Critical review of furfural and furfuryl alcohol production: Past, present, and future on heterogeneous catalysis

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Qualitative and Quantitative Review of Furfural and Furfuryl Alcohol Production: Past, Present, and Future on Heterogeneous Catalysis

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ABSTRACT

The valorization of biomass has the potential to produce molecules from renewable sources. Among them, furfural (FUR) is one of the best platform molecules due to its reactivity. It is produced from the acid dehydration of xylose (XYL), in homogenous or heterogeneous media. Besides, the FUR reduction produces furfuryl alcohol (FA), an important product to chemical industry. Based on the most-cited and also most-recent papers on this research area, the present work proposes a qualitative and quantitative review FUR and FA synthesis on heterogeneous systems. The XYL dehydration and FUR hydrogenation to FA were reviewed. Also, the direct upgrade of XYL to FA might bring new ideas to new research fields. The nature of solvents, co-solvents, and also active phases were explored and described. At the end of each section, selected results were collected. In addition, a summary of future perspectives was also provided. Then, this paper offers general and specific approaches for a better understanding of XYL, FUR and FA main reactions.

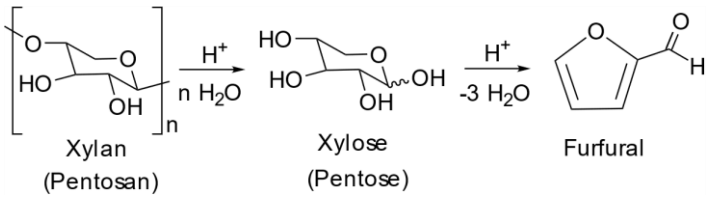
Keywords: Biomass, Xylose, Furfural, Furfuryl Alcohol, Hydrogenation, MPV Reaction.

1. INTRODUCTION

The demand for producing chemicals from renewable sources has increased in the last decade [1]. The European Climate Law recently proposed a reduction of 55% of net emissions of greenhouse gases compared to 1990 and climate neutrality by 2050 [2]. In addition, since 2010, the United States has promoted a federal program to keep a supply of biofuels, the Biomass Crop Assistance Program [3]. As for Brazil, a country with an extensive tradition in biofuels and a renewable-predominant energy matrix, a National Biofuel Policy – RenovaBio – was established in 2017 to promote the expansion of biofuels use with emphasis on the regularity of fuel supply and reduction of greenhouse gas emissions in the production, commercialization and use of biofuels [4]. In this worldwide scenario, it is essential to produce chemicals from renewable sources to form other biofuel-related products [5].

Among the most promising biobased molecules is furfural (FUR), a reactive molecule with an aldehyde group attached to a furan ring [6]. Also, FUR is produced from lignocellulosic biomass (LB) sources and may react to around 80 other compounds [6]. In 2021, the FUR market size was evaluated at around US$ 520 million, with an expected compound annual growth rate (CAGR) of 6.5% from 2022 to 2030 [7]. Those are reasons to consider it one of the candidates for the biofuels era [8]. FUR is produced from the acid dehydration of xylose (XYL), a repetition unit from the xylan, as expressed in Figure 1. The reaction was originally carried out in a homogeneous medium.

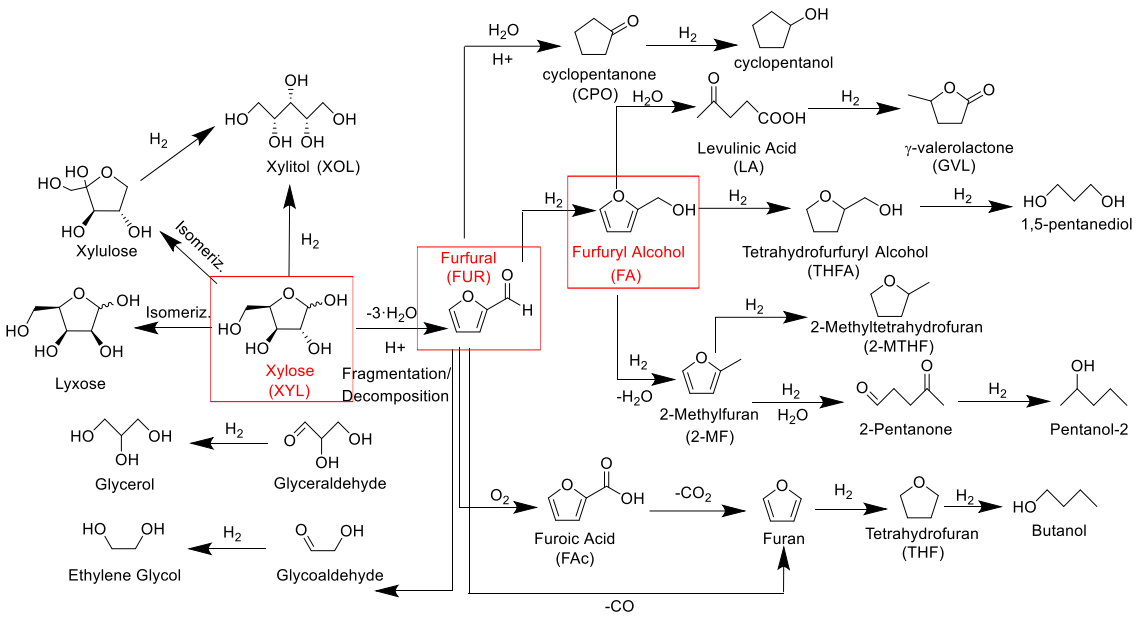
Figure 1 - Acid-catalyzed scheme for FUR production - Adapted from [9].



Nowadays, most of the FUR is produced by the Chinese Batch Process, a modification of the Quaker Oats Process, where lignin and liquor are extracted from the reaction medium, and low-pressure steam is mixed to carry out an azeotropic separation of FUR [10]. However, those methods still have issues regarding the corrosion of equipment and the separation of catalysts [11]. So then, the search for solid heterogeneous catalysts for the sustainable production of FUR is still demanding and has been extensively pursued over the last decade.

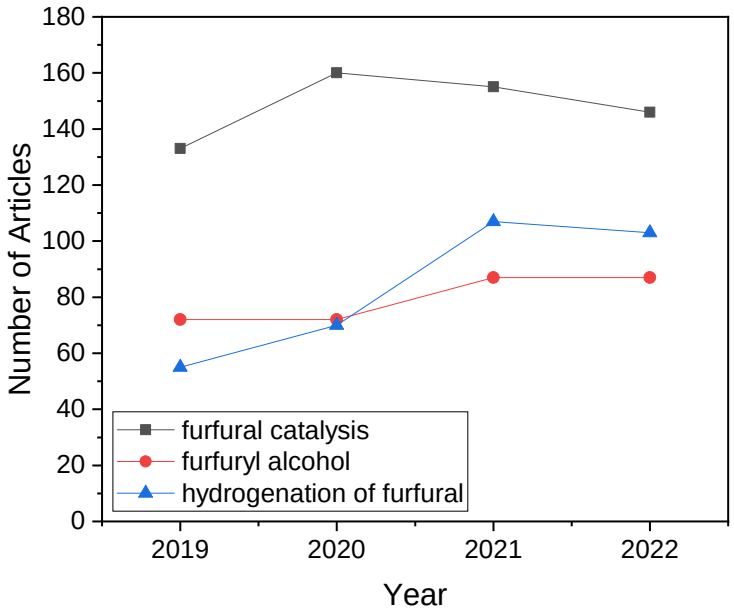
Figure 2 shows a non-exhaustive network of varied FUR-derived products. The FUR hydrogenation includes the formation of essential solvents and biofuels to the chemical industry, like furfuryl alcohol (FA), tetrahydrofurfuryl alcohol (THFA), and 2-methyltetrahydrofuran (2-MTHF). The presence of water in reaction media may provide the conversion of FA into levulinic acid (LA), which may be further converted to γ-valerolactone (GVL) in H_2. Also, in another route, H_2 can transform FUR in 2-methylfuran (2-MF), 2-pentanone, and pentanol-2. Alternatively, the presence of O_2 makes FUR react to furoic acid, furan, and tetrahydrofuran (THF).

Figure 2 - Compounds produced from hydration, hydrogenation, decarboxylation and oxidation of FUR molecule – Adapted from [12].



Although the first patents about FUR production and its derivatives are not recent [12–17], the interest in this topic has increased year by year, as provided in Figure 3 . On FUR production, the research efforts are focused on proposing solid catalysts to XYL dehydration, whereas on FUR hydrogenation to FA the studies are now focused on the liquid phase conversion over heterogeneous catalysts.

Figure 3 – Number of publications related to FUR and FA since 2019 (only articles).



Source: Web of Science – search TI = (furfural and catal*), TI = (furfuryl alcohol), TI = (furfural AND hydrogenation). Date of search: May 7th 2023..

Given this brief overall background, this review is determined to gather and analyze qualitative and quantitative information on established articles and recent updates of FUR and FA production. Furthermore, the combined approach of XYL to FA will be discussed, as well as the future trends in this area. Then, this contribution aims at being a guide to introduce researchers to the field and to provide new insights about the area.

2. FURFURAL SYNTHESIS

2.1. General Mechanisms in Cyclic and Acyclic Compounds

On XYL dehydration to FUR, several mechanisms were proposed in cyclic and acyclic forms, with a proper H^+ source, *i.e.*, a Brönsted acid [18–20]. The cyclic approach explained the FUR production via protonation of varied OH sites on XYL molecule. This mechanism may occur in two paths: 1) the attack of H^+ at the oxygen atom bonded in carbon 1, also called 1-OH protonation, including a xylosyl cation and the scission of C_5-O linkage (expressed in Figure 4) or 2) the 2-OH protonation, which provides a shorter path to FUR (illustrated in Figure 5).

Figure 4 –1-OH protonation in XYL dehydration (Adapted from [21,22]).

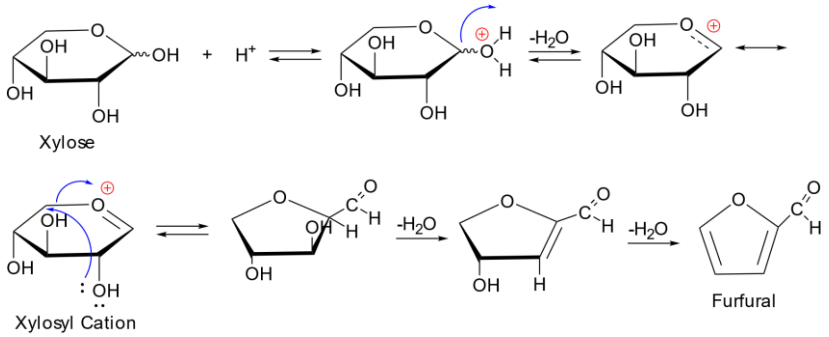
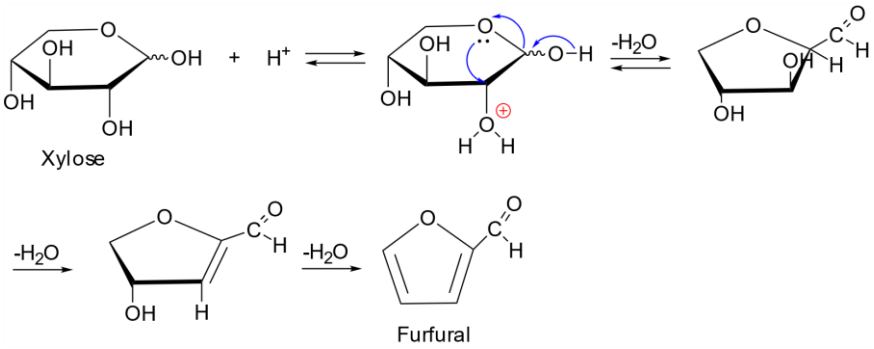


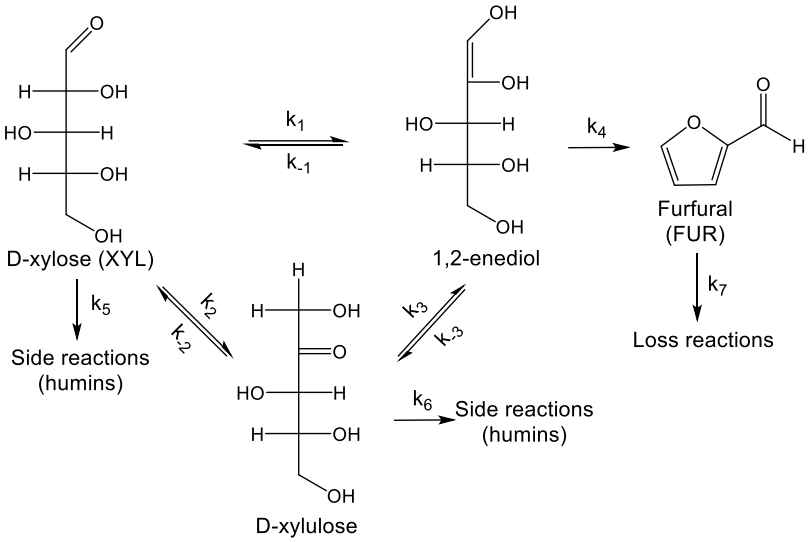
Figure 5 – 2-OH protonation in XYL dehydration (Adapted from [21,22]).



The comparison of the routes by molecular dynamic simulations in the gas phase showed that the 2-OH protonation might provide a shorter path to FUR [19]. Once no hydrogen of the solvent was exchanged in cyclic dehydration in acid media, it was concluded that the acidity modification came from Brönsted acids [21]. In reference to XYL dehydration, it is also known that xylulose, an isomer from XYL, plays a significant role in FUR synthesis [1]. However, the previous mechanisms did not account for its presence [20].

Recent quantum chemistry calculations informed new insights into the XYL conversion to FUR. According to Fang et al. (2022), the enolization of XYL and xylulose to 1,2-enediol produced FUR. In fact, this diol played a major role in XYL conversion once the one-step generation of FUR from 1,2-enediol presented lower activation energies [20]. The mechanism expressed in Figure 6 showed the formation of xylulose and a direct transformation of 1,2-enediol to FUR as the rate-limiting step, which can enhance new studies in the research field.

Figure 6 – Mechanism for XYL dehydration with 1,2-enediol – Adapted from [20].



2.2. Production of Humins (HUM) and Role of Acid Sites

During the XYL conversion to FUR, there is not only the production of the desired compound but also the formation of additional undesired substances. For example, as depicted in Figure 6, the production of xylulose and 1,2-enediol can happen. Besides, FUR is a very reactive aldehyde that can undergo several loss reactions, generating then polymeric substances [22]. Another issue of FUR already stated in the literature is the fragmentation route, i.e., situations when FUR leads to minor products, like glyceraldehyde, glycolaldehyde, formic acid, acetol, and formaldehyde, even at mild conditions [22–25].

Although the byproducts above are undesired, the most substantial concerns about XYL dehydration rely on the formation of humins - HUM. First, HUM are dark and insoluble polymeric molecules that attach to the solid catalyst due to their strong adsorption on the catalytic surface [26–28]. Second, those compounds might be produced via resinification or condensation mechanisms [29]. And third, the resinification route occurs when FUR reacts with itself, forming then larger aldehydes, whereas the condensation route is the reaction of FUR with other components, like XYL, as provided on Figure 7 and Figure 8 [29].

Figure 7 – Example of resinification reactions of FUR – Adapted from [29].

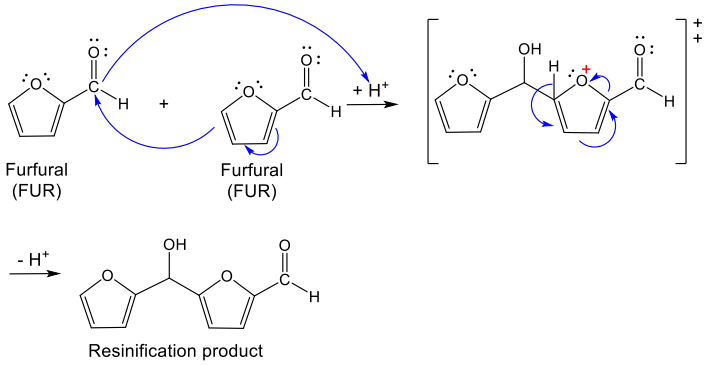
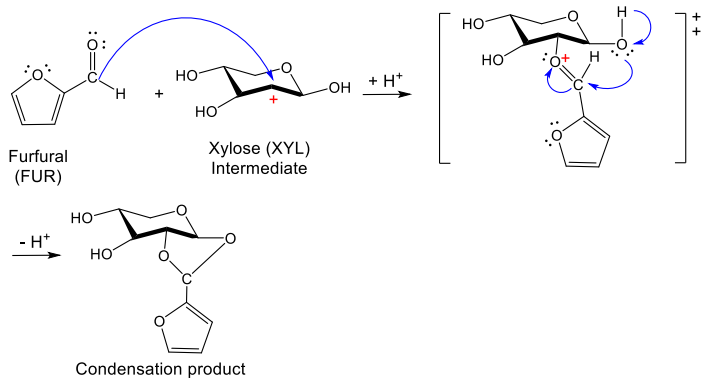


Figure 8 – Example of condensation reactions of FUR – Adapted from [29].



One of the main drawbacks of HUM production is the blocking of the catalytic sites, which decreases the FUR yield [30]. Therefore, as producing HUM is certain in FUR reaction, reducing its production is crucial for catalysts design. Among the most important factors accounted for HUM production, the diameter of pores, nature and/or strength of acid sites, and temperature can be highlighted. Several researches have indeed studied those influences.

Weingarten et al. (2011) showed important outcomes from FUR conversion to HUM [31]. As a first remark, the use of microporous materials increased the rate of disappearance of FUR, especially in water medium. In addition, this combination provided a higher affinity to HUM [31]. So then, at least from XYL to FUR reactions, the use of microporous catalysts was not recommended.

Besides, the solid catalysts have two types of acid sites: Lewis (LAS) or Bronsted (BAS). The first is related to potential electron acceptors due to a positive charge on the surface, whereas the latter corresponds to potential H^+ donors [32]. Both sites were selective during the XYL transformation to FUR, although BAS provided higher selectivity to FUR [31]. Nevertheless, there were essential outcomes related to HUM

formation. The BAS could catalyze the resinification reactions from FUR, and LAS increased the condensation products from XYL and FUR [31,32]. Besides, the presence of LAS had induced XYL decomposition, even at mild temperatures, producing stable adducts with FUR, and increasing HUM production [31]. This was also confirmed by Pholjaroen et al. (2013), who attested that an excess of LAS decreased FUR yield and took to more HUM [32]. Therefore, LAS are more active than BAS for HUM production. However, as both sites may produce resinification and condensation reactions, it is also recommended to look at the strength of acid sites.

It was demonstrated that strong LAS and BAS promoted the formation of more HUM, increasing FUR loss reactions [33]. On the contrary, the FUR yield was improved with weak to medium acid sites. In addition, an increase in the total acidity of the reaction medium was able to reduce HUM production due to higher stability in the FUR molecule, as confirmed by Doiseau et al. (2014) [33].

Pholjaroen et al. (2013) established the influences of elevated temperatures on XYL dehydration to FUR. Usually, the minimum temperature for the desired reaction was around 130 ^{o}C [32]. In order to diminish FUR side reactions, it was noted that up to 200 ^{o}C, both XYL conversion and FUR yield increased on water. However, temperatures superior to 200 ^{o}C increased pentoses conversion and also FUR decomposition into minor products [32]. Then, an ideal range for FUR production in the liquid phase would be from 160 to 180 ^{o}C.

2.3. Nature of Solvents

Hu et al. (2014) also established that pure water does not provide the necessary stable forms of XYL intermediates, decreasing the FUR yield [34]. In theory, a proper solvent for FUR production must curb its side reactions. In addition, a volatile and environmentally friendly solvent improves separation of the reaction medium using distillation or similar approaches [34]. Besides water, another option is the constitution a reaction medium with other substances, like alcohols, ethers or even furans. Table 1 displays several normal boiling points of some compounds usually selected for solvents in XYL dehydration.

Table 1 – Standard boiling points (T_b) of the FUR and most used solvents in XYL dehydration - Adapted from [35].

Substance	T_b (ºC)	Substance	T_b (ºC)
Acetone	50.6	Toluene	110.6
Methanol	64.7	FUR	162.0
Isopropanol	82.6	DMSO	189.0
Water	100.0	GVL	207.0

2.3.1 Water

Water is the most used polar protic solvent for XYL dehydration. It has the highest solubility of XYL due to its capacity of hydrogen bonds – almost 470 g/L [36]. However, this same advantage may arise several drawbacks. For instance, polar solvents modify acidity on the catalyst surface [31]. Concerning oxides on an aqueous medium, the detection of new charges on those solids was previously reported [37]. Furthermore, the formation of Lewis acid-base adducts by coordination with water molecules was assigned to the deactivation of LAS in water medium in zeolites and metal oxides [38]. As a solution, the use of materials containing water-tolerant LAS (as Nb_2O_5 or $Sc(OTf)_3$) can overcome the issues of LAS deactivation by water [39]. Aside for the higher activities, materials with elevate LAS will produced more HUM and side-reactions, decreasing FUR yield over time [40].

Another issue of water is the release of more H^+ ions at elevated temperatures, becoming then a source of BAS. This contributes to more degradation of FUR to HUM. Recently, Lin et al. (2020) demonstrated that a total aqueous medium conducted for both XYL and FUR degradations. Also, the production of formic acid was reported as one of the undesired products in that conversion [36]. Then, some options instead of a pure water medium are the use co-solvents, as polar aprotic or with lower polarity.

2.3.2 Alcohols

One advantage of the reduced chain alcohols is their reduced boiling point, as depicted in Table 1. However, their structure also displays polar (-OH) and non-polar parts (C, H), which reduces their polarity compared to water, and may favor FUR interactions [34]. The most used primary alcohols are methanol or ethanol.

The literature recorded different results for pure methanol on XYL dehydration. Hu et al. (2012) reported that methanol could stabilize XYL intermediates, avoiding further reactions [41]. However, Iglesias et al. (2016) showed that XYL reacted with methanol, providing new intermediates for the reaction, alkyl xylosides [42]. In addition, the etherification of XYL to xylosides was much faster than XYL dehydration to FUR on pure methanol. Indeed, ethanol also worsened FUR yield. Köchermann et al. (2019) had also demonstrated that higher proportions of ethanol inhibited XYL conversion and could catalyze FUR degradation reactions [43]. Then, the use of primary alcohols produced new intermediates, especially on the XYL route [44].

Lin et al. (2020) showed that pure isopropanol reduced the number of H-bonds with the XYL molecule [36]. Furthermore, the use of isopropanol and isobutanol as pure solvents prevented the side reactions of FUR due to the formation of H-bonds and steric hindrance [34]. However, despite its low polarities, pure isopropanol still conduct XYL degradation reactions [36]. This is one reason for the use of mixtures water/isopropanol as media for FUR production. Therefore, secondary alcohols are preferred over primary ones for XYL dehydration.

2.3.3 Ethers, Esters and Ketones

Ethers are non-polar substances, whereas most esters and ketones are aprotic polar solvents, *i.e.*, they lack an H^+ for donation in H-bonds [45]. Aside from the volatility and solubility in FUR, the use of pure ethers does not improve XYL dehydration to FUR. In turn, it increases FUR degradation because of its ring opening. In FUR production with diethyl ether, the researchers mentioned the formation of reactive intermediates, conducting the production of polymers from FUR [34].

The advantages of esters rely on the formation of minor acids at elevated temperatures, which may demand less acidity for heterogeneous catalysts. Nonetheless, there were issues related to the XYL access to sites on Amberlyst 70 on pure methyl formate [34]. Even with the formation of formic acid reported, it was not capable of increasing the FUR yield. Therefore, the lack of polarity in ethers create issues on pore access inside solid catalysts.

Most ketones have boiling points lower than water, around 60 ^{o}C, which may favor the separation for a heterogeneous catalyst. On the contrary, using pure ketones on FUR production, as acetone and cyclopentanone, provided a rapid FUR formation and increased the FUR degradation compared to water [34]. In addition, the ketones may

produce a self-condensation reaction with FUR, leading to more polymers. Therefore, the excess of availability of FUR in ketones is responsible for the autocatalytic degradation.

2.3.4 GVL, GBL and others

Molecular dynamics simulations showed that pure GVL and GBL formed less H-bond with XYL [36]. Nonetheless, pure GVL could not conduct FUR production from XYL in the absence of catalyst, due to reduced solubility – about 2.5 g of XYL/L [36]. Moreover, the pure solvents did not decrease XYL loss reactions.

In the case of GVL and GBL, once they are products derived from FUR, the approach on the FUR production in only one equipment is easier. Most importantly, it was concluded that the presence of BAS solids in pure GVL reduced the activation energy for XYL dehydration and increased the energy for FUR side reactions [45]. Therefore, those aprotic polar solvents tend to increase FUR yield and also curb undesired products [45]. The reason for the improvement was that water provides more stabilization for H^+ ions, leading to lower reactivity and FUR yields.

However, their main application is related to mixtures with water. Once XYL is more mixable in aqueous media, the lactone may protect FUR molecule. The GVL-H_2O and GBL-H_2O systems presented reduced H-bonds between the solvent and co-solvent, leading to about 50% FUR yield. And most of all, no formic acid was detected in the systems, leading to the conclusion of the protective shell of those lactones for FUR [36]. The application of lactones as co-solvents will be detailed further.

Other aprotic solvent used for XYL dehydration is DMSO (dimethyl sulfoxide), which can also protect FUR from resinification reactions [46]. However, the protection effect is so superior to other solvents, that it redueces XYL dehydration rates in pure medium. Nonetheless, as well as in GVL, the DMSO boiling point – close to 200 ^oC - is another drawback for industrial applications [34].

2.4. Nature of Co-Solvents

As aforementioned, FUR is a reactive molecule. Hence, it is essential to promote a selective conversion of XYL to FUR in order to minimize its degradation on acid media. Besides, using pure solvents and adding a co-solvent might improve the FUR separation, whether for extraction or solubilization.

2.4.1 Hydrocarbons

During the first researches about XYL dehydration on solid catalysts, hydrocarbons were used for FUR extraction [47,48]. It is favored in non-polar compounds once the main XYL dehydration reactions take place on the aqueous phase [47]. Besides, the most used extractor was toluene (TOL) because the non-polar part has elevated affinity with the FUR molecule [48]. Also, it was reported that TOL did not change the hydrophobic or hydrophilic properties of solid catalysts, which is another advantage [49].

However, a reaction conducted only with TOL did not achieve the XYL dehydration. Even in water mixtures, there is an optimal proportion between H_2O and TOL. For example, a ratio of 1:4 (v/v) of H_2O/TOL did not provide a suitable interface for FUR production due to excess water [50,51]. In addition, not all types of solid acid catalysts can react in a TOL medium. The addition of hydrophobic species in solid catalyst may increase FUR yield, due to its anti-adsorption on sites, that is now occupied by an non-polar chain [52]. To conclude, another issue of TOL is its toxicity and the impact on the environment. Then, the search for less aggressive solvents remains.

2.4.2 Alcohols

The minor alcohols (such as methanol or ethanol) are soluble in water, whereas larger chain alcohols (butanol-1 or pentanol-1) have limited solubility in an aqueous medium. However, the chain size is a determinant for inhibiting aldol condensation in FUR, as reported by Guo et al. (2018) [53]. Above all, the larger chain alcohols tend to be less polar, improving their extraction capacity. Parejas et al. (2017) detected that a butanol-1/ H_2O provided similar extraction capacities to TOL/H_2O [54].

The number of works using methanol or ethanol as solvents or co-solvents is reduced on the literature. As examples, Paniagua et al. (2015) detected the formation of methyl xyluloside and ethyl xyloluside with the use of methanol and ethanol on XYL dehydration [55]. Those compounds were further dehydrated to produce xylulose. Indeed, the transformation of XYL into xylulose was more pronounced on methanol than ethanol due to the lack of steric hindrance [55]. Then, it is preferable to use less polar alcohols on biphasic media in XYL dehydration.

2.4.3 Cyclopentyl methyl ether (CPME)

Besides the low solubility in water, which provides better FUR extraction, CPME has a reduced normal boiling point of 106 ^{o}C, a distant value from FUR – 162 ^{o}C. Another advantage relied on a positive azeotrope with H_2O at 83 ^{o}C, but only for concentrated

CPME amounts – about 84% of CPME to 16% of H_2O (m/m) [56]. For those reasons, it has been studied as a substitute for TOL in co-solvents for XYL dehydration.

Campos-Molina et al. (2012) detected that CPME not only extracted FUR from the aqueous phase but also prevented side reactions. In fact, FUR yields up to 100% were reported in H_2O/CPME media using a H_2SO_4 solution as an acid source [57]. Furthermore, temperatures up to 200 ^oC were used in XYL dehydration without indicating degradation products [57,58]. However, elevated concentrations of CPME curbed XYL dehydration routes and increased resinification FUR reactions with the organic layer, as stated by Wang et al. (2017) [59]. Therefore, especially with solid acid catalysts, an optimum proportion of H_2O/CPME must be maintained, normally about (1/3 – v/v) [59,60].

2.4.4 GVL

GVL is probably the most promising co-solvent used with water for biomass reactions. First, it is non-aggressive to the environment and derived from FUR products [61]. Second, the GVL medium allows the increasing of acidity without damaging the FUR yield, which is not possible on water [62]. As an example, the mixture GVL/H_2O produced FUR with almost 100% yield in biomass subtracts, as corn cob or eucalyptus sawdust [62,63]. Furthermore, in batch or continuous modes, the mixture could activate properly LAS and BAS sites of heterogeneous catalysts, such as SAPO-34 or niobia-titania solids [63,64]. Recently, another application of GVL was to provide the suitable reduction of viscosity in ionic liquids and deep eutectic solvents, also improving the FUR selectivity [65,66]. Those new liquids may act as both catalysts and solvents in the reaction medium, improving further stages of separation.

2.5. Recent Advances in XYL dehydration to FUR

Apart from homogeneous catalysts, the main challenge on FUR production field has been the search for optimal heterogeneous catalysts and solvents [1]. In the first works of XYL dehydration, zeolites were used as materials for FUR production, due to their pore sizes and LAS/BAS tuning [47]. Other solids, such as Metal-Organic Frameworks (MOFs) were also used because of their empty cavities, resistance to acidity and also hydrothermal stability [67–70].

Another class of materials used in XYL dehydration are mesoporous oxides. However, the main issue regarding to water is the deactivation of LAS [71]. Among those oxides, Nb_2O_5 and TiO_2 had emerged as natural water-tolerant LAS catalysts for biomass

conversions [38,72–77]. Recently, dos Santos et al. (2022) could also discover that mixed oxides of Sn and Mo provide both resistant LAS and BAS necessary for XYL conversion to FUR. Nonetheless, elevated selectivities for XYL isomers (about 30%), as lyxose and xylulose, were also reported due to the existence of LAS [78].

In order to tune the catalyst surface, the addition of functionalized groups has also been a trend in FUR production. The main reason relies on the addition of BAS that cannot exist on material or that was even lost after thermal treatments, as an example of Nb_2O_5 [79–82]. Other issue is the stability of functionalized groups after several reaction cycles [82–84].

Dulie et al. (2021) explored the functionalization of amorphous compounds derived from lignin for FUR production. The anchored groups were SO_3H, COOH and OH. According to the researchers, the sulfonic and carboxylic groups worked as BAS, increasing FUR yield. At the same time, the OH groups were hydrophilic and provided XYL adsorption for FUR formation [83]. In turn, the excessive polarity of OH and COOH parts was responsible for strong H bonds with aldehyde groups on FUR, leading to irreversible adsorptions. Then, there must be an optimal quantity of anchored groups on functionalization. Recently, Liu et al. (2023) synthetized a modified SBA-15 catalyst with doping of Zr and addition of P by acid treatment [85]. Both the Zn doping and grafting of phosphate groups increased the total acidity of the catalyst. Furthermore, according to the researchers, the phosphate groups increased BAS content whereas the Zr content improved LAS acidity [85]. With regard to the reaction medium, it was reported that the TOL extracted FUR and the incorporation of NaCl improved the FUR distribution coefficient on organic phase, limiting degradation reactions [85]. Their approach had 80% and 68% of FUR yields with XYL and xylan monomers, respectively [85].

Krzelj et al. (2021) could also carry out a SO_3H surface modification but in foams instead of powders. Moreover, their technique also allowed them to perform the XYL dehydration in continuous operation. Both sulfonic groups and foam format enhanced mass transfer and FUR selectivities [84]. Indeed, the FUR yield was superior to homogeneous catalysis using H_2SO_4 solutions. Therefore, the use of foams might open a new field of research in surface treatment for FUR production [84].

Aside from the surface modifications, the scale-up for XYL dehydration remains challenging. New research fields aim to process simulation and new configurations of continuous reactors. The recent work of Guo et al. (2022) studied a new configuration of

the reactor for FUR production based on biphasic slug flow microreactors. The new mode allowed lower heat and mass transfer limitations so that the converter could be modeled as a plug flow one [86]. Another interesting conclusion was the capacity to extract water/MIBK system, which could suppress the HUM formation compared to monophasic systems. In the same research field, Lu et al. (2023) designed the FUR production using micropacked bed reactors. Two solids were used as LAS and BAS sources, respectively: SO_4^{2-}/Al_2O_3 and HND-580 (ion exchange resin) [87]. In a first approach, the reactor system comprising only SO_4^{2-}/Al_2O_3 catalyst presented 90% of XYL conversion at 170 ^oC, despite 20% of FUR yield [87]. According to the authors, the Al^{3+} centers were LAS for XYL isomerization to xylulose [87]. Furthermore, the strong LAS of SO_4^{2-}/Al_2O_3 resulted in accumulation of xylulose, lacking the further FUR formation [87]. Next, the introduction of HND-580 in a mixed solid approach improved the FUR yield to 35%, due to xylulose protonation [87]. Concerning the gas flow, the use of CO_2 improved the FUR yield from 35% to 43% in 28 s of reaction. The dissolution of CO_2 in water produced unstable carbonic acid (species for protonation) and also FUR extraction, suppressing side reactions [88,89]. However, the deactivation of both catalysts was reported after 5 h of reaction: HND-580 were replaced by new solids and SO_4^{2-}/Al_2O_3 was put in thermal treatment before regeneration [87]. So, the slug flow converters allied to non-polar co-solvents and new catalysts might provide new insights into FUR production [86]

Regarding simulation studies, An et al. (2022) carried out XYL dehydration to FUR on a chemical plant using a PFR reactor and extractive distillation to separate FUR. Among the non-polar solvents, TOL, MIBK, and 2-pentanone were tested. Due to a higher partition coefficient, the 2-pentanone approach provided better FUR extraction and induced the lowest energy consumption on the process [90].

3. FURFURYL ALCOHOL SYNTHESIS ON LIQUID PHASE

3.1. Substances produced during FUR hydrogenation

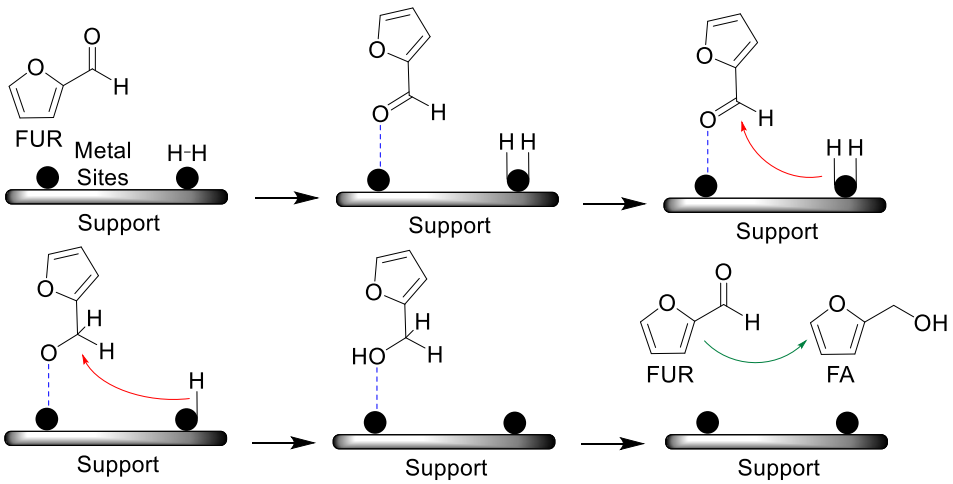
The FUR hydrogenation can produce many products in the liquid phase, as expressed in Figure 2. First, the hydrogenation of C=C bonds of FUR produces tetrahydrofurfuryl alcohol (THFA), a product with minor interest than furfuryl alcohol (FA) [91,92]. Second, FA can lead to 2-MF in a hydrogenolysis path. Third, the cleavage of the C=O bond in FUR provides decarbonylation to furan, and the presence of H_2O can promote the synthesis of LA and GVL [91–93]. Finally, the furan ring might also open, producing linear alcohols, for example butanol-1. In order to provide the FUR conversion to FA, two major approaches are commonly reported in articles: the use of H_2 gas as an external source of H or the presence of sacrificial alcohol might provide FUR reduction.

3.2. Classic Approach and MPV Reaction

Since the first studies, gaseous H_2 has been used as an H source for liquid-phase FA production from FUR [14–17]. The main idea was to increase the H_2 solubility in reaction media to reach the catalyst surface, where FUR reduction occurred. However, to provide suitable solubility in the liquid phase, an excess of H_2 must be supplied due to mass transfer limitations. This is the main reason for the elevated pressures at those operations – from 20 to 50 bar.

Figure 9 shows a graphical representation of the mechanism for FUR hydrogenation in the liquid phase. In the Langmuir-Hinshelwood-Hougen-Watson (LHHW) mechanism, there is the cleavage of the H-H bond and the adsorption of FUR on the metal sites, promoting the activation of the external C=O bond of the furan ring.

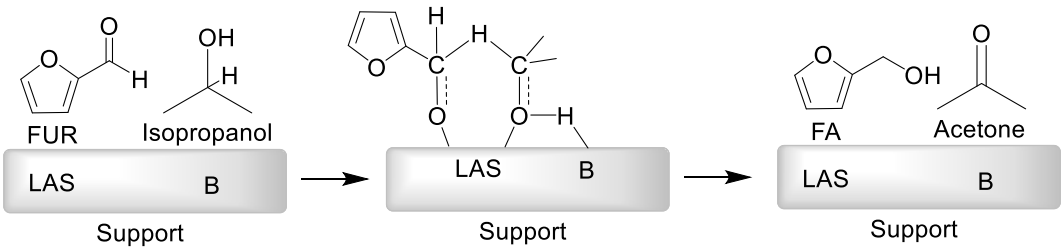
Figure 9 – Scheme for LHHW approach for FA production in the liquid phase – Adapted from [93,94].



Furthermore, the Meerwein–Ponndorf–Verley (MPV) reduction is another possibility for FA synthesis. In that approach, another H-donor is used instead of the H_2 gas. Then, the conversion to FA may be carried out at lower pressures [95]. Generally, alcohols are more used in MPV reactions because of reduced costs, renewable nature and advantages as solvents [96]. Concerning the type of alcohols, the secondary ones (*e.g.*, isopropanol, isobutanol, etc) are more efficient donors than the primary ones [96]. They have a better stabilization effect of the carbocation produced during hydride transfer [96]. However, tertiary alcohols are unable to perform MPV due to the lack of a α–H [96].

In Figure 10, the MPV mechanism uses both LAS and basic sites on heterogeneous solids [97]. The LAS bind to the hydroxyl groups of H-donors (usually the alcohol of sacrifice), generating an alkoxide species – a six-membered complex between the furan ring and the reducing agent [97]. At the same time, the basic sites attract the protons of the O-H bond, weakening the O-H bonds. Moreover, it was reported that a strong interaction between the hydroxyl oxygen and the LAS will easier the abstraction of the hydrogen by the basic sites [96]. Related to BAS, López-Asensio et al. (2018) showed that BAS did not show activity for MPV reduction [98]. However, an acid-base pair on catalytic surface is required to complete the MPV cycle, even though is not possible to have both strong LAS and basic sites on the same material [96].

Figure 10 –MPV reduction of FUR on acid-base surfaces – Adapted from [96,97].



LAS promote the adsorption of larger molecules, whereas basic sites (electron donors) are responsible for the adsorption of the reducing agent.

Either approach may be taken for FA production once technical pros or cons are considered in a technical-economic analysis (TEA). As mentioned before, using molecular H_2 would require high pressures and therefore the need for appropriate facilities. Moreover, H_2 is expensive and still mostly produced from fossil resources, which can impact the overall sustainability of FA production technology. Finally, hydrogenation catalysts demand a metal phase, which besides availability and cost,

should also be stable for liquid-phase reactions avoiding leaching. MPV-based process, on the other hand, may take the advantage of requiring metal-free catalysts, but would strongly rely on the selection of a highly efficient, low cost and renewable-based hydrogen donor to fit the sustainable requirements.

3.3. Reaction Media for FA Production

3.3.1 Water

Aside from its use in biomass reactions, the effect of water on FUR hydrogenation to FA is different. Several articles reported drawbacks in water media for FA production. It was concluded that H_2O damaged MPV reduction due to the conversion of LAS into BAS and the LAS deactivation in water [98]. Also, the FUR hydrogenation was damaged in hydrophobic catalysts on water due to a lack of FUR adsorption [99].

Furthermore, the H_2O medium provides issues related to the control of FUR hydrogenation [99–105]. As an example, the presence of an intermediate (3-hydroxy-4-cyclopentanone) favored the formation of cyclopentanone (CPO) during FUR reduction due to the H^+ release in water [101,102]. Moreover, the presence of both BAS and water shifted the FUR route not only to FA, but to further products, as LA and GVL [100]. Besides, the water medium was more spontaneous to ring opening in FA, leading to 1,2-pentanediol, as remarked by the experiments and DFT calculations of Ma et al. (2017) [103]. In another researhc, Zhou et al. (2019) confirmed that H_2O and basic sites led to cyclohexanol formation, another product derived from FA [105]. Therefore, the use of water is not suitable for providing FUR conversion to FA.

3.3.2 Alcohols

The class of alcohols presented varied behaviors concerning FUR hydrogenation to FA. The ideal alcohol should have an intermediate polarity and low molecular size to avoid competition with active catalyst sites [106–108]. As an example, minor chain alcohols, like methanol or ethanol, have promoted easier access of FUR to sites in acid media [108–110]. As a consequence, the formation of acetals, an undesired product derived from FUR, was reported [109,110]. In addition, both methanol and ethanol have elevated polarity, which can make them have similar water features.

Large chain alcohols (butanol-1 and cyclohexanol), though, did not produce acetal side products. However, their reported selectivity to FA was low because of the lack of interaction with FUR molecule [111]. Among the most cited alcohols on FUR

hydrogenation, isopropanol had the equilibrium between polarity and molecular size [112].

3.3.3 Hydrocarbons

Aside from the excessive FUR extraction capacity, the potential damage to the environment for the hydrocarbons during FUR-derived reactions is one concern [113]. The most studied compounds during FA production were toluene (TOL) and hexane (HEX). The literature did not report any acetalization during FA production assisted by TOL or HEX [110,114]. In some cases, the FA selectivity was close to 100%. However, both works stated reduced FUR conversion due to the low interaction between FUR and the hydrocarbons [110,114]. Then, despite the elevated solubility on FUR molecules, the lack of activity during hydrogenation is the major disadvantage for their use.

3.3.4 Other non-polar and aprotic substances

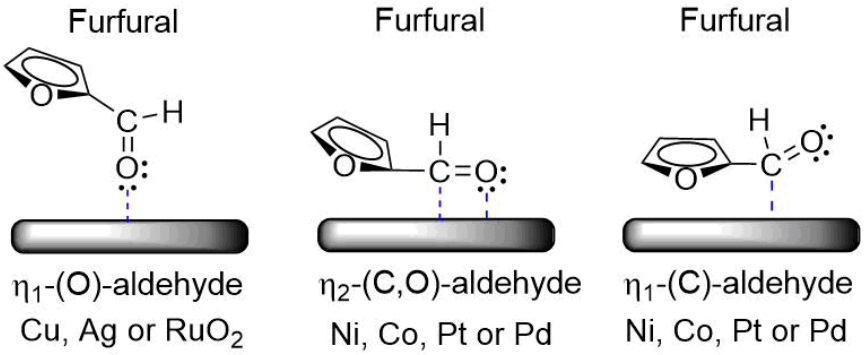
As well as the non-polar solvents, polar aprotic compounds (MIBK, DMF or CPME) do not present the donation of H. Then, this lack of acidity damaged MPV reactions, and it requires high H_2 pressures – usually superior than 10 bar [115–119]. Recently, CPME was reported as a stable compound for FUR hydrogenation to FA. At first, the use of CPME prevented self-polymerization of FUR even at 150 ^{o}C [120,121]. Also, de Souza et al. (2019) showed that CPME did not produce either etherification or secondary products during FUR reduction [115]. One of the reported applications was in continuous liquid phase FA synthesis, with *ca.* 100% of selectivity [116,119]. Another cited substance is ethyl acetate, which provided suitable stability and prevented side products during continuous FUR hydrogenation [117,118]. In short, polar aprotic substances showed promising conclusions for further studies in FA production, especially CPME.

3.4. Nature of Metals and Recent Advances

During FUR hydrogenation to FA and further substances, different adsorption modes of the furan ring were reported, as expressed in Figure 11 [122–124]. At first, the η_1-(O)-aldehyde adsorbed the C=O bond in an inclined shape, usually on Cu, Ag, and RuO_2 surfaces. As a result, this mode is not active for FUR hydrogenation to FA, due to the lack of affinity with the metal phase and furan ring [122,124]. In contrast, another reported mode was the η_2-(C,O)-aldehyde, which has stronger interaction with the furan ring in the adsorbed C and O bonds [123,124]. This mode was reported on Ni, Co, Pd, and Pt surfaces, increasing the FUR hydrogenation and further cleavage of furan ring

[123,124]. Furthermore, in temperatures up to 200 ºC, the η_2-(C,O) is changed to η_1-(C) pattern, promoting decarbonylation to furan [93,123].

Figure 11 – Adsorption modes of FUR on varied surfaces – Adapted from [123,124].



3.4.1 Palladium (Pd) and Platinum (Pt)

It was reported that Pd^0 metal sites favored C=C hydrogenation instead of C=O from carbonyl group because those sites had more affinity with non-polar groups [91]. Indeed, Pd/SiO_2 catalysts were more selective to furan and THF production, and Pd-TiO_2 produced 2-MF and 5-hydroxy-2-pentanone [124,125]. Therefore, the balance between hydrogenation and decarbonylation must be accounted on the design of Pd solids [126]. The alternatives might be the inclusion of a second metal phase (Fe, Ag or Co) or the promotion of strong metal-support interaction (SMSI) [124–127].

The mathematical modeling of FUR hydrogenation to FA using Pd-TiO_2 solids pointed out some insights. It was established that Pd sites were responsible for the hydrogenation mechanism, and the acid sites promoted FUR ring opening [125]. In addition, the adsorption of FUR, FA, and H_2 were more notable on the Pd surface compared to THFA, which reinforced the necessity of equilibrium between hydrogenation and decarbonylation routes [125]. As an example of recent discoveries, the stabilization of Pd nanoparticles could control the BAS on titania supports, reducing acetal production on MPV reactions [128]. Another reported strategy was the advantage of SMSI of Pd/TiH_2 catalysts, improving FUR conversion to FA [126]. This occurred due to more defects and oxygen vacancies on the surface, promoting suitable adsorption of C=O bonds on FUR. It was also pointed out that elevated particle sizes on Pd solids induced less FA formation [126]. Therefore, the interactions of support and metal phase were important in Pd catalysts [126].

In the examples with platinum, several DFT calculations demonstrated that Pt^0 metal sites were very active for FUR hydrogenation. However, they only presented reduced activity compared to Pd^0 sites because of differences in the adsorption energy of the FUR molecule [129]. In turn, a major issue on Pt^0 sites is the interaction with FA, allowing a total reduction to THFA [129]. Therefore, similar to Pd catalysts, the recent upgrades on FA formation rely on modifications on support or a bimetallic combination.

Tolek et al. (2021) pointed out that Pt/TiO_2 catalysts reduced at temperatures up to 500 ^oC led to Pt-TiO_x interface sites with SMSI. Those TiO_x-covered sites led to increased FA yield on FUR reduction – *ca.* 80% [130]. Furthermore, the Co addition on Pt/TiO_2 structure created higher amounts of anatase phase and increased the Pt dispersion on the catalytic surface, also improving FA yield to 98% [130]. According to the authors, the presence of cobalt promoted the rehybridization of d-orbitals in Pt sites modifying adsorption. Besides, Zahid et al. (2021) also confirmed improvements on mixture of Pt and Co for FUR hydrogenation. The research concluded that the incorporation of Co created a charge transference between both metals, improving FA selectivity [131]. Finally, it was reported that on bimetallic Pt-Co catalysts, the first sites were responsible for H_2 dissociation, whereas the second ones created LAS (Co^{2+}) for carbonyl adsorption [132]. Therefore, the proposal of second base metal on Pt solids has been improving the selective hydrogenation of FUR into FA.

3.4.2 Nickel (Ni)

Ni catalysts were reported as less expensive FUR hydrogenation options than Pd and Pt [129]. In contrast, Ni/C catalysts could not allow FA synthesis at temperatures up to 120 ^oC. In fact, the hydrogenation of the C=O aldehyde bond was initiated at 150 ^oC, but Ni was very selective for 2-MF at 200 ^oC [129]. Furthermore, several literature reports issues on Ni catalysts for FA production. As example, elevated Ni contents (above 10 wt.%) curbed the activity for FA production due to larger particles and Ni agglomeration [133]. Wang et al. (2018) also pointed out issues on NiO particles that may act as LAS and promote more production of 2-MF [134]. Besides, the presence of NiO sites were linked to the adsorption of organic species and loss of performance in FA synthesis [135]. Concerning Ni^0 sites, the non-uniformity promoted excessive hydrogenation and hydrogenolysis of FA into THFA and CPO [136]. Also, Ni^0 sites were not stable and presented leaching problems on FUR reduction in the liquid phase [134]. So, despite its hydrogenation capacity, the lack of selectivity and the presence of deoxygenation to 2-

MF are obstacles for Ni catalysts. Recent studies have however demonstrated improvements of Ni solids performance for FA production from FUR.

Kamble et al. (2021) reported that methanol as a solvent for Ni/bentonite catalysts improved the selective of FUR reduction. According to the research, the η_2-(C,O) adsorption mode with methanol could produce hydroxyalkyl species that favored FA production in a MPV route [137]. Bretzler et al. (2021) confirmed that THF suppressed the ring opening to 1,2-pentanediol compared to isopropanol. They also pointed out that Ni supported on W_xC solids promoted the ring opening of FA due to the oxophilic nature of carbides [138]. Another recent work showed that the insertion of Re on Ni/C enhanced metal dispersion and also prevented strong interactions of furan ring and adsorbed H_2, increasing FA yield [139]. Therefore, the recent works aimed for bimetallic combinations of Ni catalysts and solvents that decreased further FA conversions.

3.4.3 Ruthenium (Ru)

The Ru^0 site presented low activity for total hydrogenation of FUR to THFA in the range of 100 to 200 ^oC, due to elevated attraction between furan ring and metal [129]. In fact, the mentioned issue for reduction of furan ring provided the highest FA selectivity at 150 ^oC for Ru solids compared to Pd, Pt, Re, Rh, Ni and Cu [129]. This is also reinforced by the use of Ru as the main catalyst for the partial hydrogenation of benzene (BEN) to cyclohexene (CHE) [140]. However, monometallic Ru-based catalysts presented several problems on FUR conversion to FA.

For instance, it was reported that Ru catalysts presented successive loss of performance for both FUR conversion and FA selectivity after reaction cycles [141,142]. According to the studies, the Ru^0 site provided irreversible chemical adsorption of FA molecule [141,142]. Furthermore, the particle size of Ru was also crucial for shifting FA synthesis. Durndell et al.(2019) discovered that particle sizes superior to 10 nm on Ru/SiO_2 catalysts favored FA production instead of furan [143]. On the contrary, smaller Ru particles had unsaturated corners and edge sites, promoting FUR decarbonylation to furan and the η_2-(C,O) adsorption mode [143]. In order to overcome those problems, recent literature works studied the influence of support and the stabilization of Ru particles during FA conversion.

Music et al. (2022) verified the influence of phosphorous acid treatment on ZrO_2 supports on Ru catalysts. According to the research, weak and medium acid sites improved the formation of FA, whereas the strong ones damaged FA production. Besides,

the strong sites increased the opening of FUR ring, generating cyclopentanone and 1,2-pentanediol. In addition, the performance of Ru was improved on phosphated zirconia due to the incorporation of medium sites and also structural disorder, improving Ru activation [144]. The study also pointed out that the LAS close to metal particles could activate carbonyl groups properly and improve FA synthesis [144]. Also recently, the combination of oxygen vacancies and enhanced hydrogen spillover from Ru nanoparticles to the support have been credited for rendering highly effective catalysts, reaching high FUR conversion and up to 99% FA selectivity [145] r. Another recent article concluded that stabilizing Ru nanoparticles immobilized by ionic liquids could increase the selectivity to FA, improving hydrogenation routes. Therefore, new studies on Ru catalysts aim to modify support or stabilize the metal sites for robust FA synthesis [146].

3.4.4 Cobalt (Co) and Iron (Fe)

Cobalt and iron are non-noble metals exploited in FUR reduction to FA. However, their use is more common in oxidation studies than hydrogenation routes once some problems persist on those metals. First, the elevated oxidation degree provided issues because of the instability of Co^0 particle [147]. Mejía et al. (2017) reported temperatures higher than 600 ^oC to reduce active phases of Co/Nb_2O_5 catalysts [148]. Furthermore, the performance of Co/SiO_2 catalysts was curbed after several cycles due to poisoning and also elevated adsorption of carbon compounds [149]. Then, as well as in noble metals, the solutions for improvements on catalyst performance are based on bimetallic metal sites and modifications of supports [147].

In the support modifications, Xu et al. (2020) synthesized Co and Fe catalysts supported on N-doped carbon. The Co solid could achieve *ca.* 99% of FA yield, whereas Fe catalyst had 18%. The performance for hydrogenation was attributed to the existence of basic sites on the support that activated FUR conversion to FA with the absence of hydrogen and Co metal phase. In turn, the reason for the lower activity of Fe solid was attributed to the formation of furfuryl formate, a side product from FUR [147].

In bimetallic species, it was reported that the addition of Co in Ru/C improved the selective hydrogenation of C=O aldehyde bond. Gao et al. (2016) pointed out that Co-Ru/C solid created both Co^{2+} and $Ru^{\delta+}$ species on the surface, interacting with the aldehyde bond whereas Ru^0 promoted its hydrogenation [150]. The activation energy calculation for FUR reduction in liquid phase was about 58 kJ/mol, one of the lowest

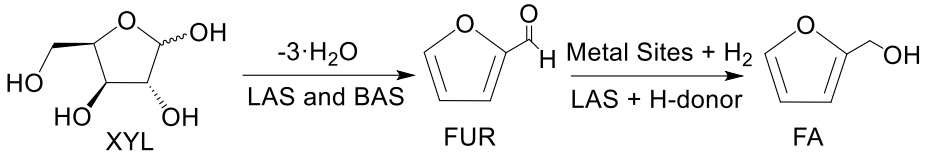
values reported on literature [150]. In another study, the incorporation of iron into the structure improved the activity of Pt (111) crystalline plan on Pt-Fe catalysts, leading to an η_1-(C,O) adsorption coordination [127]. Furthermore, adding Co in a CuAl alloy produced stronger LAS, increasing FA formation and 2-MH in the hydrogenolysis route, which corroborates the results that stronger sites damaged FA formation [144,151]. Then, changes in the conformation of the support and the addition of a second or even third metal phase improved the performance of Co and Fe catalysts.

4. DIRECT UPGRADE OF XYLOSE TO FURFURYL ALCOHOL IN THE LIQUID PHASE

4.1. Principles and Challenges for FA synthesis from XYL

Given the XYL dehydration and FUR hydrogenation in the liquid phase, it is possible to connect both routes. In other words, the production of FA is conducted with XYL as the main substrate. During this conversion, LAS and BAS develop the XYL dehydration to FUR. Next, the LAS sites and H-donor or metal sites and H_2 carry out the conversion of FUR to FA (Figure 12).

Figure 12 – Sites used in direct FA production from XYL – Adapted from [152].



This direct approach is particularly interesting considering all recent efforts on process intensification whereby more efficient and competitive technologies are pursued. Indeed, many relevant issues concerning energy consumption, waste generation and process sustainability process can be dealt with in such more compact process configuration.

Nonetheless, accomplishing high productivity is still of foremost importance and, therefore, aside for the problems from the XYL and FUR routes, like HUM and resins productions, the direct path is even more challenging. For example, if the XYL molecule is not protected, there will be a direct reduction of XYL to xylitol (XOL) that cannot be converted to FUR and FA. As expressed in Figure 2, the isomerization of XYL to xylulose does not improve either the FA formation, and in some cases, the opening of the furan ring curbs the selectivity to FA [153–159].

The literature reported several strategies for the design of systems for direct FA synthesis. First, a biphasic semi-batch reactor can be used to extract FUR and a tubular converter hydrogenates FUR to FA [160]. Second, a catalytic bed can also contain two catalysts for FUR and FA production, as reported by Cui et al. (2016) [161]. Third, a biphasic batch reactor with H_2 gas can also be tested, where the pentose is dehydrated in water and the non-polar phase extracts FUR for its reduction [162,163]. Finally, the conception of a multifunctional catalyst may also work on a homogeneous system for FA

production [153–159,164,165]. The further section will describe the advances in this research field.

4.2. Recent Advances in FA synthesis from XYL

The use of catalytic foams was explored for the XYL upgrade to FA in reaction media [162,163]. As first remark, Amberlyst-15 was used for XYL dehydration and Ru/C for FUR hydrogenation [162]. It was established that the composition of the liquid phase was crucial for the XYL upgrade in batch reactors. The monophasic water medium did not protect XYL molecule, producing elevated contents of XOL instead of FUR [162]. The phenomenon warned to the control of both dehydration and hydrogenation rates. On the contrary, a reaction medium with of water and organic solvent displayed different outcomes. The authors confirmed that cyclohexane and 2-MTHF suppressed the XYL hydrogenation to XOL and allowed the conversion of FUR to THFA [162]. In addition, the research determined that the hydrophobicity of the organic solvent was important for the control of XYL upgrade to further products [162]. The elimination of FUR side reactions was also linked to the same organic solvents, demonstrating the importance of proper FUR extraction [163].

The use of isopropanol as an auxiliary solvent in water media prevented side reactions from FUR molecule [153]. An optimal proportion of (1:3) between H_2O and isopropanol was stated, because lower ratios allowed to more XYL isomerization [153]. Also, the inactivation of LAS after several cycles showed the influence of water on direct FA synthesis [157]. According to the study, more FUR was produced instead of FA, damaging MPV conversion [157]. Moreover, the FA formation was reported reaching higher levels in THF and acetone than water, indicating the reduced protection of XYL molecule in water [158]. Therefore, elevated contents of H_2O in the reaction media might inactivate LAS because of attaching and adsorption [157,158].

Peng et al. (2020) used $H_4SiW_{12}O_{40}$, a commercial heteropolyacid, to carry out the direct conversion of XYL to FA. According to the research, the addition of tert-butanol to the reaction system protected the FA molecule of further degradation steps [166]. In addition, the glycosylation of XYL was minimized because of the hydrophobicity and steric hindrance of the tertiary alcohol. Furthermore, when formic acid was used as H-donor, the FA yield from XYL was improved to 90%. One possible reason is the generation of formic acid by the acid dehydration of tert-butanol using H^+ from the cited acid [166]. Together with the stability of tet-butanol, the XYL dehydration

was catalyzed by the LAS and the BAS on the heteropolyacid. In addition, the W atom adsorbs the H for FA production from FUR [166]. In regard to the activation energies, the proposed system had 85 kJ/mol from XYL to FUR, a lower value compared to 130 kJ/mol over water medium [167]. Therefore, the system comprised by tert-butanol and formic acid act as co-solvent and proton donor for the production of FA from XYL [166].

Aside for the type of solvents, the nature of sites is crucial in direct FA synthesis from XYL. First, it was concluded that isolated metal centers allowed direct conversion of XYL to XOL, but not to FA [154,155]. On the XYL dehydration route, the acid sites were responsible for FUR production [155]. In second place, the excess of acid groups loading curbed the FA synthesis and increased FUR yield [154,165], leading to the conclusion that the catalytic sites should not be isolated. Therefore, the design of vicinity between metal and acid sites was necessary to optimize the XYL to FA route in metal-supported catalysts [154].

Besides metal catalysts, zeolites produced FA from XYL on a metal-free approach [156,159]. As well as on metals, the vicinity of BAS and LAS sites was also important for FA production once desorption of FUR should be avoided. Furthermore, the balance between water-tolerant LAS and BAS provided different insights in the MPV route of XYL to FA. Higher BAS contents shifted the FA conversion to LA in an acid-catalyzed route. Therefore, an ideal proportion of water-tolerant LAS and BAS was required for the metal-free route [159].

As a final remark, Deng et al. (2020) studied the influence of pore sizes on the direct conversion of XYL to FA [165]. On Cu/SBA-15 solids, pores up to 120 Å decreased the carbon balance and FA production due to a combined effect of higher XYL conversion and diffusion of molecules. In turn, minor pores (about 40 Å) improved the FA formation and reduced the XOL production [165]. In short, the equilibrium of pore sizes is important for FA production from XYL.

To conclude, selected results of FA production from XYL were summarized in Table 2.

Table 2 – Researches in XYL upgrade to FA in phase with highest reported FA yield.

System	Solvents	T (ºC)	pH_2 (bar)	Y_{FA} (%)	Ref.
$Pt/SiO_2 + ZrO_2\text{-}SO_4$	H_2O/Isopropanol	130	-	33	[153]
$Pt/ZrO_2\text{-}SO_4$	H_2O/Isopropanol	130	30	16	[154]
[Al]-SBA-15	H_2O/Isopropanol	130	-	20	[157]
Zeolite beta	H_2O/Isopropanol	130	-	80	[156]
Zr-BEA zeolites	H_2O/Isopropanol	130	-	10	[168]
Pd/Nb_2O_5	H_2O/THF	130	30	23	[158]
$Cu/SBA\text{-}15\text{-}SO_3H$	H_2O/1-butanol	130	30	60	[165]
$H\beta/CuO/ZnO/Al_2O_3$*	H_2O/GBL	150	10	87	[161]
Co N-doped carbon	H_2O/1,4-dioxane	160	-	70	[164]

*: operation in continuous mode, -: absence of gaseous H_2

5. CONCLUSIONS AND FUTURE TRENDS

Along this contribution, the processes for XYL dehydration, FUR hydrogenation and direct FA synthesis from XYL were reviewed. The dehydration of XYL produces FUR in liquid phase. The LAS isomerizes XYL, and the BAS converts the isomers to FUR. However, the proportion of LAS/BAS and the strength of those cites is crucial for FUR production in heterogeneous catalysts. Strong LAS and BAS produce more HUM, decreasing FUR yield and also blocking catalytic sites. Furthermore, the excess of LAS curbs FUR yield whereas weak/medium sites improve it. Therefore, an optimum ratio and strength of LAS/BAS sites must be accounted for catalyst design.

Both solvents and co-solvents also determine the proper conversion of XYL to FUR in liquid phase. For example, water induces to more HUM formation and also deactivation of LAS on heterogeneous solids. Then, the use of another substance to extract or protect FUR molecule for side-reactions is recommended. In this sense, a new class of solvents has emerged, especially with alcohols and GVL. In water mixtures, isopropanol and n-butanol prevent FUR side reactions and GVL activates LAS and BAS properly during XYL dehydration. Regarding new studies, many upgrades occurred in XYL dehydration. The surface modification of heterogeneous catalyst has providing new ideas for FUR synthesis. SO_3H groups improve FUR production and may also act as BAS. In addition, the use of materials with water-tolerant LAS also provided more activity for FUR synthesis. Finally, the design of tubular reactors and process simulation has helped to scale-up the FUR production with sustainable process in the future.

The FUR reduction to FA can occur with H_2 gas or without an external source of H (MPV approach). The latter is the major upgrade in FA production studies. Normally isopropanol has been used as sacrificial alcohol for H donation, because water leaded to more CPO and LA production. Furthermore, the nature of metals is also important for FA production. Despite the lack of selectivity for C=C and C=O bonds, Pd^0 and Pt^0 lead to elevated hydrogenation rates. Similar phenomenon also occurs over Ni^0. Furthermore, base metals incorporation (Co and Fe) has helped to increase dispersion and change synergy in bimetallic combinations. As new areas, the surface modification of support with basic sites improves the understanding of MPV reactions. In addition, DFT studies provide new comprehension concerning interaction of FUR with metal particles.

Many works had performed the direct upgrade of XYL to FA in the same reaction medium, with a sequence of dehydration and reduction routes. Catalysts with metal, LAS,

and BAS sites can convert directly XYL to FA in the presence of H_2. However, some features are necessary for the design. The construction of solids with vicinal acid and metal sites converts XYL to FA more efficiently. After all, clustered metal sites lead to XOL directly from XYL and the excess of acid sites produces more FUR instead of FA. In addition, new researches are focused on the direct FA synthesis from XYL with the absence of metal sites, especially on zeolites. Either way, the demand for more advanced structured catalysts is foreseen. Process-driven new catalyst architectures seem to be a way to increase the resistance of metal-based systems to leaching, particularly in water-containing reaction media.

Among the further perspectives, the use of eutectic solvents in XYL dehydration can help to a transition from bench scale to industrial processes. Furthermore, the search for green and environmentally friendly solvents remains both for FUR and for FA production. Catalysts that curb the production of HUM and resins will reduce the cost in industrial applications. In addition, new studies on continuous production of FUR and FA will help in scale-up of XYL dehydration and FUR hydrogenation.

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REFERENCES

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

[2] European Commission, Off. J. Eur. Union 2021 (2021) 17.

[3] U.S. Department of Agriculture: Commodity Credit Corporation and Farm Service Agency, (2010) 1–43.

[4] B.M. of M. and Energy, (n.d.).

[5] S.G. Wettstein, D. Martin Alonso, E.I. Gürbüz, J.A. Dumesic, Curr. Opin. Chem. Eng. 1 (2012) 218–224.

[6] P. Bhaumik, P.L. Dhepe, Catal. Rev. - Sci. Eng. 58 (2016) 36–112.

[7] G.V. Research, Furfural Market Size, Share & Trends Analysis Report By Process (Quaker Batch Process, Chinese Batch Process), By Raw Material (Corncob, Sugarcane Bagasse), By Application, By End Use, And Segment Forecasts, 2022 - 203, 2021.

[8] J.P. Lange, E. Van Der Heide, J. Van Buijtenen, R. Price, ChemSusChem 5 (2012) 150–166.

[9] M. Dashtban, A. Gilbert, P. Fatehi, J. Sci. Technol. For. Prod. Process. 2 (2012) 44–53.

[10] J.F.L. Silva, M.A. Selicani, T.L. Junqueira, B.C. Klein, S. Vaz, A. Bonomi, Brazilian J. Chem. Eng. 34 (2017) 623–634.

[11] K.E. Zeitsch, ed., Sugar Series - The Chemistry and Technology of Furfural and Its Many by-Products, Elsevier Science, 2000.

[12] H.J. Brownlee, Process for Producing Furfural, 2,140,572, 1938.

[13] A.P. Dunlop, Production of Furfural, 2,536,732, 1951.

[14] H. Adkins, R. Connor, Method of Hydrogenation of Furfural to Furfuryl Alcohol, 2,094,975, 1937.

[15] F.N. Peters Jr., Method for the Reduction of Furfural and Furan Derivatives, 2,082,025, 1937.

[16] P. Mastagli, Method for the Catalytic Hydrogenation of Furfural, 2,763,666, 1956.

[17] S. Swadesh, Catalytic Production of Furfuryl Alcohol and Catalyst Therefor, 2,754,304, 1956.

[18] M.R. Nimlos, X. Qian, M. Davis, M.E. Himmel, D.K. Johnson, J. Phys. Chem. A 110 (2006) 11824–11838.

[19] H. Rasmussen, H.R. Sørensen, A.S. Meyer, Carbohydr. Res. 385 (2014) 45–57.

[20] X. Fang, M.P. Andersson, Z. Wang, W. Song, S. Li, Carbohydr. Res. 511 (2022) 108463.

[21] S.J. Eitelman, D. Horton, Carbohydr. Res. 341 (2006) 2658–2668.

[22] M. Möller, U. Schröder, RSC Adv. 3 (2013) 22253–22260.

[23] Y. Zhu, W. Li, Y. Lu, T. Zhang, H. Jameel, H.M. Chang, L. Ma, RSC Adv. 7 (2017) 29916–29924.

[24] J. Köchermann, J. Mühlenberg, M. Klemm, Ind. Eng. Chem. Res. 57 (2018) 14417–14427.

[25] K. Lamminpää, J. Ahola, J. Tanskanen, Ind. Eng. Chem. Res. 51 (2012) 6297–6303.

[26] K.R. Enslow, A.T. Bell, RSC Adv. 2 (2012) 10028–10036.

[27] L. Filiciotto, A.M. Balu, J.C. Van der Waal, R. Luque, Catal. Today 302 (2018) 2–15.

[28] N.W. Dulie, B. Woldeyes, H.D. Demsash, A.S. Jabasingh, Waste and Biomass Valorization (2020).

[29] K.R. Enslow, A.T. Bell, ChemCatChem 7 (2015) 479–489.

[30] K. Dalvand, J. Rubin, S. Gunukula, M. Clayton Wheeler, G. Hunt, Biomass and Bioenergy 115 (2018) 56–63.
[31] R. Weingarten, G.A. Tompsett, W.C. Conner, G.W. Huber, J. Catal. 279 (2011) 174–182.
[32] B. Pholjaroen, N. Li, Z. Wang, A. Wang, T. Zhang, J. Energy Chem. 22 (2013) 826–832.
[33] A.C. Doiseau, F. Rataboul, L. Burel, N. Essayem, Catal. Today 226 (2014) 176–184.
[34] X. Hu, R.J.M. Westerhof, D. Dong, L. Wu, C.Z. Li, ACS Sustain. Chem. Eng. 2 (2014) 2562–2575.
[35] D.W. Green, R.H. Perry, Perry's Chemical Engineers' Handbook, McGraw-Hill, 2008.
[36] Q. Lin, S. Liao, L. Li, W. Li, F. Yue, F. Peng, J. Ren, Green Chem. 22 (2020) 532–539.
[37] M. Kosmulski, Adv. Colloid Interface Sci. 238 (2016) 1–61.
[38] K. Nakajima, Y. Baba, R. Noma, M. Kitano, J. N. Kondo, S. Hayashi, M. Hara, J. Am. Chem. Soc. (2011).
[39] N.K. Gupta, A. Fukuoka, K. Nakajima, ACS Catal. 7 (2017) 2430–2436.
[40] M.J.C. Molina, M.L. Granados, A. Gervasini, P. Carniti, Catal. Today 254 (2015) 90–98.
[41] X. Hu, C. Lievens, C.-Z. Li, ChemSusChem 5 (2012) 1427–1434.
[42] J. Iglesias, J.A. Melero, G. Morales, M. Paniagua, B. Hernández, ChemCatChem 8 (2016) 2089–2099.
[43] J. Köchermann, J. Schreiber, M. Klemm, ACS Sustain. Chem. Eng. (2019) acssuschemeng.9b01697.
[44] C. Wu, W. Yuan, Y. Huang, Y. Xia, H. Yang, H. Wang, X. Liu, Catal. Letters 147 (2017) 953–963.
[45] M.A. Mellmer, C. Sener, J.M.R. Gallo, J.S. Luterbacher, D.M. Alonso, J.A. Dumesic, Angew. Chemie - Int. Ed. 53 (2014) 11872–11875.
[46] O.H. Pardo Cuervo, G.P. Romanelli, J.A. Cubillos, H.A. Rojas, J.J. Martínez, ChemistrySelect 5 (2020) 4186–4193.
[47] C. Moreau, R. Durand, D. Peyron, J. Duhamet, P. Rivalier, Ind. Crops Prod. 7 (1998) 95–99.
[48] A.S. Dias, M. Pillinger, A.A. Valente, J. Catal. (2005).
[49] H.S. Pawar, ChemistrySelect 5 (2020) 916–923.
[50] P. Bhaumik, P.L. Dhepe, ChemCatChem 9 (2017) 2709–2716.
[51] M. Hronec, K. Fulajtárová, Catal. Today 324 (2019) 27–32.
[52] S. Kaiprommarat, S. Kongparakul, P. Reubroycharoen, G. Guan, C. Samart, Fuel 174 (2016) 189–196.
[53] X. Guo, F. Guo, Y. Li, Z. Zheng, Z. Xing, Z. Zhu, T. Liu, X. Zhang, Y. Jin, Appl. Catal. A Gen. 558 (2018) 18–25.
[54] A. Parejas, V. Montes, J. Hidalgo-Carrillo, E. Sánchez-López, A. Marinas, F. Urbano, Molecules 22 (2017) 2257.
[55] M. Paniagua, S. Saravanamurugan, M. Melian-Rodriguez, J.A. Melero, A. Riisager, ChemSusChem 8 (2015) 1088–1094.
[56] U. Azzena, M. Carraro, L. Pisano, S. Monticelli, R. Bartolotta, V. Pace, ChemSusChem 12 (2019) 40–70.
[57] M.J. Campos Molina, R. Mariscal, M. Ojeda, M. López Granados, Bioresour. Technol. 126 (2012) 321–327.
[58] M.J. Campos-Molina, J.J. Corral-Pérez, R. Mariscal, M.L. Granados, Catal. Today

279 (2017) 155–163.
[59] Y. Wang, F. Delbecq, W. Kwapinski, C. Len, Mol. Catal. 438 (2017) 167–172.
[60] Y. Wang, T. Len, Y. Huang, A. Diego Taboada, A.N. Boa, C. Ceballos, F. Delbecq, G. Mackenzie, C. Len, ACS Sustain. Chem. Eng. 5 (2017) 392–398.
[61] J.M.R. Gallo, D.M. Alonso, M.A. Mellmer, J.H. Yeap, H.C. Wong, J.A. Dumesic, Top. Catal. 56 (2013) 1775–1781.
[62] X. Li, Q. Liu, C. Luo, X. Gu, L. Lu, X. Lu, ACS Sustain. Chem. Eng. 5 (2017) 8587–8593.
[63] X. Li, J. Yang, R. Xu, L. Lu, F. Kong, M. Liang, L. Jiang, S. Nie, C. Si, Ind. Crops Prod. 135 (2019) 196–205.
[64] C. Moreno-Marrodan, P. Barbaro, S. Caporali, F. Bossola, ChemSusChem 11 (2018) 3649–3660.
[65] W. Hui, Y. Zhou, Y. Dong, Z.J. Cao, F.Q. He, M.Z. Cai, D.J. Tao, Green Energy Environ. 4 (2019) 49–55.
[66] E.S. Morais, M.G. Freire, C.S.R. Freire, J.A.P. Coutinho, A.J.D. Silvestre, ChemSusChem 13 (2020) 784–790.
[67] R.C.G. Frem, G. Arroyos, B. Jader, S. Flor, R.C. Alves, G.N. Lucena, M. Caroline, Quim. Nova 41 (2018) 1178–1191.
[68] J. Jiang, O.M. Yaghi, Chem. Rev. 115 (2015) 6966–6997.
[69] A. Chatterjee, X. Hu, F.L.Y. Lam, Appl. Catal. A Gen. 566 (2018) 130–139.
[70] Y. Liu, C. Ma, C. Huang, Y. Fu, J. Chang, Ind. Eng. Chem. Res. 57 (2018) 16628–16634.
[71] H.Y. Luo, J.D. Lewis, Y. Román-Leshkov, Annu. Rev. Chem. Biomol. Eng. 7 (2016) 663–692.
[72] Z.C. Tang, D.H. Yu, P. Sun, H. Li, H. Huang, Bull. Korean Chem. Soc. 31 (2010).
[73] C. García-Sancho, I. Agirrezabal-Telleria, M.B. Güemez, P. Maireles-Torres, Appl. Catal. B Environ. 152–153 (2014) 1–10.
[74] T. Kitano, T. Shishido, K. Teramura, T. Tanaka, ChemPhysChem 14 (2013) 2560–2569.
[75] K. Nakajima, T. Fukui, H. Kato, M. Kitano, J.N. Kondo, S. Hayashi, M. Hara, Chem. Mater. (2010).
[76] T. Kitano, T. Shishido, K. Teramura, T. Tanaka, Catal. Today 226 (2014) 97–102.
[77] K.M.A. Santos, E.M. Albuquerque, G. Innocenti, L.E.P. Borges, C. Sievers, M.A. Fraga, ChemCatChem 11 (2019) 3054–3063.
[78] T. V. dos Santos, D.O. da Silva Avelino, D.B.A. Pryston, M.R. Meneghetti, S.M.P. Meneghetti, Catal. Today 394–396 (2022) 125–132.
[79] T. Iizuka, K. Ogasawara, K. Tanabe, Bull. Chem. Soc. Jpn. 56 (1983) 2927–2931.
[80] V. Lebarbier, M. Houalla, T. Onfroy, Catal. Today 192 (2012) 123–129.
[81] G.S. Foo, D. Wei, D.S. Sholl, C. Sievers, ACS Catal. 4 (2014) 3180–3192.
[82] A.T.Y. Wolek, M.A. Ardagh, H.N. Pham, S. Alayoglu, A.K. Datye, J.M. Notestein, J. Catal. 394 (2021) 387–396.
[83] N.W. Dulie, B. Woldeyes, H.D. Demsash, Int. J. Biol. Macromol. 171 (2021) 10–16.
[84] V. Krzelj, D.P. Ferrandez, M.F. Neira D'Angelo, Catal. Today 365 (2021) 274–281.
[85] P. Liu, S. Shi, R. Wei, L. Gao, J. Zhang, G. Xiao, ChemistrySelect 8 (2023).
[86] W. Guo, H.C. Bruining, H.J. Heeres, J. Yue, AIChE J. 68 (2022).
[87] H.-X. Lu, W.-Y. Yang, Y.-X. Shi, H.-B. Wang, H. Mao, L. Sang, Z.-P. Zhao, Chem. Eng. Sci. 266 (2023) 118256.
[88] K. Gairola, I. Smirnova, Bioresour. Technol. 123 (2012) 592–598.

[89] A.R.C. Morais, R. Bogel-Lukasik, Green Chem. 18 (2016) 2331–2334.
[90] J. An, G. Lee, J.-M. Ha, M.-J. Park, Biofuels 13 (2022) 63–67.
[91] R. Albilali, M. Douthwaite, Q. He, S.H. Taylor, Catal. Sci. Technol. 8 (2018) 252–267.
[92] G. Giorgianni, S. Abate, G. Centi, S. Perathoner, S. Van Beuzekom, S.H. Soo-Tang, J.C. Van Der Waal, ACS Sustain. Chem. Eng. 6 (2018) 16235–16247.
[93] S. Chen, R. Wojcieszak, F. Dumeignil, E. Marceau, S. Royer, Chem. Rev. 118 (2018) 11023–11117.
[94] R. V. Sharma, U. Das, R. Sammynaiken, A.K. Dalai, Appl. Catal. A Gen. 454 (2013) 127–136.
[95] J. Hidalgo-Carrillo, A. Parejas, M.J. Cuesta-Rioboo, A. Marinas, F.J. Urbano, Catalysts 8 (2018).
[96] M.J. Gilkey, B. Xu, ACS Catal. 6 (2016) 1420–1436.
[97] Z. An, J. Li, Green Chem. 24 (2022) 1780–1808.
[98] R. López-Asensio, J.A. Cecilia, C.P. Jiménez-Gómez, C. García-Sancho, R. Moreno-Tost, P. Maireles-Torres, Appl. Catal. A Gen. 556 (2018) 1–9.
[99] W.R. Silva, E.Y. Matsubara, J.M. Rosolen, P.M. Donate, R. Gunnella, Mol. Catal. 504 (2021) 111496.
[100] T. Ennaert, J. Van Aelst, J. Dijkmans, R. De Clercq, W. Schutyser, M. Dusselier, D. Verboekend, B.F. Sels, Chem. Soc. Rev. 45 (2016) 584–611.
[101] M. Hronec, K. Fulajtarová, Catal. Commun. (2012).
[102] M. Hronec, K. Fulajtarová, T. Liptaj, Appl. Catal. A Gen. 437–438 (2012) 104–111.
[103] R. Ma, X.-P. Wu, T. Tong, Z.-J. Shao, Y. Wang, X. Liu, Q. Xia, X.-Q. Gong, ACS Catal. 7 (2017) 333–337.
[104] K. Gupta, R.K. Rai, S.K. Singh, ChemCatChem 10 (2018) 2326–2349.
[105] X. Zhou, Z. Feng, W. Guo, J. Liu, R. Li, R. Chen, J. Huang, Ind. Eng. Chem. Res. 58 (2019) 3988–3993.
[106] W. Gong, C. Chen, H. Zhang, Y. Zhang, Y. Zhang, G. Wang, H. Zhao, Mol. Catal. 429 (2017) 51–59.
[107] F. Li, S. Jiang, J. Huang, Y. Wang, S. Lu, C. Li, New J. Chem. 44 (2019) 478–486.
[108] K. Alibegovic, D.G. Morgan, Y. Losovyj, M. Pink, B.D. Stein, N. V. Kuchkina, E.S. Serkova, K.E. Salnikova, Z.B. Shifrina, V.G. Matveeva, E.M. Sulman, L.M. Bronstein, ChemistrySelect 2 (2017) 5485–5491.
[109] Á. O'Driscoll, T. Curtin, W.Y. Hernández, P. Van Der Voort, J.J. Leahy, Org. Process Res. Dev. 20 (2016) 1917–1929.
[110] O'Driscoll, J.J. Leahy, T. Curtin, Catal. Today 279 (2017) 194–201.
[111] M.J. Taylor, L.J. Durndell, M.A. Isaacs, C.M.A. Parlett, K. Wilson, A.F. Lee, G. Kyriakou, Appl. Catal. B Environ. 180 (2016) 580–585.
[112] P. Panagiotopoulou, N. Martin, D.G. Vlachos, J. Mol. Catal. A Chem. (2014).
[113] X. Hu, R.J.M. Westerhof, D. Dong, L. Wu, C.Z. Li, ACS Sustain. Chem. Eng. (2014).
[114] A. Fuente-Hernández, R. Lee, N. Béland, I. Zamboni, J.M. Lavoie, Energies 10 (2017).
[115] P.M. de Souza, L. Silvester, A.G.M. da Silva, C.G. Fernandes, T.S. Rodrigues, S. Paul, P.H.C. Camargo, R. Wojcieszak, Catalysts 9 (2019) 8–10.
[116] P.N. Romano, J.M.A.R. de Almeida, Y. Carvalho, P. Priecel, E. Falabella Sousa-Aguiar, J.A. Lopez-Sanchez, ChemSusChem 9 (2016) 3387–3392.
[117] A.J. Garcia-Olmo, A. Yepez, A.M. Balu, A.A. Romero, Y. Li, R. Luque, Catal. Sci. Technol. 6 (2016) 4705–4711.

[118] W. Ouyang, A. Yepez, A.A. Romero, R. Luque, Catal. Today 308 (2018) 32–37.
[119] Y. Wang, P. Prinsen, K.S. Triantafyllidis, S.A. Karakoulia, P.N. Trikalitis, A. Yepez, C. Len, R. Luque, ACS Sustain. Chem. Eng. 6 (2018) 9831–9844.
[120] C.P. Jiménez-Gómez, J.A. Cecilia, R. Moreno-Tost, P. Maireles-Torres, Top. Catal. 60 (2017) 1040–1053.
[121] S. Chen, P.M. de Souza, C. Ciotonea, M. Marinova, F. Dumeignil, S. Royer, R. Wojcieszak, Appl. Catal. A Gen. 633 (2022) 118527.
[122] B. Liu, L. Cheng, L. Curtiss, J. Greeley, Surf. Sci. (2014).
[123] S. Bhogeswararao, D. Srinivas, J. Catal. (2015).
[124] N. Pino, S. Sitthisa, Q. Tan, T. Souza, D. López, D.E. Resasco, J. Catal. 350 (2017) 30–40.
[125] M. Pirmoradi, J.R. Kastner, Chem. Eng. J. 414 (2021) 128693.
[126] Z. Wang, X. Wang, C. Zhang, M. Arai, L. Zhou, F. Zhao, Mol. Catal. 508 (2021) 111599.
[127] L. Liu, H. Lou, M. Chen, Appl. Catal. A Gen. 550 (2018) 1–10.
[128] G.F. Tierney, S. Alijani, M. Panchal, D. Decarolis, M.B. Gutierrez, K.M.H. Mohammed, J. Callison, E.K. Gibson, P.B.J. Thompson, P. Collier, N. Dimitratos, E.C. Corbos, F. Pelletier, A. Villa, P.P. Wells, ChemCatChem 13 (2021) 5121–5133.
[129] R. Šivec, M. Huš, B. Likozar, M. Grilc, Chem. Eng. J. 436 (2022) 135070.
[130] W. Tolek, K. Khruechao, B. Pongthawornsakun, O. Mekasuwandumrong, F.J. Cadete Santos Aires, P. Weerachawanasak, J. Panpranot, Catal. Commun. 149 (2021) 106246.
[131] M. Zahid, J. Li, A. Ismail, F. Zaera, Y. Zhu, Catal. Sci. Technol. 11 (2021) 2433–2445.
[132] M.G. Dohade, P.L. Dhepe, Green Chem. 19 (2017) 1144–1154.
[133] L. Liu, H. Lou, M. Chen, Int. J. Hydrogen Energy 41 (2016) 14721–14731.
[134] Y. Wang, P. Prinsen, K.S. Triantafyllidis, S.A. Karakoulia, A. Yepez, C. Len, R. Luque, ChemCatChem 10 (2018) 3459–3468.
[135] J. He, L. Schill, S. Yang, A. Riisager, ACS Sustain. Chem. Eng. 6 (2018) 17220–17229.
[136] F. Hu, Y. Wang, S. Xu, Z. Zhang, Y. Chen, J. Fan, H. Yuan, L. Gao, G. Xiao, Catal. Letters 149 (2019) 2158–2168.
[137] P.A. Kamble, M.L. Kantam, V.K. Rathod, ChemistrySelect 6 (2021) 6601–6606.
[138] P. Bretzler, M. Huber, S. Nickl, K. Köhler, RSC Adv. 10 (2020) 27323–27330.
[139] C.R.A. de Abreu, P. Simon, R. Wojcieszak, P.M. de Souza, F.S. Toniolo, Top. Catal. 65 (2022) 902–914.
[140] L. Foppa, J. Dupont, Chem. Soc. Rev. 44 (2015).
[141] J.J. Musci, A.B. Merlo, M.L. Casella, Catal. Today 296 (2017) 43–50.
[142] C. Ramirez-Barria, M. Isaacs, K. Wilson, A. Guerrero-Ruiz, I. Rodríguez-Ramos, Appl. Catal. A Gen. 563 (2018) 177–184.
[143] L.J. Durndell, G. Zou, W. Shangguan, A.F. Lee, K. Wilson, ChemCatChem 11 (2019) 3927–3932.
[144] J.J. Musci, M. Montaña, A.B. Merlo, E. Rodríguez-Aguado, J.A. Cecilia, E. Rodríguez-Castellón, I.D. Lick, M.L. Casella, Catal. Today 394–396 (2022) 81–93.
[145] L.D. de Almeida, S.F. Bazan, P.L. Gastelois, M.A.S. Garcia, G.F. de Lima, V.W. Faria, M.A. Fraga, A.G.M. da Silva, P.A. Robles-Azocar, ACS Appl. Nano Mater. (2023).
[146] S. Doherty, J.G. Knight, T. Backhouse, T.S.T. Tran, R. Paterson, F. Stahl, H.Y.

Alharbi, T.W. Chamberlain, R.A. Bourne, R. Stones, A. Griffiths, J.P. White, Z. Aslam, C. Hardare, H. Daly, J. Hart, R.H. Temperton, J.N. O'Shea, N.H. Rees, Catal. Sci. Technol. 12 (2022) 3549–3567.
[147] L. Xu, R. Nie, X. Lyu, J. Wang, X. Lu, Fuel Process. Technol. 197 (2020) 106205.
[148] C. Hernández Mejía, J.H. den Otter, J.L. Weber, K.P. de Jong, Appl. Catal. A Gen. (2017).
[149] M. Audemar, Y. Wang, D. Zhao, S. Royer, F. Jérôme, C. Len, K. De Oliveira Vigier, Energies 13 (2020) 2–10.
[150] Z. Gao, L. Yang, G. Fan, F. Li, ChemCatChem 8 (2016) 3769–3779.
[151] M. Kalong, P. Hongmanorom, S. Ratchahat, W. Koo-amornpattana, K. Faungnawakij, S. Assabumrungrat, A. Srifa, S. Kawi, Fuel Process. Technol. 214 (2021) 106721.
[152] M.A. Fraga, R.F. Perez, Processo de Obtenção de Álcool Furfurílico Por Meio de Catalisadores Multifuncionais, BR 10 2013 025330-8 A2, 2015.
[153] R.F. Perez, M.A. Fraga, Green Chem. 16 (2014) 3942–3950.
[154] R.F. Perez, S.J. Canhaci, L.E.P. Borges, M.A. Fraga, Catal. Today 289 (2017) 273–279.
[155] S.J. Canhaci, R.F. Perez, L.E.P. Borges, M.A. Fraga, Appl. Catal. B Environ. 207 (2017) 279–285.
[156] P.N. Paulino, R.F. Perez, N.G. Figueiredo, M.A. Fraga, Green Chem. 19 (2017) 3759–3763.
[157] R.F. Perez, E.M. Albuquerque, L.E.P. Borges, C. Hardacre, M.A. Fraga, Catal. Sci. Technol. 9 (2019) 5350–5358.
[158] P.C. Oliveira, S.J. Canhaci, C.B. Gabriel, C.R. Moreira, A.M. Duarte de Farias, M.A. Fraga, Curr. Res. Green Sustain. Chem. 5 (2022).
[159] T.L. Coelho, B. Marinho, E.M. Albuquerque, M.A. Fraga, Catal. Sci. Technol. 10 (2020) 7165–7176.
[160] J.A. Dumesic, D.M. Alonso, J.Q. Bond, T. Root, M. Chia, Method to Produce, Recover and Convert Furan Derivatives from Aqueous Solutions Using Alkylphenol Extraction, US 8,389,749 B2, 2013.
[161] J. Cui, J. Tan, X. Cui, Y. Zhu, T. Deng, G. Ding, Y. Li, ChemSusChem 9 (2016) 1259–1262.
[162] V. V. Ordomsky, J.c. Schouten, J. Van Der Schaaf, T.A. Nijhuis, Appl. Catal. A Gen. 451 (2013) 6–13.
[163] V. V. Ordomsky, J.C. Schouten, J. van der Schaaf, T.A. Nijhuis, Chem. Eng. J. 231 (2013) 12–17.
[164] L. Xu, R. Nie, H. Xu, X. Chen, Y. Li, X. Lu, Ind. Eng. Chem. Res. 59 (2020) 2754–2760.
[165] T. Deng, G. Xu, Y. Fu, Chinese J. Catal. 41 (2020) 404–414.
[166] L. Peng, M. Wang, H. Li, J. Wang, J. Zhang, L. He, Green Chem. 22 (2020) 5656–5665.
[167] V. Krzelj, J. Ferreira Liberal, M. Papaioannou, J. van der Schaaf, M.F. Neira d'Angelo, Ind. Eng. Chem. Res. 59 (2020) 11991–12003.
[168] E.M. Albuquerque, P.N. Paulino, R. Sadek, L. Valentin, J.-M. Krafft, S. Dzwigaj, M.A. Fraga, Appl. Catal. A Gen. 604 (2020) 117766.