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REVIEW

# An Insight into the Valorization of Hemicellulose Fraction of Biomass into Furfural: Catalytic Conversion and Product Separation

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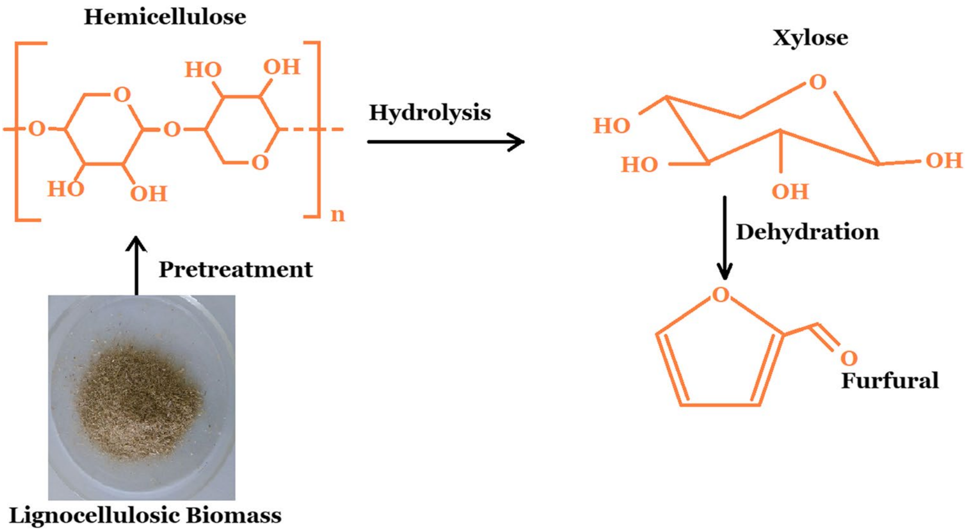
## Abstract

The global impetus to produce alternatives for the petroleum-based fuels and value-added chemicals in order to reduce greenhouse gases is currently emphasizing stringent need on the industries to diversify and valorize byproducts. This further aims at the valorization of agroindustrial by-product into furfural. A thorough investigation of research advances particularly, the pretreatment of biomass, a pertinent reaction mechanism in furfural production, separation of furfural and the various used catalysts were explored in the current review. The biomass, which contains fiber, lignin, pentosans, and pith, can be converted into furfural by the application of suitable chemical, biochemical and microbial methods. Dilute acid, alkali and hydrothermal pretreatment methods for hemicellulose separation from the biomass matrix were discussed in detail. Studies on the development of an effective and stable catalyst to overcome the limitation of the existing commercial processes were also reviewed. The strategies including the steam stripping, nitrogen stripping, supercritical carbon dioxide extraction, mono- and biphasic solvent extractions were investigated in this study, as a way forward towards the removal of furfural from the reaction medium, thereby assisting in the avoidance of the product degradation.

### Graphic Abstract



**Keywords** Furfural · Heterogeneous catalyst · Biomass · Hydrolysis · Dehydration · Furfural separation

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## Statement of Novelty

The purpose of this review is to demonstrate the gaps in producing the furfural from biomass efficiently. It provides insights and understanding of lignocellulosic biomass conversion over various catalysts in view of the production of furfural. It is intended to give a clue for the readers on the reaction mechanisms, pretreatment methods to enhance furfural yield and the various catalysts which can be applied for biomass valorization processes. This review is important as it also elucidates furfural isolation mechanisms to help readers understand the effect of the method on the yield.

## Introduction

Conversion of biomass into sustainable energy and various chemicals is recently becoming an attractive alternative to resolve the problems of mankind [1]. Lignocellulosic biomass contains cellulosic, hemicellulosic and lignin components which can be transformed into various platform chemicals such as furfural. Furfural can be produced from xylan, a five-carbon saccharide, undergoing hydrolysis reaction followed by the dehydration upon the release of the three water molecules. Most organic conversions in chemical process industries are based on the acid-base homogeneous catalysis. Mineral acids are used in industrial furfural productions and sulphuric acid is the most widely used catalyst in the production of furfural [2]. Hydrochloric acid, nitric acid, and phosphoric acid are also among the reported homogeneous catalysts used to catalyze the conversions [3, 4]. These catalysts, however, are corrosive to the reaction system and careful handling of them is required [5, 6]. The use of homogeneous acid catalysts requires extra separation steps after reaction which may lead to additional costs. The production of furfural is one of the chemical processes that involve the use of these catalysts which may be toxic, hazardous and corrosive. Besides, these catalysts are not reusable and recoverable from the reaction mixture, as either they may form a complex molecule with the product or they are highly soluble in the reaction mixture resulting in hazardous waste effluents [7]. This also leads to the formation of hazardous inorganic acids as by-products. Hence, the environment is soaringly affected by these chemical processes. Various attempts have been carried out by the researchers to mitigate the chemical pollution occurring due to the use of acid homogeneous catalysts. Heterogeneous solid acids have advantages over the conventional homogeneous acid catalysts, for instance, the simplicity in handling, decreased reactor problems, plant corrosion problems, and they can be easily recovered and reused several times without any loss of their efficiency [8].

## Lignocellulosic Biomass as a Source of Carbohydrate for the Furfural Production

Furfural is produced mainly from the lignocellulosic biomass with high hemicellulose content. Lignocellulosic biomass, the raw materials for furfural production, differ in composition and structure based on the species of the biomass and environmental growth conditions [9]. The most common sources to produce furfural are sugarcane bagasse and corncobs [10] Lignocellulosic biomass contains three main components based on their mass contributions [11]. These are cellulose, hemicellulose, and lignin which are mainly linked together by the hydrogen bond. Cellulose is a polymer composed of six carbon glucose linked to each other with $\beta$-glycosidic bonds [12–14]. Cellobiose is the repeating unit and hydrogen bonds are responsible for the high water insolubility and flexibility of cellulose crystalline structure [15]. The elementary fibrils formed by the adjacent chains contain amorphous and crystalline regions, the amorphous region is subjected to hydrolysis first [16]. Hemicellulose is a mixed polymer of both five and six-carbon monosaccharide molecules. It consists of polymers of glucose, galactose, mannose, xylose, arabinose and other five and six carbon monosaccharides [17]. Xylan, mannans, and galactans are the main amorphous polymer groups in hemicellulose [18]. The polymer xylan is the major component of sugarcane bagasse hemicellulose which is composed of thousands the monomer xylose linked to each other by the $\beta$-(1,4)-glycosidic bonds [19]. Its backbone contains xylose of more than 80% [20].

Lignin, one of the major components of lignocellulosic biomass, is a highly cross-linked hydrophobic polymer which binds the hemicellulose to cellulose [9]. It is an amorphous three-dimensional aromatic biomolecule consisting of tyrosine and phenylalanine as building blocks. The three monomer units, p-hydroxyphenylpropane (H), guaiacylpropane (G) and syringylpropane (S), synthesized from coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol respectively, polymerize by dehydrogenation to form lignin having different structure and relatively high recalcitrant property from cellulosic polysaccharides [21]. The cellulose, hemicellulose, and lignin are linked to each other by the hydrogen bonds. Besides these, the lignin is linked to hemicellulose with the covalent feruloyl ester-ether chemical bonds [22]. The presence of non-hydrolyzable C–O–C and C–C bonds in its structure and heterogeneity of the ether & C–C bonds hamper the degradation of lignin. During the acid hydrolysis for the fractionation of the lignocellulosic biomass into cellulose, hemicellulose and lignin, the formation of the complex products due to the possible formation of acid-soluble lignin-based components in the reaction, may occur [23]. Lignin has the tendency to neutralize the acidity and inhibit the formation of furfural by dehydration of the xylose in an acidic reaction medium [24]. Lamminpää et al. [24] studied the effect of the presence of lignin along with the hemicellulose on the yield of furfural and confirmed that it has a negative effect on both the conversion of xylose and the yield of furfural [24]. Daorattanacha et al. [25] reported a 24% decrease in xylose conversion and a 11% decrease in the yield of furfural upon the addition of 50 wt. % lignin loading [25]. On the other hand, the presence of lignin assists the isomerization of glucose to fructose and the subsequent conversion, provided no low catalyst loading conditions, to hydroxymethylfurfural [25]. Several methods, for example, the alkaline and alkaline peroxide pretreatment, organic solvent extraction, ultrasonication, and twin-screw extrusion treatments, and microwave treatment have been used to remove lignin [26, 27]. In alkaline treatment, the most widely used delignification method [26], a soda solution is used to solubilize and remove the lignin after the biomass is exposed to mechanical and hot water pretreatment at around 100 °C and above for about or more than an hour [28, 29]. In the acid pretreatment, dilute sulfuric acid is used to isolate hemicellulose from lignin and cellulose [30]. The combination of the two methods appears to be promising because their advantages could be coupled and minimize their disadvantages. Acid pretreatment followed by alkaline improves the removal of lignin through solubilization by breaking the ether bonds and deprotonation of ionizable groups [31]. Luo et al. [32] fractionated pubescens into 87 wt % cellulose, 93.6 wt % hemicellulose and 80.2 wt% lignin derivatives in 25% GVL/water system at 160 °C within 4 h [32].

## Biomass Pre-treatment for Isolation of Hemicellulose

Quaker Oats Technology is the oldest commercial way of producing furfural, conceived in 1921 [13]. Quaker Oats Technology or its modified versions are used to produce furfural. In the Quaker Oats Technology, biomass is treated with sulfuric acid at 153 °C for 5 h to hydrolyze the pentosan content and generate pentoses. In this process, the raw 100 kg biomass is mixed with 2.246 kg sulfuric acid without any pretreatment step and the fed to the reactor. Steam stripping is applied to recover furfural after it is formed by the dehydration of the pentoses in the subsequent stage. Low yield around 50%, high steam requirement, disposal problems due to extremely acidic waste discharge and high operating cost are the major challenges in this process [33]. Various studies have been undertaken to improve furfural production technology to achieve higher yield and lower cost and to make environmentally friendly. In this regard, the scholars have been searching for low-cost catalyst, better product separation technology and a suitable solvent. In order to facilitate, the heat and mass transfer, the biomass should undergo size reduction and then the isolation of the components is carried out [34]. Seaparation of the hemicelluloses component, in order to reduce the recalcitrant nature of the biomass or the biomass pretreatment is an important step. Pretreatment has an impact on the furfural yield by reducing the amount of lignin, which polymerizes with other compounds in acidic conditions [35]. It may also reduce operating cost if the recycling of catalyst is considered [36].

Isolation of hemicellulose can be through several pretreatment ways using chemical, biochemical, physical or physicochemical methods. This step can be performed by steam explosion, organic solvents, acids such as dilute sulfuric acid or phosphoric acid, alkali treatment using alkaline agents such as sodium hydroxide, ammonia or lime, and autohydrolysis [37]. Figure 1 illustrates the various pretreatment methods along with the possible intermediate and final products obtained from the biomass. Applications and purpose of the extraction products, mainly containing the hemicellulose, are the main considerations that should be incorporated in determining the extraction method. The degree of polymerization, reactivity, purity, and solubility are among the important characteristics of the extracted hemicellulose which can be affected by the method of isolation used [38]. Dilute acid pretreatment of bagasse produces monosaccharide and oligosaccharides, while alkaline pretreatment results in the polysaccharides [30, 38].

### Dilute Acid Pretreatment

Acid pretreatment selectively extracts hemicellulose from the cellulose, hemicellulose and lignin complex because hemicellulose is more readily separated under acidic conditions due to its amorphous nature. It is often done using dilute acids to reduce the problems associated with the use of concentrated acids like the corrosion of the reactors, other equipment and energy requirement for acid recovery [38, 39]. $H_2SO_4$, HCl and $H_3PO_4$ are commonly used to cleave the glucosidic linkage thereby solubilizing the hemicellulose component predominantly to pentose and at some extent to insoluble cellulose and lignin fractions. In this isolation method, furfural is also formed in a small amount [38]. The concentration of 0.5 to 1.5% of sulfuric acid at the temperature above 121–160 °C was reported for the hydrolysis of hemicellulose [39]. About 75 to 95% recovery of sugar can be achieved using the dilute acid treatment.

### Hydrothermal Pretreatment

Hydrothermal pretreatment is used to preferentially extract the hemicellulose from the cellulose, hemicellulose and lignin complex. Hemicellulose can be extracted in hot water at a lower temperature than the cellulose and lignin [40,

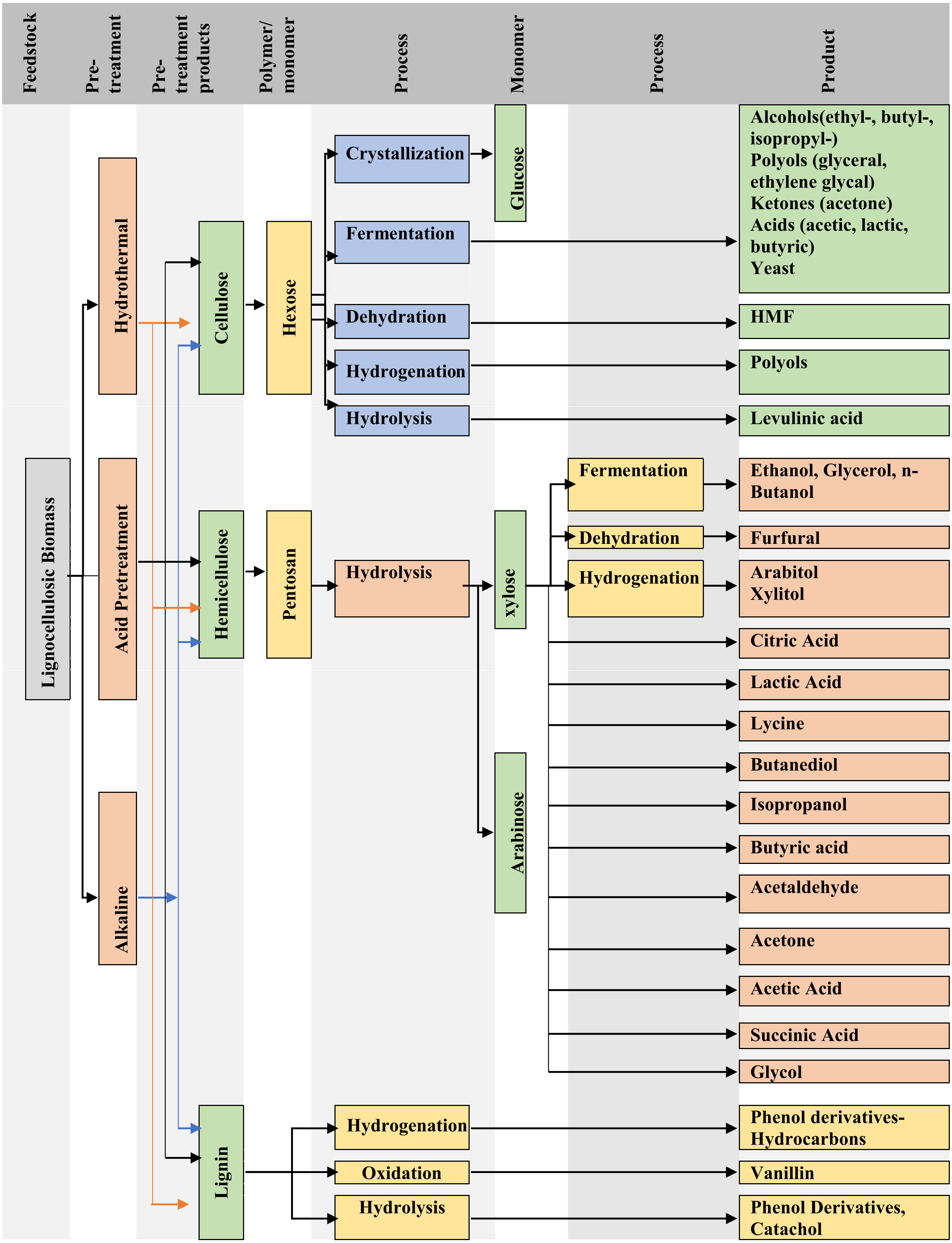


**Fig. 1** Major polymeric and monomeric sugar intermediates and products of lignocellulosic biomass processing

41]. Hot, compressed water depolymerize and solubilize the hemicellulose into pentoses and di- and poly-saccharides of pentoses. Autohydrolysis and steam explosion are the hydrothermal pretreatment methods.

#### Autohydrolysis

Autohydrolysis uses hot, compressed water usually at the temperature between 150–230 °C. Like dilute acid pretreatment, this isolation method uses hydronium ion to catalyze the hemicellulose extraction process [42]. *O*-glycosidic linkages and acetyl groups break, resulting in partial depolymerization when hydronium ion is released because of an increase in temperature. The acetate group cleaves to some extent and the pH decreases resulting in the formation of additional acetic acid. Autohydrolysis is a green process as it uses only aqueous media without the addition of chemicals [37]. The liquor resulting from the hot water pretreatment includes oligosaccharides and polysaccharides [43]. 55 to 84% of hemicellulose was obtained through the autohydrolysis [39]. The solids remaining after the pretreatment contain, mainly cellulose and lignin which can be further converted to useful chemicals [44].

#### Steam Explosion

Steam explosion is another physical pretreatment method which helps to separate the hemicellulose from the lignocellulosic material by solubilizing the soluble components. In this method, the chipped biomass is exposed to saturated steam under high pressure and then the pressure is suddenly reduced to help the biomass undergo explosive decomposition [45]. The sudden compression and expansion depolymerize the fiber and the soluble products of the pretreatment should be removed from the reactor to reduce destruction reactions. Full recovery of hemicellulose can be achieved in the presence of sulfuric acid or sulfur dioxide [45]. Steam explosion is less expensive and less energy consuming process when compared to acid pretreatment because it uses no external catalyst and requires less amount of water (around 3 to 7 times less) to pretreat the same amount of biomass [46]. Even though it is an inexpensive pretreatment method, the steam explosion has limitations like the destruction of some portion of the pentosan.

### Alkaline Pretreatment

Organic solvents and alkaline agents remove lignin together with hemicellulose as they do not selectively remove hemicellulose from the complex matrix [39, 47]. Alkaline pretreatment can be categorized into two, i.e. alkaline/alkaline earth metals and ammonia based, depending on the type of catalyst involved in fractionating the lignocellulosic components [39]. Using $Na_2CO_3$, up to 82% xylan extraction from sugarcane bagasse was achieved and low formation of furan aldehyde observed. Alkaline pretreatment under microwave radiation with improved recovery was also studied [48]. Biomass pretreatment should achieve optimized isolation of the hemicellulose component with lower recalcitrance to facilitate the successive conversion to value-added chemicals such as furfural. To mitigate issues related to disposal, the environmentally benign chemicals are required to be used during the pretreatment. Suitable, energy efficient and inexpensive pretreatment methods are also required [49].

### Microwave-Assisted Pretreatment

Electromagnetic waves with frequencies ranging from 0.3–300 GHz are useful to heat up dielectric substances with high potential to absorb microwaves [50]. Aqueous systems are very suitable for the application of microwaves because water is a highly polar substance [50]. Furthermore, microwave heating has advantages like the energy efficiency, faster reaction time and lower reaction temperature when compared to the conventional heating [51]. It directly provides energy to substances by molecular interaction with electromagnetic fields. It also saves costs by reducing the amount of chemical/solvents used to fractionate the biomass components, minimizing the by-product formation and increasing the yield. The extent of biomass fractionation depends on the microwave intensity and irradiation time. Several studies have been carried out on the extraction of the hemicellulosic components from various lignocellulosic biomass like spruce wood [52], tobacco biomass [53], aspen wood and sugarcane trash [54]. Up to 66.1 and 5.3%, xylan and xylose were obtained respectively from aspen wood at 195 °C in 20 min and up to 50% (w/w) xylan and 6% (w/w) xylose from sugarcane trash at temperatures above 170 also reported up to about 70 wt% hemicellulose from sugarcane bagasse at 185 °C in 20 min and 77% from softwood sawmill shavings at 190 °C in 10 min [55].

## Furfural

Furfural is a promising chemical platform aldehyde with empirical formula $C_5H_4O_2$. It is a colorless liquid with a characteristic 'almond-benzaldehyde' odor [56]. It was first isolated in 1821 by a German scientist, Dobereiner [57]. These days, furfural is considered as one of the top value-added chemicals with a huge potential to be produced from the lignocellulosic biomass [58]. Furfural can be produced from the agro-industrial residues, including the corncob, wood wastes and sugarcane bagasse. Sugarcane bagasse and corncob are the main raw materials used for the commercial productions [45]. It can also be produced from the fossil-based raw materials like 1,3-dienes, but this is not economical as compared to the lignocellulosic biomass-based sources [59]. As shown in Fig. 2, furfural can be subjected to other different reactions to produce various other useful chemicals [47].

## Applications of Furfural

Furfural is a platform chemical having various industrial applications. It has an excellent property for dissolving the components selectively. It can be used to extract unsaturated compounds from oil which can be used to make drying oils and remove aromatic compounds from diesel fuel and lubrication oil to improve their properties and hence produce high quality motor oil. It can also be used as very effective fungicide with better effect and faster action as compared to the formaldehyde, even if applied at low concentrations. It kills wheat smut in 3 h while formaldehyde does in 6 h at 0.5% concentration dose. The advantage of using furfural as fungicide is, its effect on the seed germination power is insignificant whereas the formaldehyde completely damages this power at concentration of 0.5% if wheat seed is soaked for 6 h [33].

Furfural can be converted to other useful compounds such as furfuryl alcohol, methyltetrahydrofuran, furoic acid, tetrahydrofurfuryl alcohol, α-Methylfurfuryl alcohol, levulinic acid, pyrrole, furfurylamine, tetrahydrofurfurylamine, piperidine furoic esters, and tetrahydrofuroic acid. Furfuryl alcohol (FA) is used to make furan resins, cement, composites and corrosion resistant fiber reinforced plastics. FA acts as viscosity reducing agent and reactive solvent in production of epoxy resins and phenolic resins respectively. Tetrahydrofuryl alcohol is specialty solvent and chemical intermediate produced through further conversion of FA (Table 1).

## Chemistry of Furfural Formation

The conversion of hemicellulose to furfural takes place through two steps [60]. The first step is the hydrolysis of polysaccharide into simple sugar. In this step, xylan is broken into the monomer xylose. Xylose is then converted to furfural in the second step through dehydration by removal of three molecules of water [57].

**Fig. 2** Possible chemicals that can be produced from furfural

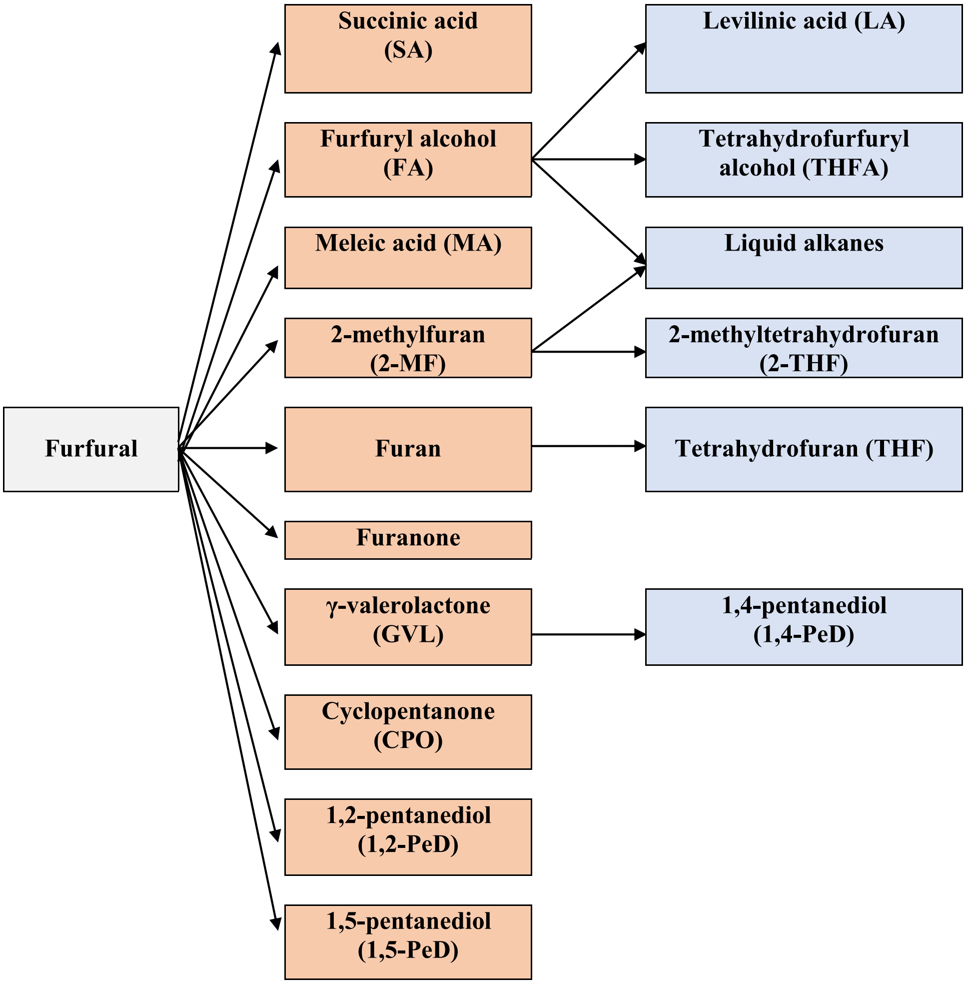
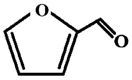
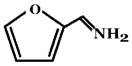
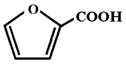
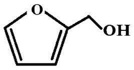
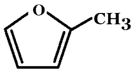
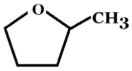
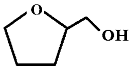
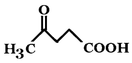
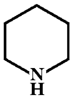


**Table 1** Applications of furfural and its derivatives

| Name of compound | Chemical structure | Applications | Refs. |
|---|---|---|---|
| Furfural |  | Used as a nematocide, fungicide and preservative<br>Solvent: extractant for aromatics from lubricating oils, Purification solvent for hydrocarbons, reactive solvent and wetting agent<br>Platform for many chemicals such as<br>Furfurylamine, furoic acid, furan, *α*-(methyl)-furfuryl alcohol, furfuryl alcohol, 2-methylfuran, furoic esters, levulinic acid, 2-methyltetrahydrofuran, tetrahydrofurfurylamine, tetrahydrofuroic acid, tetrahydrofurfuryl alcohol, α-Acetylfuran and Piperidine | [131] |
| Furfurylamine |  | A platform to produce diuretic furosemide for removal of excess water and salt from human body<br>Synthesis of herbicides, pesticides, pharmaceuticals, and piperidine derivatives | [131] |
| Furoic acid |  | Used to produce furoyl chloride, which is used in medication and insecticide manufacturing<br>Is precursor for synthesis of perfumes, cardiovascular and cancer drugs, antibiotic, alpha blockers, and corticosteroid intermediates. | [131] |
| Furan |  | Preparation of specialty chemicals such as *a*-acetylfuran, 2,5-dimethoxy-2,5-dihydrofuran, 2,2-difurylpropane, 2,2-di(tetrahydrofurfuryl)propane, and pyrrole derivatives. | [131] |
| Furfuryl alcohol |  | Production of foundry sand binders, wood protection, corrosion-resistant fiber-reinforced plastics, cements and mortars<br>Used as reactive solvent for phenolic resins in the refractory industry, as paint stripper, cleaning compound formulation, lubricants, dispersing agents, viscosity reducer for epoxy resins<br>Chemical building block for drug synthesis, synthetic fibers, rubbers, lysine and vitamin C | [131] |
| 2-Methylfuran |  | Used for antimalarial drug production<br>Used as an octane number improver | [132] |
| 2-Methyltetra-hydrofuran |  | Gasoline additives and higher boiling substitute for tetrahydrofuran as specialty solvent<br>Used in the electrolyte formulation for secondary lithium electrodes and as a component of alternative fuels | [133] |
| Tetrahydro-furfuryl alcohol |  | High-boiling solvent for dyes, printing inks, pesticides and herbicides, paint-stripping agent, industrial cleaner<br>Reactive diluent for epoxy resins<br>Preparation of disinfectants and antimetabolite drugs. | [131] |
| Levulinic acid |  | Production of succinic acid and δ-aminolevulinic acid | |
| Piperidine |  | Piperidine is used as a solvent and building block in the pharmaceutical industry | [134] |

$$C_5H_{10}O_5 \rightarrow C_5H_4O_2 + 3H_2O.$$

### Mechanism for the Hydrolysis of Pentosan

Pentosan consists predominantly of rings linked by oxygen bridges (ether bridges). As shown in Fig. 3, protonation of oxygen link is the first step of hydrolysis of pentosan and carbon-oxygen bond cleavage follows resulting in the formation of the hydroxyl group on one side oxygen bridge and carbonium ion is formed during the reaction on the other side. The addition of water molecule onto carbocation forms $H_2O^+$ group and then $H_2O^+$ group liberates hydrogen ion leaving a hydroxyl group behind. These steps of hydrolysis continue until the all oxygen bridge disappears.

### The Mechanism for the Dehydration of Pentose

Various mechanisms for the transformation of xylose to furfural have been proposed but, most studies focus on the cyclodehydration mechanism removing three molecules of water using heterogeneous catalysts. Figure 3 shows the mechanism for removal of three molecules of water from xylose to form furfural. First, protonation of the free electron pair on hydroxyl group results in trivalent positively charged oxygen and the positive charge moves to the adjacent carbon

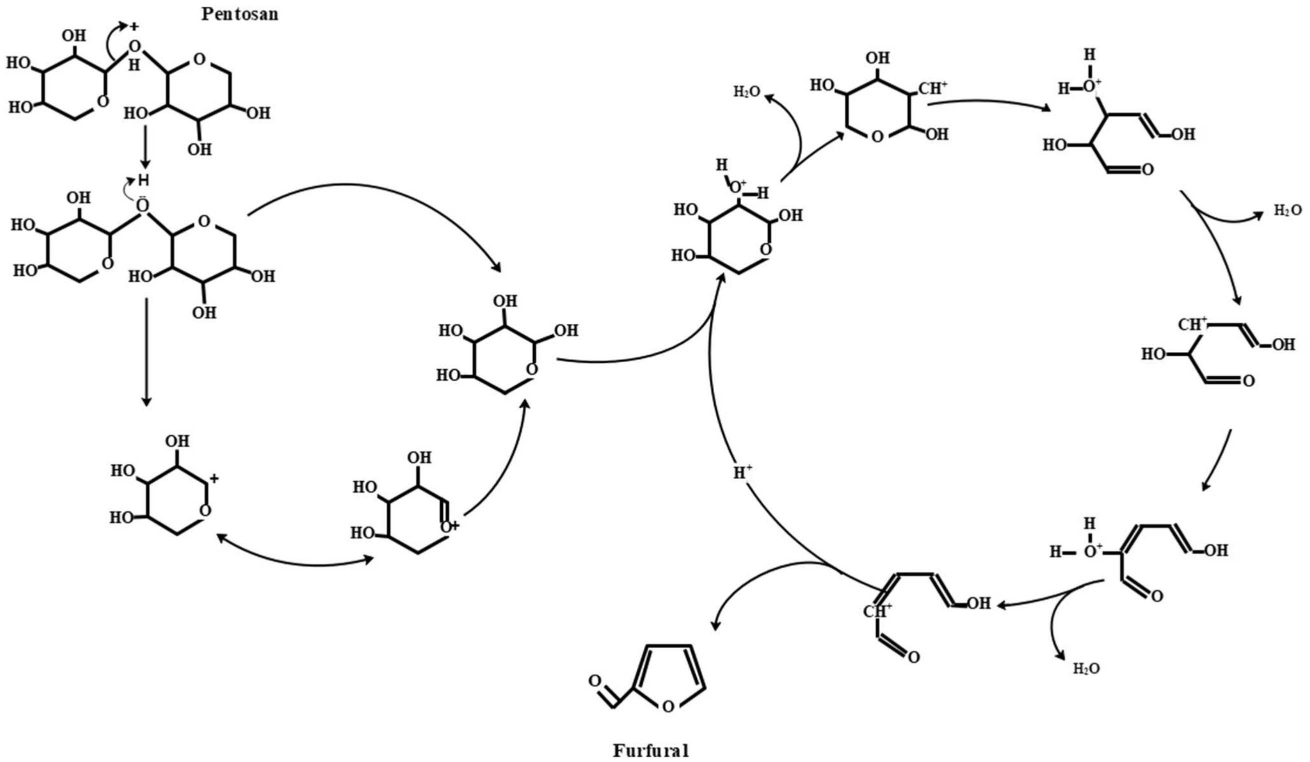


**Fig. 3** The mechanism for the hydrolysis of pentosan and the dehydration of pentose

atom to arrange itself to more stable conformation before C–O bond breaks and a water molecule is released. Then, the two electrons from the neighboring C–O bond are attracted to the C–C bond. This causes the formation of the double bond and the C–O bond breaks liberate another hydrogen ion. This hydrogen ion then attacks electron pair on the oxygen of another hydroxyl group to liberate another water molecule. The attacked site splits to another carbocation and water molecule. The resulting hydrogen ion migrates and attacks another non-bonded pair of electrons on another hydroxyl groups and other two water molecules are released upon dissociation. In the end, ring formation takes place by 1,4-elimination [45, 61]. Other reaction mechanisms such as xylose dehydration via enolization and β-elimination were also proposed as shown in Fig. 4.

Xylose dehydration to furfural through lyxose and xylulose formation by functional group rearrangement or by reconfiguration around C1 and C2 carbon atoms were also reported as it can be seen in Fig. 4. With Brønsted acids, furfural can be formed directly from xylose while Lewis acids lead to furfural through the intermediate xylulose. Choudhary et al. [62] reported that the zeolite produce xylulose from xylose and the intermediated xylulose can be quickly transferred into furfural in the presence of Brønsted-acid catalysts such as HCl and Amberlyst-15 [62]. Binder and coworkers also proposed isomerization by enolization and hydride shift mechanisms for the transformation of xylose to furfural using the chromium as a catalyst [63]. First, xylose isomerizes to xylulose by 1,2-hydride shift and the resulting xylulose then dehydrates over chromium catalyst to form furfural. Xylose also isomerizes to xylulose by enolization over chromium and enediol is formed.

## Catalysts Used to Produce Furfural from Pentoses

Different studies have been made by many researchers to increase furfural yield. Pentosan content of the feed, catalysts loading, time and temperature of hydrolysis and residence time of furfural in the reaction medium are among the determinant factors to that should be considered to optimize the yield in the production of furfural [64].

### Homogeneous Catalysts

In last decades, extensive studies on the conversion of reagent grade xylose and xylan into furfural have been performed instead of raw biomass for simplification of analysis. Homogeneous catalysts, mineral acids [65] and metal chlorides [66, 67] have been investigated for furfural production. Among the mineral acids, sulfuric acid and hydrochloric

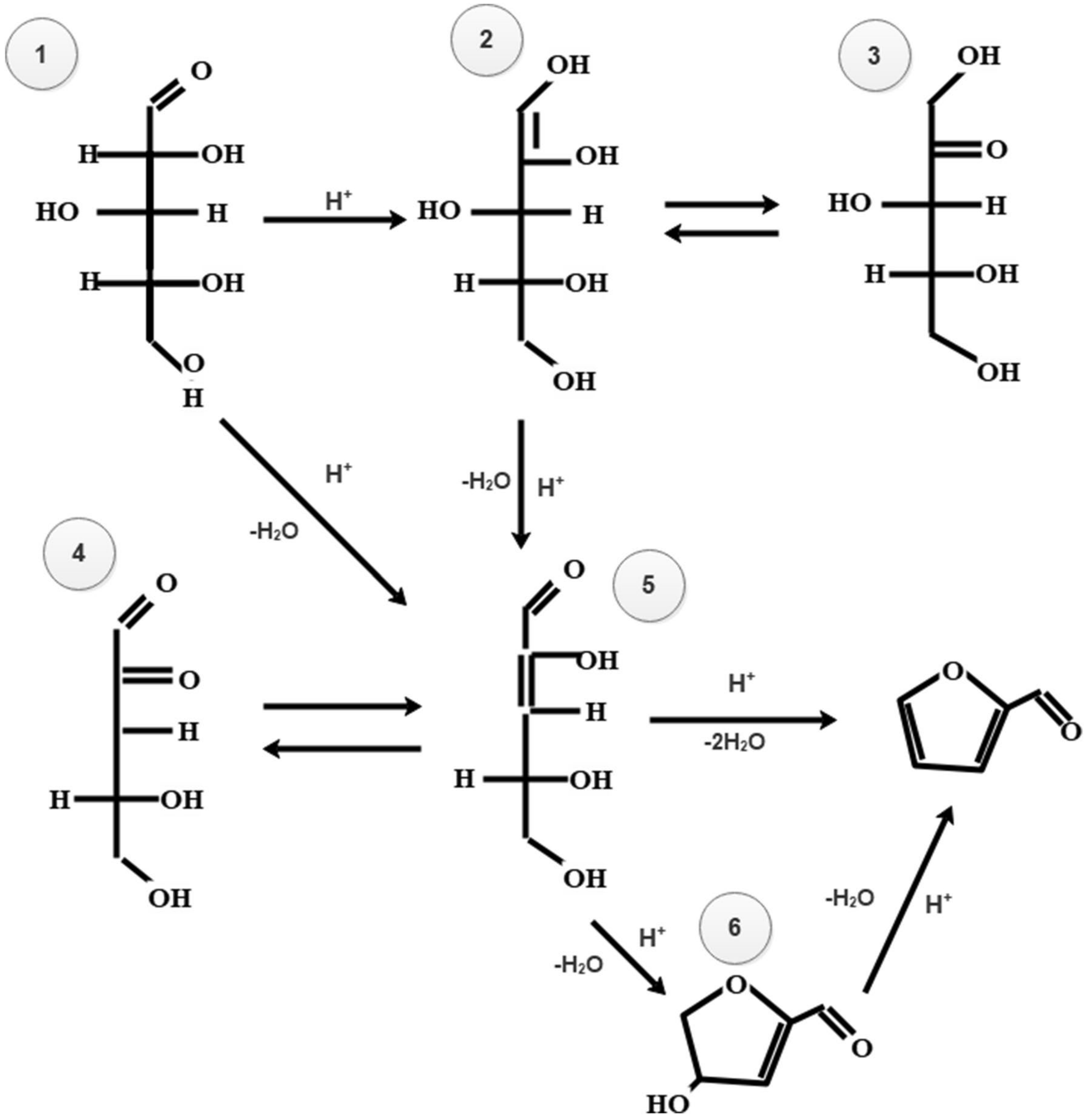


Fig. 4 Xylose dehydration mechanism via enolization and β-elimination

acid are the most widely used catalysts for the commercial production of furfural [68]. Using sulfuric acid as a catalyst, Quaker Oats produce furfural with around 50% yield at 150 °C in 5 h and similar yields have been reported for most industrial processes [69]. Undesired polymerization reactions are the causes for the formation of solid humins which are in turn responsible for the moderate yield of furfural [70]. Yemis and Mazza [65] studied and compared the catalytic activities of sulfuric acid, nitric acid, phosphoric acid, hydrochloric acid, acetic acid and formic acid targeting at the yield of furfural. The highest yield of furfural from xylose using hydrochloric acid was about 65% at 170 °C [44]. $AlCl_3$ gave 84.8% furfural yield from xylan at 170 °C in reaction time of 10 s [51].

Marcotullio and De Jong have shown the effect of $Cl^-$ ions on the dehydration rate of xylose to furfural in aqueous acidic solutions. The presence of $Cl^-$ ions have shown improvement in the yield of furfural and selectivity using conventional heating [71]. On the other hand, using microwave heating [72] investigated the effect of sodium chloride on the dehydration rate of xylose to furfural and achieved 76% furfural yield at 200 °C in less than 8 min. However, mineral acids are extremely corrosive to the equipment, recovery of the catalysts from the reaction mixtures is difficult, and we cannot reuse the catalysts [73, 74]. Various attempts have been carried by researchers to mitigate the chemical pollution occuring because of the use of acid homogeneous catalysts.

**Table 2** Catalysts used for furfural production

| Substrate | Catalyst | Solvent | Characterization BET surface area (m$^2$/g) Acid density (mmol/g) Pore size | Temperature (°C) | Time | Yield in % | References |
|---|---|---|---|---|---|---|---|
| Bagasse | Silicoaluminophosphate | Toluene/water | – | 170 | 8 h | 93 | [84] |
| Camellia oleifera shell | Sulfonated swelling mesoporous polydivinylbenzene (PDVB–$SO_3H$) | γ–Butyrolactone/water | BET 676.18 m$^2$/g<br>2.6 mmol/g | 170 | 30 min | 61.3 | [83] |
| Cassava waste | Sulfonated carbon-based catalyst | Acetone/DMSO/water | BET 1.1 m$^2$/g<br>1.46 mmol/g | 250 | 1 min | 2.1 | [135] |
| Corn stover | SC-CaCt-700 | γ-Valerolactone | BET 921 m$^2$/g<br>2.62 mmol/g | 200 | 100 s | 93 | [136] |
| Corncob | $SO_4^{2-}/SnO_2$-MMT/NaCl | Toluene | BET 93 m$^2$/g | 190 | 20 min | 66.1 | [137] |
| Corncob | $SO_4^{2-}/TiO_2–ZrO_2/La^{3+})$ | Water | – | 180 | 2 h | (6.18 g/100 g) | [138] |
| Corncob hydrolysate | $SO_4^{2-}/SnO_2$-MMT | Toluene | BET 93 m$^2$/g | 190 | 15 min | 81.69 | [137] |
| D-xylose | Acid-functionalized multi-wall carbon nanotubes (MWCNTs) | Water | BET 131 m$^2$/g<br>0.31 mmol/g<br>3.3 nm | 170 | 3 h | 57 | [99] |
| Hydrolysates from corncob | Tin-loaded montmorillonite | SBP/NaCl-DMSO | – | 190 | 10 min | 57.8 | [139] |
| Isolated hemicellulose | Silicoaluminophosphate | Toluene/water | – | 170 | 10 h | 82 | [84] |
| Maple wood | Sulfuric acid | methyl isobutyl ketone/water | – | 170 | 50 min | 85.3 | |
| Soft-wood hemicellulose | SAPO-5 | $H_2O$/toluene | BET 309 m$^2$/g<br>0.8 mmol/g | 170 | 8 h | 65 | [140] |
| Soft-wood hemicellulose | SAPO-11 | $H_2O$/toluene | BET 42 m$^2$/g<br>0.3 mmol/g | 170 | 8 h | 58 | [140] |
| Soft-wood hemicellulose | SAPO-44 | $H_2O$/toluene | BET 369 m$^2$/g<br>1.2 mmol/g<br>0.45 nm | 170 | 8 h | 63 | [140] |
| Xylan | $SO_4^{2-}$/Sn-MMT | 2-MTHF/water | BET 153.52 m$^2$/g<br>0.58 mmol/g | 160 | 1.5 h | 77.35 | [70] |
| Xylose | $CrCl_2$, LiBr | *N,N*-dimethylacetamide | – | 100 | 4 h | 56 | [63] |
| Xylose | PSZ-MCM-41 | Toluene/water | – | 160 | 4 h | 42.8 | [141] |
| Xylose | Dealumin. HNu-6 (2) | Toluene/water | – | 170 | 4 h | 47 | [104] |
| Xylose | H-mordenite 13 | Toluene/water | – | 260 | 0.05 h | 98 | [142] |
| Xylose | Arenesulfonic SBA-15 | Toluene/water | BET 568 m$^2$/g<br>0.94 mmol/g<br>2.3 nm | 160 | 20 h | 86 | [77] |
| Xylose | $SO_4^{2-}$/Sn-MMT | 2-MTHF/water-NaCl | BET 153.52 m$^2$/g<br>0.58 mmol/g | 160 | 2 h | 79.64 | [70] |
| Xylose | HY-faujasite (15) | $H_2O$/MIBK | 7.4 × 7.4 Å | 170 | 50 min | 29.7 | [143] |
| Xylose | HY-faujasite (15) | $H_2O$/toluene | 7.4×7.4 Å | 170 | 50 min | 41.82 | [143] |
| Xylose | H-mordenite (12) | $H_2O$/MIBK | 6.5×7 Å | 170 | 50 min | 20.16 | [143] |
| Xylose | H-mordenite (12) | $H_2O$/toluene | 6.5×7 Å | 170 | 50 min | 33.62 | [143] |
| Xylose | HY-ferrierite (20) | $H_2O$/toluene | BET 389.9 m$^2$/g<br>4.2×5.4 Å | 140 | 4 h | 35 | [113] |
| Xylose | HY-ferrierite (20) | $H_2O$ | BET 389.9 m$^2$/g<br>4.2×5.4 Å | 140 | 4 h | 13 | [113] |
| Xylose | HY-ferrierite (20) | DMSO | BET 389.9 m$^2$/g<br>4.2x5.4 Å | 140 | 4 h | 23 | [113] |
| Xylose | H-ZSM-5 | $H_2O$ | 0.16 mmol/g<br>1.2 nm | 200 | 30 min | 46 | [89] |
| Xylose | Sn-Beta + HCl | $H_2O$ | BET 100 m$^2$/g | 110 | 3 h | 14.3 | [62] |
| Xylose | Sn-Beta + Amberlyst | $H_2O$ | – | 110 | 3 h | 9.5 | [62] |
| Xylose | MCM-41 | $H_2O$/butanol | BET 800 m$^2$/g<br>3 nm | 170 | 3 h | 44 | [79] |
| Xylose | MCM-41-$SO_3H$ | $H_2O$/MIBK | BET 438 m$^2$/g | 140 | 24 h | 51 | [81] |
| Xylose | MCM-41-$SO_3H$ | $H_2O$/toluene | BET 438 m$^2$/g | 140 | 24 h | 76 | [81] |
| Xylose | MCM-41-$SO_3H$ | DMSO | BET 438 m$^2$/g | 140 | 24 h | 75 | [81] |

**Table 2** (continued)

| Substrate | Catalyst | Solvent | Characterization BET surface area ($m^2/g$) Acid density (mmol/g) Pore size | Temperature (°C) | Time | Yield in % | References |
|---|---|---|---|---|---|---|---|
| Xylose | H-MCM-22 (24) | $H_2O$ | BET 333 $m^2/g$<br>0.204 mmol/g | 170 | 16 h | 52 | [144] |
| Xylose | H-MCM-22 (24) | $H_2O$/toluene | BET 333 $m^2/g$<br>0.204 mmol/g | 170 | 16 h | 70 | [144] |
| Xylose | ITQ-2 (24) | $H_2O$ | BET 623 $m^2/g$<br>0.198 mmol/g | 170 | 16 h | 54 | [144] |
| Xylose | ITQ-2 (24) | $H_2O$/toluene | BET 623 $m^2/g$<br>0.198 mmol/g | 170 | 16 h | 66 | [144] |
| Xylose | Nu-6(2) | $H_2O$/toluene | – | 170 | | 23 | |
| Xylose | ITQ-18 | $H_2O$/toluene | – | 170 | | 43 | [82] |
| Xylose | SBA-15-$SO_3H$ | $H_2O$/toluene | – | 160 | 4 h | 69 | |
| Xylose | $SO_4^{2-}/ZrO_2–Al_2O_3/$ SBA-15 | $H_2O$/toluene | BET 271 $m^2/g$<br>0.91 mmol/g<br>6.59 nm | 160 | 4 h | 52.8 | [75] |
| Xylose | Nafion 117 | DMSO | – | 150 | 2 h | 60 | [98] |
| Xylose | Amberlyst-15/hydrotalcite | *N*,*N*-dimethylformamide (*N*,*N*-DMF) | – | 10 | 1 h | 37 | [145] |
| Xylose | Sulphonated graphene oxide SGO | Water | BET 680 $m^2/g$ | 200 | 35 min | 62 | [98] |
| Xylose | Graphene oxide | Water | BET 318 $m^2/g$ | 200 | 35 min | 53 | [98] |
| Xylose | Sulphonated graphene | Water | BET 634 $m^2/g$ | 200 | 35 min | 55 | [98] |
| xylose | Glu-TsOH-Ti | Methyltetrahydrofuran water | BET 42.5 $m^2/g$<br>1.03 mmol/g<br>4.5 | 180 | 30 min | 51 | [146] |
| Xylose | PTSA-POM | γ-Valerolactone | 2.2–2.4 mmol/g | 170 | 10 min | 80.4 | [109] |
| Xylose | Nb50-MCM-41 | Water/toluene | BET 1040 $m^2/g$<br>4 nm | 160 | 6 h | 38.6 | [141] |
| Xylose | H-AM-11 | Water/toluene | BET 328 $m^2/g$<br>0.17 $cm^3\ g^{-1}$ | 160 | 6 h | 49.8 | [141] |
| Xylose | Na,H-AM-11 | Water/toluene | BET 489 $m^2/g$<br>0.22 $cm^3\ g^{-1}$ | 160 | 6 h | 50 | [141] |
| Xylose | Magnetic porous carbon-based solid acids prepared from sawdust | DMSO | – | 150 | 6 h | 61 | [147] |
| Xylose | Sulfonated carbon prepared from D-glucose | γ-Valerolactone | – | 175 | 20 min | 70 | [147] |
| Xylose | WH-PTSA-220 | γ-Valerolactone | – | 170 | 2 h | 60 | [147] |
| Xylose | Al-TUD-1(21) | Water/toluene | BET 757 $m^2/$ g0.197 mmol/g | 170 | 6 h | 60 | [148] |

## Heterogeneous Catalysts

Solid acid catalysts could be regenerated and reused in catalytic processes with comparable efficiencies [17, 75–77]. Sulfonic acid functionalized mesoporous SBA-15 materials [77], modified zeolites such as HUSY, H-Beta zeolite, H-mordenite [78], and MCM-41 [79]) are among heterogeneous solid catalysts that were developed for furfural production to solve the problems associated with the use of homogeneous catalysts. Arenesulfonic SBA-15 catalysts were prepared via co-condensation for the dehydration for D-xylose to furfural [77]. These selective and hydrothermally stable catalysts incorporate high arenesulfonic-site and posse hexagonal pore arrangement. The activities of sulfonic acid functionalized mesoporous SBA-15 materials were studied with emphasis on the stability of the catalyst. At 160 °C with 99% selectivity, they obtained 82% furfural yield from D-xylose in water/toluene. Even though the solvent (toluene) used in the study for extraction of furfural from water medium is not a green chemical, arenesulfonic functionalized SBA-15 supports aged at higher temperatures show higher stability and recyclability [77]. The most studied solid catalysts are zeolites, which are thermally and chemically stable, have tunable acidities and shape [80]. Furfural yield of mostly lower than 40% was achieved on studies using a variety of H-zeolites (e.g., HY-faujasite, H-mordenite, and H-ferrierite) in water, water/methyl isobutyl ketone (MIBK), water/toluene and dimethyl sulfoxide (DMSO) in a batch reactor at 140–170 °C [81].

A sulfated tin ion-exchanged montmorillonite ($SO_4^{2-}$/Sn-MMT) in 2-Methyltetrahydrofuran (2-MTHF)/NaCl-water showed high activity and reusability with furfural yield of 79.64% from xylose at 160 °C [70]. The presence of NaCl showed a decrease in the yield of furfural from xylan. Silico-aluminophosphate (SAPO) based catalysts have shown up to 65% yield of furfural from hemicellulose in bi-phasic systems at 170 °C in 8 h [82]. Bhaumik and Dhepe [83] showed in their work that the SAPO-44 can be washed with water and reused for eight times without loss of efficiency. This catalyst contains both the Lewis and Bronsted acid cites where isomerization and dehydration reactions take place. Bhaumik and Dhepe [84] have also shown in other work that hydrothermally stable SAPO-44 can achieve up to 93% furfural yield from the raw lignocellulosic material such as bagasse, rich husk and wheat straw [85].

Sulfonated metal oxides and ion-exchange resins were also used for dehydration of xylose to produce furfural. 40-70% yield was achieved by using ion-exchange resins [80]. Metal oxides, sulfonated with $H_2SO_4$, such as $TiO_2$, $ZrO_2$, $SnO_2$, and $Al_2O_3$ were also studied and proved that $SnO_2$ gives the highest xylose conversion and furfural yield [86]. $SO_4^{2-}/ZrO_2–TiO_2$ gave a higher yield than the selected zeolite catalysts [87]. $TiO_2$ coupled nanocellulose was proved to enhance the conversion of cellulose to glucose [88]. Neill et al. [89] studied the conversion of furfural over ZSM-5 zeolite in $H^+$ form at 140–220 °Cin a batch reactor and proposed a kinetic model for the reaction as the first order with activation energy of 32.1 kcal/mol. The catalyst achieved a yield of 46% furfural from xylose at the optimum temperature of 200 °C. The effects of parameters like the catalyst pore size, time and temperature were investigated and found to be highly influential in product distribution [89].

Carbon-based solid acids have suitable catalytic properties to produce furfural by dehydration of xylose. The accessibility to xylose is good as the specific surface area and porosity of these solid acids is high. Besides, these types of catalysts have excellent electron conductivity and have relatively high chemical and thermal stability [90–92]. Carbon materials can be prepared from cheap and abundant biomass residue to be used as catalyst and catalyst support for various biomass transformation [93, 94]. Carbon black and activated carbon are prepared via different techniques. Pyrolysis of polymers or hydrocarbon at about 1500 °C can produce an amorphous carbon black with randomly cross-linked structure and roughly planar layers of $sp^2$ hybridization carbons [90]. Activated carbon is amorphous solid with high porosity and surface area. It is prepared by carbonization of carbon materials in the absence of oxygen if physical activation is required. Steam or oxygen is used as physical activation at 600–1200 °C [91]. The carbon material is carbonized after impregnated with an acid, a strong base or a salt in chemical activation [95].

Carbon materials exhibit acid-base character with different oxygen functionality. Biomass-based amorphous carbon has been studied for biomass conversion by bearing $SO_3H$, COOH, and OH groups [14, 68]. The catalyst can be easily prepared from biomass resources by incomplete carbonization and subsequent sulfonation at a high temperature greater than 160 °C with a large amount of fuming sulfuric acid (15 wt% $SO_3$) or concentrated sulfuric acid (98%) for the introduction of $SO_3H$ groups into the amorphous carbon surface. Lignin can be used to produce activated carbon and acidic sulfonated carbon for hydrolysis/dehydration of polysaccharides and polyols [96].

Porous carbon materials are becoming very attractive in recent years for their versatile use as catalysts, catalyst supports, sorbent for air and water purification, supercapacitors and fuel cells. For catalytic processes, solid acid catalysts based on the carbon sources are getting attention due to their recyclability, low cost, unique structure, environment-friendly properties, and easy preparation methods. They can be obtained from carbon precursors through carbonization and sulfonation for various applications like dehydration of xylose to furfural. Hydrothermal, ionothermal and molten salt carbonization are among the various techniques adopted to synthesize porous structured carbon materials reported in some literature. Thermochemical conversions take place in water for the case of hydrothermal carbonization and in ionic liquids and molten salt for ionothermal and molten salt carbonization respectively. Hydrothermal carbonization is an inexpensive, mild and green process involving thermal decomposition of carbon precursor in aqueous solution in the presence of heat [97].

Lam et al. [98] reported that the water-tolerant carbon catalyst sulfonated graphene oxide (SGO) with 2% loading converted xylose to furfural with selectivity of about 75% and yield of 62% in 35 min at 200 °C. At these same conditions, i.e. catalyst loading, time of reaction and temperature; graphene, graphene oxide and, sulfonated graphene achieved relatively lower yield of 51,53 and 55% as compared SGO. SGO exhibit large surface area (680 $m^2/g$), contains aryl sulfonic acid group which are active sites responsible for the dehydration process and remains active after repeated reactions.

Properties of carbon-based solid catalysts that affect the catalytic performance include acidic property, specific surface area and pore size [99]. The acidity of the catalyst is among the properties of catalyst that can significantly affect the performance of a catalyst. The strength and distribution of acid sites on the solid surfaces in addition to their nature are determinant catalytic properties of a solid acid catalyst that affect the conversion and selectivity of a reaction. A Brønsted acid donates proton while Lewis acids accept electrons. Lewis acid sites promote xylose-xylulose-furfural route instead of xylose to furfural direct conversion and Brønsted acid sites catalyze the conversion of xylulose to furfural [4]. Agirrezabal-Telleria et al. [77] used partially hydroxylated $MgF_2$ catalysts by varying the Lewis/Brønsted acid ratio to produce furfural in water/toluene [100]. Lewis acidity is due to $Mg^{2+}$ ions and hydroxyl groups are responsible for Brønsted acid property of the catalyst. Combination of Sn-beta zeolite as a Lewis acid and Amberlyst-15 as a Brønsted acid can be used to convert xylose to xylulose and then to furfural in an aqueous medium [101]. The Lewis/Brønsted acid site ratio is, therefore, one of the factors that affect the rate of dehydration reaction and furfural yield. The optimum Lewis/Brønsted loading is required to achieve the optimized conversion and yield [100]. Carbonaceous by-products will be formed at higher L/B ratio and lower L/B ratio leads to undesired polymerization reaction. The rate of reaction increases with an increase in acid content and strength, but too strong acidity accelerates undesired reactions. The variation of acidity of zeolite catalysts is mainly due to the preparation conditions and Si/Al ratio [4]. Carbon-based catalysts possess Brønsted acid sites like -$SO_3H$ and –COOH. Phenolic –OH group are also present in these types of catalysts [102].

IUPAC defines pore size less than 2 nm as micropores, 2–50 nm as mesopores and greater than 50 nm as macropores. The pore size of the catalyst should match the molecular size of xylose and furfural to facilitate the diffusion of reactants into the catalyst and removal of products in furfural production processes. Small pore size than xylose and furfural results in diffusional resistance problem by inhibiting the diffusion rate and larger sizes may be suitable for furfural rearrangement into large molecules because of longer residence time product inside the porous structure [4]. Catalyst screening by Iglesias et al. [103] showed that H-ZSM5 containing narrow pore size were unable to promote the desired transformation and probably transformations may occur on the active sites located at the outer surface of the catalyst [103]. The size of xylose and furfural were approximate to be 0.68 and 0.57 nm, respectively based on literature. Neill et al. [89] concluded in their work that zeolite with a pore size (0.8 nm) close to the size of xylose and furfural would be effective for xylose conversion to furfural [89].

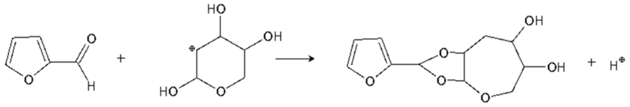
The specific surface area of the catalysts is another factor that affects the catalytic performance. Higher specific surface area promotes the performance of a catalyst by increasing the accessibility of the active sites to xylose [4]. Lima et al. [104] experimented delaminated Nu-6 zeolite with the greater surface area in about seven folds than of standard Nu-6 zeolite and increased rate of reaction in two folds with furfural yield of about 50% at 453 K [82]. Table 2 shows the summary of the reaction conditions and the yield of furfural with various catalysts.

## Conversion of Hexoses to Furfural

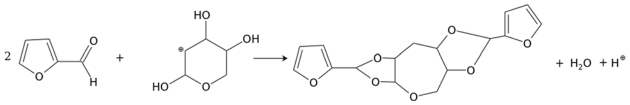
Most of the investigations towards furfural focus on the conversion of hemicellulose component of biomass, but there are also several published works that confirm the possibility of converting cellulose component into furfural. Jin et al. [105] illustrated two possible mechanisms of furfural formation from hexoses. The first pathway is the conversion of hexose to HMF and then to furfural, while the second is hexose to pentose and then to furfural [105]. In the conversion of glucose to HMF, glucose isomerizes in the rate-limiting step to fructose and fructose then dehydrates to form HMF [25]. The formed HMF then loses –$CH_2O$ by decarboxylation to form furfural [8]. The formation of pentose via retro-aldol reaction from ketose is the other plausible pathway to produce furfural from C6 sugars [106]. Aida et al. [107] investigated the effect of temperature, residence time and pressure on the yield of furfural from D-glucose in water and the yield was 12.2% at 400 °C [107]. Some literature reported the higher yield of furfural from raw biomass when compared to the pure xylose, where the possible reason could be the co-conversion of five- and six-carbon sugar in the polymer matrix. Looking for simultaneous utilization of cellulose and hemicellulose component derived sugars, 51.1 and 40.9% yield of furfural on molar basis were achieved from corncob and sugarcane bagasse respectively in γ-valerolactone at 185 °C within 85 min [108]. A maximum yield of 22.3% furfural on the molar basis was obtained from cellulose at 175 °C in 100 min using Fe-beta zeolite as a catalyst γ-valerolactone [108]. In one pot processing of corn stalk, a furfural yield of 83.8% (at 170 °C, 100 min), 84.5% (at 180 °C, 80 min) and 86.3% (at optimal conditions of 190 °C, 40 min) were obtained while a maximum yield of 80.4% was obtained from xylose (at 170 °C, 10 min) using PTSA-POM catalyst in GVL/water system [109].

## Reduction of Yield Loss Through Isolation of Furfural from the Reaction Mixture

Since furfural is very reactive, in the acidic medium it undergoes through various reactions such as polymerization which lead to lower furfural yield. Resinification and condensation reactions are the causes for the decrease in the yield of furfural [33]. These reactions occur when the furfural formed during the reaction stays dissolved in the liquid phase. Resinification reactions basically take place when furfural reacts with another furfural molecule and condensation reactions take place when furfural combines with an intermediate.



Difurfural xylose is also formed as a degradation product if additional furfural molecule reacts with an intermediate [33]. These furfural degradation reactions are possible only when furfural is present as dissolved product in the liquid phase, whereas impossible in the vapor phase where the catalytically active components are absent [33]. Table 3 shows the summary of various furfural separation approaches.



In industrial processing of biomass for the production of furfural, steam is injected into the reaction chamber to supply heat for the reaction to take place and also to preferentially remove furfural from the liquid phase. This selective removal of furfural from the liquid phase into vapor phase help the process to achieve higher furfural yield by preventing the product loss due to resinification and condensation reactions. In the analytical method the amount of furfural produced can be escalated to 100% yield because the presence of HCl saturated with NaCl raises the boiling point and result in superheating of vapor [33].

Continuous removal of furfural product from the acidic medium is required to stop the polymerization and condensation reactions which reduce yields. This can be done by steam stripping, reactive distillation, water/organic biphasic systems, use of supercritical fluids ($CO_2$) and gaseous acid catalysis (using superheated steam and HCl vapor) [110].

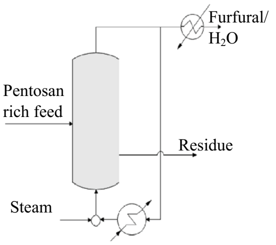
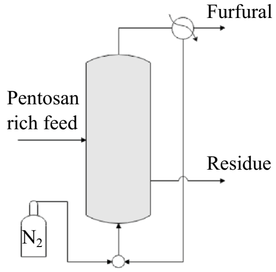
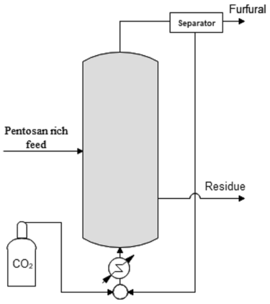
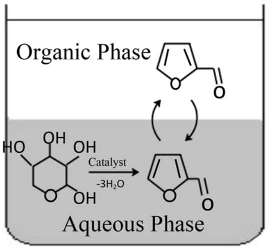
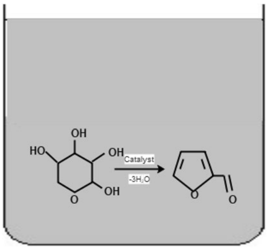
## Steam Stripping

Steam stripping is a separation process which uses steam to preferentially extract components from a liquid stream. Commercially furfural is produced from biomass using $H_2SO_4$ and recovered from the aqueous solution by steam stripping to stop the further transformation of furfural to larger molecules and purification is done by double distillation [59]. The energy consumption by this method of product recovery has been reported to be very high as it uses 25 to 35 tons of steam to produce a ton of furfural [71]. In Rosenlew process 30 to 1 ratio of steam to furfural is used to achieve 59.5% yield of furufal at 180 °C. Gandarias and Arias [73] suggested in their work that high amount of utilities are required when fresh steam is used and cooling of vapors are required. Further purification also requires high energy input if the concentration of furfural in the steam is too low [73]. Volume of steam used for stripping can affect yield of furfural. Too low amount of steam is not sufficient for fast isolation of the furfural formed during the reaction. The furfural remaining in the acidic medium will be lost due to resinification and condensation reactions. Too high steam input hinders the catalystic activity towards the formation of furfural by reducing the acidity of the medium [33]. Therefore, optimum amount of steam is required to produce higher amount of furfural as both too much and too low volume of steam reduce the product output . Costs of steam stripping appear to be high because of high steam usage to extract the furfural from the reaction medium and the high cooling requirement for stripping vapor and high energy requirement for boilers in the distillation process for the dilute furfural-water stream separation [33].

## Nitrogen-Stripping

Nitrogen is another stripping agent for producing furfural from biomass at higher yields. It is inert, easily separable and recyclable gas. Agirrezabal-Telleria et al. [111] achieved 67%, a higher yield of furfural as compared to that obtained using steam stripping [112]. Agirrezabal-Telleria et al. [77] studied partially hydroxylated $MgF_2$ catalysts by varying the Lewis/Brønsted acid ratio and simultaneous stripping with nitrogen achieved 87% furfural selectivity at 160 °C in water/toluene [100]. Introduction of the nitrogen stripping current commercial process reduces the energy requirements and allows the recycling of the stripping agent and reduces the cost up to 60%. But, high recompression is required to recycle if the reduction of the use of fresh nitrogen is to be applied [73]. High product purity, high furfural yield, lower product dilution, easy separation of catalyst and stripping agent recycling are among the advantages of nitrogen stripping [80]. Nitrogen stripping showed better industrial feasibility as compared to biphasic water/organic solvent systems. 39% furfural yield was reported in water toluene system using ion-exchange sulfonic resin (A70) as a catalyst, which is less than that obtained using nitrogen as an extracting agent at the same temperature of 175 °C [41, 80, 111]. Nitrogen stripping has also the advantage of reducing the cost of final product separation challenging the commercial production processes of furfural [95]. Considering the stripping agent recycling and product dilution, nitrogen stripping has a cost advantage over the steam stripping [111].

**Table 3** The summary of furfural separation approaches

| Process | Advantages/disadvantages |
|---|---|
| Steam stripping<br><br> | Very high energy consumption: high amount of steam is required to produce furfural<br>Azeotropic separation of furfural/water mixture required<br>High cooling requirements for the stripping vapors |
| Nitrogen-stripping<br><br> | Inert, easily separable and recyclable gas is used<br>Require lower energy than steam stripping<br>High product purity, lower product dilution, easy catalyst separation<br>Better industrial feasibility than water/organic biphasic systems<br>Recompression of stripping agent and significantly larger vacuum unit required: thus, increasing the investment. |
| Supercritical carbon dioxide<br><br> | Supercritical $CO_2$ is chemically inert, non-flammable, can be easily recycled and easily separated from the product<br>Has also the capability of acidifying the reaction system<br>The dissolving efficiency and selectively can be controlled by selection of suitable pressure/temperature combination<br>Enable extraction of furfural at a low temperature < 50 °C. |
| Water/organic biphasic systems<br><br> | Avoid azeotropic separation process of furfural/water mixture<br>Ease of catalyst and product separation<br>Higher yield than in aqueous phase alone |
| Monophasic systems<br><br> | Green solvent γ-valerolactone (GVL)<br>Feasible for laboratory scale due to multistep processing for GVL production, high boiling point and miscibility with water<br>No additional step for liquid-liquid separation to recover solvent |

## Water/Organic Biphasic Systems

Furfural can be produced in biphasic systems consisting of water and organic mixture [73]. In this system, furfural produced in the aqueous phase will be immediately transferred to the organic phase. The spontaneous transfer of furfural into organic phase protects it from undergoing further transformation to a larger molecule. The purpose of a biphasic reaction is to increase furfural yield by reducing the side reactions and to simplify the separation process by avoiding the azeotropic point of the furfural-water mixture. Organic phase includes solvents like toluene, butanol, methyl isobutyl ketone (MIBK), MIBK-2-butanol mixture, tetrahydrofuran (THF), or dichloromethane (DCM), which have a great affinity for absorbing furfural. Furfural resinification reactions appear to be negligible in the organic phase of toluene/water system. The yield of furfural was 70, 66 and 35 in water/toluene byphasic system and 52, 54 and 13 in water only in the presence of H-MMC-22(24), ITQ-2(24) and HY-ferrierite(20) respectively [113, 114]. Deng et al. [115] reported higher yield of furfural in water/dichloromethane than in water only [115]. The addition of NaCl into the water/dichloromethane further improved the yield of furfural.

With the aim to produce furfural using green process and develop an appropriate kinetic model for conversion of xylose to furfural, Hua et al. [116] achieved improved furfural yield under optimal conditions [116]. They used high-temperature water as a catalyst to dehydrate xylose to furfural and ethyl butyrate, butyl acetate, n-butanol, n-butyl ether, and toluene solvents to extract the product. Ethyl butyrate showed the highest extraction efficiency. Selection of an appropriate solvent along with a proper catalyst can give high furfural yields. Zeolites, sulfated and tungstated zirconia catalysts, and sulfonic acid materials, which have different textural, surface, and acid properties in methanol, ethanol, and 2-propanol were tested. β-zeolite achieved best results as it exhibits best Brønsted and Lewis acid site combinations among the tested catalysts and 2-propanol was found to be the best medium to hinder side reactions that may occur in aqueous media and to give higher furfural yield than methanol and ethanol [103]. 68.3% furfural yield was achieved in $H_2O$/toluene over SBA-15-$SO_3H$ [117]. The MCM-41 resulted in a furfural yield of about 44% in DMSO [81] and less than 40% in $H_2O$/1-butanol [79], while 51% in water/MIBK and 76% yield achieved in water/toluene by MCM-41-$SO_3H$ [81, 117]. With $H_3PW_{12}O_{40}$ and $Cs_3PW_{12}O_{40}$ supported on MCM-41, the yields in $H_2O$/toluene were 48% and 33%, respectively, and increased to 52% and 45% in DMSO, respectively [4].

Presence of biomass particles in water also reduce the furfural yield loss by preventing movement of furfural molecules and catalytically active components towards each other [80]. Environmental issues, solvent recovery, and process complexity are the major problems associated with biphasic systems [118]. For large scale processing, separation of the product furfural from the organic solvents consumes a substantial amount of energy and vigorous mixing of water and solvent for efficient extraction of furfural is a problem. Use of solvents with a low boiling point is another challenge in biphasic systems as heat treatment develops high pressure in the reaction vessel which in turn lead to additional capital cost [119]. In water/organic biphasic systems the use of organic solvents in commercial processes could add economic burdens because of the consumption of solvents, costs extra separation steps and waste management to protect the environment from pollution [111]. Cleaning the water effluents from these systems are difficult as high energy is required to remove the solvents and recovery of solvents is also a must to make the process economical [120].

## Monophasic systems

Gürbüz et al. [106] reported the use of a γ-valerolactone solvent as a monophasic system for conversion of xylose into furfural using a solid acid catalyst. γ-valerolactone has the advantage that it is green solvent can be produced from biomass. But, multi-step processing for γ-valerolactone production, its high boiling point, and miscibility with water makes it feasible only for laboratory [119]. Use of γ-valerolactone as a solvent has advantages like the promotion of xylose conversion rate and inhibition of the furfural degradation rate and the separation of furfural from the solvent is simple due to the difference in their volatility. There is no further step needed for liquid-liquid separation as in the case of biphasic systems to recover organic solvents from aqueous/organic phases.

## Supercritical Carbon Dioxide

Super critical carbon dioxide was also reported for the extraction of furfural from reaction solution. In this extraction type liquified $CO_2$ is introduced into a reactor containing the solution and transferred to container with cooling system. Supercritical $CO_2$ is easily recoverable, green and also has tendency to acidify the reaction system. Hydrothermal conversion of sugar under the pressure up to 12 MPa achieved 68% furfural yield [121]. Sako et al. [122] evaluated the conversion of different concentrations of xylose to furfural to envestigate the effect of supercritical $CO_2$ on the selectivity and the yield of furfural at 150 °C. From the experimental data they reported, it is clear that the yield obtained without the use of supercritical $CO_2$ is less than the yield obtained in the presence of supercritical $CO_2$ for the same xylose conversion and they obtained an improved maximum yield of 70% [122]. Sangarunlert et al. [123] reported a maximum yield of furfural aproching 90% from rice husk using supercritical $CO_2$ for extraction of the product [123]. Diffusivity, surface tension and solublity are highly desirable properties for supercritical $CO_2$ extraction. High diffusivity enhances the mass transfer, reduced surface tension is required for easy penetration and wetting of pore of biomass materials and solublity is important for selective extraction [124]. The compression of $CO_2$ takes the major part of energy requirement for supercritical extraction [125]. This method of extraction is at experimental level due to the high capital and operating costs [13].

## Challenge in Furfural Production

Solvent recycling, catalyst reuse, and product purification are very crucial factors to be considered for the economical industrial conversion of the various feedstocks to furfural. Currently, azeotropic distillation is in use for purification of furfural as the product streams contain up to 6% furfural and over 90% water in pentoses conversion processes [126]. But, it requires a large investment and high energy [127]. In producing furfural, various technologies have been developed at the experimental level. For instance, the supercritical $CO_2$ extraction technology is one of the methods applied to separate furfural from the reaction mixture in view of getting a higher yield by suppressing reactions leading to furfural loss. But, this technology is being applied only at the laboratory stage due to its high operating and material cost requirements to be applied in industrial scale [127].

To reuse a catalyst for the next catalytic runs, separating it from reaction mixture and regeneration may be required. But, catalyst reuse is still a challenge for industrial applications due to reduced activity and deactivation of catalysts upon regeneration. In catalytic valorization of biomass, difficulty in the separation of solid catalysts from the solid residue remaining in the reaction mixture is often observed [8, 128]. Washing the used catalyst with water and organic solvent to separate it from corn stover residue and the drying is a difficult task [8] and it incurs additional costs of solvents for washing and energy for drying. Up to 5% furfural yield reduction was observed in the first run after regeneration and calcination deactivated the Al-beta [108]. In the MSPFR catalyzed conversion of xylose to furfural, the yield was 77.3% when the catalyst was used for the first time, but on the 5th run, 62.5% was obtained [8]. Besides the loss of active sites due to leaching, accumulation of by-products and corn stover residue were the main reasons for the reduced performance of the catalyst. CrPO4 catalyst was tasted for furfural production by washing and drying after each use and achieved a yield of 47% from xylose on the 4th run with a significant difference of 41% from the first run and this reduced activity can be due to the partial dissolution of the catalyst [44]. The activity of H-SAPO-34 zeolite in producing furfural from eucalyptus sawdust was about 88%, but it reduced to 57.24% in the $5^{th}$ run and it couldn't be recovered by calcination [129].

Solvent recycling is one of the important processes in chemical industries for economical operations because it reduces the costs associated with waste stream management and chemical consumption [130]. Environmental pollution is a problem of high priority these days. Solvent released in waste streams from industries needs to be reduced to protect the environment. And, also to keep consistent operating conditions throughout the process in furfural production, the solvent used should be fully recovered and reused or makeup solvent is required. Generally, to reduce the amount of solvent required and to minimize the negative environmental impact associated with the disposal of solvents in waste streams, recovery and reuse of solvents is required. Recovery processes might be possible at a laboratory scale, but it would be though for commercialization [118].

## Conclusions

Significant studies have been carried out in the last several decades on the catalytic transformation of lignocellulosic biomass to furfural. This review provided an overview of the catalytic valorization process of biomass to valuable platform product, the furfural. Various catalysts employed by the researchers to achieve high catalytic activity and selectivity in converting the carbohydrate fractions of various biomass, but economical scale-up is still the challenge due to the difficulties in solvent recycling, catalyst reuse, and product purification. Isolation of hemicellulose is required to reduce the recalcitrant nature of biomass and to allow use of the other lignocellulosic fractions, like cellulose, to obtain diversified products through integration of processes with furfural production. Extracting hemicellulose with a desired characteristic such as the degree of polymerization, reactivity, purity, and solubility remains still a challenge. Researchers have also pioneered the furfural stripping methods from the reaction medium for suppressing product degradation. Resinification and condensation reactions, which cause the degradation of furfural, could be minimized by removing the furfural formed in the liquid phase and transferring the same into the vapor phase, which is devoid of the catalytically active components.

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