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Furfural and 5-(hydroxymethyl)furfural (HMF): two pivotal intermediates for bio-based chemistry

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Highlights

- Furfural and HMF offer rare opportunities for designing novel bio-based products and will play a central role in tomorrow's chemistry.
- The renewability benefit should not be overstated as it is only a part of the cumulative "carbon cost" of the derived chemicals.
- Progresses result from subtle combinations of catalyst design, solvent and process optimization, mechanistic studies and the use of cruder, cheaper raw material.
- Explorative synthetic chemistry using furfural and HMF must be developed for discovering new architectures with original molecular design, offering possible novel applicative properties and improved environmental impact.

Keywords: Furfural, HMF, bio-based chemistry; platform molecules; aldehydes; renewable

Abstract

Research on furfural and 5-(hydroxymethyl)furfural (HMF) concerns all fields of chemistry: catalysis, mechanistic studies, synthetic organic chemistry, materials sciences, chemical engineering. The purpose of this account is, by picking a selection of very recent literature, to show the vitality of the field and to illustrate how transdisciplinary approaches can help overcoming the strong overlap between catalysts, solvent and process issues. It highlights the necessity to encourage researches in two main directions, one being the optimization of the

access to industrially relevant targets, and the second being the commitment of synthetic organic chemist to explorative studies on new reactions and new architectures.

Introduction

A new chemical tree from C5-C6 carbohydrates via furfural and HMF is now established. These two furanic aldehydes offer rare opportunities for designing novel bio-based products exhibiting promising applications as commodities or specialty chemicals including monomers, solvents, fuels, and fine chemicals. [1-14]

Though renewability is an important point, its beneficial contribution (renewable *vs* fossil) to the overall products carbon footprint should not be overstated. All other contributions (reagents, catalysts, solvents, heat, separation, utilization of the product and its end of life) account indeed, to the major part of the cumulative “carbon cost”. This is why, in keeping with the modern vision of green chemistry and engineering, [15] the topic must be considered globally and address all issues, including cheaper and more sustainable raw materials, safer and cleaner processes, and diversification in molecular design of the derivatives.

The difficulty lies on the overlap between several key fundamental issues: adapting the catalyst to different starting resources, finding appropriate “catalyst/solvent” couples with higher “dehydration-isolation” efficiency, or looking for more selective and efficient subsequent transformations. In all of these directions, innovation results from a subtle combination of catalyst design, solvent and process optimization, and mechanistic considerations. Overall, several facets of green chemistry subtly overlap, such as catalyst design, use of non-edible biomass, clean solvent and processes, molecular design, selectivity, making this topic a fascinating school case.

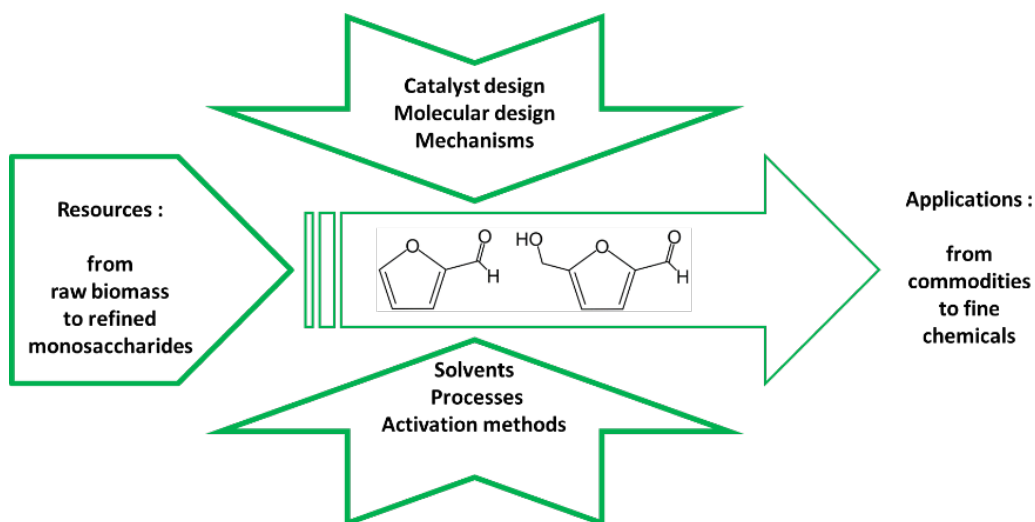


Figure 1. The overlapping challenges of furfural and HMF chemistries.

This short opinion account aims at highlighting first the variety of approaches by picking a selection of very recent papers exemplifying the “resource-catalyst-solvent” triple challenge of furfural and HMF synthesis. Next, among applications and uses, a focus is made on furfural-derived bio-based solvents and on HMF oxidations and reductions towards monomers. A short section also covers the bridge between C5-C6 chemistries. This account gives the viewpoint of synthetic organic chemists, stressing the benefits of the progress in the design of catalysts and processes, and encouraging further synthetic exploration for diversifying the realm of possible products and applications.

1. Furfural

1.1 Synthesis

Xylose is the substrate of choice for the synthesis of furfural. However, there are still some limitations to the efficacy of its dehydration to furfural, with selectivity issues due to the formation of humins necessitating to start from low xylose concentrations. Recent investigations have focused on the exploration of different catalysts, various media, and possible activation by additives.

Lam and coworkers [16] reported that activated coal fly ash at 170 °C allowed achieving 85% conversion of D-xylose and 62% yield of furfural (even 68% in the presence of NaCl). This cheap Brønsted acidic catalyst could be reused up to 6 times. A bimetallic heteropolyacid ($\text{Sn}_{0.625}\text{Cs}_{0.5}\text{PW}$) allowed Guo and coll. [17] to obtain furfural in 63 % yield from D-xylose at 200 °C in a DMSO/H₂O mixture for 3 h. The catalyst could be supported on a chitosan-derived support while keeping the same activity. Lam and coworkers [18] demonstrated the first use of

a modified Metal Organic Framework (MOF), MIL-101 (Cr), for the dehydration of xylose to furfural. Subsequently, Chang and coll. [19] obtained the furfural in 71% yield from xylose. Furfural rapidly degrades through resinification and condensation reactions under traditional diluted acid conditions, resulting in yields generally below 55% in industrial production. [6,20] This is overcome by the use of a biphasic system allowing to extract furfural from the reactive phase. The DMSO/H₂O system was shown by Guo and coll. [17], Dumesic and coll. [21] and others to efficiently yield furfural from D-xylose, DMSO allowing suppressing side reactions. [22,23] Bogel-Lukasik and Morais [24] obtained furfural in 70 mol% yield from xylose in a water-THF biphasic medium, using high-pressure CO₂ within 1 hour at 180 °C. Vigier and coworkers [25] showed that the use of the biphasic mixture of aqueous choline chloride (ChCl_{aq}) and methylisobutylketone (MIBK) led to 75% isolated yield of furfural with 50 wt% conversion of a concentrated xylose feed. They suggested the stabilization of both xylose and furfural by the solvent system and the implication of an intermediate choline xyloside exhibiting a faster dehydration than xylose. Wan and coworkers [26] showed that lignocellulose also could be fractionated and converted in a one-pot reaction in ChCl_{aq}/MIBK. Using the 1-butyl-3-methylimidazolium (BMIM) chloride /FeCl₃ system, combining an ionic liquid and a metal salt in a butanone/water (4:1) mixture, Wang and coll. [27] reported a 97% xylose conversion and a 60% yield of furfural at 150 °C in 30 min. The use of resources less refined than xylose can help developing the C5/C6-furanic chemical tree. Thus, the processes must include the initial pretreatment step leading to the reactive monosaccharides. For this, catalysts such as a new-type of Na/Fe(1.42)-solid acid catalyst have been designed, allowing the conversion of cellulose into furfural (61%) at 550 °C as reported by Yang and coll. [28] while Zhang and coll. [22] developed a bifunctional carbonaceous solid acid catalyst (HSC-SO₃H) prepared by the hydrothermal carbonization and sulfonation of sucralose, achieving 91 mol% (21 wt%) yield of furfural directly from raw corncob after 30 min at 175°C in a γ -valerolactone (GVL) water mixture. Using the same medium under microwave conditions, Huang, Pan and co-workers [29] achieved 88 wt% yield of furfural from xylan, as compared to 63, 61 and 60 wt% yields from corncobs, bagasse and poplar powder, respectively. The study indicated that the furfural yield increased with the solvent dielectric constant (GVL > MIBK > 2-MeTHF > THF).

Several other agricultural residues have been investigated. For example, an oil palm frond, the carbohydrate-rich residue of the palm oil industry, was shown by Wu and coll. [30] to produce furfural in a modest 26% yield. Pinewood and eucalyptus sawdust were used by Tanksale and

coll. [31] for the production of furfural and HMF in 2-methyl tetrahydrofuran (2-MeTHF)/water in the presence of levulinic acid (LA) as the catalyst. For facilitating the early steps of the biomass transformation, Bizzi and coll. [32] proposed the ultrasound-assisted acid hydrolysis (UAAH) of several lignocellulosic materials, leading to furfural in yields ranging from 36 to 72 mg/g using a cup horn, with even higher yields when combining ultrasounds and deep eutectic solvents (DES).

1.2 Conversions of furfural to fine chemicals and bio-based solvents

While the access to furfural is already a mature field, its downstream chemical tree is still an open space from a synthetic organic chemist's viewpoint. The production of nitrogen-containing structures from furfural using reductive amination has been intensely studied due to the wide interest of potential derivatives in the polymer or surfactant businesses. Reductive amination can be achieved under several sets of conditions. For example, furfurylamine (FAM) was prepared in 91% yield by Kawanami, Chatterjee and co-workers [33] using 5% Rh/Al₂O₃ as the catalyst, with a high selectivity using NH₄OH and H₂ as the reducing agent. Hailes and coll. [34] investigated three transaminases TAmS (CV-Tam ArRMut11 Mv-Tam) for the amination of furfural and derivatives to access furfurylamines under ambient conditions. They obtained FAM in up to 92% yield from furfural. Recently, Zhang, Liu and co-workers [35] reported the efficient and recyclable Co@NC-800 catalyst for the synthesis of primary amines. Accordingly, FAM was prepared in 82% yield from furfural. Wischert, Jérôme and coworkers [36] reported an elegant sequence towards *m*-xylilenediamine from furfural and acrylonitrile through a 100% carbon-economical pathway involving a Diels-Alder/aromatization sequence. De Oliveira Vigier, Pera-Titus and coworkers [37] found that a library of secondary and tertiary tetrahydrofurfurylamines could be efficiently prepared under mild conditions (25 °C/1 bar H₂) using Pd/Al₂O₃ as the catalyst. The same group [38] disclosed other types of amines synthesized by aldol condensation / reductive amination sequences. Other recent important pieces of work are the synthesis of a wide range of amphiphilic biobased derivatives by Hausoul, Palkovits and colleagues [39], and the interesting access to quinolone-2-carboxylic acid from furfural involving an initial partial oxidation step [40].

Besides the above transformations, furfural is an essential resource for the design of bio-based solvents. Generally, bio-based solvents benefit from a renewable production, biodegradability and lower toxicity. [3-11] The catalytic hydrogenation, dehydration and esterification of furfural and its derivatives afford bio-based solvents including 2-methyl furan (2-MF), furfuryl alcohol (FA), tetrahydrofurfuryl alcohol (THFA), tetrahydrofuran (THF), 2-methyl tetrahydrofuran (2-MeTHF), γ -valerolactone (GVL), cyclopentyl methyl ether, methyl levulinate and pentanediol (Figure. 2). [41-43] This topic is illustrated below with a few recent reports on THFA and 2-MeTHF, which are among the mostly used bio-based solvents nowadays. [44,45]

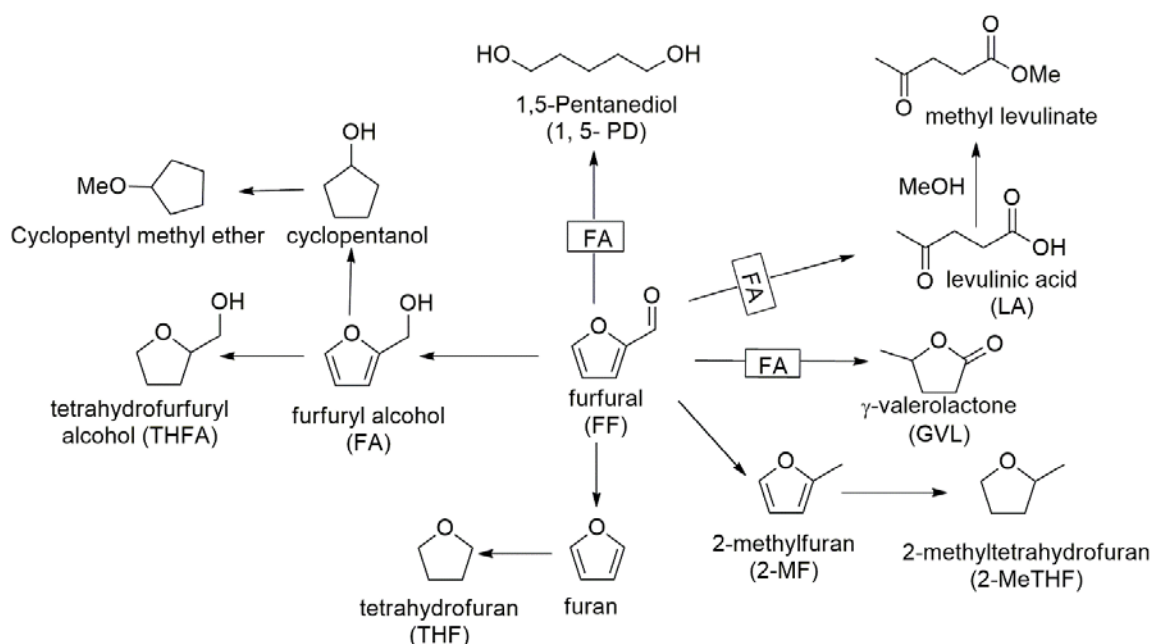


Figure 2. Bio-based solvents from furfural.

Taylor, Albilali and co-workers [46] reported the hydrogenation of furfural to THFA in 95% yield using 0.97 % of Pd-Pt/TiO₂ with a synergistic effect of Pd and Pt as confirmed by Rebrov Cherkasov and co-workers [47] and Shimazu and coll. [48] Using Ni_{0.09}Zn/NC600 as the catalyst, Wei and coll. [49] observed a 97% conversion of furfural with 86% selectivity for THFA in water at 150 °C for 1 h. For accessing 2-MeTHF, Zhu and coll. found that Cu₂Si₂O₅(OH)₂ and Pd/SiO₂ could be used as catalysts for transforming furfural in one-step and 97% yield under ambient conditions. [50] Actually, biobased solvents are still underused. Interestingly, looking back in the history of solvents, a parallel can be drawn. Indeed, dipolar aprotic solvents were first thought not to have any future due to their limited availability and high prices. Yet, they are now extensively used owing to their technical benefits. As many

solvents must be withdrawn because of environmental concerns, needs for new solvents arise, and it can be foreseen that furfural (and HMF) chemistry will contribute significantly to the field.

2. 5-Hydroxymethylfurfural (HMF)

2.1. Synthesis

HMF is the acid-catalyzed triply dehydrated product of C₆ carbohydrates. In this reaction, the key issues are the selectivity, due to the limited stability of HMF in acidic conditions, and the possible use of hexose-containing starting materials cheaper than the very reactive fructose. Many studies reported recently (Table 1) have addressed both issues, by proposing specifically designed catalysts and solvents.

Table 1. Selection of recently reported conditions for the transformation of various resources to HMF.

Entry	Resource	Conditions (catalyst, additives, solvent, temperature, time)	Yield	Ref.
1 ^a	Levogluconone	ZSM-5/H ₂ O/180°C/0.5 h	40	[51]
		Amberlyst 70/H ₂ O/180°C/0.5 h	48	
2 ^a	Fructose Sucrose	Amberlyst 15/DES/60-80°C/1-4 h	78	[52]
			69	
3 ^a	Glucose	Fe ³⁺ modified Amberlyst 15 THF-NaCl _{aq} /160°C/1 h	68	[53]
4 ^b	Glucose	Al-D41/ChCl/H ₂ O-MIBK 195 °C/1.5 h	57	[54]
5 ^b	Fructose	TiO ₂ -C/microwave/DMSO 120 °C/1 h	90	[55]
6 ^a	Glucose	Sulfonated C-based solid/THF-NaCl _{aq} 160 °C/3 h	93	[56]
7 ^b	Fructose, Glucose Sucrose, Inulin Starch, Cellobiose Cellulose, Wheat Straw	HfO(PO ₄) _{2.0} /THF-NaCl _{aq} 160-190 °C/2-4 h	95, 90 87, 80 79, 75 70,18	[57]
8 ^a	Glucose	ChCl-H-ZSM-5/MIBK/180 °C/3 h	49	[58]

9 ^a	Glucose	Yb(OTf) ₂ /HSO ₃ -MPR <i>tert</i> -butylphenol-H ₂ O/130 °C/1 h	50	[59]
10 ^b	Fructose	Betaine-based cat./ChCl/H ₂ O-MIBK 130 °C/1 h	88	[60]
	Glucose	Betaine-based cat./AlCl ₃ 6H ₂ O/MIBK 170-180 °C/1 h	66	
	Cellulose		37	
Lignocellulose	53			
11 ^a	Cellulose	Ni _{2.0} -CS/ H ₂ (6 MPa) 200 °C/ 1 h	85	[61]
12 ^a	Waste coffee grounds	H ₂ SO ₄ -Al(NO ₃) ₃ ·9H ₂ O microwave/ H ₂ O-DMSO 200W/10 min	14	[62]
	Glucose		28	
	Fructose		62	
13 ^b	Glucose	Al-mont-10/THF-NaCl _{aq} 180 °C/2.5 h	80	[63]
	Starch		60	
	Inulin		82	
14 ^a	Cellulose	RuCl ₃ /Butanol-NaCl _{aq} 220 °C/0.5 h	83	[64]
15 ^a	Fructose	CO ₂ -H ₂ O-isopropanol 190 °C/2 h	67	[65]
16 ^a	Fructose	25 MPa of CO ₂ /150 °C/3 h	80	[66]
17 ^a	Fructose	[BMIM][Cl]/Carbonaceous microspheres-SO ₃ H 80 °C/0.5 h	83	[67]
	Sucrose		45	
	Inulin		59	
18 ^a	Fructose	[1,2,3-(MIM) ₃ propane][Cl] ₃ 120-140 °C/2-5 h	93	[68]
			72	
			51	
	Sucrose	[1,2,3-(MIM) ₃ propane][Cl] ₃ -CC-SO ₃ H 130-140 °C/3-5 h	97	
			77	
			58	
19 ^a	Starch	ChCl-B(OH) ₃ /NaCl _{aq} -MIBK 195 °C/1 h	38	[69]
20 ^c	Fructose	H ₂ O/THF/NaCl, HCl (pH 2)/Na ₂ S ₂ O ₄ 170°C/2 h	98	[70]
21 ^a	Fructose	H ₂ O/DMSO/O ₂ /no catalyst 120°C/24 h	77	[71]

^aHPLC yield; ^bGC yield; ^cIsolated yield

2.2 Reactivity of HMF

The recent literature on HMF-derived products is extremely rich and diversified towards either polymers or fine chemicals. Polymers can result from polycondensation reactions mostly leading to polyesters or polyamides or C-C bond formation reactions as it is the case in the production of humins. [1,7-11, 44, 45, 72-79]. Below, we focus our survey only on oxidation and reduction reactions of HMF, two key steps towards the design of novel monomers and polymers (Figure 3).

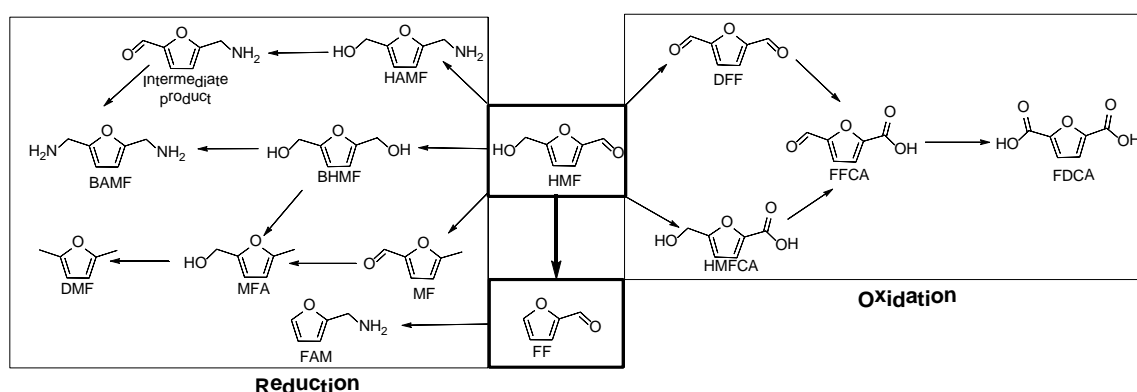


Figure 3. HMF, a key building block for monomer synthesis.

2.2.1. Oxidation of HMF

The oxidation of HMF to furanic derivatives is challenging because both the formyl and the hydroxymethyl groups can undergo oxidation to various extents leading to several possible products with variable stabilities. Indeed, while efficient access to 2,5-furandicarboxylic acid (FDCA) is the focus of many studies, the selective formation of partially oxidized intermediates is also sought with the idea of widening the downstream scope of bio-based building blocks.

2.2.1.1. Chemical oxidation

The selective access to 5-hydroxymethyl-2-furancarboxylic acid (HMFCFA) by aerobic oxidation of HMF was recently reported by Grunwaldt and coll. using the high activity of Ag/ZrO₂ (yield \geq 98%) [80] while in a related work, Xia and coll. [81] used Ag-PVP/ZrO₂(1:1) (in 98% yield). 2,5-Diformylfuran (DFF), which exhibits the same level of oxidation as HMFCFA, can be obtained using the Mn-based heterogenous catalysts described by Riisager, Chen and co-workers (HMF conversion of 33% along with 97% selectivity to DFF) [82] and Cui, Wang and co-workers (>99% DFF selectivity, 100% conversion) [83] (in 32% and 99% yield, respectively). A photocatalytic approach was proposed by Wu and coll. [84] who

performed the oxidation of HMF to DFF with 87% selectivity using $\text{WO}_3/\text{g-C}_3\text{N}_4$ as the catalyst under visible light. High DFF selectivity was also obtained by Giannakoudakis, Colmenares, Triantafyllidis and coworkers [85] by additive-free photo-assisted partial oxidation of HMF using MnO_2 nanorods as catalysts.

5-Formyl-2-furancarboxylic acid (FFCA), the one-step further oxidized compound, was selectively prepared by Dibenedetto and coll. [86] using a cheap and stable mixed oxide CuO-CeO_2 in 90% yield, using molecular oxygen as the oxidant and water as the solvent. This unstable platform was also prepared by Wu and coll. [87] (in 92% yield) using ruthenium on activated carbon in water.

To selectively prepare FDCA from HMF, Silva and coll. [88] used a trickle-bed reactor in the presence of $\text{Ru/Al}_2\text{O}_3$ catalyst (in 98% yield, scale), while Hara and coll. used a $\text{MnO}_2/\text{NaHCO}_3$ combination using O_2 as the sole oxidant in water (in 86% yield). [89] Recently, Zhang, Xin and co-workers [90] developed an ionic liquids-heteropolyacids system leading to FDCA in 48% overall yield from glucose. The selective photocatalytic oxidation of HMF to FDCA in 96% yield was reported by Zhang, Deng and co-workers [91] $\text{CoPz/g-C}_3\text{N}_4$ was used as the photocatalyst under simulated sunlight and normal air pressure.

Electrochemical oxidation of HMF is a useful alternative. Huber, Jin and co-workers [92] prepared earth-abundant bimetallic NiFe layered double hydroxide nanosheets on carbon fiber paper as the anode for the electrochemical oxidation of a highly concentrated solution of HMF to FDCA with a 99% faradic efficiency). As for Schuhmann and coll. [93] they prepared FDCA in 98% yield from HMF using a high-surface-area Ni foam modified with a high-surface-area nickel boride as the electrode. Subsequently, Sun and coll. [94] showed that NiB_x displayed excellent conversion, selectivity and faradaic efficiency values at both the anode and the cathode simultaneously using water as the oxygen and hydrogen source. Two approaches by Choi and coll. involved the use of thin and thick sets of NiOOH , or 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) and 4-acetamido-TEMPO (ACT) in mildly basic conditions. [95,96] Finally, Han, Gan and co-workers [97] reported a structure-optimized non-precious core-shell NiSe@NiO_x nanowire electrocatalyst for the quantitative oxidation of 5-HMF to FDCA, showing stability over six successive cycles. An alternative electrochemical

approach was recently reported by Han, Song and colleagues [98] who demonstrated that the activity of CoO was enhanced after Se doping, creating oxygen vacancies.

Dimethyl furan-2,5-dicarboxylate, an interesting derivative of FDCA because more soluble in many organic solvents, has been prepared quantitatively from HMF by Mejia Choi and coll. [99] using a bimetallic Ru@C and CoxOy-N@C catalytic system under ambient conditions in methanol. The latter catalyst was also shown very active for the preparation of 5-(hydroxymethyl)furan-2-carboxylate and methyl furan-2-carboxylate from HMF and furfural, respectively.

2.2.1.2. Enzymatic oxidation

Fraaije and coll. disclosed a HMF oxidase (HMFO) for the oxidation of HMF and its derivatives. The studies indicated that HMFO hydrates the aldehyde intermediates allowing an excellent catalytic activity for the production of FDCA. [100] Li, Zong and co-workers [101] developed a series of enzymes to synthesize various valuable HMF derivatives *via* selective oxidation. Hence, DFF was obtained in 92% yield from HMF using a galactose oxidase. Subsequently, a xanthine oxidase from *Escherichia coli* was used to catalyze the oxidation of HMF to HMFCFA in 94% yield and a *Panus conchatus* laccase afforded FFCA in 82% yield in the presence of TEMPO used as a mediator. [102] The enzymatic oxidation of HMF to FDCA in a one-pot reaction was achieved by Carnell and coll. [103] using the galactose oxidase M₃₋₅(GO M₃₋₅), a periplasmic aldehyde oxidase (PaoABC), catalase and a horse radish peroxidase (HRP). Remarkably, You, Qi and co-workers [104] reported the use the CotA-TJ102 laccase as the catalyst, and TEMPO as the mediator for the oxidation of HMF to FFCA in 98% yield and 98% selectivity.

2.2.2. Reduction

2.2.2.1. 2,5-Dimethylfuran

2,5-Dimethylfuran (DMF) is a promising green solvent also used as a “second generation biofuel”. [105,106] The direct hydrogenation of HMF to DMF has been abundantly investigated using a series of noble (Ru-, Pt-, and Pd-based) and non-noble metal catalysts (Ni- and Cu-based). [107] He and coll. [108] reported that under H₂, Co-(ZnO-ZnAl₂O₄) allowed to obtain DMF in 74% yield from biomass resources. Simultaneously, Zhou and coll. [109] developed an excellent Co-graphene nanomaterial catalyst for the hydrogenation of HMF to DMF (94%

yield). Fu, Li and co-workers [110] achieved 86 % yield in DMF with a total conversion of HMF, using an Fe-based catalyst. Solanki and Rode [111] reported a non-noble, reusable and recoverable bimetallic catalyst Cu-Fe (1:2), achieving an excellent conversion (97%) and selectivity (93%) to DMF from HMF. Meanwhile, Shown, Mondal and co-workers [112] synthesized bimetallic MOF-derived nanoparticles Cu-Pd@C-B to produce DMF (96% yield) from HMF. Chaudret, Asensio and co-workers [113] obtained DMF in quantitative yield from HMF using FeC@Ru NPs as the catalyst while Kim and coll. [114] developed a one-pot reaction system to produce DMF in high yield from sucrose, cellobiose, starch, and cellulose using the tandem catalyst of Cu-Pd/UiO-66(NH₂)@SGO. Fan, Li and co-workers [115] investigated the use of a non-noble bimetallic Cu-Ni electrode for the electrocatalytic production of DMF from HMF, achieving a 91% conversion and 88% faradic efficiency. A very nice access to DMF and its fully hydrogenated analog dimethyltetrahydrofuran was proposed by Royer, Marceau and colleague [116] by hydroconversion of HMF using mesoporous silica supported Ni catalysts.

2.2.2.2. Reductive amination

Hara and coll. [117] reported that the combination of Ru/Nb₂O₅ and [Ru(CO)ClH(PPh₃)₃]/xantphos system allowed to prepare 2,5-bis(aminomethyl)furan (BAMF) from HMF in 93% yield. Similarly, Mecking and coll. reported a homogenous Ru-based catalyst for the one-pot amination of HMF to BAMF (90%). [118] Wei and coll. reported the reductive amination of furfural and HMF to BAMF under benign conditions over Raney Ni (61% yield at 160°C from HMF). [119,120]

FDCA has taken the inside track and is one of the targets of choice. However, the emergence of mild and selective methods offer now efficient accesses to a wider range of partial oxidation and reduction products from HMF, multiplying the opportunities for uses as intermediates towards more complex chemical architectures.

3. Bridging the C5 and C6 branches of the furfural/HMF chemical tree:

Adding a carbon atom (+ C1) to furfural or removing a carbon atom from HMF (-C1) is also an interesting strategy to switch from C5 to C6 sugars or *vice versa*. This may be related to price and availability issues, as furfural is still significantly cheaper and more abundant than

HMF. It may also be appealing in terms of reactivity, when one useful C-5 target can be obtained more easily or only from HMF. Below, two examples illustrate the +/- C1 options.

Carbonylation of furfural to FDCA is an example of transformation allowing the transformation C5→C6, providing a bright market for furfural and CO utilizations. Yin and coll. [121] disclosed the conversion of furfural to FDCA through oxidative carbonylation. Subsequently, they developed a series of approaches involving homogeneous, biphasic and/or heterogenous conditions to efficiently achieve the conversion of C5 furfural derivatives to C6 molecular platforms. [122-124]

The reversed C6→C5 strategy was reported by Vlachos, Sandler and co-workers [125] who investigated the Lewis acid (CrCl₃)-catalyzed glucose transformation to levulinic acid (LA) in aqueous acidic (HCl) media. Liu and coll. [126] used [C₃SO₃Hmim]HSO₄ as the catalyst and cellulose as the substrate in H₂O at 170°C for 5 h for preparing LA in 86% yield even after 5 recycles. Yang and coll. [127] obtained LA in 22% yield as the main side product from starch. Teoh [128] used solid acids of amorphous silica-alumina and silica-alumina-phosphate as catalyst achieving ≥40% carbon yield of LA straight from glucose. Tsang [129] studied the valorization of paper towel waste by producing LA under various acidic conditions with best yields in LA when using in 1 M H₂SO₄ at moderate temperatures. Furfuryl alcohol (FA) can be also directly converted to alkyl levulinates in the presence of metal triflates, as shown by Jérôme and colleagues. [130] Interestingly, LA can be further transformed into useful intermediates. Hence, in the presence of amines, Andrioletti and coll. [131] reported the efficient metal-free conversion of LA to N-substituted-5-methylpyrrolidone (Yield up to 86%). Subsequently, Sakai and coll. [132] used InI₃ and Han, Song and co-workers [133] used Pt/P-TiO₂ as catalysts to produce various N-substituted-pyrrolidones from LA. Varma and coll. [134] efficiently obtained γ -valerolactone (GVL) from LA, using AgPd@g-C₃N₄ as the catalyst when Palkovits and coll. [135-138] reported a series of studies about the transformation of LA to green solvents among which GVL and 2-MeTHF. Interestingly, a (non-)Kolbe electrolysis conversion of LA was also described. Bio-based solvents and important intermediates were also efficiently prepared from the glucose-derived LA and itaconic acid in a pioneering report by Klankermayer, Leitner and co-workers. [139] Hence, 2- or 3-MeTHF were prepared from LA and itaconic acid, in the presence of a Ru-based catalyst and H₂ in > 90% yield, respectively. Such +/- C1 sequences provide thus additional opportunities for synthetic explorations aimed at transforming furfural or HMF.

Conclusions:

The vitality of the chemistry of C5 and C6 sugars is so high that furfural and HMF will very likely play a central role in tomorrow's chemistry, benefiting from efforts of chemists in all disciplines, from theoretical to engineering *via* synthesis and catalysis. While the "furfural tree" is rather mature already, the HMF one is still incomplete. Apart from the need to widen the range of resources to raw biomass that should replace refined sugars in order to improve the economic viability of the processes towards polymers and fine chemicals, the purity and grade issues of HMF and its immediate derivatives are also major challenges still to overcome. The viable future of the promising polyester furanoate (PEF) or analogues depends on these successful achievements.

The field of furfural and HMF chemistries has benefited from the creativity of the catalysis community and will continue to do so. In terms of diversity and innovation in molecular design, it needs a stronger input of the synthetic chemistry community who is strongly encouraged to develop more explorative research. On the longer term, it is a requisite for enriching the scope of functional intermediates and offer novel biobased building blocks and synthetic pathways towards original architectures with breakthrough applications in all fields of chemistry. This diversification will be facilitated by the development of bioinspired processes, combining mildness and selectivity, well adapted to the chemical sensitivity of furfural and HMF.

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