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Guanfei Shen, Bruno Andrioletti, Yves Queneau. Furfural and 5-(hydroxymethyl)furfural (HMF): two pivotal intermediates for bio-based chemistry. *Current opinion in green and sustainable chemistry*, Elsevier, In press, 10.1016/j.cogsc.2020.100384 . hal-02887644

**HAL Id: hal-02887644**

**<https://hal-udl.archives-ouvertes.fr/hal-02887644>**

Submitted on 8 Jul 2020

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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

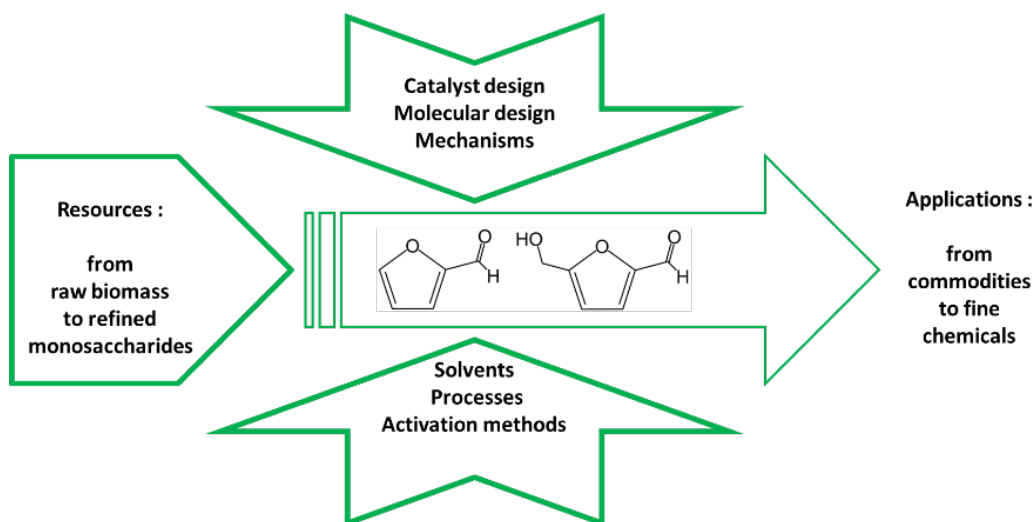
access to industrially relevant targets, and the second being the commitment of synthetic organic chemist to explorative studies on new reactions and new architectures.

## **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/H<sub>2</sub>O 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

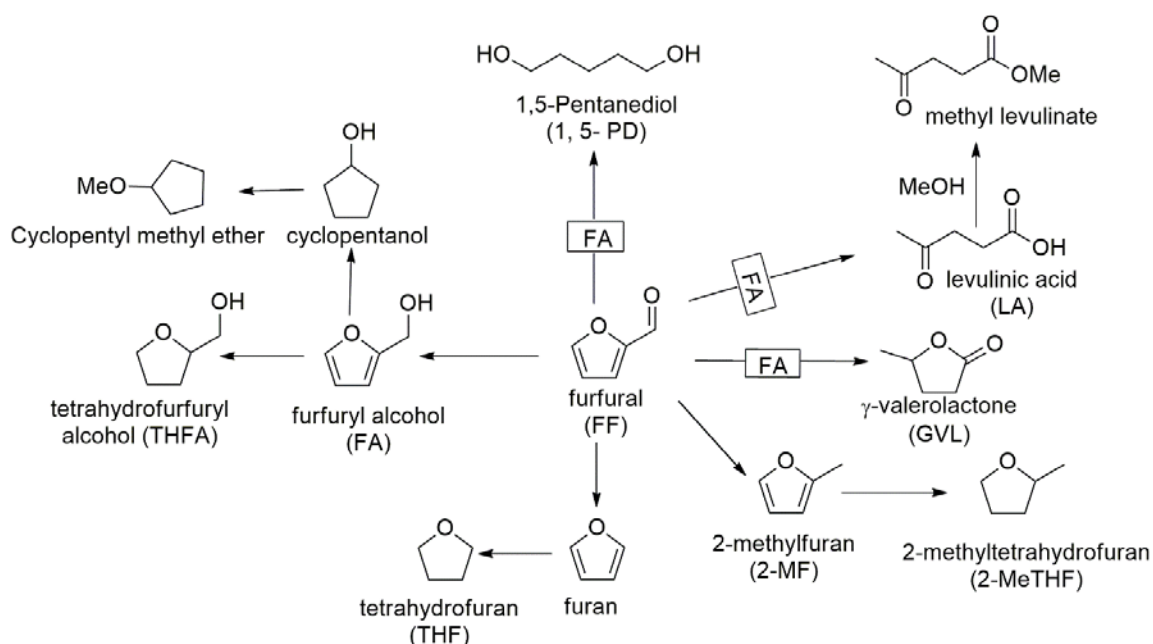
a modified Metal Organic Framework (MOF), MIL-101 (Cr), for the dehydration of xylose to furfural. Subsequently, Chang and coll. [19] obtained the furfural in 71% yield from xylose. Furfural rapidly degrades through resinification and condensation reactions under traditional diluted acid conditions, 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/H<sub>2</sub>O 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 CO<sub>2</sub> within 1 hour at 180 °C. Vigier and coworkers [25] showed that the use of the biphasic mixture of aqueous choline chloride (ChCl<sub>aq</sub>) 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<sub>aq</sub>/MIBK. Using the 1-butyl-3-methylimidazolium (BMIM) chloride /FeCl<sub>3</sub> 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-SO<sub>3</sub>H) 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  $\gamma$ -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/Al<sub>2</sub>O<sub>3</sub> as the catalyst, with a high selectivity using NH<sub>4</sub>OH and H<sub>2</sub> 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 H<sub>2</sub>) using Pd/Al<sub>2</sub>O<sub>3</sub> 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),  $\gamma$ -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/TiO<sub>2</sub> with a synergistic effect of Pd and Pt as confirmed by Rebrov Cherkasov and co-workers [47] and Shimazu and coll. [48] Using Ni<sub>0.09</sub>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 Cu<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>2</sub> and Pd/SiO<sub>2</sub> 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 C<sub>6</sub> 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 <sup>a</sup>	Levogluconone	ZSM-5/H <sub>2</sub> O/180°C/0.5 h	40	[51]
		Amberlyst 70/H <sub>2</sub> O/180°C/0.5 h	48	
2 <sup>a</sup>	Fructose Sucrose	Amberlyst 15/DES/60-80°C/1-4 h	78	[52]
			69	
3 <sup>a</sup>	Glucose	Fe <sup>3+</sup> modified Amberlyst 15 THF-NaCl <sub>aq</sub> /160°C/1 h	68	[53]
4 <sup>b</sup>	Glucose	Al-D41/ChCl/H <sub>2</sub> O-MIBK 195 °C/1.5 h	57	[54]
5 <sup>b</sup>	Fructose	TiO <sub>2</sub> -C/microwave/DMSO 120 °C/1 h	90	[55]
6 <sup>a</sup>	Glucose	Sulfonated C-based solid/THF-NaCl <sub>aq</sub> 160 °C/3 h	93	[56]
7 <sup>b</sup>	Fructose, Glucose Sucrose, Inulin Starch, Cellobiose Cellulose, Wheat Straw	HfO(PO <sub>4</sub> ) <sub>2.0</sub> /THF-NaCl <sub>aq</sub> 160-190 °C/2-4 h	95, 90 87, 80 79, 75 70,18	[57]
8 <sup>a</sup>	Glucose	ChCl-H-ZSM-5/MIBK/180 °C/3 h	49	[58]

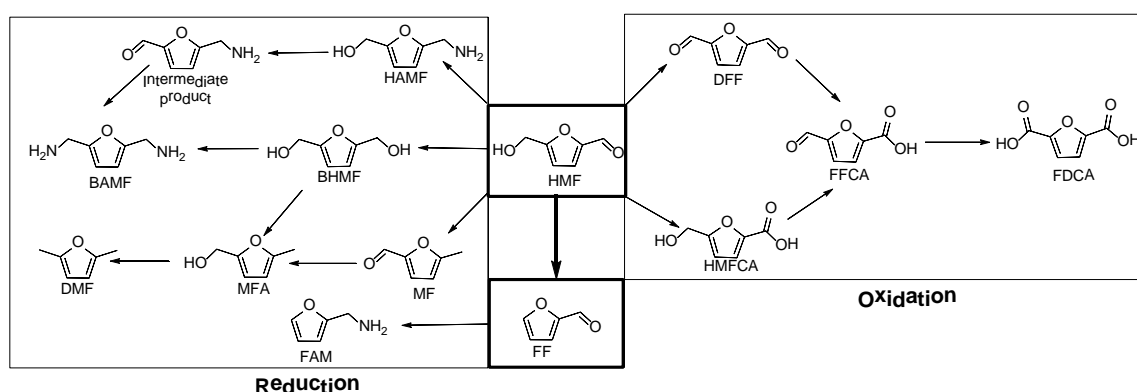


9 <sup>a</sup>	Glucose	Yb(OTf) <sub>2</sub> /HSO <sub>3</sub> -MPR <i>tert</i> -butylphenol-H <sub>2</sub> O/130 °C/1 h	50	[59]
10 <sup>b</sup>	Fructose	Betaine-based cat./ChCl/H <sub>2</sub> O-MIBK 130 °C/1 h	88	[60]
	Glucose	Betaine-based cat./AlCl <sub>3</sub> 6H <sub>2</sub> O/MIBK 170-180 °C/1 h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

<sup>a</sup>HPLC yield; <sup>b</sup>GC yield; <sup>c</sup>Isolated 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/ZrO<sub>2</sub> (yield  $\geq$  98%) [80] while in a related work, Xia and coll. [81] used Ag-PVP/ZrO<sub>2</sub>(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  $\text{MnO}_2$  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  $\text{CuO-CeO}_2$  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  $\text{O}_2$  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  $\text{NiB}_x$  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  $\text{NiOOH}$ , 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  $\text{NiSe@NiO}_x$  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 M<sub>3-5</sub>(GO M<sub>3-5</sub>), 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 H<sub>2</sub>, Co-(ZnO-ZnAl<sub>2</sub>O<sub>4</sub>) 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(NH<sub>2</sub>)@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/Nb<sub>2</sub>O<sub>5</sub> and [Ru(CO)ClH(PPh<sub>3</sub>)<sub>3</sub>]/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 (CrCl<sub>3</sub>)-catalyzed glucose transformation to levulinic acid (LA) in aqueous acidic (HCl) media. Liu and coll. [126] used [C<sub>3</sub>SO<sub>3</sub>Hmim]HSO<sub>4</sub> as the catalyst and cellulose as the substrate in H<sub>2</sub>O 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 H<sub>2</sub>SO<sub>4</sub> 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 InI<sub>3</sub> and Han, Song and co-workers [133] used Pt/P-TiO<sub>2</sub> as catalysts to produce various N-substituted-pyrrolidones from LA. Varma and coll. [134] efficiently obtained γ-valerolactone (GVL) from LA, using AgPd@g-C<sub>3</sub>N<sub>4</sub> 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 H<sub>2</sub> 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.

## Acknowledgments

The authors thank the Ministère de l'Enseignement Supérieur et de la Recherche et de l'Innovation (MESRI) and CNRS for their financial support, as well as the Chinese Scholarship Council (Université de Lyon-CSC call) for the fellowship to GS.

## References

- 1 G.W. Huber, S. Iborra, A. Corma, Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering, *Chem. Rev.* 106 (2006) 4044-4098.
- 2 R. Mariscal, P. Maireles-Torres, M. Ojeda, I. Sádbaba, M.L. Granados, Furfural: a renewable and versatile platform molecule for the synthesis of chemicals and fuels, *Energ. Environ. Sci.* 9 (2016) 1144-1189.
- 3 K. Yan, G. Wu, T. Lafleur, C. Jarvis, Production, properties and catalytic

- hydrogenation of furfural to fuel additives and value-added chemicals, *Renew. Sust. Energ. Rev.* 38 (2014) 663-676.
- 4 Y. Lee, E.E. Kwon, J. Lee, Polymers derived from hemicellulosic parts of lignocellulosic biomass, *Rev. Environ. Sci. Bio.* 18 (2019) 317-334.
  - 5 M.J. Climent, A. Corma, S. Iborra, Conversion of biomass platform molecules into fuel additives and liquid hydrocarbon fuels, *Green Chem.* 16 (2014) 516-547.
  - 6 A. Mittal, S.K. Black, T.B. Vinzant, D.K. Johnson, Production of furfural from process-relevant biomass-derived pentoses in a biphasic reaction system, *ACS Sustainable Chem. Eng.* 5 (2017) 5694-5701.
  - 7 A.A. Rosatella, S.P. Simeonov, R.F.M. Frade, C.A.M. Afonso, 5-Hydroxymethylfurfural (HMF) as a building block platform: Biological properties, synthesis and synthetic applications, *Green Chem.* 13 (2011) 754-793.
  - 8 J.G. de Vries, Green Syntheses of Heterocycles of Industrial Importance. 5-Hydroxymethylfurfural as a Platform Chemical. In: *Advances in Heterocyclic Chemistry*, Eds. Academic Press: 2017; Vol. 121, pp. 247-293.
  - 9 R.J. van Putten, J.C. van der Waal, E.D. de Jong, C.B. Rasrendra, H.J. Heeres, de J.G. Vries, Hydroxymethylfurfural, a versatile platform chemical made from renewable resources, *Chem. Rev.* 113 (2013) 1499-1597.
  - 10 F.A. Kucherov, L.V. Romashov, K.I. Galkin, V.P. Ananikov, Chemical transformations of biomass-derived c6-furanic platform chemicals for sustainable energy research, materials science, and synthetic building blocks, *ACS Sustainable Chem. Eng.* 6 (2018) 8064-8092.
  - 11 A. Farrán, C. Cai, M. Sandoval, Y. Xu, J. Liu, M. J. Hernáiz, R.J. Linhardt, *Green Solvents in Carbohydrate Chemistry: From Raw Materials to Fine Chemicals*, *Chem. Rev.* 115 (2015) 6811-6853.
  - 12 L. Hu, L. Lin, Z. Wu, S. Zhou, S. Liu, Recent advances in catalytic transformation of biomass-derived 5-hydroxymethylfurfural into the innovative fuels and chemicals, *Renew. Sust. Energy. Rev.* 74 (2017) 230-257.
  - 13 H. Li, A. Riisager, S. Saravanamurugan, A. Pandey, R.S. Sangwan, S. Yang, R. Luque, Carbon-increasing catalytic strategies for upgrading biomass into energy-intensive fuels and chemicals, *ACS Catal.* 8 (2018) 148-187.
  - 14 M.J. Hülsey, H. Yang, N. Yan, Sustainable routes for the synthesis of renewable heteroatom-containing chemicals, *ACS Sustainable Chem. Eng.* 6 (2018) 5694-



5707.

- 15 \* P.T. Anastas, J.B. Zimmerman, The periodic table of the elements of green and sustainable chemistry, *Green Chem.* 21 (2019) 6545-6566.
- 16 A. Chatterjee, H.U. Xijun, F.L.Y. Lam, Modified coal fly ash waste as an efficient heterogeneous catalyst for dehydration of xylose to furfural in biphasic medium, *Fuel* 239 (2019) 726-736.
- 17 X. Guo, F. Guo, Y. Li, Z. Zheng, Z. Xing, Z. Zhu, T. Liu, X. Zhang, Y. Jin, Dehydration of D-xylose into furfural over bimetallic salts of heteropolyacid in DMSO/H<sub>2</sub>O mixture, *Appl. Catal. A* 558 (2018) 18-25.
- 18 A. Chatterjee, X. Hu, F.L.Y. Lam, Towards a recyclable MOF catalyst for efficient production of furfural, *Catal. Today*, 314 (2018) 129-136.
- 19 Y. Liu, C. Ma, C. Huang, Y. Fu, J. Chang, Efficient Conversion of Xylose into Furfural Using Sulfonic Acid-Functionalized Metal-Organic Frameworks in a Biphasic System, *Ind. Eng. Chem. Res.* 57 (2018) 16628-16634.
- 20 Q. Wang, W. Qi, W. Wang, Y. Zhang, N. Leksawasdi, X. Zhuang, Q. Yu, Z. Yuan, Production of furfural with high yields from corncob under extremely low water/solid ratios, *Renew. Energ.* 144 (2019) 139-146.
- 21 J.N. Chheda, Y. Román-Leshkov, J.A. Dumesic, Production of 5-hydroxymethylfurfural and furfural by dehydration of biomass-derived mono-and poly-saccharides, *Green Chem.* 9 (2007) 342-350.
- 22 L. Zhang, L. Tian, R. Sun, C. Liu, Q. Kou, H. Zuo, Transformation of corncob into furfural by a bifunctional solid acid catalyst. *Bioresour. Technol.* 276 (2019), 60-64.
- 23 A.A. Marianou, C.M. Michailof, A. Pineda, E.F. Iliopoulou, K.S. Triantafyllidis, A.A. Lappas, Effect of Lewis and Brønsted acidity on glucose conversion to 5-HMF and lactic acid in aqueous and organic media, *Appl. Catal. A-Gen.* 555 (2018) 75-87.
- 24 A.R.C. Morais, R. Bogel-Lukasik, Highly efficient and selective CO<sub>2</sub>-adjunctive dehydration of xylose to furfural in aqueous media with THF, *Green Chem.* 18 (2016) 2331-2334.
- 25 \* S. Jiang, C. Verrier, M. Ahmar, J. Lai, C. Ma, E. Muller, Y. Queneau, M. Peratitus, F. Jerome, K. de Oliveira Vigier, Unveiling the role of choline chloride in furfural synthesis from highly concentrated feeds of xylose, *Green Chem.* 20 (2018)

5104-5110.

- 26 Z. Chen, X. Bai, A. Lusi, W.A. Jacoby, C. Wan, One-pot Selective Conversion of Lignocellulosic Biomass into Furfural and Co-products Using Aqueous Choline Chloride/Methyl Isobutyl Ketone Biphasic Solvent System, *Bioresour. Technol.* 289 (2019) 121708.
- 27 Y. Zhao, H. Xu, K. Wang, K. Lu, Y. Qu, L. Zhu, S. Wang, Enhanced furfural production from biomass and its derived carbohydrates in the renewable butanone-water solvent system, *Sustain. Energy Fuels.* 3 (2019) 3208-3218.
- 28 X. Bai, J. Li, C. Jia, J. Shao, Q. Yang, Y. Chen, H. Yang, X. Wang, H. Chen, Preparation of furfural by catalytic pyrolysis of cellulose based on nano Na/Fe-solid acid, *Fuel* 258 (2019) 116089-116096.
- 29 T. Yang, Y.H. Zhou, S.Z. Zhu, H. Pan, Y.B. Huang, Insight into Aluminum Sulfate-Catalyzed Xylan Conversion into Furfural in a  $\gamma$ -Valerolactone/Water Biphasic Solvent under Microwave Conditions, *ChemSusChem.* 10 (2017) 4066-4079.
- 30 B. Lee, T.Y. Wu, C.H. Ting, J.K. Tan, L.F. Siow, C.K. Cheng, J.M. Jahim, A.W. Mohammad, One-pot furfural production using choline chloride-dicarboxylic acid based deep eutectic solvents under mild conditions, *Bioresour. Technol.* 278 (2019) 486-489.
- 31 B. Seemala, V. Haritos, A. Tanksale, Levulinic acid as a catalyst for the production of 5-hydroxymethylfurfural and furfural from lignocellulose biomass, *ChemCatChem*, 8 (2016) 640-647.
- 32 C.A. Bizzi, D. Santos, T.C. Sieben, G.V. Motta, P.A. Mello, E.M. Flores, Furfural production from lignocellulosic biomass by ultrasound-assisted acid hydrolysis, *Ultrason. Sonochem.* 51 (2019) 332-339.
- 33 M. Chatterjee, T. Ishizaka, H. Kawanami, Reductive amination of furfural to furfurylamine using aqueous ammonia solution and molecular hydrogen: an environmentally friendly approach, *Green Chem.* 18 (2016) 487-496.
- 34 A. Dunbabin, F. Subrizi, J.M. Ward, T.D. Sheppard, H.C. Hailes, Furfurylamines from biomass: transaminase catalyzed upgrading of furfurals, *Green Chem.* 19 (2017) 397-404.
- 35 Z. Yuan, B. Liu, P. Zhou, Z. Zhang, Q. Chi, Preparation of nitrogen-doped carbon supported cobalt catalysts and its application in the reductive amination, *J. Catal.* 370 (2019) 347-356.

- 36 \* I. Scodeller, S. Mansouri, D. Morvan, E. Muller, K.D.O. Vigier, R. Wischert, F. Jérôme, Synthesis of Renewable meta-Xylylenediamine from Biomass-Derived Furfural, *Angew. Chem. Int. Ed.* 57 (2018) 10510-10514.
- 37 S. Jiang, E. Muller, F. Jérôme, M. Pera-Titus, K.D.O. Vigier, Conversion of furfural to tetrahydrofuran-derived secondary amines under mild conditions, *Green Chem.* 22 (2020) 1832-1836.
- 38 S. Jiang, C. Ma, E. Muller, M. Pera-Titus, F. Jérôme, K.D.O. Vigier, Selective synthesis of THF-derived amines from biomass-derived carbonyl compounds, *ACS Catal.* 9 (2019) 8893-8902.
- 39 \* L. Kipshagen, L.T. Vömel, M.A. Liauw, A. Klemmer, A. Schulz, C. Kropf, P.J.C. Hausoul, R. Palkovits, Anionic surfactants based on intermediates of carbohydrate conversion, *Green Chem.* 21 (2019) 3882-3890.
- 40 M. Li, X. Dong, N. Zhang, F. Jérôme, Y. Gu, Eco-efficient synthesis of 2-quinaldic acids from furfural, *Green Chem.* 21 (2019) 4650-4655.
- 41 D.M. Alonso, S.G. Wettstein, J.A. Dumesic, Gamma-valerolactone, a sustainable platform molecule derived from lignocellulosic biomass, *Green Chem.* 15 (2013) 584-595.
- 42 Y. Gu, F. Jérôme, Bio-based solvents: an emerging generation of fluids for the design of eco-efficient processes in catalysis and organic chemistry, *Chem. Soc. Rev.* 42 (2013) 9550-9570.
- 43 V. Pace, P. Hoyos, L. Castoldi, P. Dominguez de Maria, A.R. Alcantara, 2-Methyltetrahydrofuran (2-MeTHF): a biomass-derived solvent with broad application in organic chemistry, *ChemSusChem.* 5 (2012) 1369-1379.
- 44 J.N. Tan, M. Ahmar, Y. Queneau, Bio-based solvents for the Baylis-Hillman reaction of HMF, *RSC Adv.* 5 (2015) 69238-69242.
- 45 W. Fan, Y. Queneau, F. Popowycz, The synthesis of HMF-based  $\alpha$ -amino phosphonates via one-pot Kabachnik-Fields reaction, *RSC Adv.* 8 (2018) 31496-31501.
- 46 R. Albilali, M. Douthwaite, Q. He, S.H. Taylor, The selective hydrogenation of furfural over supported palladium nanoparticle catalysts prepared by sol-immobilisation: effect of catalyst support and reaction conditions, *Catal. Sci. Technol.* 8 (2018) 252-267.
- 47 N. Cherkasov, A.J. Expósito, M.S. Awz, J. Fernández-García, S. Huband, J. Sloan,

- L. Paniwnyk, E.V. Rebrov, Active site isolation in bismuth-poisoned Pd/SiO<sub>2</sub> catalysts for selective hydrogenation of furfural, *Appl. Catal. A* 570 (2019) 183-191.
- 48 M.D. Astuti, D.R. Mujiyanti, U.T. Santoso, S. Shimazu, Novel preparation method of bimetallic Ni-In alloy catalysts supported on amorphous alumina for the highly selective hydrogenation of furfural, *Mol. Catal.* 445 (2018) 52-60.
- 49 Z. Li, X. Wei, G. Liu, X. Meng, Z. Yang, S. Niu, D. Zhang, H. Gao, Z. Ma, Z. Zong, Highly selective hydrogenation of furfural and levulinic acid over Ni<sub>0.09</sub>Zn/NC<sub>600</sub> derived from ZIFW-8, *Mol. Catal.* 480 (2020) 110651-110657.
- 50 F. Dong, Y. Zhu, G. Ding, J. Cui, X. Li, Y. Li, One-step conversion of furfural into 2-methyltetrahydrofuran under mild conditions, *ChemSusChem*. 8 (2015) 1534-1537.
- 51 X. Huang, S. Kudo, J. Sperry, J.I. Hayashi, Clean Synthesis of 5-Hydroxymethylfurfural and Levulinic Acid by Aqueous Phase Conversion of Levoglucosenone over Solid Acid Catalysts, *ACS Sustainable Chem. Eng.* 7 (2019) 5892-5829.
- 52 \* S. Marullo, C. Rizzo, F. D'Anna, Activity of a Heterogeneous Catalyst in Deep Eutectic Solvents: The Case of Carbohydrate Conversion into 5-Hydroxymethylfurfural, *ACS Sustainable Chem. Eng.* 7 (2019) 13359-13368.
- 53 S. Xu, C. Yin, D. Pan, F. Hu, Y. Wu, Y. Miao, L. Gao, G. Xiao, Efficient conversion of glucose into 5-hydroxymethylfurfural using a bifunctional Fe<sup>3+</sup> modified Amberlyst-15 catalyst, *Sustain. Energy Fuels*. 3 (2019) 390-395.
- 54 Y. Feng, G. Yan, T. Wang, W. Jia, X. Zeng, J. Sperry, Y. Sun, X. Tang, T. Lei, L. Lin, Synthesis of MCM-41-Supported Metal Catalysts in Deep Eutectic Solvent for the Conversion of Carbohydrates into 5-Hydroxymethylfurfural, *ChemSusChem*. 12 (2019) 978-982.
- 55 M.M. Songo, R. Moutloali, S.S. Ray, Development of TiO<sub>2</sub>-Carbon Composite Acid Catalyst for Dehydration of Fructose to 5-Hydroxymethylfurfural, *Catalysts*. 9 (2019) 126-140
- 56 M. Nahavandi, T. Kasanneni, Z.S. Yuan, C.C. Xu, S. Rohani, Efficient Conversion of Glucose into 5-hydroxymethylfurfural using a Sulfonated Carbon-based Solid Acid Catalyst: An Experimental and Numerical Study, *ACS Sustainable Chem. Eng.* 7 (2019) 11970-11984.

- 57 Z. Cao, Z. Fan, Y. Chen, M. Li, T. Shen, C. Zhu, H. Ying, Efficient preparation of 5-hydroxymethylfurfural from cellulose in a biphasic system over hafnium phosphates, *Appl. Catal. B* 244 (2019) 170-177.
- 58 N.R. Peela, S.K. Yedla, B. Velaga, A. Kumar, A.K. Golder, Choline chloride functionalized zeolites for the conversion of biomass derivatives to 5-hydroxymethylfurfural, *Appl. Catal. A* 580 (2019) 59-70.
- 59 Wang, C. Liang, Q. Zhang, F. Zhang, Synergistic Catalysis of Brønsted Acid and Lewis Acid Coexisted on Ordered Mesoporous Resin for One-Pot Conversion of Glucose to 5-Hydroxymethylfurfural, *ACS Omega*. 4 (2019) 1053-1059.
- 60 \* Y. Feng, M. Li, Z. Gao, X. Zhang, X. Zeng, Y. Sun, X. Tang, T. Lei, L. Lin, Development of Betaine-Based Sustainable Catalysts for Green Conversion of Carbohydrates and Biomass into 5-Hydroxymethylfurfural, *ChemSusChem*. 12 (2019) 495-502.
- 61 Q. Wu, G. Zhang, M. Gao, S. Cao, L. Li, S. Liu, C. Xie, L. Huang, S. Yu, A.J. Ragauskas, Clean production of 5-hydroxymethylfurfural from cellulose using a hydrothermal/biomass-based carbon catalyst, *J. Clean. Prod.* 213 (2019) 1096-1102.
- 62 R.J.J. Ganado, D.E. Yu, F.C. Franco, Microwave-Assisted Conversion of Simple Sugars and Waste Coffee Grounds into 5-Hydroxymethylfurfural in a Highly Aqueous DMSO Solvent System Catalyzed by a Combination of  $\text{Al}(\text{NO}_3)_3$  and  $\text{H}_2\text{SO}_4$ , *Ind. Eng. Chem. Res.* 58 (2019) 14621-14631.
- 63 Cao, M. Ma, J. Liu, Y. Yang, H. Liu, X. Xu, J. Huang, H. Yue, G. Tian, S. Feng, Highly effective transformation of carbohydrates to 5-Hydroxymethylfurfural with Al-montmorillonite as catalyst, *Appl. Catal. A* 571 (2019) 96-101.
- 64 Yan, R. Ma, H. Wei, L. Li, B. Zou, Y. Xu, Ruthenium trichloride catalyzed conversion of cellulose into 5-hydroxymethylfurfural in biphasic system, *Bioresour. Technol.* 279 (2019) 84-91.
- 65 H. Lin, Q. Xiong, Y. Zhao, J. Chen, S. Wang, Conversion of carbohydrates into 5-hydroxymethylfurfural in a green reaction system of  $\text{CO}_2$  water-isopropanol, *AIChE J.* 63 (2017) 257-265.
- 66 H. Labauze, S. Camy, P. Floquet, B. Benjelloun-Mlayah, J.S. Condoret, Kinetic study of 5-Hydroxymethylfurfural synthesis from fructose in high pressure  $\text{CO}_2$ -Water two-phase system, *Ind. Eng. Chem. Res.* 58 (2018) 92-100.

- 67 X. Li, Y. Wang, X. Xie, C. Huang, S. Yang, Dehydration of fructose, sucrose and inulin to 5-hydroxymethylfurfural over yeast-derived carbonaceous microspheres at low temperatures, *RSC Adv.* 9 (2019) 9041-9048.
- 68 P.V. Rathod, R.B. Mujmule, W.J. Chung, A.R. Jadhav, H. Kim, Efficient Dehydration of Glucose, Sucrose, and Fructose to 5-Hydroxymethylfurfural Using Tri-cationic Ionic Liquids, *Catal. Lett.* 149 (2019) 672-687.
- 69 A. Mukherjee, M.J. Dumont, A. Cherestes, Production of 5-Hydroxymethylfurfural from Starch through an Environmentally-Friendly Synthesis Pathway, *Catal. Lett.* 149 (2019) 283-291.
- 70 \* R.F.A. Gomes, Y.N. Mitrev, S.P. Simeonov, C.A.M. Afonso, Going Beyond the Limits of the Biorenewable Platform: Sodium Dithionite-Promoted Stabilization of 5-Hydroxymethylfurfural, *ChemSusChem.* 11 (2018) 1612-1616.
- 71 \* M.R. Whitaker, A. Parulkar, P. Ranadive, R. Joshi, N.A. Brunelli, Examining Acid Formation During the Selective Dehydration of Fructose to 5-Hydroxymethylfurfural in Dimethyl Sulfoxide and Water, *ChemSusChem.* 12 (2019) 2211-2219.
- 72 \* W. Fan, Y. Queneau, F. Popowycz, HMF in multicomponent reactions: utilization of 5-hydroxymethylfurfural (HMF) in the Biginelli reaction, *Green Chem.* 20 (2018) 485-492.
- 73 C. Verrier, S. Moebs-Sanchez, Y. Queneau, F. Popowycz, The Piancatelli reaction and its variants: recent applications to high added-value chemicals and biomass valorization, *Org. Biomol. Chem.* 16 (2018) 676-687.
- 74 W. Fan, C. Verrier, Y. Queneau, F. Popowycz, 5-Hydroxymethylfurfural (HMF) in organic synthesis: a review of its recent applications towards fine chemicals, *Curr. Org. Synt.* 16 (2019) 583-614.
- 75 van Zandvoort, E.J. Koers, M. Weingarth, P.C.A. Bruijninx, M. Baldus, B.M. Weckhuysen, Structural characterization of <sup>13</sup>C-enriched humins and alkali-treated <sup>13</sup>C humins by 2D solid-state NMR, *Green Chem.* 17 (2015) 4383-4392.
- 76 S.K.R. Patil, J. Heltzel, C.R.F. Lund, Comparison of structural features of humins formed catalytically from glucose, fructose, and 5-hydroxymethylfurfuraldehyde, *Energ. Fuel.* 26 (2012) 5281-5293.
- 77 G. Tsilomelekis, M.J. Orella, Z. Lin, Z. Cheng, W. Zheng, V. Nikolakis, D.G. Vlachos, Molecular structure, morphology and growth mechanisms and rates of 5-

- hydroxymethyl furfural (HMF) derived humins, *Green Chem.* 18 (2016) 1983-1993.
- 78 T.M.C. Hoang, E.R.H. van Eck, W.P. Bula, J.G.E. Gardeniers, L. Lefferts, K. Seshan, Humin based by-products from biomass processing as a potential carbonaceous source for synthesis gas production, *Green Chem.* 17 (2015) 959-972.
- 79 \* V. Maruani, S. Narayanin-Richenapin, E. Framery, B. Andrioletti, Acidic hydrothermal dehydration of D-glucose into humins: Identification and characterization of intermediates, *ACS Sustainable Chem. Eng.* 6 (2018) 13487-13493.
- 80 Schade, K.F. Kalz, D. Neukum, W. Kleist, J.D. Grunwaldt, Supported gold-and silver-based catalysts for the selective aerobic oxidation of 5-(hydroxymethyl) furfural to 2, 5-furandicarboxylic acid and 5-hydroxymethyl-2-furancarboxylic acid, *Green Chem.* 20 (2018) 3530-3541.
- 81 J. An, G. Sun, H. Xia, Aerobic Oxidation of 5-Hydroxymethylfurfural to High-Yield 5-Hydroxymethyl-2-furancarboxylic Acid by Poly (vinylpyrrolidone)-Capped Ag Nanoparticle Catalysts, *ACS Sustainable Chem. Eng.* 7 (2019) 6696-6706.
- 82 Chen, W. Yang, Z. Gui, S. Saravanamurugan, A. Riisager, W. Cao, Z. Qi, MnOx/P25 with tuned surface structures of anatase-rutile phase for aerobic oxidation of 5-hydroxymethylfurfural into 2, 5-diformylfuran, *Catal. Today.* 319 (2019) 105-112.
- 83 Q. Ke, Y. Jin, F. Ruan, M.N. Ha, D. Li, P. Cui, Y. Cao, H. Wang, T. Wang, X. Han, X. Wang, Boosting the activity of catalytic oxidation of 5-hydroxymethylfurfural to 2, 5-diformylfuran over nitrogen-doped manganese oxide catalysts, *Green Chem.* 21 (2019) 4313-4318.
- 84 Q. Wu, Y. He, H. Zhang, Z. Feng, Y. Wu, T. Wu, Photocatalytic selective oxidation of biomass-derived 5-hydroxymethylfurfural to 2, 5-diformylfuran on WO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> composite under irradiation of visible light, *Mol. Catal.* 436 (2017) 10-18.
- 85 D.A. Giannakoudakis, V. Nair, A. Khan, E.A. Deliyanni, J.C. Colmenares, K.S. Triantafyllidis, Additive-free photo-assisted selective partial oxidation at ambient conditions of 5-hydroxymethylfurfural by manganese (IV) oxide nanorods, *Appl. Catal. B-Environ.* 256 (2019) 117803-117812.

- 86 Ventura, M. Aresta, A. Dibenedetto, Selective Aerobic Oxidation of 5-(Hydroxymethyl) furfural to 5-Formyl-2-furancarboxylic Acid in Water, *ChemSusChem*. 9 (2016) 1096-1100.
- 87 \* C.T. Chen, C.V. Nguyen, Z.Y. Wang, Y. Bando, Y. Yamauchi, M.T. Bazziz, A. Fatehmulla, W.A. Farooq, T. Yoshikawa, T. Masuda, K.C. Wu, Hydrogen Peroxide Assisted Selective Oxidation of 5-Hydroxymethylfurfural in Water under Mild Conditions, *ChemCatChem*. 10 (2018) 361-365.
- 88 A. Danielli da Fonseca Ferreira, M. Dorneles de Mello, M.A.P. da Silva, Catalytic Oxidation of 5-hydroxymethylfurfural to 2, 5-furandicarboxylic acid over Ru/Al<sub>2</sub>O<sub>3</sub> in a Trickle-bed Reactor, *Ind. Eng. Chem. Res.* 58 (2018) 128-137.
- 89 \* E. Hayashi, Y. Yamaguchi, K. Kamata, N. Tsunoda, Y. Kumagai, F. Oba, M. Hara, Effect of MnO<sub>2</sub> crystal structure on aerobic oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid, *J. Am. Chem. Soc.* 141 (2019) 890-900.
- 90 R. Chen, J. Xin, D. Yan, H. Dong, X. Lu, S. Zhang, Highly Efficient Oxidation of 5-Hydroxymethylfurfural to 2, 5-Furandicarboxylic Acid with Heteropoly Acids, *ChemSusChem*. 12 (2019) 2715-2724.
- 91 S. Xu, P. Zhou, Z. Zhang, C. Yang, B. Zhang, K. Deng, S. Bottle, H. Zhu, Selective oxidation of 5-hydroxymethylfurfural to 2, 5-furandicarboxylic acid using O<sub>2</sub> and a photocatalyst of Co-thioporphyrazine bonded to g-C<sub>3</sub>N<sub>4</sub>, *J. Am. Chem. Soc.* 139 (2017) 14775-14782.
- 92 \* J. Liu, L. Dang, Z. Xu, H.Q. Yu, S. Jin, G.W. Huber, Electrochemical oxidation of 5-Hydroxymethylfurfural with NiFe layered double hydroxide (LDH) nanosheet catalysts, *ACS Catal.* 8 (2018) 5533-5541.
- 93 \* S. Barwe, J. Weidner, S. Cychy, D.M. Morales, S. Dieckhöfer, D. Hiltrop, J. Masa, M. Muhler, W. Schuhmann, Electrocatalytic Oxidation of 5-(Hydroxymethyl) furfural Using High-Surface-Area Nickel Boride, *Angew. Chem. Int. Ed.* 57 (2018) 11460-11464.
- 94 \* Zhang, X. Sheng, X. Chen, Z. Fang, J. Jiang, M. Wang, F. Li, L. Fan, Y. Ren, B. Zhang, B.J. Timmer, M.S.G. Ahlquist, L. Sun, Paired Electrocatalytic Oxygenation and Hydrogenation of Organic Substrates with Water as the Oxygen and Hydrogen Source, *Angew. Chem. Int. Ed.* 58 (2019) 9155-9159.
- 95 \* B.J. Taitt, D.H. Nam, K.S. Choi, A comparative study of nickel, cobalt, and iron



- oxyhydroxide anodes for the electrochemical oxidation of 5-hydroxymethylfurfural to 2, 5-furandicarboxylic acid, *ACS Catal.* 9 (2018) 660-670.
- 96 A.C. Cardiel, B.J. Taitt, K.S. Choi, Stabilities, Regeneration Pathways, and Electrocatalytic Properties of Nitroxyl Radicals for the Electrochemical Oxidation of 5-Hydroxymethylfurfural, *ACS Sustainable Chem. Eng.* 7 (2019) 11138-11149.
- 97 Gao, Z. Liu, J. Ma, L. Zhong, Z. Song, J. Xu, S. Gan, D. Han, L. Niu, NiSe@ NiOx core-shell nanowires as a non-precious electrocatalyst for upgrading 5-hydroxymethylfurfural into 2, 5-furandicarboxylic acid, *Appl. Catal. B-Environ.* 261 (2020) 118235-118242.
- 98 X. Huang, J. Song, M. Hua, Z. Xie, S. Liu, T. Wu, G. Yang, B. Han, Enhancing the electrocatalytic activity of CoO for the oxidation of 5-hydroxymethylfurfural by introducing oxygen vacancies, *Green Chem.* 22 (2020) 843-849.
- 99 \*A. Salazar, P. Hünemörder, J. Rabeah, A. Quade, R.V. Jagadeesh, E. Mejía, Synergetic Bimetallic Oxidative Esterification of 5-hydroxymethylfurfural (HMF) under mild conditions, *ACS Sustainable Chem. Eng.* 7 (2019) 12061-12068.
- 100 W.P. Dijkman, M.W. Fraaije, Discovery and characterization of a 5-hydroxymethylfurfural oxidase from *Methylovorus* sp. strain MP688, *Appl. Environ. Microb.* 80 (2014) 1082-1090.
- 101 W.P. Dijkman, D.E. Groothuis, M.W. Fraaije, Enzyme-catalyzed oxidation of 5-hydroxymethylfurfural to furan-2, 5-dicarboxylic acid, *Angew. Chem. Intern. Ed.* 2014, 53, 6515-6518.
- 102 Y.Z. Qin, Y.M. Li, M.H. Zong, H. Wu, N. Li, Enzyme-catalyzed selective oxidation of 5-hydroxymethylfurfural (HMF) and separation of HMF and 2, 5-diformylfuran using deep eutectic solvents, *Green Chem.* 17 (2015) 3718-3722.
- 103 S.M. McKenna, P. Mines, P. Law, K. Kovacs-Schreiner, W.R. Birmingham, N.J. Turner, S. Leimkühler, A.J. Carnell, The continuous oxidation of HMF to FDCA and the immobilisation and stabilisation of periplasmic aldehyde oxidase (PaoABC), *Green Chem.* 19 (2017) 4660-4665.
- 104 C. Zhang, X. Chang, L. Zhu, Q. Xing, S. You, W. Qi, R. Su, Z. He, Highly efficient and selective production of FFCA from CotA-TJ102 laccase-catalyzed oxidation of 5-HMF, *Int. J. Biol. Macromol.* 128 (2019) 132-139.
- 105 A. Rothamer, J.H. Jennings, Study of the knocking propensity of 2, 5-dimethylfuran-gasoline and ethanol-gasoline blends, *Fuel* 98 (2012) 203-212.

- 106 S. Nishimura, N. Ikeda, K. Ebitani, Selective hydrogenation of biomass-derived 5-hydroxymethylfurfural (HMF) to 2, 5-dimethylfuran (DMF) under atmospheric hydrogen pressure over carbon supported Pd-Au bimetallic catalyst, *Catal. Today*. 232 (2014) 89-98.
- 107 X. Wang, X. Liang, J. Li, Q. Li, Catalytic hydrogenolysis of biomass-derived 5-hydroxymethylfurfural to biofuel 2, 5-dimethylfuran, *Appl. Catal. A* 576 (2019) 85-95.
- 108 Z. An, W. Wang, S. Dong, J. He, Well-distributed cobalt-based catalysts derived from layered double hydroxides for efficient selective hydrogenation of 5-hydroxymethylfurfural to 2, 5-methylfuran, *Catal. Today*. 319 (2019) 128-138.
- 109 F. Yang, J. Mao, S. Li, J. Yin, J. Zhou, W. Liu, Cobalt-graphene nanomaterial as an efficient catalyst for selective hydrogenation of 5-hydroxymethylfurfural into 2, 5-dimethylfuran, *Catal. Sci. Technol.* 9 (2019) 1329-1333.
- 110 J. Li, J.L. Liu, H.Y. Liu, G.Y. Xu, J.J. Zhang, J.X. Liu, G.L. Zhou, Q. Li, Z.H. Xu, Y. Fu, Selective Hydrodeoxygenation of 5-Hydroxymethylfurfural to 2, 5-Dimethylfuran over Heterogeneous Iron Catalysts, *ChemSusChem*. 10 (2017) 1436-1447.
- 111 B.S. Solanki, C.V. Rode, Selective hydrogenation of 5-HMF to 2, 5-DMF over a magnetically recoverable non-noble metal catalyst, *Green Chem*. 21 (2019) 6390-6406.
- 112 C. Sarkar, P. Koley, I. Shown, J. Lee, Y.F. Liao, K. An, J. Tardio, L. Nakka, K.H. Chen, J. Mondal, Integration of Interfacial and Alloy Effects to Modulate Catalytic Performance of Metal-Organic-Framework-Derived Cu-Pd Nanocrystals toward Hydrogenolysis of 5-Hydroxymethylfurfural, *ACS Sustainable Chem. Eng.* 7 (2019) 10349-10362.
- 113 \* J.M. Asensio, A.B. Miguel, P.F. Fazzini, P.W.N.M. van Leeuwen, B. Chaudret, Hydrodeoxygenation Using Magnetic Induction: High-Temperature Heterogeneous Catalysis in Solution, *Angew. Chem. Int. Ed.* 58 (2019) 11306-11310.
- 114 R. Insyani, D. Verma, H.S. Cahyadi, S.M. Kim, S.K. Kim, N. Karanwal, J. Kim, One-pot di-and polysaccharides conversion to highly selective 2, 5-dimethylfuran over Cu-Pd/Amino-functionalized Zr-based metal-organic framework (UiO-66 (NH<sub>2</sub>))@ SGO tandem catalyst, *Appl. Catal. B* 243 (2019) 337-354.

- 115 \* Y. Zhang, B. Wang, L. Qin, Q. Li, Y. Fan, A non-noble bimetallic alloy in the highly selective electrochemical synthesis of the biofuel 2, 5-dimethylfuran from 5-hydroxymethylfurfural, *Green Chem.* 21 (2019) 1108-1113.
- 116 S. Chen, C. Ciotonea, K.D.O. Vigier, F. Jérôme, R. Wojcieszak, F. Dumeignil, E. Marceau, S. Royer, Hydroconversion of 5-hydroxymethylfurfural to 2, 5-dimethylfuran and 2, 5-dihydroxymethyltetrahydrofuran over non-promoted Ni/SBA-15, *ChemCatChem.* 12 (2020) 2050-2059.
- 117 T. Komanoya, T. Kinemura, Y. Kita, K. Kamata, M. Hara, Electronic effect of ruthenium nanoparticles on efficient reductive amination of carbonyl compounds, *J. Am. Chem. Soc.* 139 (2017) 11493-11499.
- 118 D. Pinggen, J.B. Schwaderer, J. Walter, J. Wen, G. Murray, D. Vogt, S. Mecking, Diamines for Polymer Materials via Direct Amination of Lipid-and Lignocellulose-based Alcohols with NH<sub>3</sub>, *ChemCatChem.* 10 (2018) 3027-3033.
- 119 \* K. Zhou, H. Liu, H. Shu, S. Xiao, D. Guo, Y. Liu, Z. Wei, X. Li, A comprehensive study on the reductive amination of 5-hydroxymethylfurfural into 2, 5-bisaminomethylfuran over Raney Ni through DFT calculations, *ChemCatChem.* 11 (2019) 2649-2656.
- 120 Y. Liu, K. Zhou, H. Shu, H. Liu, J. Lou, D. Guo, Z. Wei, X. Li, Switchable synthesis of furfurylamine and tetrahydrofurfurylamine from furfuryl alcohol over Raney nickel, *Catal. Sci. Technol.* 7 (2017) 4129-4135.
- 121 S. Zhang, G. Shen, Z. Chen, G. Yin, Accessing the HMF derivatives from furfural acetate through oxidative carbonylation, *Chemistry Select.* 2 (2017) 7096-7099.
- 122 G. Shen, S. Zhang, Y. Lei, Z. Chen, G. Yin, Synthesis of 2, 5-furandicarboxylic acid by catalytic carbonylation of renewable furfural derived 5-bromofuroic acid, *Mol. Catal.* 455 (2018) 204-209.
- 123 G. Shen, S. Zhang, Y. Lei, J. Shi, Y. Xia, F. Mei, Z. Chen, G. Yin, Catalytic carbonylation of renewable furfural derived 5-bromofurfural to 5-formyl-2-furancarboxylic acid in oil/aqueous bi-phase system, *Mol. Catal.* 463 (2019) 94-98.
- 124 \* G. Shen, J. Shi, Y. Lei, Z. Chen, B. Andrioletti, G. Yin, Aqueous Carbonylation of Furfural Derived 5-Bromofuroic Acid to 2, 5-Furandicarboxylic Acid with Supported Palladium Catalyst, *Ind. Eng. Chem. Res.* 58 (2019) 22951-22957.
- 125 V. Choudhary, S.H. Mushrif, C. Ho, A. Anderko, V. Nikolakis, N.S. Marinkovic, A.I. Frenkel, S.I. Sandler, D.G. Vlachos, Insights into the interplay of Lewis and

- Brønsted acid catalysts in glucose and fructose conversion to 5-(hydroxymethyl) furfural and levulinic acid in aqueous media, *J. Am. Chem. Soc.* 135 (2013) 3997-4006.
- 126 H. Ren, B. Girisuta, Y. Zhou, L. Liu, Selective and recyclable depolymerization of cellulose to levulinic acid catalyzed by acidic ionic liquid, *Carbohydr. Polym.* 117 (2015) 569-576.
- 127 \* Y. Peng, X. Li, T. Gao, T. Li, W. Yang, Preparation of 5-methylfurfural from starch in one step by iodide mediated metal-free hydrogenolysis, *Green Chem.* 21 (2019) 4169-4177.
- 128 G.K. Beh, C.T. Wang, K. Kim, J. Qu, J. Cairney, Y.H. Ng, A.K. An, R. Ryoo, A. Urakawa, W.Y. Teoh, Flame-made amorphous solid acids with tunable acidity for the aqueous conversion of glucose to levulinic acid, *Green Chem.* 22 (2020) 688-698.
- 129 A. Chappaz, J. Lai, K.D.O. Vigier, D. Morvan, R. Wischert, M. Corbet, B. Doumert, X. Trivelli, A. Liebens, F. Jérôme, Selective Conversion of Concentrated Feeds of Furfuryl Alcohol to Alkyl Levulinates Catalyzed by Metal Triflates, *ACS Sustainable Chem. Eng.* 6 (2018) 4405-4411.
- 130 S.S. Chen, L. Wang, K.M. Iris, D.C. Tsang, A.J. Hunt, F. Jérôme, S. Zhang, Y.S. Ok, C.S. Poon, Valorization of lignocellulosic fibres of paper waste into levulinic acid using solid and aqueous Brønsted acid, *Bioresource technol.* 247 (2018) 387-394.
- 131 \* A. Ledoux, L. S. Kuigwa, E. Framery, B. Andrioletti, A highly sustainable route to pyrrolidone derivatives-direct access to biosourced solvents, *Green Chem.* 17 (2015) 3251-3254.
- 132 Y. Ogiwara, T. Uchiyama, N. Sakai, Reductive amination/cyclization of keto acids using a hydrosilane for selective production of lactams versus cyclic amines by switching of the indium catalyst, *Angew. Chem. Int. Ed.* 55 (2016) 1864-1867.
- 133 \* C. Xie, J. Song, H. Wu, Y. Hu, H. Liu, Z. Zhang, P. Zhang, B. Chen, B. Han, Ambient Reductive Amination of Levulinic Acid to Pyrrolidones over Pt Nanocatalysts on Porous TiO<sub>2</sub> Nanosheets, *J. Am. Chem. Soc.* 141 (2019) 4002-4009.
- 134 K. Tadele, S. Verma, M.A. Gonzalez, R.S. Varma, A sustainable approach to empower the bio-based future: upgrading of biomass via process intensification,

- Green Chem. 19 (2017) 1624-1627.
- 135 M.G. Al-Shaal, M. Calin, I. Delidovich, R. Palkovits, Microwave-assisted reduction of levulinic acid with alcohols producing  $\gamma$ -valerolactone in the presence of a Ru/C catalyst, Catal. Commun. 75 (2016) 65-68.
- 136 Obregón, I. Gandarias, M.G. Al-Shaal, C. Mevissen, P.L. Arias, R. Palkovits, The role of the hydrogen source on the selective production of  $\gamma$ -valerolactone and 2-methyltetrahydrofuran from levulinic acid, ChemSusChem. 9 (2016) 2488-2495.
- 137 L. Negahdar, M.G. Al-Shaal, F.J. Holzhäuser, R. Palkovits, Kinetic analysis of the catalytic hydrogenation of alkyl levulinates to  $\gamma$ -valerolactone, Chem. Eng. Sci. 158 (2017) 545-551.
- 138 \* F.J. Holzhäuser, J.B. Mensah, R. Palkovits, (Non-) Kolbe electrolysis in biomass valorization-a discussion of potential applications, Green Chem. 22 (2020) 286-301.
- 139 F.M. Geilen, B. Engendahl, A. Harwardt, W. Marquardt, J. Klankermayer, W. Leitner, Selective and flexible transformation of biomass-derived platform chemicals by a multifunctional catalytic system, Angew. Chem. Int. Ed. 2010, 49, 5510-5514.

## Annotated references

\*15 P.T. Anastas, J.B. Zimmerman, The periodic table of the elements of green and sustainable chemistry, *Green Chem.* 21 (2019) 6545-6566. Anastas and Zimmerman share their vision of green and sustainable chemistry, which is one element at the intersection of several others, including economic, ethical ones, towards a sustainable future.

\*25 S. Jiang, C. Verrier, M. Ahmar, J. Lai, C. Ma, E. Muller, Y. Queneau, M. Peratitus, F. Jerome, K. de Oliveira Vigier, Unveiling the role of choline chloride in furfural synthesis from highly concentrated feeds of xylose, *Green Chem.* 20 (2018) 5104-5110. Vigier and coworkers showed that the use of the biphasic mixture of aqueous choline chloride ( $\text{ChCl}_{\text{aq}}$ ) and 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.

\*36 I. Scodeller, S. Mansouri, D. Morvan, E. Muller, K.D.O. Vigier, R. Wischert, F. Jérôme, Synthesis of Renewable meta-Xylylenediamine from Biomass-Derived Furfural, *Angew. Chem. Int. Ed.* 57 (2018) 10510-10514. A smart strategy based on a cycloaddition – aromatization sequence offers a general access to aminated xylenes, useful scaffolds in fine chemistry.

39\* L. Kipshagen, L.T. Vömel, M.A. Liauw, A. Klemmer, A. Schulz, C. Kropf, P.J.C. Hausoul, R. Palkovits, Anionic surfactants based on intermediates of carbohydrate conversion, *Green Chem.* 21 (2019) 3882-3890. This paper illustrates the interest of furfural and HMF derivatives in the design of bio-based surfactants.

\*52 S. Marullo, C. Rizzo, F. D'Anna, Activity of a Heterogeneous Catalyst in Deep Eutectic Solvents: The Case of Carbohydrate Conversion into 5-Hydroxymethylfurfural, *ACS Sustainable Chem. Eng.* 7 (2019) 13359-13368. D'Anna used Amberlyst for the efficient preparation of 5-HMF in 78% and 69% yields from fructose and sucrose respectively.

\*60 Y. Feng, M. Li, Z. Gao, X. Zhang, X. Zeng, Y. Sun, X. Tang, T. Lei, L. Lin, Development of Betaine-Based Sustainable Catalysts for Green Conversion of Carbohydrates and Biomass into 5-Hydroxymethylfurfural, *ChemSusChem.* 12 (2019)

495-502. Some bio-based catalysts, such as betaine-based catalysts reported by Zeng and co-workers, afford 5-HMF in up to 88% yield from fructose, glucose, cellulose and lignocellulosic materials.

\*70 R.F.A. Gomes, Y.N. Mitrev, S.P. Simeonov, C.A.M. Afonso, Going Beyond the Limits of the Biorenewable Platform: Sodium Dithionite-Promoted Stabilization of 5-Hydroxymethylfurfural, *ChemSusChem*. 11 (2018) 1612-1616. A major contribution in the field is the observation by Afonso et al. that sodium dithionite promoted the thermal stabilization of HMF, effective at the preparative stage or in the downstream uses towards fine chemicals.

\*71 M.R. Whitaker, A. Parulkar, P. Ranadive, R. Joshi, N.A. Brunelli, Examining Acid Formation During the Selective Dehydration of Fructose to 5-Hydroxymethylfurfural in Dimethyl Sulfoxide and Water, *ChemSusChem*. 12 (2019) 2211-2219. Brunelli *and coll.* Have contributed to the field by highlighting the influence of the H<sub>2</sub>O/DMSO ratio on the catalytic activity of catalysts.

\*72 W. Fan, Y. Queneau, F. Popowycz, HMF in multicomponent reactions: utilization of 5-hydroxymethylfurfural (HMF) in the Biginelli reaction, *Green Chem*. 20 (2018) 485-492. The first use of HMF in the Biginelli reaction is reported in this paper, illustrating that the sensitivity of HMF to acidic conditions can be overcome.

\*79 V. Maruani, S. Narayanan-Richenapin, E. Framery, B. Andrioletti, Acidic hydrothermal dehydration of D-glucose into humins: Identification and characterization of intermediates, *ACS Sustainable Chem. Eng.* 6 (2018) 13487-13493. This work shows that during the decomposition of D-glucose into humins, besides HMF, other water-soluble oligomers of D-glucose (WSO) have been identified, leading to the proposition of a slight modification of the humins structure as compared to what is commonly admitted.

\*87 C.T. Chen, C.V. Nguyen, Z.Y. Wang, Y. Bando, Y. Yamauchi, M.T. Bazziz, A. Fatehmulla, W.A. Farooq, T. Yoshikawa, T. Masuda, K.C. Wu, Hydrogen Peroxide Assisted Selective Oxidation of 5-Hydroxymethylfurfural in Water under Mild Conditions, *ChemCatChem*. 10 (2018) 361-365. FFCA can be in 92% yield using ruthenium on activated carbon in water.

\*89 E. Hayashi, Y. Yamaguchi, K. Kamata, N. Tsunoda, Y. Kumagai, F. Oba, M. Hara, Effect of MnO<sub>2</sub> crystal structure on aerobic oxidation of 5-hydroxymethylfurfural

to 2,5-furandicarboxylic acid, *J. Am. Chem. Soc.* 141 (2019) 890-900. Hara and coll. used a  $\text{MnO}_2/\text{NaHCO}_3$  combination using  $\text{O}_2$  as the sole oxidant in water to selectively prepare FDCA in 86% yield from HMF.

\*92 J. Liu, L. Dang, Z. Xu, H.Q. Yu, S. Jin, G.W. Huber, Electrochemical oxidation of 5-Hydroxymethylfurfural with NiFe layered double hydroxide (LDH) nanosheet catalysts, *ACS Catal.* 8 (2018) 5533-5541. Huber, Jin and co-workers demonstrate that electrochemical processes are efficient an alternative for the oxidation of HMF. They used a bimetallic NiFe-based catalyst as the anode for the electrochemical oxidation of a highly concentrated solution of HMF to FDCA with a 99% faradic efficiency.

\*93 S. Barwe, J. Weidner, S. Cychy, D.M. Morales, S. Dieckhöfer, D. Hiltrop, J. Masa, M. Muhler, W. Schuhmann, Electrocatalytic Oxidation of 5-(Hydroxymethyl) furfural Using High-Surface-Area Nickel Boride, *Angew. Chem. Int. Ed.* 57 (2018) 11460-11464. Schuhmann and coll. have 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.

\*94 P. Zhang, X. Sheng, X. Chen, Z. Fang, J. Jiang, M. Wang, F. Li, L. Fan, Y. Ren, B. Zhang, B.J. Timmer, M.S.G. Ahlquist, L. Sun, Paired Electrocatalytic Oxygenation and Hydrogenation of Organic Substrates with Water as the Oxygen and Hydrogen Source, *Angew. Chem. Int. Ed.* 58 (2019) 9155-9159. Sun and coll. showed that  $\text{NiB}_x$  displayed excellent conversion, selectivity and faradaic efficiency values at both the anode and the cathode simultaneously using water as the oxygen and hydrogen source.

\*95 B.J. Taitt, D.H. Nam, K.S. Choi, A comparative study of nickel, cobalt, and iron oxyhydroxide anodes for the electrochemical oxidation of 5-hydroxymethylfurfural to 2, 5-furandicarboxylic acid, *ACS Catal.* 9 (2018) 660-670. Choi and coll. involved the use of thin and thick sets of  $\text{NiOOH}$ , or 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) and 4-acetamido-TEMPO (ACT) in mildly basic conditions.

\*99 A. Salazar, P. Hünemörder, J. Rabeah, A. Quade, R.V. Jagadeesh, E. Mejía, Synergetic Bimetallic Oxidative Esterification of 5-hydroxymethylfurfural (HMF) under mild conditions, *ACS Sustainable Chem. Eng.* 7 (2019) 12061-12068. Dimethyl furan-2,5-dicarboxylate (FDCM) can be prepared quantitatively from HMF using a bimetallic  $\text{Ru@C}$  and  $\text{Co}_x\text{O}_y\text{-N@C}$  catalytic system under ambient conditions in methanol. The reaction is also efficient for the preparation of methyl furan-2-carboxylate from furfural.



\*113 J.M. Asensio, A.B. Miguel, P.F. Fazzini, P.W.N.M. van Leeuwen, B. Chaudret, Hydrodeoxygenation Using Magnetic Induction: High-Temperature Heterogeneous Catalysis in Solution, *Angew. Chem. Int. Ed.* 58 (2019) 11306-11310. Chaudret, Asensio and co-workers obtained DMF in quantitative yield from HMF using FeC@Ru NPs as the catalyst.

\*115 Y. Zhang, B. Wang, L. Qin, Q. Li, Y. Fan, A non-noble bimetallic alloy in the highly selective electrochemical synthesis of the biofuel 2, 5-dimethylfuran from 5-hydroxymethylfurfural, *Green Chem.* 21 (2019) 1108-1113. Fan, Li and co-workers demonstrate that the use of a non-noble bimetallic Cu-Ni electrode can be used efficiently for the electrocatalytic production of DMF from HMF, achieving a 91% conversion and a 88% faradic efficiency.

\*119 K. Zhou, H. Liu, H. Shu, S. Xiao, D. Guo, Y. Liu, Z. Wei, X. Li, A comprehensive study on the reductive amination of 5-hydroxymethylfurfural into 2, 5-bisaminomethylfuran over Raney Ni through DFT calculations, *ChemCatChem.* 11 (2019) 2649-2656. 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).

\*124 G. Shen, J. Shi, Y. Lei, Z. Chen, B. Andrioletti, G. Yin, Aqueous Carbonylation of Furfural Derived 5-Bromofuroic Acid to 2, 5-Furandicarboxylic Acid with Supported Palladium Catalyst, *Ind. Eng. Chem. Res.* 58 (2019) 22951-22957. Building on previous papers by Yion and coll, this paper is a nice illustration of the smart use of furfural as a resource for C6 targets.

\*127 Y. Peng, X. Li, T. Gao, T. Li, W. Yang, Preparation of 5-methylfurfural from starch in one step by iodide mediated metal-free hydrogenolysis, *Green Chem.* 21 (2019) 4169-4177. Besides HMF, the direct transformation of starch also provides levulinic acid (LA) in 22% yield as the main side product. It opens the way to several C5 downstream derivatives.

\*131 A. Ledoux, L. S. Kuigwa, E. Framery, B. Andrioletti, A highly sustainable route to pyrrolidone derivatives-direct access to biosourced solvents, *Green Chem.* 17 (2015) 3251-3254. A beautiful example of low E-factor (0.2) process: no additive, no-solvent, catalyst-free route to a biobased methylpyrrolidone in one step from levulinic acid and easy isolation by distillation.

\*133 C. Xie, J. Song, H. Wu, Y. Hu, H. Liu, Z. Zhang, P. Zhang, B. Chen, B. Han, Ambient Reductive Amination of Levulinic Acid to Pyrrolidones over Pt Nanocatalysts

on Porous TiO<sub>2</sub> Nanosheets, *J. Am. Chem. Soc.* 141 (2019) 4002-4009. Han, Song and co-workers develop novel catalysts to produce various N-substituted-pyrrolidones from LA, thus widening the scope of possible derivatives of LA.

\*138 F.J. Holzhäuser, J.B. Mensah, R. Palkovits, (Non-) Kolbe electrolysis in biomass valorization-a discussion of potential applications, *Green Chem.* 22 (2020) 286-301. The review highlights the fascinating potential of both Kolbe and (Non-) Kolbe electrochemical processes for the transformation of biomass.