selectivity would be improved. Therefore, designing strategy for the selective dissolution of hemicellulose to obtain xylan or xylose type products that benefit for the follow-up reaction by the assistance of solvent and catalyst is necessary. It also needs to develop high effective catalytic system for the further conversion of hemicellulose derivatives to produce furfural by the design of novel efficient catalysts and new efficient solvent system. Hence, we expect that replacement of fossil resource-based production of furfural by more sustainable technologies based on renewable biomass will continue to grow.

**Acknowledgements**

This work is financially supported by the National Natural Science Foundation of China (No. 21536007), 111 Project (No. B17030) and Sichuan Science and Technology Program(No.2018JY0207).

**Notes and references**

[1] J. S. Luterbacher, D. M. Alonso, J. A. Dumesic, Green Chem., 16(2014), 4816-4838.

[2] P. Peng, D. She, Carbohydr. Polym. 112(2014), 701-720.

[3] E. L. Kunkes, D. A. Simonetti, R. M. West, J. C. Serrano-Ruiz, C. A. Gärtner, J. A. Dumesic, Science, 322(2008), 417-421.

[4] J. Q. Bond, D. M. Alonso, D. Wang, R. M. West, J. A. Dumesic, Science, 327(2010), 1110-1114.

[5] T. P. Vispute, H. Y. Zhang, A. Sanna, R. Xiao, G. W. Huber, Science, 330(2010), 1222-1227.

[6] J. R. Rostrup-Nielsen, Science, 308(2005), 1421-1422.

[7] D. R. Dodds, R. A. Gross, Science, 318(2007), 1250-1251.

[8] N. Sella Kapu, H. L.Trajano, Biofuels, Bioprod. Biorefin., 8(2014), 857-870.

[9] B. Kamm, P. R. Gruber, M. Kamm, Wiley-VCH Verlag GmbH & Co. KGaA, 2006.

[10] L. Negahdar, I. Delidovich, R. Palkovits, Appl. Catal., B, 184(2016), 285-298.

[11] K. Sanderson, Nature, 474(2011), 12-14.

[12] [S. V.Vassilev,](http://www.sciencedirect.com/science/article/pii/S0016236111005904#!) [D. Baxter,](http://www.sciencedirect.com/science/article/pii/S0016236111005904#!) [L. K.Andersen,](http://www.sciencedirect.com/science/article/pii/S0016236111005904#!) [C. G.Vassileva,](http://www.sciencedirect.com/science/article/pii/S0016236111005904#!) [T. J. Morgan](http://www.sciencedirect.com/science/article/pii/S0016236111005904#!), Fuel, 94(2012), 1-33.

[13] H. V. Scheller, P. Ulvskov, Annu. Rev. plant Biol., 61(2010), 263-289.

[14] L. Negahdar, I. Delidovich, R. Palkovits, Appl. Catal., B., 184(2016), 285-298.

[15] K. Tekin, S. Karagöz, S. Bektas, Renewable Sustainable Energy Rev.,40(2014),6733-687.

[16] D. O. Otieno, B. K. Ahring, Carbohydr. Res., 360(2012), 84-92.

[17] R. Sahu, P. L. Dhepe, ChemSusChem, 5(2012), 751-761.

[18] G. S. Yi, Y. G. Zhang, ChemSusChem, 5(2012), 1383-1387.

[19] J. Bian, F. Peng, X. P. Peng, P. Peng, F. Xu, R. C. Sun, Bioresour. Technol., 127 (2013), 236-241.

[20] B. S. Weeks, P. P. Perez, Med. Sci. Monit., 15(2009), 43-46.

[21] N. M. Hansen, D. Plackett, Biomacromolecules, 9(2008), 1493-1505.

[22] J. W. Agger, T. Isaksen, A.Várnai, S.Vidal-Melgosa, W. G. Willats, R. Ludwig, S. J. Horn, V. G. H. Eijsink, B. Westereng, Proc. Natl. Acad. Sci., 111(2014), 6287-6292.

[23] P. Langan, L. Petridis, H. M. O'Neill, S. V. Pingali, M. Foston, Y. Nishiyama, R. Schulz, B. Lindner, B. L. Hanson, S. Harton, W. T. Heller, V. Urban, B. R. Evans, S. Gnanakaran, A. J. Ragauskas, J. C. Smith, Green Chem., 16(2014), 63-68.

[24] F. Carvalheiro, L. C. Duarte, F. M. Gírio, J. Sci. Ind. Res., (2008), 849-864.

[25] H. M. Hernández-Hernández, J. J. Chanona-Pérez, A. Vega, P. Ligero, J. A. Mendoza-Pérez, G. Calderón-Domínguez, E. Terres, R. R. Farrera-Rebollo, Ind. Crops Prod., 86(2016), 163-172.

[26] A. R. C. Morais, M. D. D. Matuchaki, J. Andreaus, R. Bogel-Lukasik, Green Chem., 18(2016), 2985-2994.

[27] T. A. Werpy, G. Petersen, O. Ridge, US Department of Energy, Oak Ridge, USA, 2004.

[28] D. Montané, J. Salvadó, C. Torras, X. Farriol,Biomass Bioenergy, 22(2012),295-304.

[29] R. Mariscal, P. Maireles-Torres, M. Ojeda, I. Sádaba, M.López Granados, Energy Environ. Sci, 9(2016), 1144-1189.

[30] M. C. Mccann, N. C. Carpita, J. Exp. Bot., 66(2015), 4109-4118.

[31] M. E. Himmel, S. Y. Ding, D. K. Johnson, W. S. Adney, M. R. Nimlos, J. W. Brady, T. D. Foust, Science, 315(2007), 804-807.

[32] M. S. Mettler, D. G. Vlachos, P. J. Dauenhauer, Energy Environ. Sci., 5(2012), 7797-7809.

[33] X. B. Zhao, L. H. Zhang, D. H. Liu, Biofuels, Bioprod. Biorefin., 6(2012), 561-579.

[34] Y. Zheng, J. Zhao, F. Q. Xu, Y. B. Li, Prog. Energy Combust. Sci., 42(2014), 35-53.

[35] L. Kratky, T. Jirout, Chem. Eng. Technol., 34(2011), 391-399.

[36] J. Lee, J. Biotechnol., 56(1997), 1-24.

[37] Y. Sun, J. Y. Cheng, Bioresour. Technol., 83(2002), 1-11.

[38] V. B. Agbor, N. Cicek, R. Sparling, A. Berlin, D. B. Levin, Biotechnol. Adv., 29(2011), 675-685.

[39] R. P. Swatloski, S. K. Spear, J. D. Holbrey, R. D. Rogers, J. Am. Chem. Soc., 124 (2002), 4974-4975.

[40] Z. Liu, F. S. Zhang, Energy Convers. Manage., 49(2008), 3498-3504.

[41] D. M. Alonso, S. G. Wettstein, J. A. Dumesic, Green Chem., 15(2013), 584-595.

[42] S. Brethauer and C. E. Wyman, Bioresour. Technol., 2010, 101, 4862-4874.

[43] L. Shuai, J. Luterbacher, ChemSusChem, 9(2016), 133-155.

[44] F. Carvalheiro, L. C. Duarte, F. M. Girio, J. Sci. Ind. Res., 67(2008), 849-864.

[45] M. J. Taherzadeh, K. Karimi, BioResources, 2(2007), 707-738.

[46] I. Finore, A. Poli, P. Di Donato, L. Lama, A. Trincone, M. Fagnano, M. Mori, B. Nicolaus, A. Tramice, Green Chem., 18(2016), 2460-2472.

[47] P. Kaur, N. K. Bhardwaj, J. Sharma, Carbohydr. Polym., 145(2016), 95-102.

[48] P. D. Carà, M. Pagliaro, A. Elmekawy, D. R. Brown, P. Verschuren, N. R. Shiju, G. Rothenberg, Catal. Sci. Technol., 3(2013), 2057-2061.

[49] M. S. Holm, S. Saravanamurugan, E. Taarning, Science, 328 (2010), 602-605.

[50] R. Karinen, K. Vilonen, M. Niemelä, ChemSusChem, 4(2011), 1002-1016.

[51] H. G. Bernal, L. Bernazzani, A. M. R. Galletti, Green Chem., 16(2014), 3734-3740.

[52] S. Dutta, S. De, B. Saha, M. I. Alam, Catal. Sci. Technol., 2(2012), 2025-2036.

[53] E. I. Gürbüz, S. G. Wettstein, J. A. Dumesic, ChemSusChem, 5(2012), 383-387.

[54] A. Corma, S. Iborra, A. Velty, Chem. Rev., 107(2007), 2411-2502.

[55] M. A. T. Hansen, H. Jørgensen, K. H. Laursen, J. K. Schjørring, C. Felby, Biomass Bioenergy, 56(2013), 572-581.

[56] J. P. Lange, E. Van der Heide, J. Van Buijtenen, R. Price, ChemSusChem, 5(2012), 150-166.

[57] M. A. Mellmer, C. Sener, J. M. R. Gallo, J. S. Luterbacher, D. M. Alonso, J. A. Dumesic, Angew. Chem. Int. Ed., 53(2014), 11872-11875.

[58] J. M. R. Gallo, D. M. Alonso, M. A. Mellmer, J. H. Yeap, H. C. Wong, J. A. Dumesic, solvent. Top. Catal., 56(2013), 1775-1781.

[59] E. I. Gürbüz, J. M. R. Gallo, D. M. Alonso, S. G. Wettstein, W. Y. Lim, J. A. Dumesic, Angew. Chem. Int. Ed., 52(2013), 1270-1274.

[60] G. Marcotullio, W. De Jong, Green Chem., (12)2010, 1739-1746.

[61] J. M. R. Gallo, D. M. Alonso, M. A. Mellmer, J. H. Yeap, H. C. Wong, J. A. Dumesic, Top Catal., (56)2013, 1775-1781.

[62] H. L. Li, J. L. Ren, L. J. Zhong, R. C. Sun, L. Liang, Bioresour. Technol., 176(2015), 242-248.

[63] O. Yemis, G. Mazza, Bioresour. Technol.,102(2011), 7371-7378.

[64] N. Sweygers, J. Harrer, R. Dewil, L. Appels, J. Clean. Prod., 187(2018), 1014-1024.

[65] L.X. Zhang, H. B. Yu, P. Wang, Y. Li, Bioresour. Technol.,151(2014), 355-360.

[66] W. J. Wang, J. L. Ren, H. L. Li, A. J. Deng, R. C. Sun, Bioresour. Technol., 183(2015), 188-194.

[67] Y. Yang, C. W. Hu, M. M. Abu-Omar, ChemSusChem, 5(2012), 405-410.

[68] T. Yang, Y. H. Zhou, S. Z. Zhu, H. Pan, Y. B. Huang, ChemSusChem, 10(2017), 4066-4079.

[69] Q. X. Lin, H. L. Li, X. H. Wang, L. F. Jian, J. L. Ren, C. F. Liu, R. C. Sun, Catalysts, 7(2017), 118-131.

[70] A. S. Mamman, J. M. Lee, Y. C. Kim, I. T. Hwang, N. J. Park, Y. K. Hwang, J. S. Chang, J. S. Hwang, Biofuels, Bioprod. Biorefin., 2(2008), 438-454.

[71] A.M. C. Lopes, A. R. C. Morais, R. M. Lukasik, Production of Platform Chemicals from Sustainable Resources, chapter 2, Springer Singapore, 2017, 45-80.

[72] S. Van den Bosch, W. Schutyser, R. Vanholme, T. Driessen, S. F. Koelewijn, T. Renders, B. D. Meester, W. J. J. Huijgen, W. Dehaen, , C. M. Courtin, B. Lagrain, W. Boerjan, B. F. Sels, Energy Environ. Sci., 8(2015), 1748-1763.

[73] M. Hakola, A. Kallioinen, M. Kemell, P. Lahtinen, E. Lankinen, M. Leskelä, T. Repo, T. Riekkola, M. Siika-aho, J. Uusitalo, S. Vuorela, N. V. Weymarn, ChemSusChem, 3(2010), 1142-1145.

[74] D. Q. Ding, J. J. Wang, J. X. Xi, X. H. Liu, G. Z. Lu, Y. Q. Wang, Green Chem., 16(2014), 3846-3853.

[75] J. J. Fan, M. De Bruyn, V. L. Budarin, M. J. Gronnow, P. S. Shuttleworth, S. Breeden, D. J. Macquarrie, J. H. Clark, J. Am. Chem. Soc., 135(2013), 11728-11731.

[76] Y. Sun, J. Y. Cheng, Bioresour. Technol.,83(2002), 1-11.

[77] M. Sasaki, T. Adschiri, K. Arai, Bioresour. Technol., 86(2003), 301-304.

[78] Y. P. Luo, Z. Li, Y. N. Zuo, Z. S. Su, C. W. Hu, ACS Sustainable Chem. Eng.*, 5*(2017), 8137-8147.

[79] D. M. Alonso, S. G. Wettstein, M. A. Mellmer, E. I. Gurbuz, J. A. Dumesic, Energy Environ. Sci., 6 (2013), 76-80.

[80] J. Li, D. J. Ding, L. J. Xu, Q. X. Guo, Y. Fu, RSC Adv., 4(2014), 14985-14992.

[81] P. Brazdausks, N. Vedernikovs, M. Puke, I. Kruma, Key Eng. Mater., 64(2014), 245-248.

[82] J. S. Luterbacher, J. M. Rand, D. M. Alonso, J. Han, J. T. Youngquist, C. T. Maravelias, B. F. Pfleger, J. A. Dumesic, Science, 343(2014), 277-280.

[83] T. J. Wang, K. Li, Q. Y. Liu, Q. Zhang, S. B. Qiu, J. X. Long, L. G. Chen, L. L. Ma, Q. Zhang, Appl. Energy, 136(2014), 775-780.

[84] X. Y. Li, Q. L. Liu, C. H. Luo, X. C. Gu, L. F. Lu, X. B. Lu, ACS Sustainable Chem. Eng. 5(2017), 8587-8593.

[85] P. LaxmikantáDhepe, RSC Adv., 4(2014), 26215-26221.

[86] W. Z. Li, Y. S. Zhu, Y. J. Lu, Q. Y. Liu, S. N. Guan, H. M. Chang, H. Jameel, L. L. Ma, Bioresour. Technol., (245)2017, 258-265.

[87] L. X. Zhang, G. Y. Xi, J. X. Zhang, H. B. Yu, X. C. Wang, Bioresour. Technol., (224)2017, 656-661.

[88] Y. P. Luo, L. B. Hu, D. M. Tong, C. W. Hu, RSC Adv., 4 (2014), 24194-24206.

[89] M. Stöcker, Angew. Chem. Int. Ed., 47(2008), 9200-9211.

[90] Q. Qing, B. Yang, C. E. Wyman, Bioresour. Technol., 101(2010), 9624-9630.

[91] Y. Kim, E. Ximenes, N. S. Mosier, M. R. Ladisch, Enzyme Microb. Technol., 48(2011), 408-415.

[92] R. R. Singhania, R. K. Sukumaran, A. K. Patel, C. Larroche, A. Pandey, Enzyme Microb. Technol., 46(2010), 541-549.

[93] J. D. DeMartini, S. Pattathil, J. S. Miller, H. Li, M. G. Hahn, C. E. Wyman, Energy Environ. Sci. 6(2013), 898-909.

[94] K. Dussan, B. Girisuta, M. Lopes, J. J. Leahy, M. H. Hayes, ChemSusChem. 9(2016), 492-504.

[95] A. V. Carvalho, A. M. da Costa Lopes, R. Bogel-Łukasik, RSC Adv., 5(2015), 47153-47164.

[96] P. Zhang, S. J. Dong, H. H. Ma, B. X. Zhang, Y. F. Wang, X. M. Hu, Ind. Crops Prod., 76 (2015), 688-696.

[97] C. K. Nitsos, K. A. Matis, K. S. Triantafyllidis, ChemSusChem, 6(2013), 110-122.

[98] C. K. Nitsos, T. C. Papadopoulou, K. A. Matis, and Kostas S. Triantafyllidis, ACS Sustainable Chem. Eng., 4 (2016), 4529-4544.

[99] J. Luo, Y. Xu, L. J. Zhao, L. L. Dong, D. M. Tong, L. F. Zhu, C. W. Hu, Bioresour. Technol., 101(2010), 8873-8880.

[100] S. Peleteiro, V. Santos, G. Garrote, J. C. Parajo, Carbohydr Polym, 146(2016), 20-25.

[101] Y. P. Luo, J. J. Fan, V. L. Budarin, C. W. Hu, J. H. Clark, Green Chem., 2017, 19, 4889-4899.

[102] Y. Xu, L. B. Hu, H. T. Huang, D. M. Tong, C. W. Hu, Carbohydr. Polym., 88(2012), 1342-1347.

[103] L. Q. Jiang, A. Q. Zheng, Z. L. Zhao, F. He, H. B. Li, W. G. Liu, Bioresour. Technol., 182(2015), 364-367.

[104] S. Mateo, J. G. Puentes, S. Sánchez, A. J. Moya, Carbohydr. Polym., 93(2013), 416-423.

[105] J. Yi, T. He, Z. C. Jiang, J. M. Li, C. W. Hu, Chi. J. Catal., 34(2013), 2146-2152.

[106] C. Zhong, C. M. Wang, F. Huang, F. X. Wang, H. H. Jia, H. Zhou, P. Wei, Carbohydr. Polym., 131(2015), 384-391.

[107] W. Fang, H. Sixta, ChemSusChem, 8(2015), 73-76.

[108] T. He, Z. C. Jiang, P. Wu, J. Yi, J. M. Li, C. W. Hu, Sci. Rep., 6(2016), 38623-38633

[109] M. C. Molina, R. Mariscal, M. Ojeda, M. L. Granados, Bioresour. Technol., 126(2012), 321-327.

[110] C. M. Cai, T. Zhang, R. Kumar, C. E. Wyman, Green Chem., 15(2013), 3140-3145.

[111] B. S. Santucci, P. Maziero, S. C. Rabelo, A. A. Curvelo, M. T. B. Pimenta, Bioenergy Res., 8(2015), 1778-1787.

[112] Y. Y. Bai, L. P. Xiao, R. C. Sun, Biomass Bioenergy, 75(2015), 245-253.

[113] E. S. Kim, S. Liu, M. M. Abu-Omar, N. S. Mosier, Energy Fuels, 26(2012), 1298-1304.

[114] A. Mittal, S. K. Black, T. B. Vinzant, M. O. Brien, M. P. Tucker, D. K. Johnson, ACS Sustainable Chem. Eng., (5)2017,5694-5701.

[115] A. R. C. Morais, M. D. D. Matuchaki, J. Andreaus, R. Bogel-Lukasik, Green Chem., 18(2016), 2985-2994.

[116] R. Xing, W. Qi, G. W. Huber, Energy Environ. Sci., 4(2011), 2193-2205.

[117] H. L. Li, X. F. Chen, J. L. Ren, H. Deng, F. Peng, R. C. Sun, Biotechnol. Biofuels, 8(2015), 127-138.

[118] H. L. Gao, H. T. Liu, B. Pang, G. Yu, J. Du, Y. D. Zhang, H. S. Wang, X. D. Mu, Bioresour. Technol., (172)2014, 453-456.

### [119] H. Q. Lê, A. Zaitseva, J. Pokki, M. Ståhl, V. Alopaeus, H. Sixta, ChemSusChem, (9)2016, 2939-2947.

[120] D. Steinbach, A. Kruse, J. Sauer, Biomass Conv. Bioref., Biomass Conv. Bioref., (2) 2017, 247-274.