

Review

Towards the Green Synthesis of Furfuryl Alcohol in A One-Pot System from Xylose: A Review

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Abstract: In the pursuit of establishing a sustainable biobased economy, valorization of lignocellulosic biomass is increasing its value as a feedstock. Nevertheless, to achieve the integrated biorefinery paradigm, the selective fractionation of its complex matrix to its single constituents must be complete. This review presents and examines the novel catalytic pathways to form furfuryl alcohol (FuOH) from xylose in a one-pot system. This production concept takes on chemical, thermochemical and biochemical transformations or a combination of them. Still, the bulk of the research is targeted to develop heterogeneous catalytic systems to synthesize FuOH from furfural and xylose. The present review includes an overview of the economic aspects to produce this platform chemical in an industrial manner. In the last section of this review, an outlook and summary of catalytic processes to produce FuOH are highlighted.

Keywords: xylose; catalyst; furfuryl alcohol; biorefinery; furfural

1. Introduction

Owing to the continuous global demand and concerns related to chemicals, fuels and materials produced from the oil industry (i.e., coal, natural gas and gasoline), which currently supplies most of these substances consumed on the planet, and the dependency of the global economy on them, alternative renewable resources have gained momentum in industry and academia. In this sense, lignocellulosic biomass is becoming an attractive alternative to substitute fossil derivatives in the production of fuels and chemicals in liquid, solid and gas form [1]. Furthermore, this type of biomass is the most abundant (after atmospheric CO₂), non-contaminant, inexpensive renewable carbon source. Valorization of by-products from the pulp and paper industry emerges as a notably promising feedstock, considering that it does not compete with food consumption. Moreover, pulp and paper mills in the Nordics are struggling to keep profiting as a consequence of the digitalization of literature, the climate crisis and especially the competitive growing market in equatorial and sub-equatorial regions with larger tree-growing rates and low-cost labor [2]. This current tendency can bring new markets to current forest firms to further expand their product portfolios with biobased chemicals and biofuels, as an extension to their cellulose-based products, such as paper and packaging materials. This situation forces the shift of their bulk production of paper-grade pulp on the way to other products with lower production volumes but higher profit, such as bio-oil from lignin [3], and value-added chemicals like xylitol [4], furfural (FUR), 5-hydroxymethylfurfural (HMF) and acetic acid from hydrolysate liquor from the dissolving pulp production [5,6].

The peculiar layout of biomass (highly oxygenated compounds) causes its conversion into chemicals and fuels to be energy-intensive and comprises profound chemical transformations [7]. One option to handle the complex matrix of biomass feedstock considers its conversion into simpler fractions, which could be further transformed downstream. Promising biomass-derived molecules

have recently been highlighted, the so-called building blocks or platform molecules [8], which consist of numerous functionalities in their structures, and therefore can be further converted to a broad spectrum of useful chemical compounds. Among the various appealing biobased platform molecules, furanic compounds like FUR, HMF, furan-2,5-dicarboxylic acid, ethanol, glycerol, isoprene, sorbitol, xylitol, lactic acid, succinic acid and levulinic acid can be produced from C₅ and C₆ sugars, which are incorporated in the hemicellulose fraction of the lignocellulosic biomass [9]. In the case of FUR, more than 70% of its market is devoted to the synthesis of furfuryl alcohol (FuOH), whose market is growing continuously [10]. Other important and widely utilized FUR derivatives in the chemical industry are tetrahydrofurfuryl alcohol (THFA) and 2-methylfuran (MF).

Furfuryl alcohol (FuOH, C₄H₃OCH₂OH, 2-furylmethanol, 2-furancarbinol) has applications in the fabrication of foundry resins, the ingredient production of P-series fuels, in liquid alkanes and in food production [11–13]. It is also a very important intermediate in fine chemical synthesis and the polymer industry, and it is used as a chemical intermediate for the synthesis of lysine, vitamin C and levulinic acid and employed as a lubricant and as a dispersing agent [14].

In order to synthesize FuOH from FUR, FUR typically is reduced at 120 °C under atmospheric pressure [15]. Currently, industrial production of derivatives from FUR has been achieved on the Cu-Cr catalyst [16], which involves various drawbacks, such as harsh conditions regarding the high H₂ pressure (3 MPa), high reaction temperature (403–473 K) and high toxicity of chromium compounds [17,18], and Cu-chromite goes through rapid deactivation associated with coke formation or via a change in the Cu oxidation state during reaction [19–21]. The first reported laboratory synthesis of FuOH was in 1864 using amalgam to reduce FUR [22]. Further studies were performed due to its presence in coffee beans [23]. Its commercial feasibility was investigated in 1934 by the Quaker Oats Company in the United States, which achieved a 99% conversion of FUR to FuOH [24]. Wojcik [25] reported in 1948 that the copper-chromium oxide catalyst yields around 96–99% FuOH in theory at 175 °C and the catalyst has little or no effect on the furan ring at 175 °C.

In addition, under liquid-phase and gas-phase systems, the chromium-based catalyst suffers from deactivation. Hence, various types of chromium-free catalysts, including noble metals (Pt, Pd, Ru, Rh and Ir) [26–30], non-noble metals (Fe, Co, Ni and Cu) [31–34] and alloyed bimetallic metals (Pt-, Ni-, Fe- and Cu-M) [35–38] have been developed to study the hydrogenation of FUR in liquid phase [39]. Moreover, liquid-phase systems are preferred, since the hydrogenation of FUR in gas phase typically results in a higher amount of by-products and higher energy requirements, due to the vaporization of FUR. Besides, it is desirable to produce FuOH in aqueous solution at mild conditions and utilize less toxic components. Hydrogenation is the most fundamental reaction in reductive conversions. The products of the hydrogenation of FUR are FuOH, MF, tetrahydrofurfural and tetrahydrofurfuryl alcohol [40] (Figure 1). Moreover, xylose and its isomerization product, xylulose, can be directly hydrogenated to xylitol on metal sites, or converted into glyceraldehyde via tetro-aldol condensation, and ultimately reduced to glycerol and ethylene glycol [41]. Additionally, xylose can be converted to xylonic acid with in situ cofactor regeneration catalyzed by co-immobilized xylose dehydrogenase and alcohol dehydrogenase [42]; it can also be converted to levulinic acid employing HY zeolite [43]. FUR, an intermediate product, can be converted into some useful chemicals through selective hydrogenation that starts by the reduction reaction of the carbonyl group and/or the furan ring, including FuOH, tetrahydrofuran (THF), tetrahydrofurfural, THFA and furan. Meanwhile, FuOH, may also continue to undergo side reactions, yielding levulinic acid and hydrogenolysis of the C-O bond (hydrodeoxygenation) forming MF notably at temperatures above 200 °C [44]. Additionally, many other compounds derived from secondary reactions like hydrogenolysis of the C-O bond, decarbonylation, hydrogenation and furan ring opening can occur, such as 2-methyltetrahydrofuran (MTHF), 2-pentanone (PN) and 2-pentanol (POL). Furthermore, when alcohols are present (methanol, ethanol, isopropanol), etherification and acetalization products may be formed such as 2-furaldehyde dimethyl acetal [40], difurfuryl ether [45] and 2-furaldehyde diethyl acetal [46–49]. Along these lines, in order to produce FuOH efficiently and selectively, it is decisive to avert over-hydrogenation by

selectively hydrogenating the C=O bonds rather than the C=C bonds, and unselectively cracking the C-C bonds. The coking process via the condensation of xylose and/or FUR derivatives also reduces the carbon efficiency [27]. The selective hydrogenation of FUR towards FuOH depends on various elements governing the intramolecular selectivity of the hydrogenation of α,β -unsaturated aldehydes [50], such as metal–support interaction, electronic and steric influence of the support, morphology of the metal particles, selective poisoning, influence and nature of the second metal, pressure and the steric effects of substituents at the conjugated double bond.

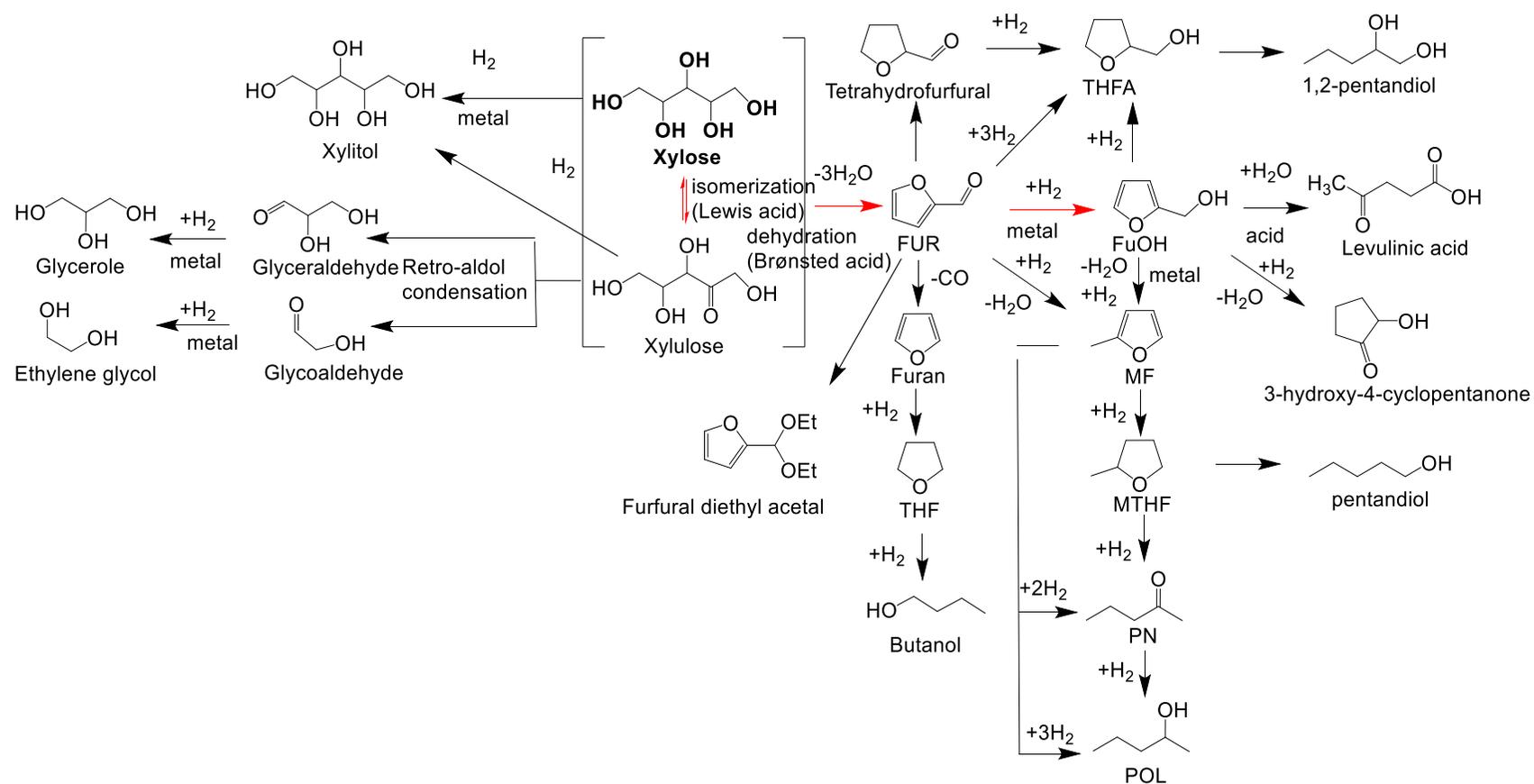


Figure 1. Possible reaction routes of the one-pot transformation of xylose to furfuryl alcohol. Adapted from [37,51–53].

2. Scope of the Review

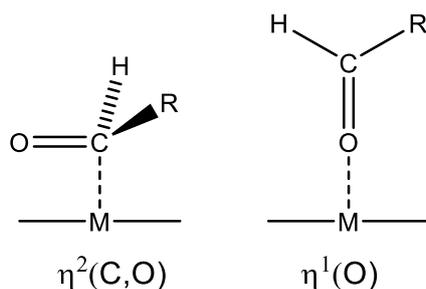
Catalytic conversion of lignocellulosic biomass represents a potential tool to selectively produce value-added materials, chemicals and fuels in solid, liquid and gas form. Among the appealing biomass-based chemicals, furfuryl alcohol is a highly attractive compound due to its wide range of applications and its sustainable production possibilities [54].

A recent review has reported advances in the catalytic production of attractive molecules from lignocellulosic biomass, which includes promising furanic compounds [5]. Moreover, readers may encounter other interesting reviews that cover the field of FUR-upgrading in a broader perspective [55,56]. Furthermore, other important reviews have collected the recent developments in the formation of FUR [57] from hemicelluloses [58] using solid acid catalysts [59] and biphasic systems [60]. A review written by Nakagawa et al. [40] gives a good perspective on the reductive conversion of FUR and HMF for catalyst development. Additionally, this review relies on helpful earlier research and reviews on furfuryl alcohol manufacture and hydrogenation, as well as catalyst characterization techniques and literature published in the field [10,54,61,62]. The reaction mechanisms to form FuOH are presented and discussed. As the following sections demonstrate, recent breakthroughs in the catalytic conversion of xylose and biomass-based feedstocks to FuOH have been developed and reviewed in the present paper. As it has been reported previously [63], xylose is the most abundant pentose in birch hydrolysate liquor found typically in the process stream of a pulp and paper company in the Nordics. Therefore, xylose was the focus feedstock for this review paper to form FuOH. Biochemical routes are shortly reviewed here since a research paper recently published covers this topic [64]. Further applications of FuOH are also mentioned and the economic aspects of its production and its market are reviewed. Nonetheless, since the present review concentrates on the formation of FuOH, the further step of synthesis of its derivatives is shortly discussed. The last sections provide an outlook of the field and conclusions that could form the basis for future studies.

3. Reaction Mechanisms

From the thermodynamic and kinetic perspective, a C=C bond is more easily hydrogenated than a C=O bond. Consequently, the selective hydrogenation of unsaturated aldehydes, including α,β -unsaturated aldehydes, to unsaturated alcohols remains a challenge. Thus, in order to hydrogenate FUR, significant studies to comprehend the reaction mechanisms have been included in the present review.

Typically, when employing Cu-based catalysts, it is conceivable to achieve selective hydrogenation of the C=O bond and at the same time keep the C=C bond intact in the furan ring. Aldehydes adsorbed onto metal surfaces take place via two types of bonding configurations: η^1 -(O) and η^2 -(C,O) [65] (Scheme 1). In a previous study, the hydrogenation of FUR over Cu-based catalysts took place through a η^1 -(O)-aldehyde (perpendicular) binding mode [33]. In this case, the aldehyde group is bonded to the surface of the active site through the carbonyl O atom with the C=C bond continuing mostly unaltered and away from the metallic surface [33]. On a Pd (1 1 1) surface, the η^2 -(C,O) configuration is preferred [65]. A strong metal-support interaction increases the selectivity of FUR hydrogenation over Pt/TiO₂ [66]. When this catalyst was used, the synergy between the metal and support enhanced the hydrogen spill over. This, in turn, led to the hydrogenation of a furfuryl-oxy intermediate that was attached to the support at oxygen vacancies. Nevertheless, the configuration on the Ni surface has been less investigated. It has been observed that both states of acetaldehyde occur on a Ni (1 1 1) crystal at 105 K [67]. Nakagawa et al. [68] introduced a reaction mechanism on the surface of a Ni/SiO₂ catalyst for FUR hydrogenation to FuOH (Figure 2), in which a strongly adsorbed FUR molecule with a η^2 -(C,O)-type configuration on the Ni metal surface is attacked by two adsorbed hydrogen atoms. The adsorbed hydrogen atoms are situated in the threefold hollow site that is a stable adsorption site on the Ni (1 1 1) surface [69].



Scheme 1. Types of bonding configurations for aldehydes adsorbed onto metal surfaces (Reproduced from [68] with the permission of John Wiley and Sons, 2012).

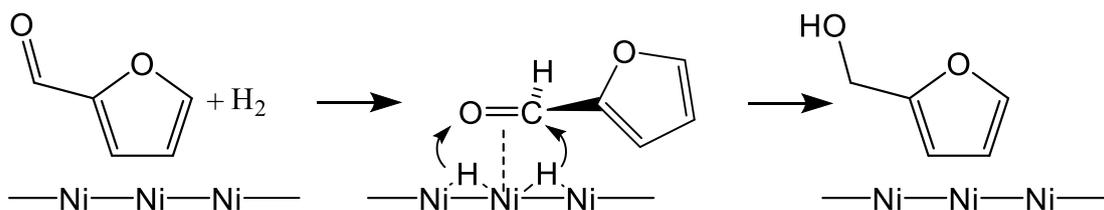
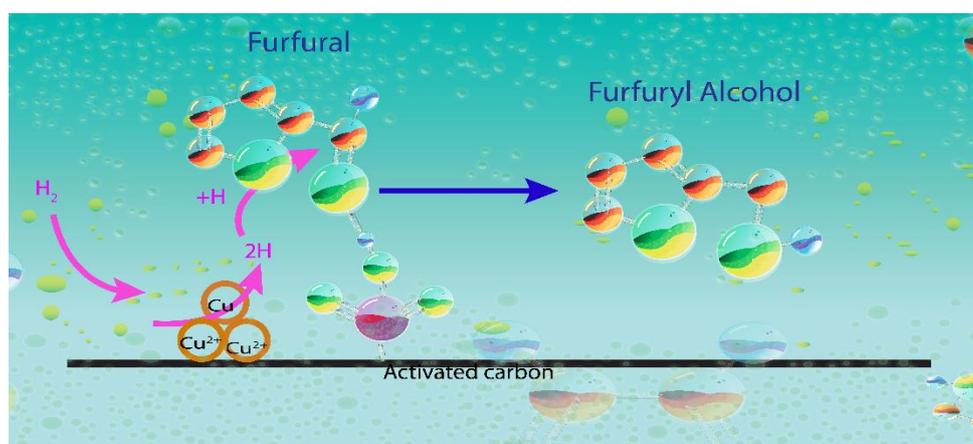


Figure 2. Proposed reaction mechanism for the hydrogenation of furfural over Ni/SiO₂ (Reproduced from [68] with the permission of John Wiley and Sons, 2012).

Gong et al. [31] proposed the liquid-phase hydrogenation process over the sulfonated activated carbon-supported Cu catalyst (Cu/AC-SO₃H) in four steps (Scheme 2):

1. FUR can be adsorbed through the carbonyl group over both Lewis acid sites (Cu(I)) and Brønsted acids sites (–SO₃H group).
2. The metallic Cu(0) provides the sites for H₂ dissociation, whereas the Cu(I) species can adsorb and activate the –C=O bond of FUR molecules.
3. The reduction reaction takes place when the active hydrogen atom attacks the bound aldehyde group on the active surface and FUR is converted into FuOH.
4. FuOH is desorbed from the surface of the catalyst with the aid of the solvent (2-propanol) and the stirring effect.

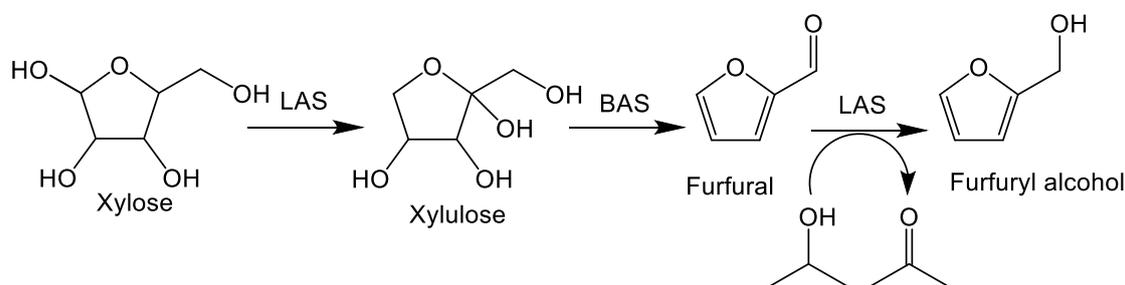


Scheme 2. Possible reaction pathway for hydrogenation of FUR according to Gong et al. [31].

Metals like Pt and Ni strongly adsorb FUR in a flat orientation, exposing both the carbonyl group and the C=C bonds to hydrogenation, giving a low selectivity towards FuOH [68]. In the search to better orient unsaturated aldehydes to adsorb solely at the carbonyl group, oxophilic metals

such as Sn and Ti have been added to the catalyst, exempting C=C bonds from hydrogenation [70]. Gallezot and Richard [71] proposed that the catalytic hydrogenation of α,β -unsaturated aldehydes may be improved over a Pt-based catalyst if a second metal is included as a promoter. The high conversion and selectivity associated with the inclusion of promoters has two main benefits: (1) the catalytic active sites interacting with the promoter [72,73]; (2) the electron contributions from the promoters, such as increasing the basicity of the zeolite, hindering the dispersion of Pt, increasing the stability of the catalyst and promoting the formation of electron-rich platinum species ($\text{Pt}^{\delta-}$) [74].

Another option for the adoption of transition metals is the reduction of FUR via the Meerwein–Ponndorf–Verley (MPV) mechanism [75,76]. This technique requires an alcohol, mainly a secondary alcohol that donates hydrogen species (sacrificing alcohol), through an intermolecular hydride transfer catalyzed by a Lewis acid, to reduce the carbonyl group of an aldehyde or ketone in the analogous alcohol via a six-membered intermediate [77,78]. At the beginning, homogeneous Lewis catalysts were used to carry out the MPV reaction [79–81]. However, these catalysts are associated with high costs and limited catalytic activity, due to their sensitivity towards moisture. Nevertheless, solid catalysts offer advantages such as easy recovery and regeneration. A reaction mechanism for the MPV reduction step was proposed by Paulino et al. [82]. In the tandem reaction, xylose is dehydrated to FUR on the zeolite Brønsted acid sites. The aldehyde is later coordinated to the Lewis acid sites by its C=O bond, establishing a cyclic six-membered transition state, formed by adsorption of an alcohol molecule, and is shifted to the carbonyl group. By now, it is known that both Lewis and Brønsted acid sites on catalysts are active and take part in a significant part in the conversion of C₅ sugars to FuOH. In this reaction, Perez et al. [83] proposed a tandem transformation of xylose/xylulose dehydration to FUR that rests principally on Brønsted acid sites [84–86], whereas the following stage (FUR transfer hydrogenation) takes place on the Lewis acid sites [87–89]. The surface sites engaged in each reaction step are highlighted in Scheme 3.

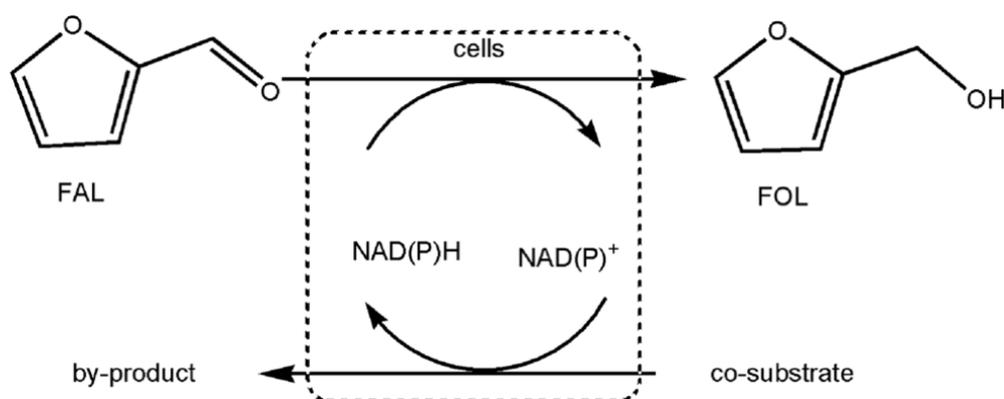


Scheme 3. Simplified scheme of xylose conversion into furfuryl alcohol (Reproduced from [83] with permission of The Royal Society of Chemistry, 2019).

4. Biochemical Conversion of FUR to FuOH

A new approach for conventional routes to produce chemicals from biomass is the use of bio-catalysis. Numerous advantages stand out from this technological strategy, such as mild reaction conditions, high yields and environmental friendliness [90].

The reduction of FUR has been biochemically proven for yeasts like *Methanococcus deltae* [91], *Saccharomyces cerevisiae* [92], *Pichia stipites* [93], *Escherichia coli* [94,95] and *Bacillus coagulans* [90,96] (Scheme 4).



Scheme 4. Simplified biotransformation of furfural to furfuryl alcohol (Reproduced from [90] with permission of The Royal Society of Chemistry, 2018).

A methanogenic bacteria, *Methanococcus deltae*, was capable of transforming FUR to FuOH in an almost stoichiometric amount [91]. He et al. [94] biosynthesized FuOH from FUR employing a recombination of *E. coli* CCZU-A13 harboring a NADH-dependent reductase (SsCR) (Table 1). The maximum activity of the enzyme was found at 30 °C and the optimum pH was observed at 6.5. They investigated also the effect of the FUR concentrations fluctuating from 20 to 300 mM. FuOH yields of 100% were obtained when the FUR concentration was ≤ 200 mM. However, for concentrations of 200 and 300 mM of FUR, the FuOH yields decreased to 94% and 74%, respectively. Studying these effects supported their next research stage to employ a combination of a solid acid catalyst and the cells to produce FuOH directly from biomass-derived xylose. A one-pot chemo-enzymatic process to dehydrate corncob-derived xylose was developed using $\text{SO}_4^{2-}/\text{SnO}$ -Kaoline and a bioreduction of FUR to FuOH with *E. coli* CCZU-T15 [97]. This chemo-enzymatic catalysis yielded 74% FUR from corncob-derived xylose and a subsequent 100% FuOH yield. Moreover, *Bacillus coagulans* NL01 has also been employed to produce FuOH from FUR, producing about 98 mM FuOH within 24 h with a conversion of 92% and a selectivity of 96% [90].

Table 1. Selected bio-catalytic systems for formation of FuOH from FUR.

Strain	Reaction Conditions Furfural Concentration [mM]	FUR Conversion (%)	FuOH Yield (%)	Reference
<i>B. coagulans</i> NL01	42 mM FUR, 15–20 g/L glucose, 9 mg/mL, 50 °C, 6 h	97	87 ^a	[90]
<i>M. deltae</i> ΔLH	10 mM FUR, H ₂ -CO ₂ as substrate, 48 h	100	100	[91]
<i>E. coli</i> CCZU-A13	300 mM FUR, 1 mM glucose/mM FUR, 0.1 g wet cells/mL, pH = 6.5, 30 °C, 12 h	100	100	[94]
<i>E. coli</i> CCZU-T15	50.5 mM FUR, 12.5 mM OP-10, 1.6 mM glucose/mM FUR, 1:3 toluene water (v/v), pH = 6.5, 30 °C, 2 h	100	100	[97]
<i>E. coli</i> CCZU-K14	200 mM FUR, 1.5 mol glucose/mol furfural, pH = 6.5, 30 °C, 24 h	100	100	[98]

^a selectivity to FuOH.

5. Patents on Furfuryl Alcohol Formation

The top five assignees registering patents on FuOH have been Quaker Oats Company (Chicago, IL, USA), Texaco Inc. (San Ramon, CA, USA), Halliburton Energy Services, Inc. (Houston, TX, USA), Jinan Shengquan Group Co. Ltd. (Shandong, Jinan, China) and Kao Corporation (Chuo City, Tokyo, Japan). Additionally, other companies in the USA and China have registered patents in FuOH. Most of the patents related to FuOH are associated with the manufacture of resins, binders, molds, foams, coatings, polymers and waxes [99–105].

Quaker Oats Co. began patenting their knowledge on FuOH by a continuous process to produce FuOH from FUR in the vapor phase employing CuO and Na₂O-SiO₂, yielding around 99% FuOH [106,107]. Furthermore, a patent submitted by Lillwitz in 1978 [108] describes the production of FuOH using HMF as the feedstock in liquid phase with Pd and Rh at ≥135 °C. FuOH is continuously extracted and the pH value is in the range of 6.5 to 9.0. The highest yield obtained was 79% with an HMF conversion of 87% in a continuous flow without the presence of solvents at 200 °C and 0.02 MPa. A method for the catalytic conversion of FUR to FuOH involving a Ru-supported and N-doped graphene material has been recently patented [109]. Furthermore, a patent reports the formation of FuOH from FUR in liquid phase employing a copper-aluminium alloy and 5.5% of Ni-Fe at 130–140 °C with a H₂ pressure of 3 MPa, that results in a FUR conversion of 99.5% and a selectivity to FuOH of 97.6% [110]. In contrast, 2-zirconium hydroxyphosphinyl acetate has been employed to convert FUR (98.1%) to FuOH (96.5% yield) at 150 °C in 1.5 h [111]. In this application, the inventors used isopropanol as a hydrogen source and as a solvent. Furthermore, the catalyst was reused three times, leading to a reduction in the catalytic activity to 92.5% FuOH yield. In a similar invention, ZrO₂@SBA-15 was used as a catalyst to form FuOH from FUR by transfer hydrogenation in a reaction temperature range of 130–160 °C and a hydrogenation reaction time of 1–4 h [112].

Additionally, a process of especial interest to obtain FuOH through multifunctional catalysts from carbohydrates (xylose) derived from lingocellulosic material was developed by Fraga and Perez in 2013 [113]. Even though various catalysts were reported, such as Pt/SiO₂-SO₃H, Pt/ZrO₂-SO₄²⁻ and Pt/ZrO₂, the patent claims that the highest selectivity to FuOH of 93% with a conversion of 19% is reached using a Pt/SBA-15-SO₃H catalyst at 130 °C, 3 MPa and a reaction time of 90 min.

6. Formation of Furfuryl Alcohol from Xylose in One-Pot Reactions

Recent advances in one-pot cascade conversion of xylose to FuOH over solid acid catalysts have attracted much attention from the industry and academia. The synthesis of FuOH from xylose employing bifunctional catalysts that incorporates acid and metal sites in one reactor brings challenges in avoiding side reactions to optimize the yield of FuOH. Furthermore, most of the studies of one-pot conversion of xylose to FuOH over bifunctional catalysts involve precious metals like Pt and Pd, and metal oxides and mesoporous silica with acid sites, such as sulphate or sulfonic groups. Nevertheless, the adequate conversion of xylose to FuOH adopting a one-step process is very attractive as it is more cost-effective and the energy-intensive separation of FUR might be avoided.

In one of the pioneering works of the one-step production of FuOH from xylose, Perez and Fraga [114] investigated a dual catalyst system consisting of Pt/SiO₂ and sulfated ZrO₂ as metal and acid catalysts, respectively. The highest selectivity to FuOH (51%) is achieved at 130 °C in 6 h employing a 1:3 aqueous to 2-propanol phase ratio at a xylose conversion of 65% (Table 2). Under these experimental conditions, reusability tests were performed. However, after the first reusability cycle, the selectivity to FuOH declined progressively after each run, reaching 29% in the third cycle. The authors suggested that the solid acid catalyst underwent deactivation, due to the unaffected formation of other products, which are dependent on metal sites (either SiO₂ or Pt). Additionally, a multifunctional catalyst based on sulphated zirconia was investigated in the one-pot formation of FuOH from xylose [115]. The highest selectivity to FuOH (27%) was obtained at a xylose conversion of 32% with an acid/metal ratio of 142 at 130 °C and 3 MPa. An interesting effect that was studied in the article shows the role of isolated metal centers, which afford the production of xylitol, whereas the presence of sole acid sites leads to

the formation of FUR. A following paper from the same research group reported a high selectivity to FuOH (75%) over a metal-free catalyst (zeolite beta) via MPV [82]. This high selectivity to FuOH was linked to the configuration of tetrahedral-framework Al centers tailored by the Al-O-Si bond distance and the characteristic typology of the catalyst. In another contribution from Fraga's group, multiwalled carbon nanotubes-supported noble metal catalysts (Ru, Pt, Au, Pd and Rh) were assessed for the one-pot conversion of xylose in aqueous phase [116]. Under the experimental conditions (6 h at 130 °C, 3 MPa H₂, using water/2-propanol (1:1)), Ru displayed the highest catalytic activity to hydrogenate xylose to xylitol and FuOH, providing 84% and 9% yield, respectively, at 100% xylose conversion. The highest FuOH yield was obtained with the Pd-functionalized catalyst (12%) at a 66% xylose conversion. The authors also studied SBA-15 catalysts incorporating Al as a heteroatom at different Si/Al ratios ([Al]-SBA-15) in the formation of FuOH from xylose [83]. The alterations to the surface of [Al]-SBA-15 guided the product distribution, FuOH being the main product and only FUR in a minor quantity despite the Si/Al ratio. All the modified mesoporous catalysts reached selectivities to FuOH of around 90%. Reusability tests were completed at 130 °C in 4 h using a water/2-propanol medium (1:1), where it can be seen that after three reusability cycles, the catalytic activity loss is insignificant (pentose conversion remains around 15%). However, the selectivity to FuOH decreased from 90 to 80%, and the selectivity to FUR increased from 10 to 20%. This effect might be a result of the Lewis acid sites losing activity after each run that results in lower conversions of the adsorbed FUR intermediate favoring the aldehyde to desorb. This developed system was designed because it requires neither molecular hydrogen nor noble metal sites for xylose conversion to FuOH, which raises costs. Brønsted acid sites come across to be active for the pentose dehydration reaction, whereas Lewis acid sites promote the transfer hydrogenation of the adsorbed FUR intermediate to FuOH [83].

Deng et al. [51] synthesized and employed a bifunctional Cu/SBA-15-SO₃H catalyst to form FuOH from xylose in a one-pot catalytic system. The highest FuOH yield (63%) was obtained at 4 MPa, 140 °C and 6 h in a biphasic water/*n*-butanol solvent mixture at a total xylose conversion. Under these experimental conditions, the authors also identified three main side-products, xylitol, FUR and xylulose. They observed that the relative high hydrogen pressure led to the side hydrogenation reaction of xylose to xylitol and the relative high reaction temperature led to the further hydrogenation to MF. Nevertheless, a study on the hydrothermal stability of the catalyst is missing and it would be of great concern to observe the catalytic activity of the functionalized Cu/SBA-15 through several reusability cycles under the same experimental conditions.

Canhaci et al. [117] converted xylose to FuOH on a single organic-inorganic hybrid mesoporous silica-supported catalyst. They employed Pt/SBA-15-SO₃H bearing different acid/metal site ratios and found negligible sole sugar dehydration to FUR and a striking production of FuOH. When they tested the catalyst reusability, the catalytic activity decreased and the product distribution changed after each reaction cycle. Nevertheless, their work demonstrated that sulfonated ordered mesoporous silica-supported catalysts deliver active and highly selective systems for the generation of FuOH from xylose. High selectivities were accomplished (83–87%) in this system.

Cui et al. [118] converted xylose to FuOH and MF. Firstly, they dehydrated xylose to FUR using a H β zeolite catalyst in a fixed-bed reactor with a high xylose conversion (>99%) and FUR yield (87.6%) when using γ -butyrolactone (GBL) and water. Secondly, they added the ternary Cu/ZnO/Al₂O₃ catalyst, which they reported in previous work to form MF from FUR [119,120], to hydrogenate FUR. A high yield of FuOH (87.2%) and MF were obtained at 150 °C and 190 °C, respectively. After a time-on-stream of 162 h in the reactor, a decline in the yield of FuOH was observed, due to the deactivation of the H β zeolite catalyst, but after reactivation, the catalytic activity could be recovered.

Table 2. Production of FuOH from xylose.

Catalyst	Substrate	Pore Width (nm)	Surface Area (m ² g ⁻¹)	Metal Loading (wt%)	Total Acidity (μmol g ⁻¹)	Temperature (°C)	Time (min)	Pressure (MPa)	Solvent	Xylose Conversion (%)	FuOH Yield (%)	Reference
Cu/SBA-15-SO ₃ H	Xylose	4.1	433.2	18.3	980	140	360	4	water/ <i>n</i> -butanol	94	63	[51]
Zeolite Beta	Xylose	N/R	551	11 ^b	1516	130	60	3	water/isopropanol	N/R	75	[82]
[Al]-SBA-15	Xylose	6.3	894	2.1	390	130	240	3 ^e	water/2-propanol	13 ^f	11 ^f	[83]
SO ₄ ²⁻ /SnO ₂ -MMT + <i>E. coli</i> CCZU-K14	Xylose	5.6	120.35	N/R	N/R	170	20	N/R	water	100	93.4	[98]
						30	1440					
Pt/SiO ₂ + ZrO ₂ -SO ₄	Xylose	6.8–4.7	207–137	0.8	317	130	360	3	2-propanol	65	51 ^a	[114]
Pt/ZrO ₂ -SO ₄	Xylose	N/R	137	Pt = 1, S = 2.9	293	130	60	3	water/isopropanol	32	27 ^a	[115]
Pd/MWCNT	Xylose	N/R	439 ^d	N/R	N/R	130	360	3	water/2-propanol	66	12	[116]
Pt/SBA-15-SO ₃ H	Xylose	N/R	N/R	N/R	N/R	130	360	3	water/isopropanol	65	83 ^a	[117]
Hβ + Cy/ZnO/Al ₂ O ₃	Xylose	N/R	N/R	N/R	361	150	600 ^c	0.1	water/γ-butyrolactone	100	87.2	[118]
Formic acid + Co-N-C	Xylose	N/R	N/R	N/R	N/R	160	300	0.5	water/1,4-dioxane	100	69.5	[121]

N/R: not reported; ^a selectivity to FuOH; ^b total Si/Al ratio; ^c As observed from a published figure based on data using a continuous fixed-bed reactor. ^d Surface area of the support.

^e Pressurized with N₂. ^f Observed from a figure in the referred article.

Furthermore, Xu et al. [121] used formic acid both as an acid catalyst and as a hydrogen donor together with a mesoporous N-doped carbon-confined Co catalyst (Co-N-C) to convert xylose to FuOH. They reported a 69.5% FuOH yield at 160 °C in 3 h from xylose, and after five reusability cycles, it was observed that the Co-N-C catalyst possesses high stability for the xylose conversion. Moreover, Ordonsky et al. [122] developed a biphasic system to dehydrate xylose and hydrogenate FUR employing Amberlyst-15 and a hydrophobic Ru/C catalyst, which is located in the organic phase. However, due to the experimental conditions, the main products of xylose dehydration with hydrogenation of FUR are THFA, γ -valerolactone, levulinic acid and pentanediols. The low amount of FuOH formed under these conditions could be the result of the high pressure (4 MPa) and high temperature (165 °C), which could have hydrogenated FuOH further to THFA.

7. Formation of Furfuryl Alcohol from Biomass-Derived Xylose in One-Pot Reactions

The use of biomass-derived xylose in the formation of FuOH has been limited. Nevertheless, a combination of thermochemical and biochemical processes has been used in a two-stage process.

He et al. used $\text{SO}_4^{2-}/\text{SnO}_2$ with different strains of *E. coli* such as CCZU-A13 [94], CCTU-T15 [97] and CCZU-K14 [98] with a xylose-rich hydrolysate liquor from corncob to produce FuOH. They employed a biocompatible solid acid catalyst ($\text{SO}_4^{2-}/\text{SnO}_2$ -APG) and *E. coli* CCZU-A13 to dehydrate the sugar-rich hydrolysate and bioreduce the intermediate FUR, respectively. At 170 °C in 20 min, 91% of xylose was converted to 52 mM of FUR. Then, after a pH adjustment, *E. coli* CCZU-A13 cells incorporating reductase SsCR were added. After another 3 h of reaction, FUR was converted to FuOH, reaching a yield of 44% determined from the initial xylose. The recycling experiments performed showed a 7% catalytic activity loss (from 100% to 93%) after five cycles, which demonstrates the relative stability of both the solid acid catalyst and the immobilized cells (Table 3). In a similar manner, corncob-derived xylose was converted in a one-pot tandem reaction to FuOH using $\text{SO}_4^{2-}/\text{SnO}_2$ -kaoline and recombination *E. coli* CCZU-T15 in toluene water media [97]. In this case, a FUR yield of 74.3% was achieved in a toluene/water medium (1:2, v/v) at 170 °C in 30 min containing 10 mM OP-10. Afterwards, FUR was converted to FuOH with *E. coli* CCZU-T15, yielding 13% based on starting material corncob. However, it was considered that 100% FuOH yield was obtained from the bioreduction step of FUR. Moreover, they used $\text{SO}_4^{2-}/\text{SnO}_2$ -Montmorillonite as a catalyst and *E. coli* CCZU-K14 to obtain FuOH in a tandem reaction [98]. The highest FUR yield (41.9%) was obtained from xylose at 170 °C in 20 min. The yield of FuOH was obtained at 100% by *E. coli* CCZU-K14 whole cells from 200 mM FUR at 30 °C in 24 h, at a pH of 6.5 and 1.5 mol glucose/mol FUR.

Table 3. Production of FuOH from biomass-derived xylose in one-pot systems.

Catalyst	Substrate	Pore Width (nm)	Surface Area (m ² g ⁻¹)	Metal Loading (wt%)	Total Acidity (μmol g ⁻¹)	Temperature (°C)	Time (min)	Pressure (MPa)	Solvent	Xylose Conversion (%)	FuOH Yield (%)	Reference
SO ₄ ²⁻ /SnO ₂ -APG + <i>E. coli</i> CCZU-A13	Corncob-derived xylose	7.1	128	3.6	N/R	170	20	N/R	water	100	44	[94]
						30	180					
SO ₄ ²⁻ /SnO ₂ -KL+ <i>E. coli</i> CCTU-T15	Corncob-derived xylose	6.3	40	N/R	N/R	170	30	N/R	toluene-H ₂ O	100	74.3	[97]
						30	360					

N/R: not reported.

8. Effect of Solvents in the Formation of Furfuryl Alcohol

The solvent effects in heterogeneous catalysis have been justified by correlating reaction rates and product distributions with two main properties: the solvent polarity and/or the dielectric constant. The results reported by various authors [117,123,124] on the formation of FUR from xylose when using zeolites indicate that the presence of water has a negative effect on the dehydration of xylose. Therefore, organic solvents are added to boost the catalytic activity of xylose dehydration and the selectivity toward the aimed compound to be formed. Biphasic systems including an aqueous and an organic phase with a high partition coefficient for FUR have been widely studied in the formation of FUR [14,63,125,126]. The organic solvent protects the FUR formed from side reactions and potentially allows for easier separations of the products. The solvent effects can influence the kinetics of both polar and non-polar substrates like Singh et al. [127] discussed in their article. It is known that a polar solvent enhances adsorption of the non-polar reactant, while a non-polar solvent enhances the adsorption of a polar reactant. However, the specificity of metals on solvent effects is not yet known.

Typically, the hydrogenation of aldehydes with alcohol as the solvent initiates the generation of secondary products such as acetals. This is caused by the reaction between the substrate and the solvent. When Merlo et al. [35] used ethanol as the solvent in the conversion of FUR to FuOH, the ether 2-isopropoxymethylfuran was found as a consequence of the reaction between FuOH and ethanol. However, FuOH and the solvent did not seem to form by-products when *n*-heptane and toluene were employed.

López-Asensio et al. [75] evaluated three alcohols in the MPV reaction in the presence of two catalysts, such as *i*-propanol, 2-butanol and cyclohexanol, as sacrificing alcohols. The results show that when 2-butanol is used, a slight increase in FUR conversion occurred for both Zr-doped mesoporous SBA-15 catalysts, in comparison to *i*-propanol and cyclohexanol. This effect is due to the fact that the long aliphatic chain reduces the polarity of the secondary alcohol and promotes the generation of a more stable six-membered intermediate with the Lewis acid sites, which facilitates the relocation of the hybrid species. On the other hand, when employing cyclohexanol, the poorest catalytic results are observed under the experimental conditions, probably attributable to steric hindrance in the development of six-membered intermediates.

Related research was accomplished by Gong et al. [31] comparing 2-propanol, ethanol, water and toluene. The protic solvents (2-propanol, ethanol and water) exhibited higher catalytic activity than the nonpolar solvent (toluene). This could be due to the hydrogen bonding between the carbonyl oxygen of FUR and the hydroxyl group of the protic solvents. In a surprising manner, Tamura et al. [26] were able to form FuOH from FUR in water under mild reaction conditions, for instance, low H₂ pressure (0.8 MPa) and low temperature (130 °C), employing Ir-ReO_x/SiO₂ as a highly active and selective solid catalyst. The authors claimed that not only FUR can be hydrogenated to FuOH in this system, but various unsaturated aldehydes can be transformed to the corresponding unsaturated alcohols due to the synergy created between Ir metal and ReO_x, which increases the selectivity and activity without losing the activity of the noble metals. Bonita et al. [128] compared the conversion of FUR and the selectivity to FuOH in isopropanol, toluene and hexanes. It was noted that the FUR conversion and the selectivity to FuOH declined significantly in toluene and hexanes, compared to the system involving isopropanol.

A study comparing various water/isopropanol mixture compositions uncovered the significant roles performed by the solvent polarity and the amount of the hydrogen donor in the formation of FuOH [82]. The study demonstrated that the highest FuOH yield (~80%) was obtained when a zeolite beta was used with the lowest water/isopropanol mixture (0.0026:1). Therefore, extensive amounts of water were shown to reduce the catalytic activity as it has been previously evidenced [129]. This effect has been correlated with the interaction between water molecules from the reaction medium and/or formed upon reaction with the surface acid sites [130–132]. Subsequently, the water molecules may be kept linked to the acid centers reducing its inherent activity [83].

Moreover, water, 1-butanol, MTHF and cyclohexane have been studied on FUR hydrogenation [122] over an Ru/C catalyst. Hydrogenation of FUR in MTHF and 1-butanol affords different compounds as opposed to the reaction in water. When employing MTHF as the solvent at a 91% conversion of FUR, the main compounds formed are FuOH (42%), THFA (11%) and MF (19%).

Therefore, solvent selection plays a great role in the selectivity to FuOH and FUR conversion. Moreover, a recent article reviewed different heterogeneous catalysts that were employed with diverse organic solvents to boost furan yields from sugar dehydration reactions [60]. Nevertheless, further research has to be completed in an effort to comprehend the influence that aqueous systems have on heterogeneous catalysts and how solvent properties alter the reaction.

9. Economic Aspects

As discussed in the previous section, FuOH covers more than 60% of applications of FUR, and some market studies even report that more than 80% of all FUR produced is converted to FuOH [133,134]. The global FuOH market is mainly driven by the consistent growth in the foundry industry, in which FuOH competes with phenol that is therefore used to produce phenolic resins. The FuOH market was estimated to be EUR 493 million in 2019, projected to reach EUR 630 million by 2024 and it is expected to reach EUR 1350 million by 2028 [134]. It is estimated that the market size of FuOH will expand, especially in the polymer, solvent and adhesives industries and in its application as a wetting agent [135]. The largest FUR-consuming region in the world is Asia-Pacific (led by China) with an estimated share of 61% in 2017 and 77% in 2018 [133,134]. China is the leading producer of FUR followed by South Africa and the Dominican Republic [136]. Moreover, the production capacity is continuously expanding with more players entering the global FuOH market. This market growth is attributed to the increasing demand of FuOH and other FUR-based derivatives [137]. A process to produce FuOH from FUR developed by Tseng et al. [138] reported an annual cost of EUR 744,000/year [139] to produce 50 kmol/h.

10. Summary and Outlook

The valorization of non-edible biomass and the active diversification of pulp and paper companies are thriving topics to achieve the biorefinery paradigm. In the present review, several successful cases have been discussed, highlighting the diverse options to obtain furfuryl alcohol in a chemoselective way from xylose and biomass-derived xylose.

The current commercial production of FuOH from FUR is performed on a Cu-Cr catalyst, which is associated with toxic effluents from chromium compounds, rapid deactivation and harsh process conditions. Besides, the former dehydration step of xylose to FUR needs to be completed in a different reactor. Nevertheless, the process yields high amounts of FuOH (>90%).

This review highlights new promising catalytic pathways for the one-pot formation of FuOH from biomass. It can be observed that bifunctional catalytic systems owning precious metals like Pt and Pd are employed with sulfonated or sulfated catalysts to form FuOH from xylose and biomass-derived feedstocks. Besides, protic solvents such as water and isopropanol are frequently used, due to their advantages in the formation of FuOH.

There is an abundance of elements that could affect the activity of the catalysts, such as the acidity of the support, the interaction between the metal and the support, the surface area and the metal content. Therefore, it is clear that the acidic properties of the solid acid catalyst and the solvent employed in the system contribute significantly to the reaction pathway. In relation to the transition metal catalyst, the renowned toxicity of chromium contains a likely risk both to health and the environment. The employment of solid catalysts offers the special advantage to design the catalyst for the system and the reaction. Nevertheless, hydrothermal stability issues under these conditions can lead to leaching, which turns the system into homogenous reactions. Thus, innovative technological systems are urgently needed that can still move on over numerous sequential stages in potential heterogeneous catalytic systems or through a single-step reaction directly from xylose over multifunctional catalysts.

The proof-of-concept of the biochemical catalytic conversion of FUR to FuOH is promising and further technical development is needed. The advantages of this kind of system are the low temperature condition, atmospheric pressure and low demand of hydrogen. A critical technological feature is the opportunity of enzymes to catalyze reactions with furans both in the presence and absence of water. Nevertheless, the biggest challenges in the biocatalytic conversion of FUR remain in delivering optimization and techno-economic feasibility to achieve efficient biorefinery concepts.

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