

Review

A review of recent advances in the production of furfural in batch system

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ABSTRACT

The production of biobased furfural has been known for a long time. Nevertheless, two recent concepts, namely bioeconomy and circular economy, have motivated the research line towards improving production schemes and diversifying potential applications. Accordingly, this review will put the spot on the recent advances of furfural production from organic feedstock rich in free sugars and/or structural or reserve polysaccharides. The review will highlight the recent progress in the furfural production in batch system following different pathways, including (i) non-catalytic routes, (ii) use of various homogeneous catalysts like mineral or organic acids, metal salts or ionic liquids, (iii) feedstock dehydration using diverse solid acid catalysts; (iv) feedstock dehydration over supported catalysts, and (v) other heterogeneous catalytic routes.

1. Introduction

Currently, the need of basic compounds grows constantly through time. In parallel, fossil resources are getting reduced, which contributes to the increase of fossil fuel-based materials price and to the increase of greenhouse gas emissions [1–3]. In addition, green chemistry presents now a very important field. It supports a new point of view in chemistry, forwarding the use of green feedstocks, solvents and process in order to limit the chemical production that can damage our environment [4–9]. To this end, it's mandatory to work on the intensive production of biorenewable resources as well as related residues to open the access to useful chemicals. In this frame, plant side-products or wastes can be considered as recycled feedstocks and one of the alternatives that aim to reduce the fossil oil dependence and its related problems [10,11]. Chemical companies produce biofuels from such renewable resources. Consequently, they opened a green pathway to get fine chemicals, agro-chemicals and compounds with precise specialty like bio-based solvents and other [12–15]. Renewable resources can be converted, biologically or chemically, into a wide range of building blocks like ethanol, glycerol, lactic acid, succinic acid, levulinic acid. The economic importance of these entities often lies in projections of their use in the short or medium term, as well as in the environmental benefits of their production and final use [16–22]. Particularly, furanic compounds, such as 2-furaldehyde (furfural) and 5-hydroxymethylfurfural (HMF) offer

several industrial applications [23–31]. Commonly, these two compounds are low yielded from the conversion of plant matrices that requires many consecutive technical steps. On the other hand, several investigations demonstrated the efficiency of one-pot synthesis of furans that could be performed based on biomass resources by following well-optimized procedures that include an appropriate selection of catalyst(s), solvent(s), equipment configuration, and process technology upgrades [32,33]. In general, hemicelluloses are the common source of furfural in addition to the other polysaccharides rich in pentoses [34]. More research has demonstrated that other carbohydrates sources can be exploited to produce furfural, such as the alginate derivatives [35]. The importance of furfural as a platform chemical relies in its large ability to be converted into a wide range of valuable derivatives including, notably, solvents, polymers or fuel additives (Scheme 1).

Numerous batch and continuous processes have been developed in industrial operations for digesting lignocellulosic biomass to produce furfural. Several key furfural production technologies and their respective conditions and yields are summarized (Table 1). These technologies are used in the main multinational industries including Transfuran Chemicals (Belgium), Central Romana Corporation (Dominican Republic), Pennakem (USA), Silvateam (Italy), Illovo Sugar (South Africa), Hongye Holding Group Corporation (China), KRBL (India), Lenzing (Austria), Tanin (Slovenia) and Shandong Crownchem industries (China). The global furfural market size was valued at USD 551 million

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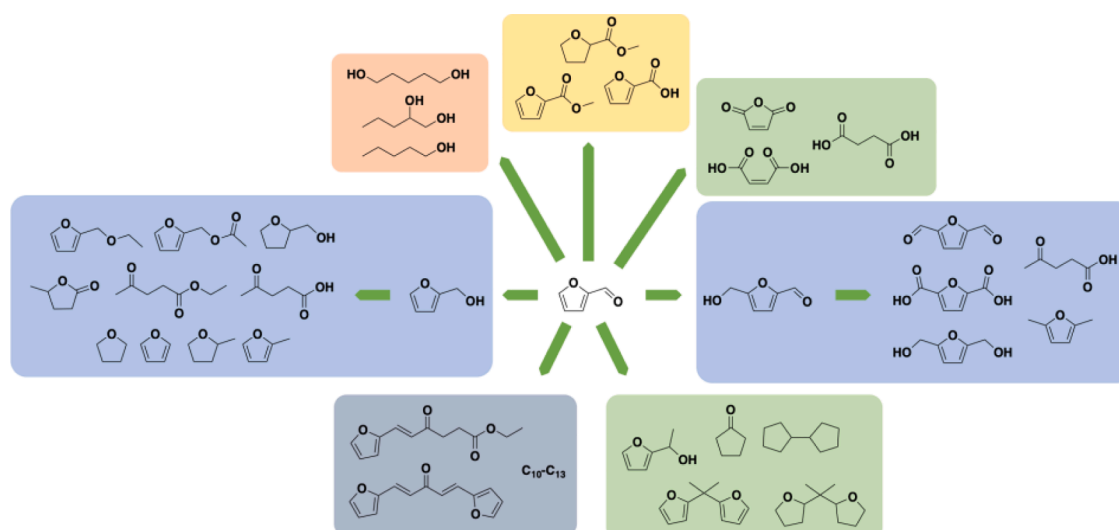
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Scheme 1. Representative synthesis of chemicals and fuel additives from furfural.

Table 1
Summary of key furfural production technologies [29].

Technology	Reactor	Biomass	Catalyst	Temperature (°C)	Furfural yield (%)
Quaker Oats	Batch	Oat hull	H ₂ SO ₄	153	40–52
Chinese batch	Batch	Corn cob	H ₂ SO ₄	160–165	50
Quaker Oats	Continuous	Bagasse	H ₂ SO ₄	184	55
Westpro/Huaxia	Continuous	Lignocellulosic residues	H ₂ SO ₄	160–165	35–50
Rosenlew	Continuous	Bagasse	Autocatalysis	180	60
Suprayield	Continuous	N/A	H ₃ PO ₄	180–240	50–70
Multi-Turbine-Column	Continuous	Straw	H ₂ SO ₄	180	86
Vedernikovs	Continuous	Birch wood saw dust	H ₂ SO ₄	188	75
Biofine	Continuous	Ground hardwood, paper sludge	H ₂ SO ₄	210–220 then 190–200	70

in 2019 and is expected to experience a compound annual growth rate of 7% from 2023 to 2030 [36] with a production of 350 metric tons worldwide.

The purpose of the present review is to continue the summary that we have started before in a previous paper [24], in which we put the spotlight on the literature of furfural production from free sugars and polysaccharides using homogeneous and heterogeneous catalyzed strategies.

2. Catalyst-free process for furfural production – conventional batch process

The synthesis of furfural was previously described without added catalyst and some side-products (carboxylic acids) or intermediates were systematically produced, underlining a lack of selectivity in reactions conducted without catalyst [37]. In this frame, the authors developed the autocatalyzed furfural production in biphasic microwave-assisted batch system in three immiscible “water-organic solvent” mixtures using: isophorone, 2-methyltetrahydrofuran (2-MTHF) or cyclopentyl methyl ether (CPME). It is noteworthy that whatever the catalysis (homogeneous, heterogeneous and without catalyst), this strategy was developed to extract the furfural and to limit the formation of humins [38–42]. The optimum aqueous-to-organic phase ratio for the three organic solvents tested was found to be 1:1 (v/v) that ensured the *in situ* extraction of furfural from D-xylose dehydration. The best selectivity towards furfural (93%) was recorded when using the CPME as an organic solvent under the well-controlled conditions of temperature (170 °C) and time (90 min). As expected, the best production of furfural starting by birch hydrolysate rich in D-xylose and D-arabinose, was achieved after 120 min of hydrothermal

reaction at 190 °C.

In a free catalyst system, Lin et al. tested series of solvents to produce furfural from D-xylose [43]. Solvents used for this study were: water, dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), isopropanol (ISO), γ -butyrolactone (GBL) and γ -valerolactone (GVL). Different parameters were studied: (1) the D-xylose solubility, (2) α/β anomers ratio, (3) the distribution of the solvent around D-xylose-furfural, (4) the hydrogen bonding between them and (5) the degradation behavior of solvents. In pure solvents, the hydrogen bonding occurred with the D-xylose resulted in different products. Among them, water and DMSO were both the best solvents to transform D-xylose into furfural because less formic acid was formed. In mixed solvents, with water, GBL and GVL were the two organic solvents that provide weak affinity to D-xylose and the volume ratio of H₂O-cosolvent was 1:1 (v/v). This work resulted with 46% of furfural yield in H₂O-GBL at 180 °C within 150 min of reaction time without presence of catalyst. Based on kinetics study, Lin et al. compared the furfural production in its six effective and commonly used biphasic solvents [44]. Based on the D-xylose conversion and furfural yield, the efficiency order of biphasic systems which is dichloromethane (DCM)-H₂O > 2-MTHF-H₂O > butan-2-ol-H₂O \approx methylisobutylketone (MIBK)-H₂O > CPME-H₂O > toluene-H₂O in 5:5 volume ratio was obtained. The highest furfural yield (82%) was achieved in the DCM-H₂O system under hydrothermal reaction with free catalyst conditions at 180 °C for 60 min.

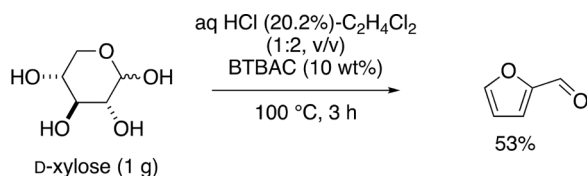
In the purpose of valorization of food industry residues, Ozbek et al. proved an eco-friendly and sustainable method that combine the CO₂ with hydrothermal processes [45]. In this study, the high-pressure CO₂/H₂O was used to valorize pistachio shell by producing hemicellulose-derived, oligomeric and monomeric sugars followed by further transformation to furfural. The production of furfural from

Table 2

Selected homogeneous catalytic dehydration processes of D-xylose and biobased derivatives for production of furfural in batch reactor.

Entry	Substrate	Catalyst	Solvent and additives	Reaction conditions	Conversion (%)	Yield (%)	Ref.
1	D-xylose	HCl (0.12 M)	H ₂ O-DCE (1:2, v/v), BTBAC	100 °C, 3 h	nd	53	[46]
2	D-xylose	HCl (nd)	H ₂ O-MIBK (2:1, wt/wt)	170 °C, 7.5 min, MW	93	76.4	[47]
3	D-xylose	H ₂ SO ₄ (0.36 M)	H ₂ O-EtOH (1:1, wt/wt)	220 °C, 5 min	100	89.8	[49]
4	D-xylose	H ₃ PO ₄ (30.5 wt%)	H ₂ O-acetone (3:7, v/v)	150 °C, 10 min	nd	53.7	[51]
5	D-xylose	H ₂ SO ₄ (pH 1)	H ₂ O-toluene-sulfolane (1:1:1, v/v/v), PBA	180 °C, 3.5 h	100	95	[52]
6	D-xylose	Acetic acid (0.5 mol L ⁻¹)	H ₂ O	178 °C, 10 b	98	97	[53]
7	D-xylose	Terephthalic acid (0.15 g)	H ₂ O-toluene (1:2, v/v)	190 °C, 3 h	92	71	[54]
8	D-xylose	Sulfamic acid (10 mol%)	H ₂ O-GVL (1:9, v/v), sulfamic acid (10 mol%)	190 °C, 15 min	nd	70.19	[55]
9	D-xylose	NaCl (9 g)	H ₂ O-THF (1:1, v/v)	190 °C, 2 h	99	77	[56]
10	D-xylose	FeCl ₃ (0.06 mol L ⁻¹)	H ₂ O-MIBK (1:4, v/v)	180 °C, 15 min	98	75.55	[60]
11	D-xylose	1-(4-Sulfonic acid) butyl-3-cetyl-2-methyl imidazolium hydrogen sulfate (0.5 g)	H ₂ O	160 °C, 180 min	95	67	[69]
12	D-xylose	[C ₄ mim]HSO ₄ (0.6 g) H ₂ SO ₄ (20 wt%)	H ₂ O	140 °C, 4 h	86.7	84	[70]
13	D-xylose	[Bmim]Cl/FeCl ₃ (0.1 mol L ⁻¹),	H ₂ O-butanone (1:4, v/v)	140 °C, 90 min	99	75	[71]
14	D-xylose	SnCl ₄ (10 mol%)	[Emim]Br (1 g)	130 °C, 1 h	98.9	71.1	[74]
15	D-xylose	3,3'-methylenebis(1-methyl-1H-imidazol-3-ium) hexafluorophosphate	H ₂ O	205 °C, 8 min	nd	49.76	[75]
16	D-xylose	[GlyIm][HSO ₄] (10 eq)	H ₂ O-5-MTHF (1:4, v/v)	180 °C, 10 min, MW	nd	87	[76]
17	D-xylose	Al ₂ (SO ₄) ₃ (0.2 g)	H ₂ O-GVL (9:1, w/w)	140 °C, 3 h	95.5	50.16	[59]
18	E. globulus wood	HCl (nd)	H ₂ O, MIBK	170 °C, 10 min, MW	nd	67.8	[47]
19	Corncob	HCl (nd)	H ₂ O, MIBK	170 °C, 20 min, MW	nd	72.5	[47]
20	Laccase-treated pre-hydrolysis liquor from Eucalyptus dissolving kraft pulp	H ₂ SO ₄ (2 wt%)	H ₂ O	160 °C, 60 min	92.82	37.60	[50]
21	Bagasse	H ₃ PO ₄ (30.5 wt%)	H ₂ O-acetone (3:7, v/v)	150 °C, 5 min	nd	45.8	[51]
22	Tung shell	Sulfamic acid (10 mol%)	H ₂ O-GVL (1:9, v/v), sulfamic acid (10 mol%)	200 °C, 30 min	nd	92	[55]
23	Corncob	KHSO ₄ (6 wt%)	H ₂ O	190 °C, 2 h	nd	11	[58]
24	Tung shell	FeCl ₃ (0.06 mol L ⁻¹)	H ₂ O-MIBK (1:4, v/v)	180 °C, 60 min	100	100	[60]

nd non determined.

**Scheme 2.** Schematic conversion of D-xylose into furfural, under optimal reaction conditions.

hemicellulose hydrolysates gave 40% yield with a selectivity of 40% under optimum conditions (160 °C, 18 min in a 30 mL aqueous solution of tetrahydrofuran (THF)).

3. Homogeneous catalysis for furfural production – conventional batch process

Dehydration of D-xylose and derivatives was studied in presence of either mineral acids (H₂SO₄, KHSO₄, HCl, H₃PO₄), organic acid (acetic acid, terephthalic acid, sulfamic acid, ionic liquids) or metal salts (NaCl, FeCl₃, SnCl₄, Al₂(SO₄)₃) in water or in aqueous biphasic systems using conventional thermal activation or microwave technology. The main results for the dehydration of D-xylose and other organic raw materials using homogeneous catalysis were summarized in Table 2.

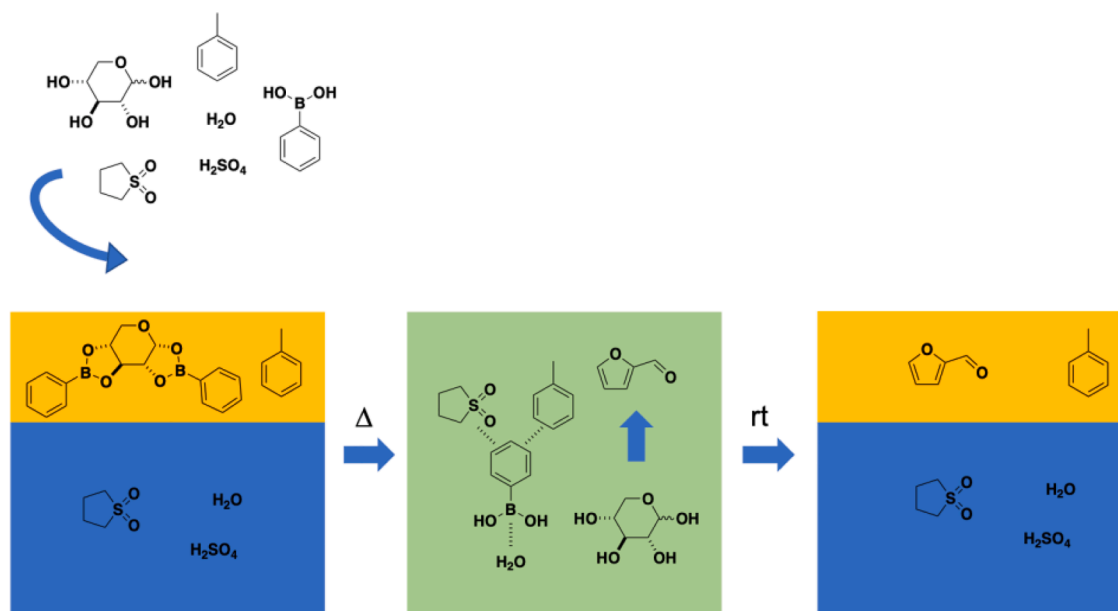
3.1. Dehydration in presence of mineral acids

The main mineral acids for the synthesis of furfural were aqueous H₂SO₄, KHSO₄, HCl and H₃PO₄ which had the advantages to be less expensive. The use of benzyltributylammonium chloride (BTBAC) as a

phase transfer catalyst in an aqueous HCl-1,2-dichloroethane (DCE) biphasic system was reported to dehydrate D-xylose into furfural [46]. The best conditions for D-xylose (1 g) dehydration were at 100 °C for 3 h in aqueous HCl (20.2%)-DCE (60 mL, 1:2, v/v) and BTBAC (10 wt%) (Scheme 2). In these conditions, furfural was isolated in 53% yield. Noteworthy, furfural was obtained after evaporation under reduced pressure as light-yellow oil. In addition, a mixture of pentose (0.5 g) and hexose (0.5 g) as a feedstock was used to coproduce furfural and 5-(chloromethyl)furfural (CMF) under the optimized conditions (BTBAC (10 wt%), 100 °C, 3 h in a mixture of aqueous HCl (20.2%)-DCE (1:2, v/v)). Furfural and CMF were obtained in 53% and 17% yields, respectively, from the sugar mixture in addition to 31% of levulinic acid extracted from aqueous phase. BTBAC allowed furfural to be extracted from the aqueous solution as soon as it is formed. In this case, BTBAC is a substitute for the aqueous NaCl biphasic mixture.

Furfural production was performed using various feedstocks such as D-xylose, hemicellulosic saccharides from *Eucalyptus globulus* wood or corncobs in biphasic media (H₂O-MIBK) assisted microwave heating [47]. HCl or H₂SO₄ were the catalysts used to promote the production of furfural. The best furfural yield obtained from *E. globulus* wood (10 min, 1% HCl) and corncobs (20 min, 0.5% HCl) were 68% and 72% respectively at 170 °C. The furfural yield from D-xylose was 76.4% with 82.3% of selectivity for 7.5 min in presence of 1% of HCl. Obviously, D-xylose furnished better results in term of productivity whereas biomass such as *E. globulus* wood and corncobs required longer time.

The effect of sulfuric acid concentration (from 0.1 to 2 M) and temperature (between 120 and 160 °C) on D-xylose dehydration was studied by Krzelj et al. who developed a kinetic model to predict the experimental results [48]. In this study, the side products are form from the interaction of furfural and D-xylose dehydration intermediates and



Scheme 3. Schematic approach of solvent composition of the system and its phase behavior for the furfural synthesis.

no D-xylose itself that results in selectivity loss. The established kinetic model can predict the conversion of D-xylose with 95% of accuracy. It is well known that the furfural yield is likely reduced by humins formation. However, the use of short chain alcohol like ethanol can suppress such side reaction [49]. Therefore, Köchermann et al. developed the D-xylose (25 g) dehydration catalyzed by H_2SO_4 (4.5 mL of 1.8 M H_2SO_4 , pH of 1.6) in H_2O -ethanol system at temperature range of 180–220 °C. Three different H_2O -ethanol weight ratios: 9:1, 4.5:1, and 1:1 (wt/wt), and in the absence of ethanol, were deeply investigated. It was noteworthy that the presence of ethanol as hydrogen-donor improved the furfural yield from D-xylose dehydration and showed an increase from 45% to 90%, combined to a decrease, by about 60%, of the humins formation.

To improve the application of the pre-hydrolyzed liquor (PHL) biomass in biorefinery, sulfuric acid was used to produce furfural with success. In this context, Eucalyptus dissolving kraft pulp pre-hydrolysis liquor (PHL) can be useful due to its enrichment in sugar and other biomass resources [50]. However, PHL contains lignin that favors side reactions during improving PHL value. After depolymerization of lignin in the presence of laccase enhancing its removal from the reaction medium, the delignified pre-hydrolysis liquor (LPHL) was converted to furfural by the action of 2 wt% H_2SO_4 . It is noteworthy that the selectivity and yield of D-xylose to furfural in LPHL (removing more than 50% of lignin) are nearly 5% higher than those of PHL (from PHL, D-xylose conversion = 94.34%, yield = 32.39 while from LPHL, D-xylose conversion = 92.82%, yield = 37.60). This phenomenon indicates that the removal of lignin in PHL is beneficial to furfural production.

A novel pressurized phosphoric acid acetone-water system (PPAWS) was developed to produce platform chemicals with the minimum of waste from hemicellulose or cellulose in one-pot [51]. Two feedstocks (1.5 wt% of bagasse which is composed of 38.5% glucan (42.8% glucose), 18.2% xylan (20.7% D-xylose), and 24.8% K-lignin or pure D-xylose) were studied. Starting from bagasse, furfural was obtained in 45.8% yield at 150 °C and 15 bar of nitrogen in a system of H_2O -acetone (7:3, v/v) within 5 min in presence of H_3PO_4 (30.5 wt%). Under the same conditions, D-xylose could reach 53.7% yield within 10 min in the PPAWS.

Whether using HCl , H_2SO_4 or H_3PO_4 the synthesis of furfural generally required a temperature above 100 °C and a two-phase mixture (H_2O -DCE, H_2O -MIBK, H_2O -ethanol and H_2O -acetone) was recommended, although a single solvent can also synthesize furfural in good

yield. Using a mixture of H_2O -MIBK, microwave-assisted dehydration as the alternative technology was efficiently for the production of furfural starting from D-xylose and other carbohydrates-containing resources.

3.2. Dehydration in presence of organic acids

Different organic acids such as boronic acid, acetic acid, terephthalic acid and sulfamic acid were described for the synthesis of furfural. The production of furfural was improved by three solvents system consisting of an apolar aromatic solvent, a polar organic solvent and acidic water [52]. In such a system, a transition from biphasic to monophasic is established by the effect of phenylboronic acid (PBA) that can extract D-xylose and gave a furfural yield above 90%. The transition from biphasic to monophasic contributes to the increase of the medium polarity because of the mixing of aromatic solvent with water-polar organic phase. This increase of polarity most likely improved the furfural selectivity. The aromatic solvent interacts with the PBA and guarantees the phase transition. Finally, under 180 °C, pH = 1 (adjusted by H_2SO_4), within 3.5 h a full conversion of D-xylose (97 mM) was performed in presence of PBA (> 20 mM) with a furfural yield of 95% in either a system of toluene-sulfolane- H_2O (6 mL, 1:1:1, v/v/v) or a system of nitrobenzene-DMSO- H_2O (6 mL, 1:1:1, v/v/v) (Scheme 3). In this process, furfural was recovered by distillation.

Based on the concept of industrial process intensification, Arpornwichanop's group investigated the production of furfural via reactive distillation (RD) from lignocellulosic biomass [53]. The biomass hydrolysate derived from sugarcane bagasse as a feedstock, in the presence of acetic acid as a catalyst, was selected as a benchmark and the process performances were evaluated by exergy and exergo-economic analyses. In this work, the decrease of the reboiler duty with the increase of D-xylose concentration improved the system efficiency by the reduction of its exergy input. Interestingly, the production of furfural was 82 kg h^{-1} with D-xylose conversion of 98% and 97% of furfural yield with high purity starting with 2 wt% of D-xylose and 0.5 mol L^{-1} of acetic acid at a pressure of 10 bar.

Terephthalic acid (TPA) from cheap polyethylene terephthalate waste was used as a catalyst for D-xylose dehydration into furfural in H_2O -toluene biphasic system [54]. TPA is a homogeneous catalyst under the reaction conditions selected but it conveniently precipitates at ambient temperature allowing to be quantitatively recovered in an easy way. D-Xylose (8.9 wt%) in the presence of catalyst (0.15 g) in a mixture

of H₂O-toluene (1:2, v/v) was converted in 92% and furfural was obtained in 71% yield at 190 °C within 3 h. Finally, TPA provided good recyclability for up to five runs.

A bifunctional solid organocatalyst, sulfamic acid was studied to produce furfural [55]. Two forms of sulfamic acid existed, one can catalyze the dehydration of D-xylose to furfural, while the other one catalyzes its isomerization into D-xylulose. Specifically, the zwitterionic form (H₃N⁺SO₃⁻) of it leads to the isomerization due to its electron-rich sulfonate that favors the attack of the hydrogen position leading to an isomerization. On the other hand, NH₂SO₃H can dehydrate the xylulose to furfural. In this work, different biomass species such as corncob, *Miscanthus × giganteus*, the hull and shell of *Camellia oleifera* (tea) fruit and *Aleurites fordii* Hems L. (tung) fruit were studied. Under the optimized conditions of 190 °C for 15 min in a biphasic system H₂O-GVL (1:9, v/v) in the presence of sulfamic acid (10 mol%) furfural was obtained in 70.19% yield from D-xylose as monomer, while furfural yield reached 92% when tung shell as starting material was used at 200 °C for 30 min. It was notable that the organic solvent used in this process was GVL that can be obtained from biobased cellulose.

Using commercial simple boronic acid, acetic acid, TPA and sulfamic acid, furfural was recovered at high temperature above 180 °C in an aqueous biphasic mixture (H₂O-toluene and H₂O-GVL) or in an aqueous monophasic mixture at 180 °C.

3.3. Dehydration in presence of metal salts

Dehydration of D-xylose and derivatives in the presence of various metal salts such as NaCl, KHSO₄, Al₂(SO₄)₃ and FeCl₃ were also reported. Simple NaCl promoted the D-xylose dehydration into furfural in water [56] as the presence of NaCl enhanced the phase separation. A system that consists of NaCl-H₂O-THF could promote the D-xylose dehydration without addition of other catalyst. In this frame, D-xylose (0.5 g) in a mixture of H₂O-THF (50 mL, 1:1, v/v) in the presence of NaCl (9 g) at 190 °C for 2 h afforded furfural in 77% yield with a selectivity of 78% and a quantitative conversion.

The acidic salt KHSO₄, as a low-cost metal salt, was reported as a catalyst for furfural production from corncob (hemicellulose 32.1%, cellulose 36.3%, and lignin 16.8%) and as an alternative to the conventional toxic and corrosive H₂SO₄ [57]. At 190 °C for 2 h, initial corncob in the presence of catalyst (6 wt%) in water produced furfural in 11% yield. This work proved the advantage of KHSO₄ over H₂SO₄ specially in term of its insolubility in water at ambient temperature and so the possibility of its recovery and reuse. Therefore, the recovery of the catalyst and its remaining catalytic efficiency were studied as well [58]. The catalyst was easily removed by simple washing with hot water followed by a solid-liquid separation. They investigated the effect of the mass ratio of hot water to the wet solid mixture, washing time and its number on the catalyst recovery. This work resulted in 87.7% of total catalyst recovery and five successive catalytic runs. Another sulfate derivative, Al₂(SO₄)₃ allowed the production of furfural from hemicellulose and waste lignocellulosic residues in H₂O-GVL system [59]. Indeed, Al₂(SO₄)₃ was the best catalyst known to promote furfural production from xylans. In this work, GVL interacts with the active acid site which contributed to a furfural yield above 50% from xylan (2.0 g xylan, 0.2 g of catalyst) converted by 95 wt% in a system of H₂O-GVL (1:9, w/w, 40.0 g global mass) at 140 °C in 3 h. The authors found that [Al(OH)₂(aq)]⁺ species gave access to both the isomerization and dehydration processes. And it is so important to put the appropriate quantity of water which restrain the humins formation and promote the efficient conversion of hemicellulose.

The production of furfural was described using FeCl₃ as Lewis acid catalyst [60,61]. Starting from D-xylose (0.4 g) in a biphasic mixture containing an aqueous solution of FeCl₃ (0.06 mol L⁻¹) and MIBK at 180 °C for 15 min, the furfural was obtained in 76% yield after 15 min. Using similar conditions, the use of Tung shell at 180 °C for 60 min furnished furfural in 100% yield.

Table 3

D-Xylose conversion and furfural selectivity obtained with different [Rmim] HSO₄ ionic liquids.

Entry	Catalyst	Co-catalyst	Conversion (%)	Selectivity (%)
1	[C ₄ mim]HSO ₄	H ₂ SO ₄	86.7	96.9
2	[C ₆ mim]HSO ₄	H ₂ SO ₄	81.4	94.9
3	[C ₈ mim]HSO ₄	H ₂ SO ₄	78.8	91.7
4	[C ₁₀ mim]HSO ₄	H ₂ SO ₄	74.5	90.3
5	[C ₄ mim]HSO ₄	H ₂ SO ₄	76.1	92.5
6	[C ₄ mim]HSO ₄	-	75.8	93.7
7	-	H ₂ SO ₄	75.9	93.6

Commercial NaCl, KHSO₄, Al₂(SO₄)₃ and FeCl₃, at temperatures above 140 °C, allowed to produce efficiently furfural. It was notable that NaCl alone played the key role for the extraction of furfural and the role of catalyst. As mentioned before, an aqueous biphasic mixture was preferred for the furfural production and the azeotropic mixture of water and toluene was an efficient candidate.

3.4. Dehydration in ionic liquids (ILs)

ILs are organic salts composed solely of cations and anions. Their unique properties like low volatility, chemical and thermal stability, good dissolving capacity, flame retardancy and others permitted to consider ILs as green solvent [62–64]. Nevertheless, ILs have some drawbacks as described by our group. In particular, fire-induced toxicity and ecological disturbance for organism have been reported [65–69]. 1-(4-Sulfonic acid) butyl-3-cetyl-2-methyl imidazolium hydrogen sulfate was used as an ionic liquid to catalyze the dehydration of D-xylose into furfural [70]. This IL has the advantage of heterogeneous and homogeneous catalyst because of its different solubility with temperature variation. High D-xylose conversion (95%) combined to high furfural yield (67%) were obtained at 160 °C for 180 min in water (25 mL) over 0.5 g of IL as catalyst. In the same way, a catalytic system, consisting of strong protic Brønsted acid (H₂SO₄) and weaker acidic hydrogen sulfate imidazolium ILs, was reported to produce furan aldehydes from carbohydrates feedstocks [71]. The structural parameters of the IL as well as the addition or not of Brønsted acid (co-catalyst) affected the conversion of carbohydrates. Using the optimized conditions: D-xylose (1.3 g), ILs (0.6 g) as a catalyst and H₂SO₄ (20 wt%) as a cocatalyst in water (50 mL) at 140 °C for 4 h the conversion and selectivity in furfural were higher than 74% and 90%, respectively. Surprisingly, the selectivity towards furfural (92–97%) was not affected by the nature of the catalyst and co-catalyst (Table 3).

Zhao et al. worked on the dehydration of D-xylose to produce furfural in H₂O-butanone system and demonstrated the role of [Bmim] Cl/FeCl₃ of ionic liquid catalyst [72]. Several metal chlorides and imidazolium ionic liquids to catalyze this conversion were compared and more the Lewis acidity of the metal ions is stronger more the D-xylose conversion and furfural yield are improved. For example, the best D-xylose conversion of 99% with 75% of furfural yield were obtained at 140 °C for 90 min using 3 mg/mL D-xylose, 0.1 mol L⁻¹ of [Bmim] Cl/FeCl₃ as catalyst in H₂O-butanone (1:4, v/v) system. Furthermore, the efficiency of [Bmim]Cl/FeCl₃ on D-xylose, arabinose, and xylan conversion to produce furfural in the same previous framework was studied. In their hands, best furfural yields were 60%, 46% and 36%, respectively, from D-xylose, xylans, and corn stalk [73]. Depending on the starting material, AlCl₃ gave better result than that of FeCl₃ [74]. Indeed, arabinose afforded furfural in 46% yield in the presence of [Bmim]Cl/FeCl₃ and 60% yield in the presence of [Bmim]Cl/AlCl₃.

SnCl₄ was used as a catalyst in a reaction medium of ionic liquid 1-ethyl-3-methylimidazolium bromide (EmimBr) [75]. Starting from D-xylose (200 mg) in the presence of SnCl₄ (10 mol%) and EmimBr (1 g) at 130 °C for 1 h, furfural was obtained in 71% yield with a large amount of D-xylose loading 20 wt%. In addition, the effect of combination of two catalysts 5 mol% SnCl₄ and 5 mol% MgCl₂ was examined, and these two

Table 4

Selected heterogeneous catalytic dehydration processes of D-xylose and biobased derivatives for production of furfural in batch reactor.

Entry	Substrate	Catalyst	Solvent and additives	Reaction conditions	Conversion (%)	Yield (%)	Ref.
	D-xylose	C-Co-S (50 mg)	H ₂ O-GVL (3:17, v/v)	170 °C, 30 min	95	75.12	[78]
	D-xylose	Starbon®450-SO ₃ H (21 mg)	H ₂ O-CPME (1:3, v/v)	175 °C, 18 h	100	70	[79]
	D-xylose	ISC-CCA (0.4 g)	GVL	170 °C, 30 min	nd	74.4	[81]
	D-xylose	SO ₄ ²⁻ /CX-DMSn (0.32 g)		180 °C, 5 h	95	66	[82]
	D-xylose	SC-GCa-800 (50 mg)	1,4-dioxane	140 °C, 40 min	99.7	76.9	[83]
	D-xylose	SG-SO ₃ H (28 mg)	GVL	150 °C, 40 min	nd	96	[84]
	D-xylose	C-SO ₃ H (200 mg)	H ₂ O-MIBK (3:7, v/v)	175 °C, 3 h, 20 b	99	66	[86]
	D-xylose	OMC-SO ₃ H (60 mg)	H ₂ O-GVL (15:85, v/v)	200 °C, 45 min, 30 b	100	76.7	[87]
	D-xylose	DFCSA (0.05 g)	H ₂ O	170 °C, 2 h, MW	94	69.7	[89]
	D-xylose	KIT-5-TFA-15 wt% (80 mg)	H ₂ O-toluene (1:2, v/v)	120 °C, 6 h	nd	75	[90]
	D-xylose	DICAT-3C	H ₂ O-toluene (1:5, v/v)	120 °C, 120 min	100	88	[91]
	D-xylose	DMSI-SA (72.5 mg)	ethanol	170 °C, 24 h	100	99	[92]
	D-xylose	H-β zeolite (6.24 g L ⁻¹)	H ₂ O-toluene (1:1, v/v)	160 °C, 4 h	nd	57	[96]
	D-xylose	PAL-SO ₃ H (0.05 g)	H ₂ O-GVL (5:95, v/v)	180 °C, 60 min	nd	87	[97]
	D-xylose	SAPO-34/5A (0.048 g)	H ₂ O	190 °C, 3 h	95	45	[98]
	D-Fructose	HY-3 zeolite (0.1 g)	H ₂ O-GBL (1:12, v/v)	150 °C, 50 min, 20 b	99	37.8	[99]
	D-xylose	H-β-SO ₃ H (0.11 g)	ISO	150 °C, 7 h	100	76.8	[100]
	D-xylose	HZ-Na-50 (0.25 g)	H ₂ O-GBL (1:8, wt/wt)	150 °C, 60 min, 20 b	99.1	63	[101]
	D-xylose	WO ₃ -ZrO ₂ (200 mg)	Butan-1-ol	170 °C, 2 h	92	51	[102]
	D-xylose	Nb ₂ O ₅ (0.04 g)	H ₂ O-THF (4:1, v/v)	130 °C, 120 min	95.4	46.8	[103]
	D-xylose	Nb ₂ O ₅ (0.8 g)	H ₂ O	160 °C, 6 h, 40 b	76.8	46.1	[104]
	D-xylose	Nb ₂ O ₅ /Al ₂ O ₃ (0.8 g)	H ₂ O	160 °C, 6 h, 40 b	87.4	30.7	[104]
	D-xylose	Zn doped CuO NP	H ₂ O	150 °C, 12 h	nd	86	[105]
	D-xylose	NbA:NbP (1 g, 1:1, w/w)	H ₂ O	160 °C, 30 min	44	33	[106]
	D-xylose	MIL-101 (Cr) (0.1 g)	H ₂ O-toluene (3:7, v/v).	150 °C, 180 in	93.9	86.7	[108]
	D-xylose	MC-SnOx-450 (0.1 g)	2-MTHF	180 °C, 20 min	97	53.9	[109]
	D-xylose	(0.25)Cr ³⁺ /P-SBA-15 (30 wt%)	H ₂ O-THF(1:3, v/v)	170 °C, 90 min	98	91	[112]
	D-xylose	Sn _{0.625} Co _{0.5} PW (0.08 g)	H ₂ O-DMSO (1:1, v/v)	200 °C, 3 h	99	63.6	[113]
	D-xylose	SO ₄ ²⁻ /SnTRP (10 wt%)	H ₂ O-toluene-DMSO (2:8:1, v/v/v)	170 °C, 3 h	97	82.91	[114]
	Corn cob	C-Co-S (50 mg)	H ₂ O-GVL (3:17, v/v)	170 °C, 120 min	96.16	73.62	[78]
	Corn straw	C-Co-S (50 mg)	H ₂ O-GVL (3:17, v/v)	170 °C 60 min	92.07	70.32	[78]
	Eucalyptus sawdust	C-Co-S (50 mg)	H ₂ O-GVL (3:17, v/v)	170 °C, 120 min	94.77	72.14	[78]
	Corn stover	ISC-CCA (0.05 g)	GVL	190 °C, 120 min	nd	70.2	[81]
	Corn cover	SO ₄ ²⁻ /CX-DMSn (0.32 g)	H ₂ O	180 °C, 5 h	98	66	[82]
	Corn stalk	SG-SO ₃ H (35 mg)	GVL	190 °C, 50 min	nd	48	[84]
	Hemicellulose	C600-S (0.03 g)	H ₂ O	200 °C, 2.5 h	nd	50	[88]
	Corn stover	MSPFR (0.2 g)	GVL	190 °C, 100 min	nd	43.4	[93]
	Corn stover	Cl _{0.3} -S-R (0.2 g)	H ₂ O-1,4-dioxane (1:9, v/v)	190 °C, 80 min	nd	38.1	[94]
	Camellia oleifera shells	PDVB-SO ₃ H (10 mg)	H ₂ O-GBL (0.5:2, v/v)	170 °C, 30 min	nd	61.3	[95]
	Bagasse pre-hydrolyzate	FePO ₄ (50 mg)	H ₂ O-2-MTHF (1:1, v/v), NaCl (160 mg)	190 °C, 120 min	96.4	88.7	[107]
	Corn stover	SO ₄ ²⁻ /SnO ₂ -Al ₂ O ₃ -CFA (2 wt%)	H ₂ O-toluene (1:1 v/v), NH ₄ Cl (100 mM)	180 °C, 30 min	93.5	84.7	[112]
	Corn stover	SO ₄ ²⁻ /SnTRP (10 wt%)	H ₂ O-toluene-DMSO (2:8:1, v/v/v)	190 °C, 3 h	nd	77.82	[114]

catalysts performed a high furfural yield of 69% which was like the use of just 10 mol% of SnCl₄.

Xiong's group synthesized functionalized alkyl imidazolium hexafluorophosphate ILs to catalyze the conversion of D-xylose (0.3 g (0.002 mol)) into furfural using microwave activation as alternative technology [76]. As expected, the catalytic activity of diimidazole hexafluorophosphate was higher than that of the corresponding monoimidazole, and the length of carbon atom chain between imidazole rings affected the yield of the reaction. At the end, 3,3'-methylenebis (1methyl-1H-imidazol-3-ium) hexafluorophosphate was the most efficient catalyst that yielded 49.76% of furfural at 205 °C within 8 min in water (5 mL). The catalyst ensured its same catalytic activity for five successive runs.

Valorization of sugarcane bagasse C5-fraction by furfural production mediated by renewable glycine-based ionic liquid [77]. An aqueous mixture of glycine (1.5 g) as amino-acid and formaldehyde (37%) was mixed at room temperature for 24 h to form the zwitterionic intermediate. Then, H₂SO₄ (10 mmol) was added and heated at 95 °C for 30 min to form the bifunctional glycine-based ionic liquid [GlyIm][HSO₄]. Starting from D-xylose (0.1 mmol) and the selected ionic liquid (10 eq) in a biphasic mixture of H₂O-MTHF (1:4, v/v) at 180 °C for 10 min, furfural was produced in 87% yield.

The strategic use of ILs as solvent and/or as catalyst was developed. Most often the acid feature was included as a moiety of the ionic liquid. Whether the nature of the designed IL, the requested temperature was above 95 °C which was lower than conventional temperature for the

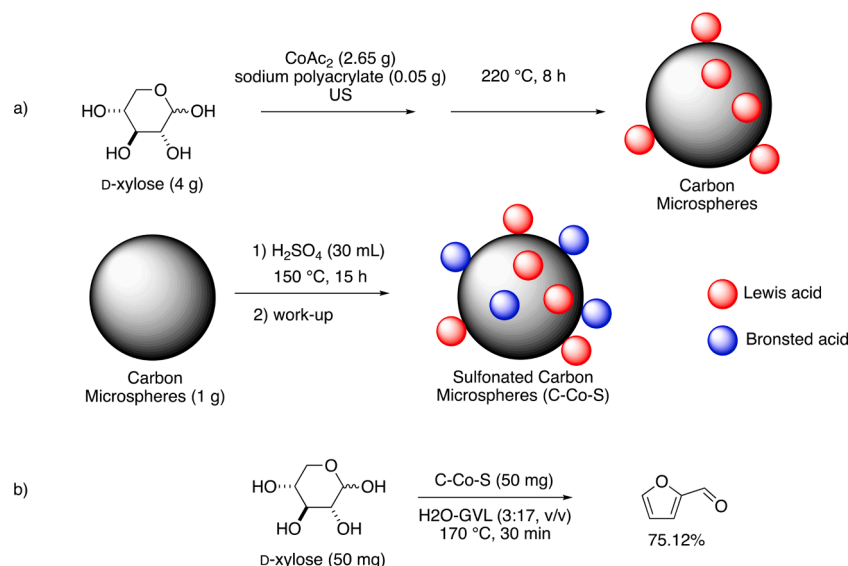
dehydration of biobased resources. It was notable that microwave-assisted dehydration in the presence of ionic liquid was an efficient process as ionic liquid was a good candidate for this alternative technology.

4. Heterogeneous catalysis for furfural production – conventional batch process

Dehydration of D-xylose and biobased derivatives was studied using various heterogeneous catalysts such as functionalized carbon supports, silica derivatives, of ions-exchange resins, clays, zeolite, oxides, and phosphates. The main results related to the dehydration of D-xylose and other carbohydrates-containing matrices, using heterogeneous catalysis, are summarized in Table 4.

4.1. Dehydration in presence of carbon acids

Functionalized carbon supports such as carbohydrate materials, graphene, lignin, and furfural precursor as well can behave as solid acid catalysts and they are frequently used in acid catalysis in many applications due to their high chemical activity, high thermal stability and low production costs. Sulfonated carbon microspheres (C-Co-S) displaying Brønsted and Lewis acid sites were used by Si's group as catalysts to produce furfural from D-xylose and the hemicellulose [78]. It was notable that the carbon material was obtained starting from D-xylose. In this way, an aqueous solution of D-xylose (4.0 g), cobalt



Scheme 4. (a) Preparation of C-Co-S starting from D-xylose and (b) dehydration of D-xylose for the furfural synthesis.

acetate (2.65 g) and sodium polyacrylate (0.05 g) was first ultrasonicated and then heated at 220 °C for 8 h to provide the carbon material. This one (1 g) was then treated with H₂SO₄ (30 mL) and then heated at 150 °C for 15 h. After work-up, C-Co-S was obtained and fully characterized. The sulfonation improved the density of Brønsted acid so the dehydration efficiency of D-xylose. In a biphasic system of H₂O-GVL (3:17, v/v) solvent, the furfural yield could reach the 75.12% using 50 mg C-Co-S as a catalyst at 170 °C within 30 min from D-xylose (50 mg) (Scheme 4). In addition, the group tested this catalyst using real biomass (50 mg) which are: corncob (120 min), corn straw (60 min) and Eucalyptus sawdust (120 min) in GVL (3.4 mL) and water (0.6 mL) at 170 °C and C-Co-S (50 mg) in all cases the furfural yield was up to 70%.

Carbohydrates were used as starting material to produce carbon-based acid catalysts. After conventional treatment of starch from potato, calcinated Starbon®450 material was obtained and its treatment with H₂SO₄ furnished after 4 h at 80 °C the sulfonated Starbon®450-SO₃H as catalyst [79,80]. At 175 °C for 18 h in a biphasic system of H₂O-CPME (1:3, v/v), the highest selectivity in furfural was 70% with complete D-xylose conversion at 175 °C within 18 h. To date, CPME is considered as an eco-friendly solvent. The benefit of reusing the catalyst was proved for three cycles with remaining the same selectivity towards furfural at complete D-xylose conversion. Another source of carbohydrate was used by Pei's group [81]. To this end, different carbon precursors: sucrose-derived disordered mesoporous carbon (C-CCA); ordered mesoporous carbon CMK-3; glucose-based hydrothermal carbon and activated carbon were studied. The two first were successfully sulfonated (ISC-CCA and S-CMK-3) while the last two were not. To evaluate the catalytic activity, the dehydration of D-xylose and corn stover to furfural was studied. However, -SO₃H density was higher in the ISC-CCA (8.3 vs 4.1 (mmol NH₃ g⁻¹)), which gave higher performance in the production of furfural. The best furfural yields using ISC-CCA were 74% at 170 °C for 30 min in the presence of ISC-CCA (0.4 g) in GVL (18 mL) starting from D-xylose (0.40 g) while starting from corn stover (0.1 g), furfural yield (70%) was obtained at 190 °C for 120 min in the presence of ISC-CCA (0.05 g) in GVL (4.5 mL). It was noteworthy that only organic solvent was used, in these optimized conditions, and it seems that an aqueous solution was not necessary.

An interesting work was reported the efficient and green synthesis of a core-shell sulfonated tin-loaded diatomite (SO₄²⁻/CX-DMSn) as catalyst [82]. Diatomite (DM), as a natural porous silica material, was mixed with a solution of SnCl₄ and aqueous HCl (2 M) and after classical work-up, the solid was maintained at 500 °C for 3 h. Then, DM-SnO₂ was immersed in an aqueous solution of H₂SO₄ (1 M) for 6 h and different

thermal treatments were used to produce DMSn. After treatment of this one in the presence of D-xylose in water, a solid CX-DMSn intermediate was dried and calcined at 800 °C for 3 h, this step permitted to cover diatomite derivative with carbon material. Acidification of CX-DMSn with H₂SO₄ for 6 h afforded the target SO₄²⁻/CX-DMSn catalyst having Lewis and Brønsted acid sites. Obviously, the sulfonation took place on the carbon layer in the surface of the DMSn. With this catalyst in hands, dehydration of D-xylose in water at 180 °C for 5 h furnished furfural in 66% yield with a selectivity of 70%. Under same conditions, the corn cob conversion resulted in 66% of furfural yield and 67% of selectivity. In this work, the treatment of D-xylose and biomass afforded, more or less, the same productivity.

Modified carbohydrate was investigated by Yang et al. to obtain a novel carbon-based solid acid catalyst (SC-GCa-800) to promote the production of furfural [83]. SC-GCa was prepared in two steps. The first one was the carbonization of calcium gluconate at high temperature (600, 700 and 800 °C) to produce porous carbon supports. After convention work-up, SC-GCa was sulfonated in the presence of sulfanilic acid, sodium nitrite in water at room temperature for 24 h. This process was interesting as the sulfanilic acid and sodium nitrite furnished the corresponding 4-diazoniobenzene sulfonate that can be grafted to the carbon support in a one-pot two steps process. After full characterization of the catalysts, the authors reported that surface area of the catalyst support increased from 612.95 to 813.07 m² g⁻¹ for 600 °C and 800 °C and the pore volume increased from 0.56 cm³ g⁻¹ to 1.07 cm³ g⁻¹ in the same temperature range. After sulfonation, the BET surface areas of SC-GCa-600, SC-GCa-700 and SC-GCa-800 are 516.49, 627.53 and 605.59 m² g⁻¹. Similarly, the pore volume obviously decreased with increasing the calcination temperature. Based on the sulfur contents, the acid site concentration was identified and found to be 0.96, 1.18 and 1.33 mmol g⁻¹ for SC-GCa-600, SC-GCa-700 and SC-GCa-800, respectively. Since the increase in the surface area and pore volume of the catalyst implied a higher acid density, SC-GCa-800 as catalyst was studied. The best results showed 99.7% of D-xylose (100 mg) conversion in presence of 50 mg of SC-GCa-800 in 5 ml of 1,4-dioxane at 140 °C within 40 min. the furfural yield obtained was 76.9% with a selectivity of 77.1%. In addition, the catalyst proved its advantage of recyclability for five cycles without remarkable reduction of its catalytic activity. It is notable that the dehydration process was done in 1,4-dioxane as organic solvent and the use of water to have a biphasic system was not necessary.

The sulfonated graphene (SG) as a carbon solid catalyst was reported to promote the production of furfural from corn stalk and D-xylose [84]. Classically, the authors prepared the graphite oxide (GO) following the

Hummer's method [85] and the obtained GO was sulfonated to have the SG in which the density of SO_3H is 2.05 mmol g^{-1} . The best results obtained from D-xylose conversion were 96% of furfural yield starting from D-xylose (60 mg) with the catalyst (28 mg) in GVL (10 mL) at 150°C within 40 min. It was notable that no biphasic system was developed and only biobased GVL as solvent was used. Decreasing the temperature from 150°C to 140°C afforded furfural in 71.9% yield with the use of D-xylose-SG mass ratio of 10.7. In GVL (10 mL), corn stalk (75 mg) was converted to furfural in 48% of yield at 190°C for 50 min. Interestingly, 10 min were enough to get 40% of furfural yield when using a 2.14 mass ratio (corn/SG).

Another source of carbon material is lignin derivatives. In this context, a carbonaceous acid catalyst from the bio-ethanol plant derived crude lignin was developed [86]. An acid pretreatment liquid derived from bio-ethanol plant permitted to obtain carbon material. After treatment of this material with H_2SO_4 (1 N), the carbon catalyst was mixed with D-xylose in a mixture of H_2O -MIBK (3:7, v/v) at 175°C for 3 h at 20 b to produce furfural in 66% yield. The recyclability was limited to 3 cycles to maintain an acceptable yield. Another laboratory produced sulfonated lignin-derived ordered mesoporous carbon ($\text{OMC-SO}_3\text{H}$) solid acid to promote the conversion of hemicellulose-derived D-xylose to furfural [87]. For the catalyst synthesis, the authors followed two steps: (i) preparation of solution containing organosolv lignin and phloroglucinol with a mass ratio of 4:1 dissolved in acetone (40 mL) and (ii) a solution containing triblock copolymer Pluronic F127 dissolved in acetone (25 mL). The mixture of the two solutions gave a uniform solution. After few treatments, an obtained film will be ready to be carbonized at 600°C . The ordered mesoporous carbon obtained can be then sulfonated by sulfuric acid at 130°C using conventional methodology. After basic work-up, the sulfonated ordered mesoporous carbon was obtained and fully characterized. For the best furfural yield of 76.7% and D-xylose conversion of 100%, the conditions were found to be 200°C for 45 min in a biphasic system of H_2O -GVL (15:85, v/v).

An interesting process for the dehydration of D-xylose to produce furfural was reported by Lin et al. [88]. The carbon source was an industrial byproduct from furfural production. Without further explanation from the authors, humins can be considered but without certainty. The dried furfural residue was pyrolyzed under N_2 in the temperature range of $400\text{--}700^\circ\text{C}$ with a rate of $10^\circ\text{C min}^{-1}$ for 5 h. Then the sulfonation of the non-activate carbonized material using H_2SO_4 at 150°C for 5 h was done. After conventional work-up the corresponding sulfonated non-activated carbon-based catalyst was obtained and fully characterized. Using similar strategies, KOH-activated carbon-based catalyst and ZnCl_2 -activated carbon-based catalyst were produced with a good efficiency. From hemicellulose (0.2 g), the non-activated carbon-based catalyst gave in aqueous solution a maximum yield of furfural 50% at 200°C for 2.5 h. Starting from D-xylose the same conditions permitted to afford furfural in 55% yield after 1.5 h. It was noteworthy that the activation improved the surface area of the solid catalyst but decrease the SO_3H density negatively affecting the conversion of D-xylose to furfural.

One original work was reported using Luan. A dual-functional carbon-based solid acid catalyst consisting of Brønsted/Lewis acid sites to promote the conversion of saccharides to produce furfural was studied by Xiong et al. [89]. Dried Luan powder (8 g) was added to a solution of HNO_3 , H_3PO_4 and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and then heated at 80°C for 24 h. After frying the mixed solution, the solid was ground and pyrolyzed at 600°C for 2 h in an N_2 atmosphere. Then the carbon material was sulfonated using H_2SO_4 for 24 h at 100°C . The catalyst showed a good efficiency with yielding 69.7% of furfural from D-xylose (94% of conversion) at 170°C for 2 h under microwave activation. The process was efficient as a good recyclability for ten runs without significant loss of catalytic activity was observed.

Even if Brønsted/Lewis acid sites were important for the dehydration of D-xylose and derivatives, the acidity of the carbon support was generally obtained by sulfonation to have Brønsted acid groups. A two-

phase mixture (H_2O -GVL, H_2O -CPME, H_2O -MIBK) or a monophasic solution (water, 1,4-dioxane, GVL) were reported for the heterogeneous catalytic dehydration. The use of liquid monophasic solution means that the problem of humins formation as side-compounds was less important. The minimum of temperature for the dehydration was 130°C to have an efficient productivity.

4.2. Dehydration in presence of silica derivatives

In parallel with the studies of carbon acid catalyst, the studies of silica acid catalyst were realized. Baruah's group highlighted the use of KIT-5 mesoporous material functionalized with trifluoromethanesulfonic acid to dehydrate D-xylose [90]. Unfortunately, the preparation of the catalyst was not reported and only its characterization was described. Among different catalysts such as KIT-5, KIT-5-TFA-5 wt%, KIT-5-TFA-10 wt%, KIT-5-TFA-15 wt% and KIT-5-TFA-20 wt%, KIT-5-TFA-15 wt% was the best one to promote the production of furfural from D-xylose. D-Xylose in the presence KIT-5-TFA-15 wt% (80 mg) in a biphasic solution of H_2O -toluene (1:2, v/v) at 120°C for 6 h furnished the target furfural in 75% yield.

Another source of silica material was studied using the same biphasic solvents: H_2O -toluene (1:5, v/v). Starting from commercial poly hydroxyethyl methacrylate seabed resin, sulfonic acid groups were anchored to furnish the corresponding DICAT-3 [91]. Hydroxy seabed resin (1 mg) in ethylene dichloride (10 mL) were mixed and chlorosulfonic acid (CSA) was added over 15–20 min at room temperature under nitrogen flow. After 1 h at room temperature and 30 min at reflux traditional work-up was developed to furnish DICAT-3 with well-defined surface morphology. The acidity of each DICAT-3 was modified by varying the molar concentration of CSA. Thus, the acidity was increased from DICAT-3A to DICAT-3C where the further increase of acidity to DICAT-3D did not add significant change on the catalyst acidity. The highest yield of furfural (88%) was performed with the use of DICAT-3C with a complete conversion of D-xylose at 120°C within 120 min with a feed stock of 12.5% w/v D-xylose concentration. The advantage of reusing the catalyst was proved for five consecutive runs. In addition, it exhibits a high thermal resistance up to 360°C .

Furfural was produced using sulfonated dendritic mesoporous silica nanospheres as a catalyst [92]. The functionalized support was obtained in two steps: (i) formation of dendritic mesoporous silica nanospheres and (ii) sulfonation of the dendritic mesoporous silica nanospheres. An aqueous mixture of cetyltrimethylammonium chloride and triethanolamine was stirred at 60°C for 1 h and then a solution of tetraethylorthosilicate in cyclohexane was then added dropwise. After 20 h at 60°C and conventional work-up, the prepared nanospheres was added to an aqueous solution sodium chloride under vigorous stirring at room temperature for 30 min. Then, 3-mercaptopropyl trimethoxysilane was added and the resulting mixture was heated at 100°C for 24 h. After work-up, the corresponding thiol groups were then converted into the target sulfonic materials by a mild oxidation protocol using hydrogen peroxide as the oxidant at room temperature for 24 h. By reacting D-xylose (1 mmol) in ethanol (3 mL, D-xylose-ethanol, 1:51, mol/mol) with 72.5 mg (5 mol%) of the sulfonic acid-functionalized dendritic mesoporous silica nanospheres (DMSi-SA) as catalyst in a sealed vial for 24 h at 170°C , furfural was obtained in 99% yield.

As expected, the use of silica material for the dehydration of D-xylose and derivatives was equivalent to the use of carbon-based materials.

4.3. Dehydration in presence of ions-exchange resins

Ions-exchange resins as heterogeneous catalyst were largely described in the literature. The main drawback of the resins was the low stability in high temperature meaning a low recyclability property. p-Hydroxybenzenesulfonic acid-formaldehyde resin acid catalyst (MSPFR) was studied to promote the production of furfural from raw corn stover [93]. An aqueous solution of chitosan (0.45 g) and acetic acid (0.6 mL)

was mixed and then p-hydroxybenzenesulfonic acid hydrate (3.1 g) and formaldehyde solution (3 mL) were added successively, and the mixture was heated at 120 °C for 10 h. After work-up the corresponding resin was obtained and characterized. This morphology increased the number of acidic sites to be in contact with the reactants. The characterization of the catalyst revealed $24.8 \text{ m}^2 \text{ g}^{-1}$ and $0.08 \text{ cm}^3 \text{ g}^{-1}$ respectively for the BET specific surface areas and total pore volumes and proved the presence of $-\text{SO}_3\text{H}$ groups. With a mixture of corn stover (0.4 g), catalyst (0.2 g) and GVL (16.5 mL) at 190 °C for 100 min, furfural was obtained 43.4% yield with 30.7% of HMF. This yield was increased to 50.3% with the increase of MSPFR/corn stover mass ratio to 1. It is noteworthy that his catalyst showed a satisfied thermal stability for furfural production up to 200 °C. New sulfonated resin-based solid acid catalyst was obtained using a similar reaction described by Zhang et al. [93] by polymerizing o-chlorophenol and p-hydroxybenzenesulfonic with formaldehyde through hydrothermal method [94]. Using $\text{Cl}_{0.3}\text{-S-R}$ catalyst, furfural was obtained in 38.1% yield starting from corn stover feed stock under 190 °C for 80 min in a biphasic system of H_2O -1,4-dioxane (1:9, v/v).

Another type of modified resin was reported by Zhang et al. [95]. Divinylbenzene (2 g) and AIBN (0.05 g) in a mixture of THF (20 mL) and water (2 mL) were stirred at room temperature for 4 h before being heated at 100 °C for 48 h. Polydivinylbenzene was obtained and sulfonated with CSA in CH_2Cl_2 at 100 °C for 3 h. The authors mentioned that two additions of CSA were requested. Starting from camellia oleifera shells (20 mg) in the presence of PDVB- SO_3H as catalyst (10 mg) in a mixture of H_2O -GBL (0.5:2, v/v) at 170 °C for 30 min, furfural was obtained 61.3% yield. The authors reported that camellia oleifera shell exhibited a high potential as feedstock to produce furfural in high yields.

The use of ions-exchange resins for the dehydration of biomass derivatives adopted similar strategy using sulfonic group as acid sites. Whatever the material used, the sulfonation of the material was conventional.

4.4. Dehydration in presence of clays

To our knowledge, the use of clays to produce furfural has not been too much investigated during the last years. Several delaminated and fluorinated hectorites to produce furfural from commercial D-xylose and from an acid biomass extract of almond shells were reported by Sánchez et al. [96]. The catalytic performances of delaminated hectorites (Na^+ and H^+) and fluorohectorites (Li^+ and H^+) were compared with one H-beta zeolite reference catalyst. In a short reaction time (1 h), H-FH was the best catalyst for both commercial D-xylose (36 g L^{-1}) and from almond shell and yielded, respectively, 20% and 60% of furfural, at 160 °C with 20% of catalyst in biphasic system of H_2O -toluene (1:1, v/v). The low furfural yield of 20% was explained by the higher Lewis acidity that contributes to the formation of condensation products. For longer reaction times (up to 4 h), furfural yielded 90% using either the reference catalyst or the H-DH system, and yields ranged between 52 and 60% when using the other catalysts. From D-xylose, within 4 h, the efficiency of catalysts was ordered: $\text{H-}\beta > \text{H-FH} > \text{blank} > \text{Li-FH} \approx \text{H-DH} > \text{Na-DH}$ with a maximum furfural yield of 57%.

The preparation of sulfonated palygorskite solid acid catalyst [97] was designed and produced via mechanochemical technology to generate furfural. To do that, the authors grafted the thiol groups ($-\text{SH}$) onto the palygorskite with 3-mercaptopropyltrimethoxysilane under mild conditions. The grafted groups were then oxidized to SO_3H groups by H_2O_2 . The actual concentration of SO_3H in the resulted catalyst (PAL- SO_3H) was found to be 1.78 mmol g^{-1} . With this catalyst in hands, the dehydration of D-xylose with different concentrations (20 to 120 g L^{-1}) was done with a quantitative conversion. The optimized conditions (D-xylose 20 g L^{-1} , 0.05 g of catalyst, H_2O -GVL 5:95, v/v at 180 °C, for 60 min) afforded furfural in 87% yield. When decreasing the D-xylose concentration to 10 g L^{-1} the furfural yield decreased to 73% and this was explained by the excess of active catalytic sites that promote the

degradation of the formed furfural and thus decreasing its yield. In addition, the increase of D-xylose concentration to 40, 80 and 120 g L^{-1} , the furfural yield decreased to 83, 75 and 70%, respectively. This fact was related to the high concentration of D-xylose that increase the probability of the collision between D-xylose, formed furfural and other intermediates.

The use of clays such as delaminated and fluorinated hectorites and sulfonated palygorskite solid acid was studied to produce furfural. As expected, the sulfonated clays were efficient in a biphasic system at temperature higher up to 180 °C for 60 min.

4.5. Dehydration in presence of zeolites

Microporous zeolites such as H-beta zeolite, SAPO-34 zeolite, HZSM-5 zeolites and HY zeolite and derivatives with large internal surfaces of up to $2000 \text{ m}^2/\text{g}$ and pore or cage diameters in the range of 0.5 to 1.2 nm were studied as catalyst for the dehydration of D-xylose and derivatives. Romo et al. worked on the preparation of SAPO-34 zeolite crystals grown on zeolite 5A beads to be used to produce furfural and HMF respectively from D-xylose and D-glucose [98]. To prepare a gel of SAPO-34, an aqueous solution of aluminum isopropoxide was stirred for 1 h to form a homogeneous solution. Then, successive addition of phosphoric acid, Ludox AS-40 colloidal, and DPA were added, and the final gel was stirred at 50 °C for 4 days. SAPO-34 gel and pure zeolite 5A beads were carried out at 230 °C for 6 h. After convention work-up, SAPO-34/5A was obtained with a surface area of $454 \text{ m}^2 \text{ g}^{-1}$ and micropore area of $378 \text{ m}^2 \text{ g}^{-1}$. Treatment of D-xylose (2 wt%) in the presence of catalyst (48 mg) in water (4 mL) at 190 °C for 3 h furnished the furfural in 45% yield.

It is notable that furfural can be obtained from cellulose and hexoses, the most abundant resource in nature. This way remained a challenge and Wang et al. reported a nice works in that sense using commercial HZ zeolite [99]. When D-fructose (0.75 g) was treated with HY-3 zeolite (0.1 g) in a mixture of H_2O -GBL (1:12, v/v) at 150 °C for 50 min in 20 bar of nitrogen afforded furfural in 37.8% yield and HMF in almost 20% yield. The HY zeolite with apertures of 7.4 Å was found to promote the formation of acyclic D-fructose from cyclic D-fructose (8.6 Å) in the synergy with GBL. The Brønsted acid sites in the channels of HY favored the selective cleavage of the C-C bond in acyclic D-fructose to D-xylose and promoted the following dehydration of D-xylose to furfural, simultaneously.

The increase of acid amount of zeolite was achieved by grafting of sulfonic acid group ($\text{SO}_3\text{-H}$) onto the zeolite [100]. As expected, the increase of sulfonating agent above 3% (9.8% H- β - $\text{SO}_3\text{-H}$) contributed to the decrease in surface area and pore volume. The conversion of D-xylose (0.47 g of D-xylose (40 g L^{-1})) in the presence of H- β - SO_3H (25 wt%) at 150 °C for 7 h furnished furfural and furfuryl alcohol. The catalyst was recovered and treated with H_2O_2 , the furanic compounds yield decreased by 25% after three runs of using the catalyst.

Another strategy was developed using HZSM-5 zeolites [101]. Among different catalysts, HZ-Na-50 was prepared typically to gel molar compositions of SiO_2 (100), Al_2O_3 (10), NaCl (25), tetrapropylammonium hydroxide (830), water and then the mixture was stirred at 80 °C for 24 h and crystallized at 170 °C for 72 h, successively. After calcination $\text{NH}_4\text{Z-Na-50}$ at 550 °C for 6 h in air, HZ-Na-50 exhibited an irregular spherical structure with relatively same micropore volumes and surface areas for both. HZ-Na-50 (surface area $590.3 \text{ m}^2 \text{ g}^{-1}$) contains Brønsted acids sites (middle strong $111 \text{ }\mu\text{mol/g}$ and strong $179 \text{ }\mu\text{mol/g}$) that favor the production of furfural from D-xylose. The weak acid site ($48 \text{ }\mu\text{mol/g}$) could favor the production of soluble oligomers. With HZ-Na-50 (0.25 g) in a biphasic system H_2O -GBL (1:8, wt/wt) at 150 °C for 60 min in 20 bar of nitrogen, D-xylose (0.625 g) furnished furfural in 63% yield with 99.1% of D-xylose conversion.

Zeolite and modified zeolites permitted to produce furfural from D-xylose and biomass derivatives. Depending on the nature of the catalyst, water, or biphasic system the temperature was higher than 150 °C for a

reaction time higher than 50 min. The sizes of the pore and the surface areas were an important parameter in the model reaction.

4.5.1. Dehydration in presence of oxides and derivatives

Pattnaik et al. developed the hydrolysis of *Phragmites karka*, a perennial grass and a highly invasive crop species, to monomeric sugars followed by their dehydration to furfural [102]. A series of oxides catalyst were used to promote the dehydration of the sugar-rich hydrolysate produced from the water hydrolysis of phragmites. The list of catalyst included ZrO_2 , TiO_2 , $\text{Zr}_{0.5}\text{Ti}_{0.5}\text{O}_2$, $\text{WO}_3\text{-ZrO}_2$, $\text{WO}_3\text{-TiO}_2$ and $\text{WO}_3\text{-Zr}_{0.5}\text{Ti}_{0.5}\text{O}_2$. The best conversion was obtained with $\text{WO}_3\text{-ZrO}_2$ as a catalyst. This latter had $56.6 \text{ m}^2 \text{ g}^{-1}$ of BET surface area, 11.6 nm of pore diameter, 1.6 mmol g^{-1} of amount of acid sites and 0.028 mmol m^2 of acid site density. It promoted the reaction under the optimized conditions: hydrolysate:butan-1-ol = 25:25 v/v, 200 mg of catalyst at 170°C for 2 h. This catalysis performed a conversion of 92% and a yield of 51% furfural. The authors mentioned that the activity of $\text{WO}_3\text{-ZrO}_2$ was correlated to the synergetic effect of Lewis and Brønsted acid sites.

Gallo et al. investigated the use of niobium oxide to promote the production of furfural from D-xylose with reasonable selectivity [103]. For the D-xylose conversion, niobium oxide behaves as an actual bifunctional Lewis/Brønsted acid catalyst, being efficient in the isomerization/epimerization and in the dehydration. Hence, no additional Brønsted acid catalyst was required. Furfural selectivities were up to 46.8%, which is comparable to catalytic systems previously reported using mineral acids. Some other works reported on the performance of two catalysts in the dehydration of D-xylose, which are: the amorphous niobium oxide (Nb_2O_5) and niobium oxide supported on $\gamma\text{-Al}_2\text{O}_3$ [104]. For the first one, they calcinated the niobic acid ($\text{Nb}_2\text{O}_5\cdot n\text{H}_2\text{O}$) at 300°C and they labelled it NB. For the second, 12 wt% $\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$, they calcinated the support $\gamma\text{-Al}_2\text{O}_3$ and then it is impregnated with the precursor (ammoniacal niobium oxalate $(\text{NH}_4\text{NbO}(\text{C}_2\text{O}_4)_2\cdot(\text{H}_2\text{O})_n)$, the obtained catalyst was labelled NB-AL. XRD analysis revealed that $\gamma\text{-Al}_2\text{O}_3$ had non crystalline structure, which make it suitable for the synthesis of solid catalysts. The average pore diameters of NB and NB-AL were 44 and 76 Å respectively which is suitable to allow the access of D-xylose (6.8 Å) and furfural (5.7 Å) to the active sites. In addition, the surface areas of $142 \text{ m}^2 \text{ g}^{-1}$ and $108 \text{ m}^2 \text{ g}^{-1}$, respectively for NB and NB-AL provide the good availability of active sites to occur the reaction. The total acidity was $859.3 \mu\text{molNH}_3/\text{g}$ for NB mainly shared in weak and medium strength acid sites. And it was $530.6 \mu\text{molNH}_3 \text{ g}^{-1}$ for $\gamma\text{-Al}_2\text{O}_3$ in which more acid sites were added after its impregnation process to give an increase of 20% of acidity from 530.6 to $617.8 \mu\text{molNH}_3 \text{ g}^{-1}$ for NB-AL solid. The pure NB catalyst owned 13 times more Brønsted acid sites than the NB-AL. this fact contributed to different performances in furfural production from D-xylose. The results of this paper showed that the NB performed better D-xylose dehydration than NB-AL under different reaction conditions evaluated. Applying 4 g of D-xylose (20 g kg^{-1} (200 mL total solution)) in deionized water with 0.8 g of catalyst (catalyst/substrate ratio = 20%) at 160°C and 40 bar NB catalyst showed a superior selectivity towards furfural of 60.1% instead of 35.1% with the NB-AL catalyst.

Mishra et al. worked on using heterogeneous catalyst made of Zn doped CuO nanoparticles (NPs) [105]. A promising catalyst obtained by sonochemical technology dehydrated the D-xylose completely without any side products confirmed by the analysis done by HPLC, ^{13}C NMR and ^1H NMR. They compared the activity of Zn doped CuO NP with different Bulk or NPs of Copper oxide (CuO NPs, CuO bulk) or zinc oxide (ZnO NPs, ZnO bulk). The best yield of furfural was obtained at 150°C within 12 h using Zn doped CuO NP as a catalyst characterized by a large surface area.

Metal oxides and derivatives showed good activity when they were used alone (Nb_2O_5). Association of two metal oxides ($\text{WO}_3\text{-ZrO}_2$) or niobium oxide supported on $\gamma\text{-Al}_2\text{O}_3$ gave good activity as well. Whatever the catalysts used, a temperature up to 150°C was necessary to dehydrate furfural and biomass derivatives. It was noteworthy that

ultrasound technology was developed for the preparation of a designed catalysts showing the importance of alternative technologies in bio-refining approaches.

4.5.2. Dehydration in presence of phosphates

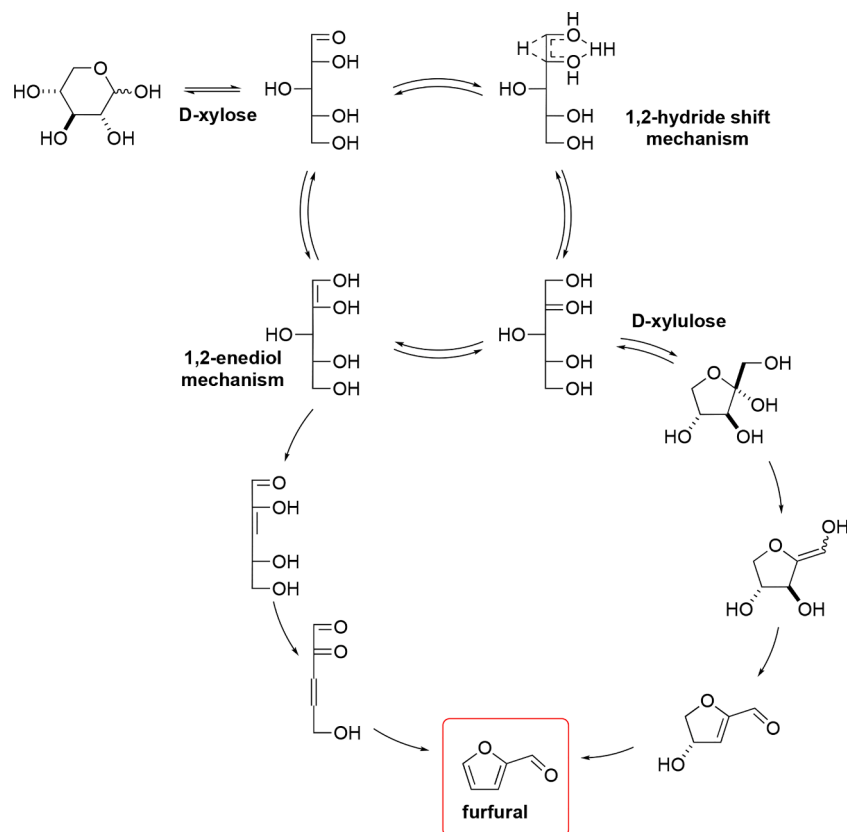
Different phosphates associated with Niobium, iron and tin were used as catalysts for the dehydration of pentose derivatives. Niobic acid (NbA) and niobium phosphate (NbP) as catalysts were associated and thermally activated at 120°C for 5 h to produce furfural from D-xylose [106]. NbA:NbP presented a BET surface area of $164.22 \text{ m}^2 \text{ g}^{-1}$, $0.18 \text{ cm}^3 \text{ g}^{-1}$ of pore volume and 6.36 nm of average pore diameter. The optimized conditions (D-xylose (2 wt%), NbA:NbP (1 g, 1:1, w/w), water, 160°C , 30 min) permitted to provide furfural with a selectivity of 74.71% and a D-xylose conversion of 44.05%. This catalyst remained its activity for five continuous runs. Recyclable ionic phosphates (FePO_4) catalysts were investigated to produce furfural from dilute-oxalic acid pretreated bagasse hydrolysate in heterogeneous system [107]. In a biphasic mixture of H_2O -2-MTHF (1:1, v/v) in the presence of NaCl (160 mg) and FePO_4 (50 mg) at 190°C for 120 min, furfural yield was 88.7%. The important feature of this catalyst is its solubility up to 170°C as the homogeneous catalyst and its capability of precipitation again after cooling system at room temperature.

Metal-organic-framework (MOF) was used to form a new hybrid material. In this way, MIL-101 (Cr) and mesoporous tin phosphate nanoparticles was developed [108]. Among the different catalyst designed, SnP-MOL-101 (Cr) - composite (MP) was obtained by mixing SnP (2 g), TPA (1.66 g) and glacial acid (0.58 mL) in water (50 mL). After 30 min, $\text{Cr}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (4 g) was added and the resulting solution was heated at 220°C for 8 h. showed the best activity. The two sites of Brønsted ($0.052 \text{ mmol pyridine g}^{-1}$ catalyst) and Lewis acids were expressed by the phosphate groups of the composite and the Cr and Sn atoms ($0.359 \text{ mmol pyridine g}^{-1}$ catalyst), respectively. MIL-101 (Cr) was characterized by $2820 \text{ m}^2 \text{ g}^{-1}$ of surface area, 2.6 nm of average pore size and 1.75 cc g^{-1} of pore volume with 0.68 nm and 0.57 nm, respectively, for D-xylose and furfural molecules size. The bifunctional acids make of the material a suitable solid acid catalyst D-xylose dehydration into furfural. It performed in 86.7% of furfural yield and 92.3% of selectivity within 180 min at 150°C starting with 300 mg of D-xylose in a H_2O -toluene system (3:7, v/v). The addition of 35 ppt of NaCl solution could improve the yield and selectivity to 92.4% and 96.6%, respectively. The composite showed a higher stability for ten runs compared to the composite that remained stable for just 4 runs.

Whatever the nature of the phosphate, phosphate used alone or as a new hybrid catalyst associating MOF, furfural was obtained in good yields.

5. Supported catalysis for furfural production – conventional batch process

Various supports were studied to dehydrate biomass starting materials. Recently, micro-mesoporous carbon, industrial biobased ash, metal-organic-framework, mesoporous silica sieve and heteropoly acid. The micro-mesoporous carbon supported tin oxide catalyst (MC-SnOx) was introduced to convert the D-xylose into furfural with the minimum of sodium chloride (NaCl) in acid-free biphasic system [109]. This work was interesting as the catalyst was obtained starting from D-fructose as biobased chemical. A mixture of SnCl_4 (8.7 g), D-fructose (2 g), P-123 (1 g) and F-127 (3 g) were dissolved in water (70 mL) and then stirred at room temperature for 2 h and at 180°C for 24 h, successively. After conventional work-up and annealed at 450°C , MC-SnOx-450 was obtained and fully characterized with the highest tin concentration on the surface of 5.31%. The increase of annealing temperature affected the stability of Sn species which decrease the acid concentration and the performance of the catalyst. Finally, an aqueous solution containing 20 g L^{-1} D-xylose (5 mL) in 2-MTHF (5 mL) in the presence of MC-SnOx-450 (0.1 g) at 180°C for 20 min afforded furfural in 53.9% yield with a good



Scheme 5. Plausible mechanism pathway for the synthesis of furfural from D-xylose in acidic media.

catalyst recyclability.

In parallel, industrial waste coal fly ash was valorized to obtain heterogeneous catalyst. To improve the activity of solid acid catalyst and eliminate the impurities, coal fly ash (50 g) was first treated with an aqueous solution of NaOH (2.5 M) for 3 h and then filtered and desiccated at 110 °C for 12 h. Mixing the coal fly ash with crystallized SnCl_4 , $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and successive treatment afforded the corresponding activated coal fly ash (10–80 wt%) with a Sn–Al (4:1–15:1, mol/mol) [110]. This catalyst showed good activity towards furfural production. In aqueous NH_4Cl –toluene biphasic system (1:1 v/v) at 180 °C for 30 min, the highest conversion of 93.5% with furfural yield of 84.7% were obtained from D-xylose-rich corn stover hydrolysate conversion. They also proved the good recovery of the catalyst and its reuse up to five times. The preparation and the use of the composite of metal-organic-framework (MOF) and activated fly ash as a catalyst tested to dehydrate the D-xylose into furfural was reported [111]. This work was done by the same group using MIL-101 (Cr) and mesoporous tin phosphate nanoparticles [108].

New composites associating mesoporous SBA-15 modified with phosphoric acid and adsorption of Cr^{3+} ions furnished a good candidate for the dehydration of furfural [112]. The preparation of catalyst (x) Cr^{3+} /P-SBA-15 was done in two steps: (i) dehydration of the molecular sieve (SBA-15) surface with phosphoric acid to obtain P-SBA-15; (ii) adsorption of Cr^{3+} ions by placing a different concentration of an aqueous solution of CrCl_3 (1.0 g of P-SBA-15 and x g of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$). Comparing different Cr^{3+} content into the composites, the best one was (0.25) Cr^{3+} /P-SBA-15. Under the optimized conditions (D-xylose (5 wt %), (0.25) Cr^{3+} /P-SBA-15 (30 wt%) in a biphasic mixture of H_2O –THF (1:3, v/v) at 170 °C for 90 min furnished furfural in 91% yield. In addition, the catalyst remained its catalytic activity for up to five runs recovery.

Catalytic performance of heteropolyacids (HPAs) in the dehydration of D-xylose to furfural in different solvent system was studied. In this

context, Jin's group reported the dehydration of D-xylose catalyzed by bimetallic salts of a heteropolyacid in a mixture of H_2O –DMSO [113]. Specifically, the Sn/Cs bimetallic salts of 12-tungstophosphoric acid (PW) adopted Keggin crystal structure of PW with Sn/Cs molar ratio, $\text{Sn}_{0.625}\text{Cs}_{0.5}\text{PW}$ owning the best activity in D-xylose dehydration. D-xylose (0.1 g) was almost totally converted and gave 63% of furfural yield with the selectivity of 63.6% under the best conditions at 200 °C in 3 h in H_2O –DMSO (1:1, v/v) in the presence of $\text{Sn}_{0.625}\text{Cs}_{0.5}\text{PW}$ (0.08 g).

It was noteworthy that the use of modified sporopollenin to produce furfural reported by Len's group was a source of valorization [41]. After cleaning the rape pollen (5 g), the remaining solid was fixed by a mixed solution of formaldehyde and ethanol (50 mL) for 1 h and then immersed in sulfuric acid solution (12 M, 50 mL) at 80 °C for 4 h at 80 °C [114]. Then, the carbonized rape pollen obtained was washed with DI water until a neutral pH reached. The treated rape pollen was obtained after dried out at 80 °C for 24 h. A mixture of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (1.75 g) was dissolved in hydrochloric acid (2 M) and added dropwise in the dispersed treated rape pollen. With the tin-loaded rape pollen in hands, addition of H_2SO_4 (2 M) and conventional treatment furnished the SO_4^{4-} /SnTRP. at 80 °C for 6 h. In the presence of SO_4^{4-} /SnTRP (10 wt%), a mixture of D-xylose in toluene, DMSO and an aqueous solution of NaCl were mixed at 170 °C. After 3 h, furfural was obtained in 82.91% yield. Starting from corn stover, similar conditions permitted to produce furfural in 77.82% yield.

Different supports such as micro-mesoporous carbon, industrial biobased ash, metal-organic-framework, mesoporous silica sieve and heteropoly acid were studied for the dehydration of D-xylose and biomass derivatives. It was notable that D-fructose was developed for the formation of new supported catalyst, nevertheless the cost of this ketose is probably a limiting point.

6. Mechanism for the synthesis of furfural

Various mechanisms for the formation of furfural from D-xylose have been identified and described in the literature. These mechanisms involve different key steps, such as 1,2-enolization, β -elimination and isomerization via 1,2-hydride shift, which can occur through either cyclic or acyclic pathway. A plausible mechanism has been proposed based on mechanistic and kinetic aspects in aqueous media using homogenous catalysis (Scheme 5) [115]. Starting from acyclic D-xylose, the isomerization via 1,2-hydride shift or 1,2 enediol mechanism produces the corresponding ketose, which is the key intermediate for assuming the cyclic pathway in the mechanism. On the other hand, the 1,2-enediol derivative can supply the 2,3-unsaturated aldehyde as a key intermediate if the assumption of the acyclic pathway is made. However, such uncertainties are reflected in the contradictory kinetic models and data presented in the literature, which prevent scientists from reaching a common and coherent interpretation. The presence of calcium derivatives such as CaCl_2 and acidic catalysts has shown a significant effect on the production of furfural. The presence of CaCl_2 shifts the α -xylopyranose and β -xylopyranose anomeric toward the α -form, which is more favorable for initiating the dehydration process [116].

7. Conclusion

This review summarized all catalytic processes, reported so far, for biobased furfural synthesis. These catalytic processes, which were classified according to the nature of the catalytic system, are amongst the most relevant in recent years. The crucial application of a catalyst was evaluated in terms of its efficiency, cost, chemical/thermal stability, recycling and reusability. Regarding homogeneous catalysis, organic and inorganic catalysts were mainly Brønsted acids. These catalysts must overcome a high activation barrier for the dehydration of xylose to furfural. On the other hand, Lewis acid salt catalysts allowed the isomerization of D-xylose to D-xylulose which is a more reactive intermediate for furfural synthesis. Therefore, the combination of Brønsted and Lewis catalysts was found as a more promising option, as lower energy was required and higher furfural yield and selectivity could be achieved. However, corrosion, environmental and handling issues needed to be properly considered with this type of catalyst which is not always mentioned in the published works. Concerning ionic liquids, they led to extraordinary results, although their separation from the reaction medium remains a major hindrance for an efficient process in a biorefinery. Regarding heterogeneous catalysts, they were described as more difficult to prepare and therefore more expensive. In addition, they are usually inefficient in the long term due to inhibition of the active sites during the hydrolysis reaction. Despite some disadvantages, some heterogeneous catalysts displayed interesting properties such as sulphated carbonaceous materials, zeolites among others.

Regardless of whether homogeneous or heterogeneous catalysis is used, the main challenge remains the lifetime of the catalysts, the limitations of the by-products obtained and the extraction and purification technology for the furfural. In most reported works, furfural yields were determined by chromatographic analysis without furfural isolation. To date, the purification of furfural remains still a major problem that should be further developed in the coming years.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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