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Furfural: A renewable and versatile platform molecule for the synthesis of chemicals and fuels

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The production of future transportation fuels and chemicals requires the deployment of new catalytic processes that transform biomass into valuable products under competitive conditions. Furfural has been identified as one of the most promising chemical platforms directly derived from biomass. With an annual production close to 300 kTon, furfural is currently a commodity chemical, and the technology for its production is largely established. The aim of this review is to discuss the most relevant chemical routes for converting furfural to chemicals, biofuels, and additives. This review focuses not only on industrially produced chemicals derived from furfural, but also on other not yet commercialised products that have a high potential for commercialisation as commodities. Other chemicals that are currently produced from oil but can also be derived from furfural are also reviewed. The chemical and engineering aspects such as the reaction conditions and mechanisms, as well as the main achievements and the challenges still to come in the pursuit of advancing the furfural-based industry, are highlighted.

1. Introduction

Modern society requires the development of economical and energy-efficient processes for the sustainable production of fuels and chemicals. This requirement primarily results from the combination of a variety of factors, including the sharp increase in the demand for fuel and chemicals driven by global population growth, decrease in petroleum resources, high oil prices, and political (energy security) and environmental concerns (CO_2 emissions and global warming effect). In 2008, the European Parliament approved a directive with mandatory targets to increase energy efficiency by 20% from the present levels, decrease greenhouse gas emissions by 20% compared to the 1990 levels, and reach a 20% renewable energy share of the final consumption by the year 2020.[1] Other countries (USA, China, etc.) are also developing policies in the same direction. Recently, the use of food crops (sugar cane, corn, wheat, sugar beet, etc.) to produce renewable fuels (known as first-generation biofuels) has been criticised for the following reasons: *i*) the impact on food prices and biodiversity; *ii*) these fuels are often not cost competitive with existing fossil fuels without subsidies; and *iii*) reductions in greenhouse gas emissions are very limited. In contrast, the use of lignocellulosic biomass (non-edible) to produce the so-called 2nd generation biofuels and biomass-derived chemicals does not present the aforementioned drawbacks and is considerably more beneficial from geopolitical and environmental perspectives. Within this scenario, the use of lignocellulosic biomass appears to be one of the most attractive and promising options for achieving environmentally friendly and sustainable production of fuels and chemicals.[2-9]

At present, the production of bioethanol from biomass-derived carbohydrates is undoubtedly the most important large-scale commercial process for producing second-generation liquid transportation biofuels. In addition to biofuels, biomass-based chemicals also appear to be a very interesting option, and these chemicals have gained a better competitive position against oil derivatives in recent years. The spectrum of potential routes for transforming biomass (gasification, pyrolysis, fermentation, and chemical routes) into chemicals is very broad.[2,9-11]

In this context, furfural (FUR) has recently been emphasised as one of the top value-added chemicals derived from biomass,[3] being identified as one of the key chemicals produced in the so-called lignocellulosic biorefineries. FUR is produced from renewable agricultural sources such as food crop residues and wood wastes. The synthesis of FUR from fossil-based raw materials (e.g., *via* the catalytic oxidation of 1,3-dienes) is not economically competitive. The largest producer of FUR is China (~70% total production capacity). Other countries with significant FUR production include the Dominican Republic (Central Romana Corporation, 32 kTon/year, world's largest single producer) and South Africa (20 kTon/year). These three countries account for approximately 90% of the global FUR production capacity (280 kTon).[12]

The commercial utility of FUR was first discovered in 1921.[13] At present, FUR is commercially produced through the acid-catalysed transformation of pentosan sugars present in biomass; the C_5 polysaccharides are first hydrolysed by H_2SO_4 to monosaccharides (primarily xylose), which are subsequently dehydrated to FUR (Figure 1). FUR is then recovered from the liquid phase by steam stripping to avoid further degradation, and purified by double distillation.[12,14]

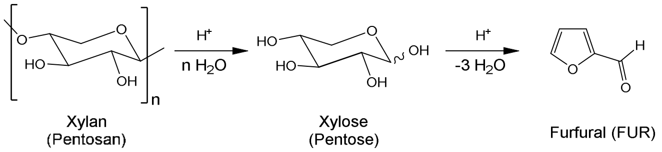

Figure 1. Simplified reaction scheme for the acid-catalysed conversion of pentosan into furfural (FUR).

Furfural production is limited by major drawbacks, including relatively low yields (~50%) resulting from undesired reactions. These include the formation of humins *via* FUR condensation with reaction intermediates, FUR resinification, and finally, fragmentation or decomposition reactions of xylose.[14-18]

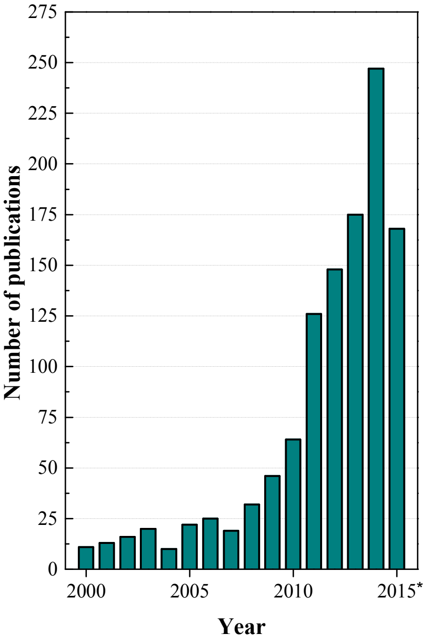

Figure 2. Number of publications on furfural (FUR) per year (Jan 2000–Dec 2014). Source: Web of Science (keywords: FUR and catal*). Year 2015 includes references up to September.

Current efforts are focused on developing new technologies to obtain FUR in an inexpensive and environmentally sustainable manner. For example, FUR degradation reactions can be partially inhibited at high temperatures/pressures (Supratherm and Stake processes) or by adiabatic flash distillation (SupraYield).[4,14] The use of N_2 rather than steam as the stripping agent for H_2O/FUR mixtures has resulted in much higher yields.[19,20] Another interesting approach is the use of H_2O-organic solvent biphasic systems.[21-29] The theory behind this approach involves utilizing the coefficient for partition of FUR between H_2O and the organic solvent. FUR exhibits higher affinity for the organic phase, where degradation reactions are mostly inhibited because of the absence of a catalyst. Another approach to increase the FUR yield, as well as to facilitate catalyst recovery and reutilisation, involves the use of solid catalysts. In this field, a large variety of materials (zeolites and zeotypes,[25-27,30-34] sulfonic ion-exchange resins,[19] sulfonic-acid modified mesoporous silicas,[23,35-37] sulfonated metal oxides,[38-40] Keggin heteropolyacids,[35,41,42] mesoporous niobium phosphate,[43] and vanadyl pyrophosphates,[44] etc.) have been investigated in recent years. A detailed review of all the solid catalysts employed in the literature for dehydration of xylose to FUR is beyond the scope of this manuscript. Interested readers are directed to the mentioned publications or to other reviews addressing the state-of-the-art in the development of heterogeneous catalysts for the production of FUR from carbohydrates and references therein.[18,45,46]

Chemically, FUR ($C_5H_4O_2$, furan-2-carbaldehyde, 2-furaldehyde) is a heteroaromatic furan ring with an aldehyde functional group. The principal direct application of FUR is as a selective solvent. The aromatic character of the furan ring and its polarity provide FUR with good solvent selectivity towards aromatics and, in general, unsaturated compounds. Furthermore, FUR has intermediate polarity, and is therefore partially soluble in both highly polar and non-polar substances.[14]

The two functionalities (aldehyde group and the aromatic ring) are responsible for the high chemical reactivity of FUR. FUR can undergo the typical reactions of aldehydes, such as acetalisation, acylation, aldol and Knoevenagel condensations, reduction to alcohols, reductive amination to amines, decarbonylation, oxidation to carboxylic acids, and Grignard reactions. The aromatic furan ring can be subjected to alkylation, hydrogenation, oxidation, halogenation, and nitration reactions. Due to the electron-withdrawing effect of the carbonyl group, the furan ring of FUR is less susceptible to hydrolytic ring cleavage and Diels–Alder cycloaddition reactions.[47,48] Currently, the most relevant use of FUR as a chemical feedstock is in the production of furfuryl alcohol and other 5-membered oxygen-containing heterocycles (furan, methylfuran, furfurylamine, furoic acid, and so on). FUR, as well as its derivative furfuryl alcohol, can either be used alone or with phenol, acetone, or urea to produce solid resins. One important application of FUR is in the synthesis of tetrahydrofuran, which is used as an important industrial solvent. However, a large number of transformations of FUR are possible, and indeed, the use of renewable FUR to produce fine and commodity chemicals and fuels is, at present, an underdeveloped area. Furan chemistry experienced its golden age during the first half of the 20th century due to the applicability of FUR as a solvent and the manufacturing of phenol–FUR resins. In the 1950s, FUR was used in the manufacture of nylon-6,6. This process was discontinued in the 1960s when tetrahydrofuran, the key intermediate, became a petrochemical.[9,48,49] However, interest in using FUR as a feedstock for biofuels and bio-based chemicals is currently increasing, as evidenced by the number of publications on catalytic technologies for FUR production and/or transformation, particularly in the past five years (Figure 2).

The main focus of this review is to present the most relevant chemical transformations of FUR to biofuels and bio-based chemicals. Other recent reviews addressing the transformation of FUR to biofuels are either focused on a wider context of biomass valorisation, or do not discuss all of the possibilities that FUR offers as a feedstock for biofuels.[2,7,10,11,46,50,51] The aim of this review is to provide a comprehensive overview of the possibilities of FUR through an updated, detailed, and critical examination of the current state-of-the-art. Focus will be directed towards both the chemical and engineering aspects, providing critical comments on the main achievements and the challenges still to come in pursuing a FUR bio-based industry. Some of the critical aspects and challenges are common to the different FUR transformations. For the sake of simplicity, these common issues will be addressed in the last section of the review, which is devoted to the main challenges of FUR-based biorefineries, whereas the more specific aspects will be dealt with in the relevant corresponding sections. The intention is to provide a solid and comprehensive foundation and complete overview for those interested in the implementation of FUR-based biorefineries.

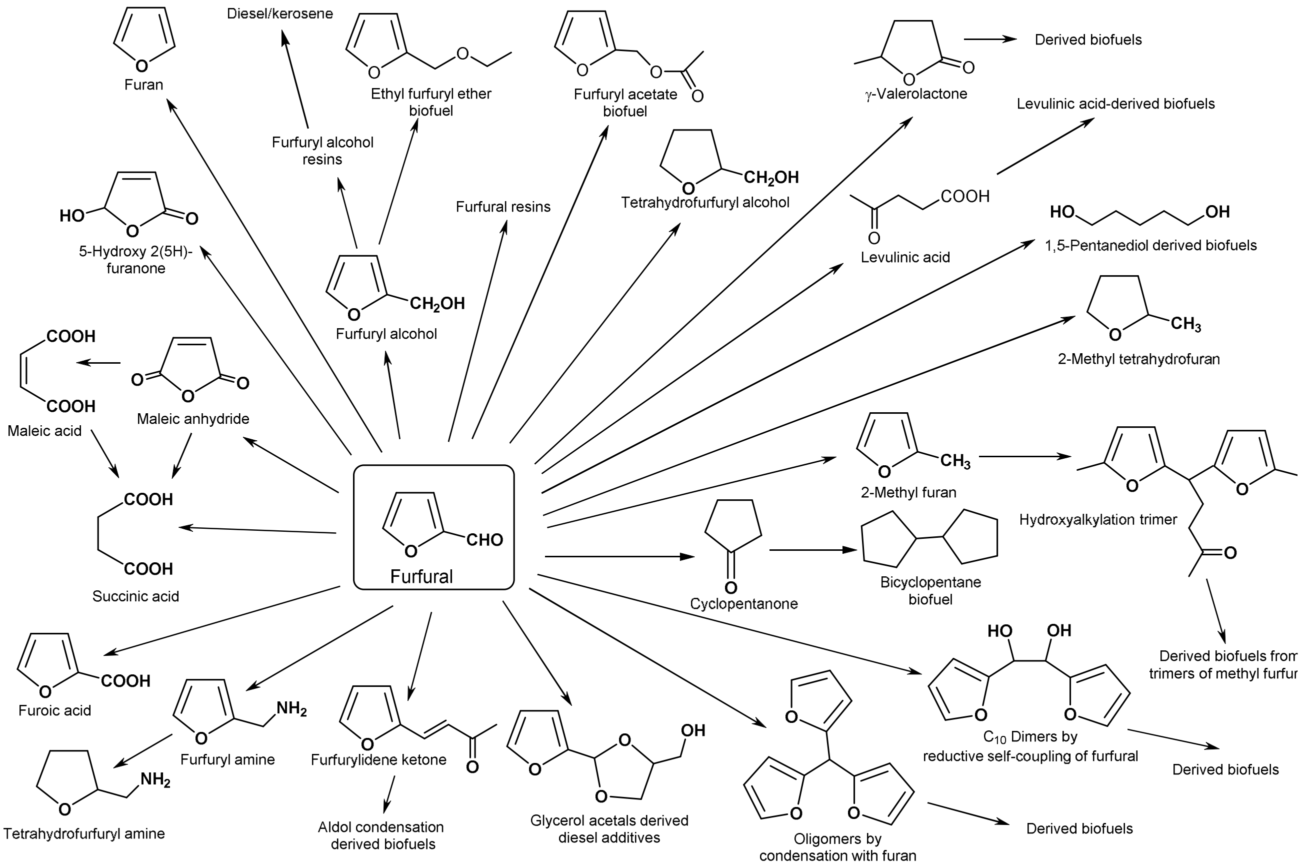

Figure 3. Summary of the furfural-derived chemicals and biofuels described in this review.

The number of potential routes for transforming FUR into fuels and useful chemicals is colossal. Reportedly, more than 80 chemicals have been derived directly or indirectly from FUR.[9] Assessing all of these transformations is clearly beyond the scope of this review for practical reasons; not all of the FUR transformations generate the same interest and/or will have the same industrial and economic impact. Rather, we examine the FUR-derived products that fulfil some of the following criteria (Figure 3):

1. Biofuels that can be derived either directly from FUR or from any of the chemicals obtained from FUR.
2. Commercial furanic chemicals that can be produced directly from FUR with important applications in the chemical industry.
3. Non-commercial chemicals that are directly derived from FUR through routes that have been technologically well demonstrated and that present high potential for commercialisation as commodities.
4. Commercial products currently derived from oil that can potentially be created directly from FUR.

Chemicals with a foreseen low consumption volume are not included in this review. Moreover, a considerable number of chemicals that are or can be derived from the different products are discussed in this review. For simplicity, these chemicals will only be mentioned to emphasise the relevance of FUR as a chemical platform, but such chemicals will not be discussed in depth.

The review is divided into three sections; the first is devoted to products that initially involve reactions of the aldehyde group; the second family of products involves removal of the aldehyde group; and the final section is directed towards describing the most important resins produced from FUR by polymerisation. Figure 3 outlines the main products and reactions that are described in this review.

2. Chemicals and biofuels from reactions involving the aldehyde group

This section examines the products derived from hydrogenation, amination, oxidation, acetalisation, and condensation of the aldehyde group.

2.1. Hydrogenation reactions

The section on hydrogenation reactions is the longest section as it encompasses a wide number of products, most of them already commercialised. These include products and biofuels derived from furfuryl alcohol, tetrahydrofurfuryl alcohol, methylfuran, tetrahydromethylfuran, and cyclopentanone.

2.1.1. Furfuryl alcohol and derivatives

Furfuryl alcohol (2-furanmethanol, FOL) is the most important chemical derived from FUR, having a broad spectrum of applications in the chemical industry (Figure 4). FOL production utilizes 65% of the overall FUR produced.[48] FOL is primarily used for the production of resins for use as high-quality cores and moulds for metal casting in the foundry industry (Section 4.2), as a reactive solvent for phenolic resins in the refractory industry, as a viscosity reducer for epoxy resins, in the manufacture of polyurethane foams and polyesters, and as a chemical building block for the synthesis of tetrahydrofurfuryl alcohol (THFA) and pharmaceuticals (such as antiulcer ranitidine), and in the manufacture of fragrances.[47,48] Other relevant chemicals that can be obtained from FOL include ethyl furfuryl ether (EFE), levulinic acid (LA), γ-valerolactone (GVL); the latter two products, as explained later, can also be obtained directly from FUR.

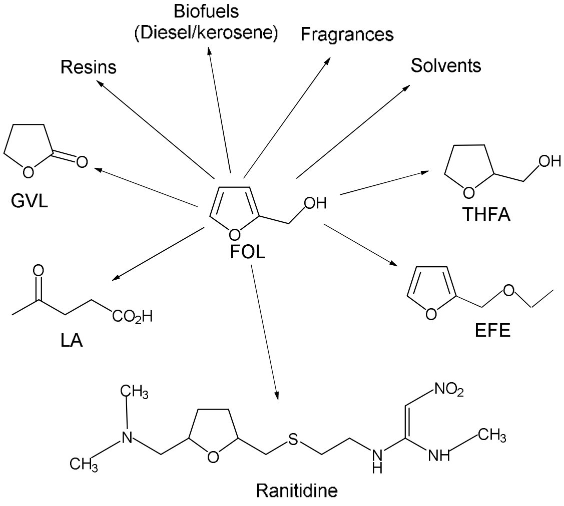

Figure 4. Chemicals and biofuels derived or that can be derived from furfuryl alcohol (FOL).

The industrial synthesis of FOL is performed *via* the catalytic hydrogenation of FUR, which can be accomplished in gas or liquid phase. The gas-phase Cu-catalysed hydrogenation of FUR is the preferred industrial route. The major hurdle limiting the liquid-phase batchwise operation process is the economical unattractiveness for large-scale applications due to the high operating costs of using batch reactors, the expensive equipment required for the high pressure conditions, and the length of time between successive reactions.

FUR hydrogenation can also lead to the formation of other chemicals besides FOL (Figure 5), such as 2-methylfuran (MF, *via* hydrogenolysis of the C-OH bond), tetrahydrofurfuryl alcohol (THFA, *via* hydrogenation of the furan ring of FOL), and 2-methyl tetrahydrofuran (MTHF, from the hydrogenation of MF).[52] Other minor products include furan and THF, different pentanediols, 2-pentanone and 2-pentanol, cyclopentanone and cyclopentanol. As shown later in this review, the trend in the selectivity for these products strongly depends on the reaction conditions and on the nature of the catalyst used.

Figure 5 also includes other FUR hydrogenation processes that are treated in this review and provides a comprehensive overview of all the products than can be found during hydrogenation of FUR. This figure depicts the pathway for formation of these products.

Gas-phase hydrogenation of furfural

The industrial gas-phase process is essentially conducted by feeding FUR into an evaporator system comprising a packed column, a circulating pump, and a heater to maintain the FUR temperature at 393 K.[14,48] H_2 is introduced at the bottom of the reaction column in a countercurrent of liquid FUR that flows downwards. The reaction products are condensed, and FOL is separated by distillation.

The gas-phase process was first reported in 1929 by using Cu on asbestos as the catalyst,[53] whereas the use of copper chromite was patented in 1931 by Du Pont de Nemours.[54] Later, Quaker Oats Company achieved furfuryl alcohol yields of 99% at 405–450 K by employing Cu supported on $Na_2O{\cdot}x SiO_2$.[55] Since then, many other catalytic systems based on Cu and other metals (Pd, Pt, Co, Fe, Ni, and Zn) have been proposed for this process, mainly to overcome the environmental concerns associated with the presence of chromium in copper chromite catalysts. The experimental conditions and catalytic results for most of these systems are summarised in Table 1. Most of the catalytic systems that are active for gas-phase hydrogenation of FUR to FOL contain copper as the active phase and silica as the support. Comparison of the catalytic results reported in the literature is complicated because the experimental conditions vary widely. The H_2/FUR molar ratio used in various studies range from 2 to 900 and the reaction temperatures range between 403 and 573 K for time-on-stream (TOS) values ranging from 0.25 to 80 h. However, it can be inferred from Table 1 that the best catalytic performance is achieved with the $CuCa/SiO_2$ catalyst,[56] which remained stable after 80 h of TOS and provided a FOL yield of 99% with a low H_2/FUR molar ratio of 5 at the lowest reaction temperature (403 K). However, in the absence of Ca,[57] and at higher reaction temperature (443 K), a FOL yield of 97% was obtained after 5 h of TOS with a similar liquid hourly space velocity (LHSV) of 0.5 h^{-1}.

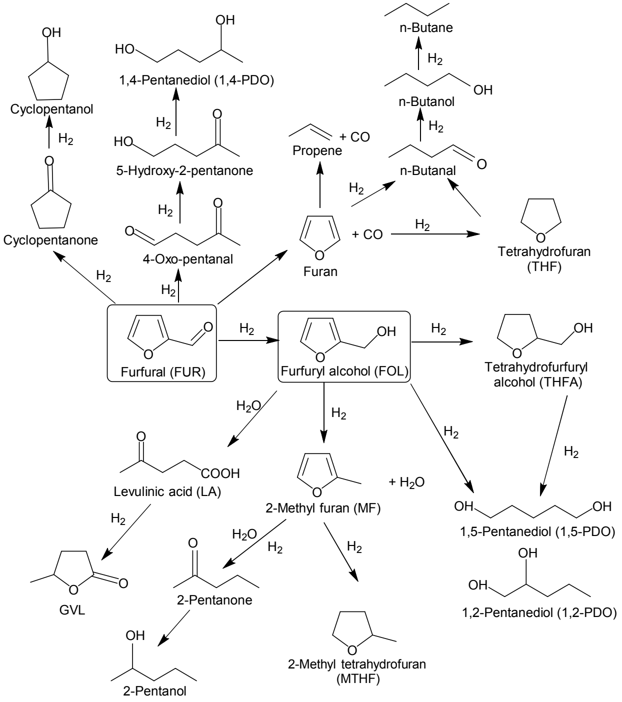

Figure 5. Various products formed during hydrogenation of furfural (FUR) to furfuryl alcohol (FOL).

Table 1. Summary of gas-phase hydrogenation of furfural (FUR) to furfuryl alcohol (FOL) with different catalysts

Catalyst	Reaction conditions				Furfural conv. (%)	FOL yield (%)	Ref.
	Space velocity (h^{-1})	H_2/FUR mol. ratio	Temp. (K)	Time[a] (h)			
$Cu_2Cr_2O_5$	n/a[b]	72	413	n/a	17 μmol/g/s[c]	(70% select.)[d]	58
$Cu_2Cr_2O_5$	52 (WHSV)	25	473	4	22 μmol/g/s[b]	(98% select.)[c]	60
Cu/SiO_2	0.5 (LHSV)	5	443	4	98	97	57
Cu/SiO_2	2.3 (WHSV)	25	563	0.25	77	63	59
Cu/SiO_2	0.5 (WHSV)	17	413	10	98	73	61
Cu/SBA-15	1.5 (WHSV)	12	443	1	92	85	62
Cu/carbon	n/a	146	498	1	1.6 μmol/g/s[b]	(68% select.)[c]	63
Cu/MgO	4.8 (WHSV)	2.5	453	5	98	96	64
Cu/ZnO	0.5 (WHSV)	17	493	10	95	31	61
Cu-Ni-Mg-Al oxides	4000 (GHSV)	10	493	36	80	64	65
$CuCa/SiO_2$	0.33 (LHSV)	5	403	80	100	99	66
$CoCu/SiO_2$	3.1 (WHSV)	6	473	12	65	64	67
$CuCr/TiO_2$	1.2 (WHSV)	900	413	0.5	90	79	68
PdCu/zeolite-Y	7.7–32.9 (WHSV)	0.08–2.27	573	n/a	58	58	69
Pt/TiO_2-V_2O_5-SiO_2	2.0 (WHSV)	2	423	0.5	87	79	56
Pt/TiO_2	1300 (GHSV)	10	473	0.5	0.2 μmol/g/s[b]	(13% select.)[c]	70
Ni/SiO_2	10 (WHSV)	25	493	n/a	84	31	71

[a] Time-on-stream at which catalytic properties were determined

[b] n/a: Not available

[c] Reaction rate was presented in the reference instead of conversion values

[d] Selectivity to FOL values were given in the reference instead of yield

From the perspective of kinetics, it has been shown that the Langmuir-Hinshelwood model fits the reaction rate data.[58,59] Whether the active sites of Cu-based catalysts in the vapour phase involve Cu^0 or Cu^+ species remains controversial.[60,63,72]

Density functional theory (DFT) calculations, along with other infrared (IR) spectroscopic techniques, have provided a model for the modes of adsorption of the different intermediates as well as plausible reaction pathways. Two different routes have been proposed: one for Cu-based catalysts[59] and one for group VIII metals.[59,71,73-75] In the first case, Resasco *et al.* proposed that the adsorption of FUR occurs preferentially *via* the lone pair of electrons on oxygen adopting a top η^1(O)-aldehyde binding mode (Figure 6).[59] The FUR molecule lies perpendicular to the catalyst surface, and the aromatic ring experiences net repulsion due to overlap of the 3d band of the surface Cu atoms with the aromatic furan ring. Thus, the reaction can proceed *via* either an alkoxide (H addition to the C atom of the carbonyl group) or a hydroxyalkyl (H attack on the O atom of the carbonyl group) intermediate. The latter mechanism is preferred because of its lower activation energy barrier, which is explained by the stabilising effect of the aromatic furan ring on the hydroxyalkyl intermediate.

The repulsion between the furan ring and the metal surface is absent with Group VIII metals (Pd, Ni, or Pt) and a flat η^2(C-O) binding mode is favoured.[73-75] The preferred elementary route to FOL occurs in 2 steps (Figure 6): hydrogenation of the carbonyl group of the flat adsorbed η^2(C-O)-FUR to generate a hydroxyalkyl intermediate, followed by hydrogenation of the carbon bearing the hydroxyl group to generate adsorbed FOL. The energetic barrier of the latter transformation (77 kJ·mol^{-1}) is smaller than that of transformation of FUR to furan *via* the formation of a η^2(C)-acyl intermediate and subsequent decarbonylation (92 kJ·mol^{-1}; see Section 3.1.1 for further details). Therefore, although decarbonylation to generate furan is, in principle, thermodynamically favoured, hydrogenation to furfuryl alcohol is kinetically preferred. DFT calculations suggest that MF formation involves a direct pathway involving the hydrogenation of adsorbed FUR to an alkoxy intermediate that is subsequently deoxygenated and hydrogenated to MF (Figure 6) and an indirect route from FOL involving dehydration of the adsorbed FOL and subsequent hydrogenation to MF, both with higher energetic barriers than the FOL synthesis.[74] DFT calculations were conducted at low hydrogen coverages (low H_2 pressure); an increase in the H coverage can change the preference for a given pathway considering the relatively small differences in the activation energies.

Therefore, the challenge in the gas-phase hydrogenation of FUR to FOL lies in the inhibition of the pathways that generate 2-methylfuran and furan when high conversions of FUR are attained because it is difficult to stop the reaction at FOL. In this regard, The so-called strong metal support interaction (SMSI) metal oxides can also play a role, as demonstrated by

Somorjai *et al.* with TiO_2-supported Pt catalysts.[76] An active furfuryl-oxy intermediate species, formed by a charge-transfer interaction between an O-vacancy on TiO_2 and furfural, is rapidly hydrogenated. The role of the Pt/TiO_2 interface is simply to facilitate H spill over to this furfuryl-oxy intermediate *via* this reaction pathway is an order of magnitude faster than when Pt is not supported on TiO_2.

The occurrence of catalyst deactivation complicates the application of Cu-based catalysts in gas-phase processes. This deactivation is more severe at higher FUR partial pressures, making a thorough kinetic study of FUR hydrogenation difficult.[58] As possible explanations of the observed catalyst deactivation, the formation of coke, catalyst poisoning by adsorption of FUR or other reaction products, a change in the oxidation state of the copper species, and sintering of the copper particles during the catalytic process have been proposed.

Recently, the strong adsorption of species derived from FUR and FOL was proposed as the main cause for deactivation of copper chromite catalysts.[60] Moreover, covering of the Cu sites by Cr species formed by the decomposition of copper chromite significantly decreases the selectivity to FOL. Nevertheless, it has very recently been demonstrated that the stability of copper chromite can be improved by deposition of a thin alumina layer *via* atomic layer deposition (ALD), which precluded coke formation, Cu sintering, and occlusion of the copper particles by chromite species.[72]

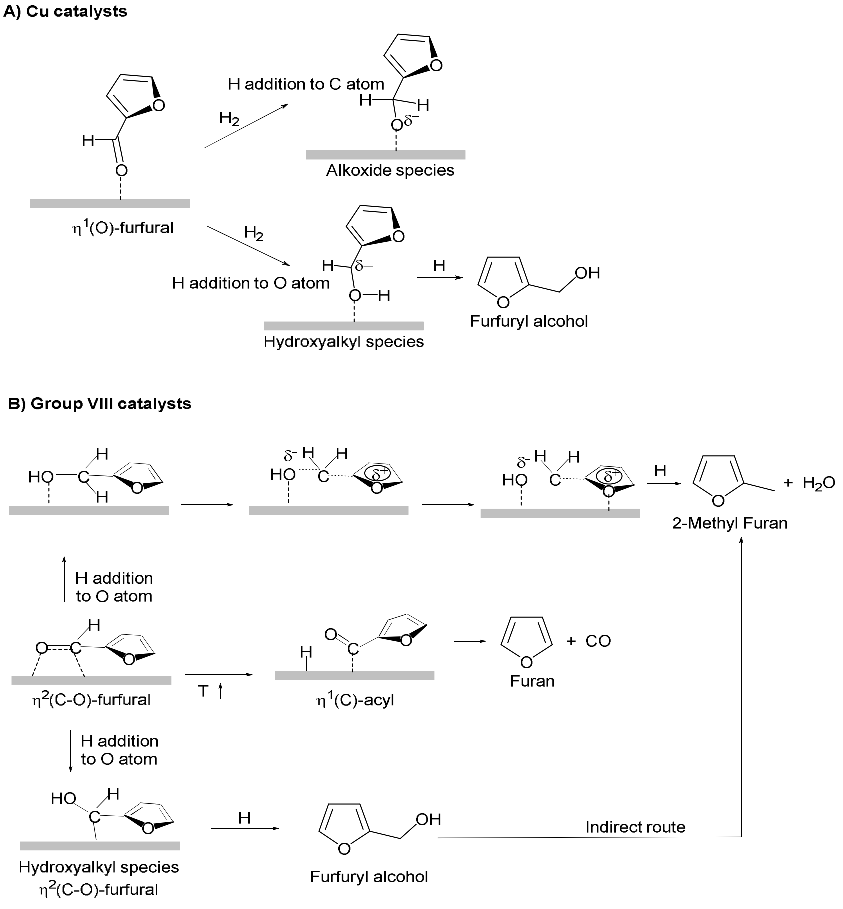

Figure 6. Mechanism of furfural (FUR) hydrogenation to furfuryl alcohol with Cu (A) and Group VIII metals (B) (adapted from References 59,71).

Finally, it must be mentioned that catalytic transfer hydrogenation (CTH) in the gas phase has also been attempted. This reaction is based on the Meerwein-Ponndorf-Verley (MPV) reduction of an aldehyde (or ketone) coupled with the oxidation of a secondary alcohol.[77,78] The main advantage of this strategy is that this process does not require a supply of external hydrogen. Moreover, this CHT process minimises the formation of by-products (MF, THFA, and furan) that are frequently generated in the conventional gas-phase H_2 reaction. The alcohol can be chosen to produce an aldehyde or a ketone with industrial applicability. Thus an 85% FOL yield was obtained by gas-phase MPV reduction of FUR coupled with oxidation of cyclohexanol to cyclohexanone with Cu-MgO-Cr_2O_3.[79,80] Cyclohexanone is used as an intermediate in the production of nylon-6 and nylon-6,6. Unfortunately no information regarding the deactivation was provided, which is a key consideration for correct assessment of the technical viability of this process.

Liquid-phase hydrogenation of furfural

The liquid-phase hydrogenation of FUR was first reported in 1928 by Quaker Oats Company.[81] A Ni/MgO catalyst was used, but the process required accurate control to avoid the formation of THFA. Reduced copper chromite has widely been used under high H_2 pressures and temperatures, with FOL yields greater than 90%. The FOL selectivity was further improved to 98% at 413 K using 10 MPa H_2 by adding alkaline earth oxides (CaO, BaO) in copper chromite.[82] Copper chromite promoted by CaO afforded an FOL yield close to 98% at lower H_2 pressures.[83]

For practical industrial operations, it has been proposed that the liquid-phase hydrogenation of FUR can be performed by mixing copper chromite with FUR to form a slurry, which is continuously fed into a tubular bubble reactor along with H_2.[14] The slurry is depressurised, and excess H_2 is re-injected into the reactor, where the liquid phase and liquefied head vapours of the column are rectified to obtain pure furfuryl alcohol. Catalyst fines and high-boiling polymers are discarded.

The main drawback of chromium-based catalysts is the environmental concern associated with their toxicity, and for this reason, extensive effort has been devoted to developing more environmentally friendly catalysts. Table 2 summarises the other catalytic systems used for this reaction. Liquid-phase hydrogenation of FUR leads to better catalytic results than achieved in the gas-phase process, and the range of catalysts that can produce FOL yields close to 100% is larger, although high H_2 pressures are required. Most studies utilize H_2 pressures of 1–2 MPa and reaction temperatures between 333 and 473 K. As with the gas phase data, the differences in the experimental conditions used in the studies preclude straightforward comparison of the catalytic results. In general, FOL yields of 100% have been attained under very different experimental conditions and with multicomponent systems in which Ni and Cu are mainly present as the active sites. Full or close to full conversion to FOL

Table 2. Performance of different catalysts in the liquid-phase hydrogenation of furfural (FUR) to furfuryl alcohol (FOL)

Catalyst	Reaction conditions						FUR conv. (%)	FOL yield (%)	Ref.
	FUR (wt.%)	Solvent	H_2 (MPa)	Temp. (K)	Time (h)	cat./FUR (wt.)			
Ni-Alloy	100	None	0.7	373	6	0.1	100	100	96
$Ni_{74.5}P_{12.1}B_{13.4}$	1.7	Ethanol	1.7	353	0.25	0.129	100	80	84,97,98
$Ni_{34.1}Fe_{36.0}B_{29.9}$	32.9	Ethanol	1	373	4	0.086	100	100	99
$NiSn_{0.2}/SiO_2$	5.6	Isopropanol	1	373	4	0.108	43	34	100
NiMoB/γ-Al_2O_3	24	Methanol	5	353	3	0.2	99	90	89
$(NH_4)_6Mo_7O_{24}$/Raney Ni	35	Isopropanol	2.1	333	6	0.057	99.9	98	101
$Cu_{3/2}PMo_{12}O_{40}$/Raney Ni	60	Ethanol	2	353	1	0.043	98	97	102
Pt-$Sn_{0.3}/SiO_2$	5.6	Isopropanol	1	373	4	0.108	100	96	92
$RhSn_{0.2}/SiO_2$	5.6	Isopropanol	1	373	4	0.108	14	13	100
Pd/SiO_2	25	*n*-Octane	n/a	n/a	n/a	0.09	75	53	90
Ru/Zr-MOF	1.2	Water	0.5	293	4	0.862	95	95	103
Ir-ReO_x/SiO_2	10	Water	6	323	n/a	0.1	100	97	104
Mo-doped Co-B amorp. alloy	14	Ethanol	1	373	3	0.172	100	100	91
Ce-doped Ni-B amorp. alloy	32.9	Ethanol	1	353	3	0.086	96.8	close to 96.8	88
Co-B amorphous alloy	32.9	Ethanol	1	383	0.5	0.086	100	100	105
Co/SBA-15	10	Ethanol	2	423	1.5	0.05	92	88	86
Ru(II) bis(diimine) complexes	1.45	Ethanol	5.1	373	2	0.096	99	99	87
Cu-Zn/Kieselguhr	200	Water	12.4	423	2.5	0.1	95	71	106
Cu-Co/SBA-15	18.6	Isopropanol	2	443	4	0.064	99	80	85
Pd-Cu/MgO	5.7	Water	0.6	383	1.3	0.08	100	99	107
Cu-Al-Fe oxides/$Ca(OH)_2$	100	None	11.8	433	0.3	0.0065	99.8	98	108
Cu-Cr oxides	41	*n*-Octane	6	473	4	0.082	95	78	109
CuFe oxides	41	*n*-Octane	6	473	4	0.082	87	84	110
Cu/Al_2O_3	0.96	Water	2	363	2	2.08	81	81	111
Cu-MgAl mixed oxides	1.2	Isopropanol	1	383	1	0.174	63.2	63	93
CuNi-MgAl mixed oxides	33	Ethanol	1	473	2	0.029	93	83	112
Cu-Zn-Cr-Zr oxides	16.8	Isopropanol	2	443	3.5	0.108	100	96	113

n/a: Not available

have been reported by using pure FUR[84,85] or FUR diluted in ethanol,[86-90] water,[91] or isopropanol.[92,93]

Kinetic analysis of the liquid-phase hydrogenation has been undertaken using Pt/C catalysts.[94] The experimental data fit most adequately to the Langmuir-Hinshelwood dual-site mechanism with different active sites for the molecular adsorption of H_2 and FUR/FOL species. The reaction between adsorbed FUR and adsorbed hydrogen is the rate-limiting step.

The deactivation of Cu-based catalysts is associated with the sintering and leaching of copper species. Atomic layer deposition has recently been demonstrated to be a suitable technique for stabilising copper-based catalysts for liquid-phase catalytic reactions.[95] With this approach, atomic layer deposition of an alumina overcoat is first conducted, resulting in encapsulation of the Cu particles by an amorphous alumina overcoat. Calcination at high temperature produces a pore structure in the alumina overcoating, thereby exposing the copper underneath but still maintaining the stabilising interaction with low coordination copper sites on the surface that prevent leaching and sintering. In contrast, Pt/C catalysts have been reported to not undergo deactivation after being used for three runs.[94]

A very interesting alternative to the liquid phase hydrogenation of FUR to FOL is the one-step hydrogenation-esterification (OHE) of FUR to yield furfuryl esters (Figure 7). These furfuryl esters can be used as fuel-blending agents and possess a high energy density.[114] The OHE of FUR-like compounds to furfuryl esters was originally proposed in a context that differs from the focus of this review, i.e., as an alternative to upgrade the quality and the stability of fast pyrolysis bio-oils rather than to valorise FUR. FUR-like chemicals and organic acids are among the primary components of bio-oils, and this reaction would allow the removal of FUR compounds and organic acids from bio-oils, leading to the formation of less corrosive and more stable bio-oils with improved properties. Zheng *et al.* investigated the OHE reaction of FUR with acetic acid to afford furfuryl acetate in the liquid phase under 20 MPa H_2 at 423 K with supported Pd, Pt, Cu, and Ni catalysts.[115,116] Unfortunately, the best yield of furfuryl acetate achieved to date is still too low for practical applications (13% with 5 wt.% Pd supported on $Al_2(SiO_3)_3$

and Al-SBA-12). FOL was the major product (~43%), with MF as a minor by-product. The authors reported that acid sites near the hydrogenating centres are required to promote the esterification, but this is accompanied by a serious drawback that must be resolved in further studies, i.e., the resinification of furfuryl alcohols, which is also driven by acid sites. No reutilisation tests were performed to assess the reusability of the catalysts.

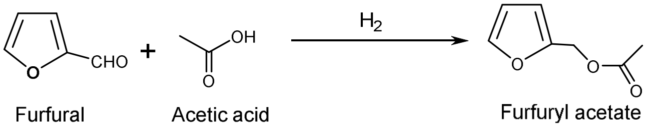

Figure 7. One-step hydrogenation-esterification (OHE) of furfural (FUR) with acetic acid.

Liquid phase hydrogenation of FUR to FOL has also been attempted under non-conventional conditions, namely, catalytic transfer hydrogenation (CTH), the use of supercritical CO_2, and electrocatalytic reduction. CTH *via* the MPV reaction between FUR and secondary alcohols has produced remarkable results. Indeed, selective conversion of FUR to FOL only has recently been reported with a Cu-based catalyst obtained by reducing a spinel-like Cu-Al-Mg oxide and using isopropanol as the hydrogen donor.[117] Unfortunately, no reutilisation studies were conducted to assess the catalyst deactivation. Similarly, a 95% FOL yield was obtained with a Ni-Cu/Al_2O_3 catalyst and the same donor agent at 473 K under 4.5 MPa N_2.[118]

The use of supercritical CO_2 has been demonstrated to be an excellent approach for conducting the hydrogenation of FUR to different furanic compounds. The selectivity towards the different products involved in the hydrogenation of FUR, that is, FOL, THFA, MF, MTHF and furan, can be tuned by using two catalytic beds with copper chromite and Pd/C at the adequate respective temperatures.[119] Thus, a 98% FOL yield was obtained by using only the first copper chromite reactor under conditions of 393 K, 15 MPa H_2, 1 mL/min CO_2, and 0.05 mL/min FUR.

Another interesting approach for the synthesis of FOL is the aqueous electrocatalytic hydrogenation of FUR using a sacrificial Ni or Ni/Fe alloy anode.[120] The generation of atomic hydrogen is performed *in situ* through the reduction of hydronium ions on the cathode surface using external electrons. A FOL yield of 63%, with a yield of MF lower than 5%, was achieved by modulating the current density and the nature of both the electrolyte solution and electrodes. Similarly, Huber *et al.* employed a continuous-flow electrocatalytic membrane reactor for the reduction of an aqueous solution of FUR.[121]

Different catalysts have been tested for the cathode,[121,122] but the reduction of FUR was better accomplished on a Pd/C cathode, with a selectivity to FOL of 54–100% at 303–343 K. Moreover, FOL, THFA, MF, and MTHF were also detected, and the product selectivity varied as a function of the applied voltage. The current efficiency was 24–30%; the unaccounted for current was utilized in the production of H_2 rather than FUR hydrogenation.

2.1.1.1. Etherification to ethyl furfuryl ether biofuel

An interesting derivatisation reaction of furfuryl alcohol (FOL) is etherification with ethanol to form ethyl furfuryl ether (EFE), also known as 2-(ethoxymethyl)-furan (Figure 8). The production and uses of pure EFE as a fuel have been patented by Shell.[123] EFE can be blended with gasoline up to 30 wt.% levels.[124] There are various advantages of using EFE rather than furfuryl alcohol itself in the fuel, such as higher stability and a higher octane number. Table 3 shows the effects of adding EFE to a normal fuel. Despite the increase in the RON (research octane number), the addition of stabilising additives was still required to improve the stability of the EFE-blended gasoline under mild and accelerated oxidation conditions (washed gum and induction period tests, respectively).[7]

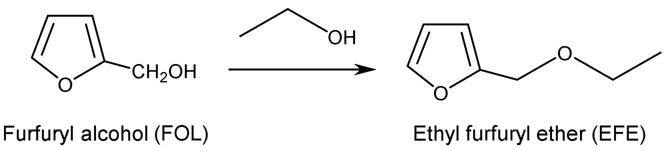

Figure 8. Etherification of furfuryl alcohol (FOL) with ethanol.

Lange and co-workers studied the production of EFE using zeolites.[7] The authors reported yields of 50 mol.% EFE at 80% furfuryl alcohol conversion using the HZSM-5 zeolite at 398 K.; 20 mol.% of heavy products was formed in this reaction along with other minor compounds such as ethyl levulinate or angelica lactone. The use of dilute H_2SO_4 as the catalyst (<0.1 wt.%) led to lower selectivities. Although the authors did not document the reusability of the catalyst, heavy products, including furanic oligomers, were also formed, which can threaten the stability of the catalyst due to the coke deposition phenomenon.[7]

Table 3. Properties of ethyl furfuryl ether (EFE) as a fuel[7]

Property	Base fuel	5 vol.% EFE in base fuel	10 vol.% EFE in base fuel
Density (g/mL)	746.5	759.9	771.6
RON	96.1	98.0	98.4
MON	85.1	85.3	85.1
Washed gum (mg/100mL)	<1	97.6	98.0
Vapour pressure (kPa)	67.7	62.8	59.4
Induction (min)	1378	237	101

2.1.1.2. Diesel and kerosene production via furfuryl alcohol oligomerisation-hydrogenation

A patent filed by van Buijtenen *et al*. describes the synthesis of a mixture of C-C coupled oligomers from FOL. These oligomers are subsequently hydrogenated to a mixture of hydrocarbons with the tetrahydrofuran skeleton (Figure 9). The C_9–C_{20} hydrocarbon fraction is suitable for use as kerosene and diesel components. The higher fraction could be fed into a catalytic cracking or hydrocracking unit after separation by distillation, and also converted into diesel, kerosene, and gasoline fractions.[125]

The synthesis of C_9–C_{20} hydrocarbon oligomers can be performed under batch conditions or in continuous mode. The latter process involves feeding an aqueous solution of FOL (35 wt.%) containing H_2SO_4 (0.01 wt.%) through a bed packed with glass beads. A FOL conversion of 76 mol.% was obtained, with an oligomer yield of 41 mol.% using a residence time of 2.1 h at 363 K. In contrast, the batch mode gave rise to 95 mol.% conversion and 52 mol.% oligomer yield under the optimum batch conditions (348 K, 24 h residence time, and 0.001 M H_2SO_4 in toluene extracting solvent). The oligomerisation of

FOL can also be performed under heterogeneous conditions, reaching a similar conversion and yield (52 mol.%) using Amberlyst-15 as catalyst (0.002 wt.%) with the same residence time and temperature. Unreacted FOL is removed from the oligomers by washing with water. Subsequent hydrogenation of the C_9–C_{20} carbon-carbon coupled oligomers is performed with a Ni/Al_2O_3 catalyst at 373 K. The hydrogenated product is distilled to isolate the diesel fraction, which can be blended (10 vol.%) with a base fuel. Determination of the key parameters in the European diesel specification EN 590 indicates that the C_9–C_{20} fraction obtained from FOL can be used for blending.

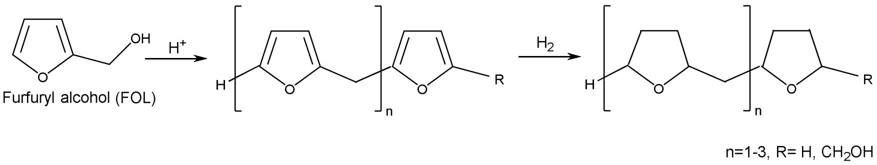

Figure 9. Synthesis of diesel/kerosene fuels by furfuryl alcohol (FOL) oligomerisation and subsequent hydrogenation reactions.

2.1.2. Levulinic acid: Derived chemicals and biofuels

Synthesis. Levulinic acid (LA, 4-oxopentanoic acid) is a product with interesting direct applications. A number of routes for LA synthesis involve petrochemical feedstocks, but LA can also be obtained from cellulose or hemicellulose. The inhibitive production costs have precluded the commercialisation of LA as a commodity.[126,127] The Biofine process was the first commercial attempt to obtain biomass-derived LA from the glucose present in cellulose. This process employs the aqueous H_2SO_4-catalysed hydrolysis of cellulose to release the glucose with further dehydration to LA (~50% yield).[9,126,127,128]

The production of LA from the pentoses present in hemicellulose has also been demonstrated, indicating that LA could, therefore, be an entry point for both hemicellulose and cellulose sugars into biorefineries. The most investigated route for production of LA from FUR involves several steps conducted in different reactors. FUR is first produced and then hydrogenated to FOL, which is then transformed into LA via acid-catalysed ring-opening in H_2O. This is not a direct route as it requires the isolation of FOL. This technique is not discussed further herein because this review is essentially devoted to direct products, but more information can be found elsewhere.[129-134] The ring opening of FOL can also be conducted in the presence of alcohols rather than H_2O;[129,133] the alcoholysis subsequently affords alkyl levulinates, which can be later hydrolysed to furnish LA.

Remarkably, the one-pot direct transformation of FUR into alkyl levulinates, not requiring the isolation of FOL, has been reported by Chen *et al.* using a bifunctional catalyst comprising Pt nanoparticles supported on a ZrNb binary phosphate solid acid under conditions of 5 MPa H_2, 403 K, and 6 h, reaching 92% conversion and 76% ethyl levulinate yield.[135] Specifically, the best catalytic performance was obtained using $Pt/ZrNbPO_4$ (2 wt.% Pt; Zr/Nb = 1:1) as the catalyst. The deactivation of the catalyst was investigated, and there were no marked changes after three runs; however, 17% of the initial catalyst activity was lost in the fifth run. More research is needed in this direction.

Derived chemicals and biofuels. Because of its high functionality (keto and carboxyl groups), LA is considered to be an attractive chemical platform for obtaining higher value-added chemicals, liquid fuels, and fuel additives.[2,3,136] Figure 10 shows the main products that can be generated from LA.

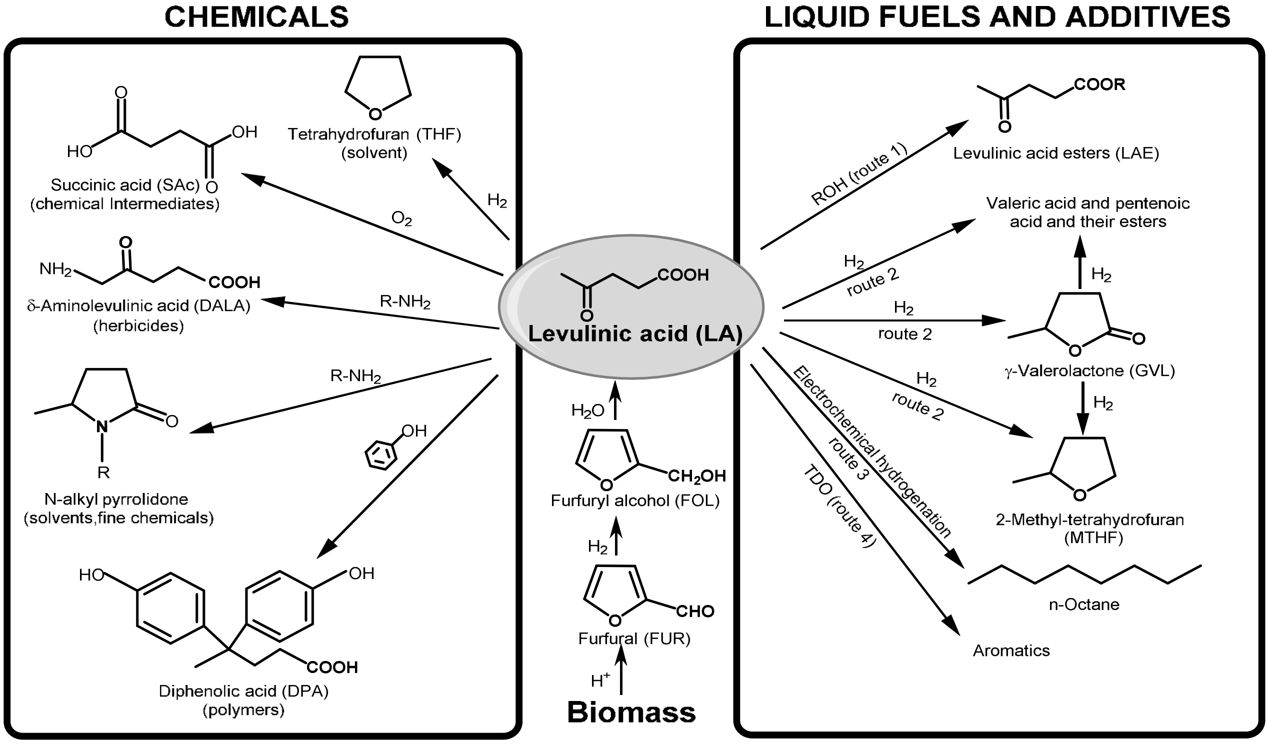

Figure 10. Use of levulinic acid (LA) as a platform for fuels and chemicals.[3]

Several approaches have been proposed for obtaining liquid transportation fuels and additives from LA. These approaches do not specifically start from FUR, and in most cases they require prior isolation of LA; thus, for the sake of simplicity, these transformations will simply be briefly summarised. Nevertheless, they have been included in this review as LA can be obtained from FUR and because, in some cases, the direct synthesis of these species from FUR has been accomplished. The following four routes are described:

<u>*Esterification to levulinate esters*</u>. Levulinic acid esters can be used as a blending component in biodiesel. Although these esters possess a very low cetane number, they are suitable for use as gasoline and diesel transportation fuel additives because of their numerous excellent properties such as low toxicity, high lubricity, flash point stability, and moderate flow properties under low temperature conditions.[137,138] Most investigations of this reaction have been conducted in alcoholic medium by starting either from isolated LA or directly from C6 carbohydrates. This approach has been extensively reviewed elsewhere and more details can be found in other publications.[139-143]

Another indirect,, though more FUR-oriented route, involves the alcoholysis of FOL. Most of the relevant research has been conducted with isolated FOL and by using homogeneous acid catalysts such as HCl or H_2SO_4 or a variety of solid acid catalysts such as strongly acidic resins,[128,129,133] acidic zeolites like ZSM-5,[7] Al-TUD-1 mesoporous aluminosilicates,[144,145] and ionic liquids functionalised with acidic anions.[146-148] Solid catalysts are, in principle, preferred because they can be reutilised and present less corrosion and downstream problems.

Interestingly, direct conversion of FUR was reported to be possible through one-pot transformation of FUR into alkyl levulinates involving initial hydrogenation of FUR to FOL, which proceeded *via* ring opening in the presence of an alcohol. A bifunctional catalyst composed of a Pt/ZrNb binary phosphate solid acid was reported to be very efficient and moderately stable with use at 5 MPa H_2, 403 K, and 6 h, reaching 92% conversion and 76% ethyl levulinate yield.[135] The possibility of performing this reaction by starting from hemicellulosic biomass still remains a challenge.

<u>*Selective hydrogenation*</u>. Figure 11 clearly illustrates the hydrogenation pathways to the relevant biofuels that can be obtained from hydrogenation of LA, i.e., either valeric acid or MTHF. The different intermediate products are classified as a function of their H and O contents. The energetic density increases as the oxygen content decreases or the hydrogen content increases. Routes requiring the isolation of GVL, the most stable intermediate, are also possible as mentioned in the ensuing section.

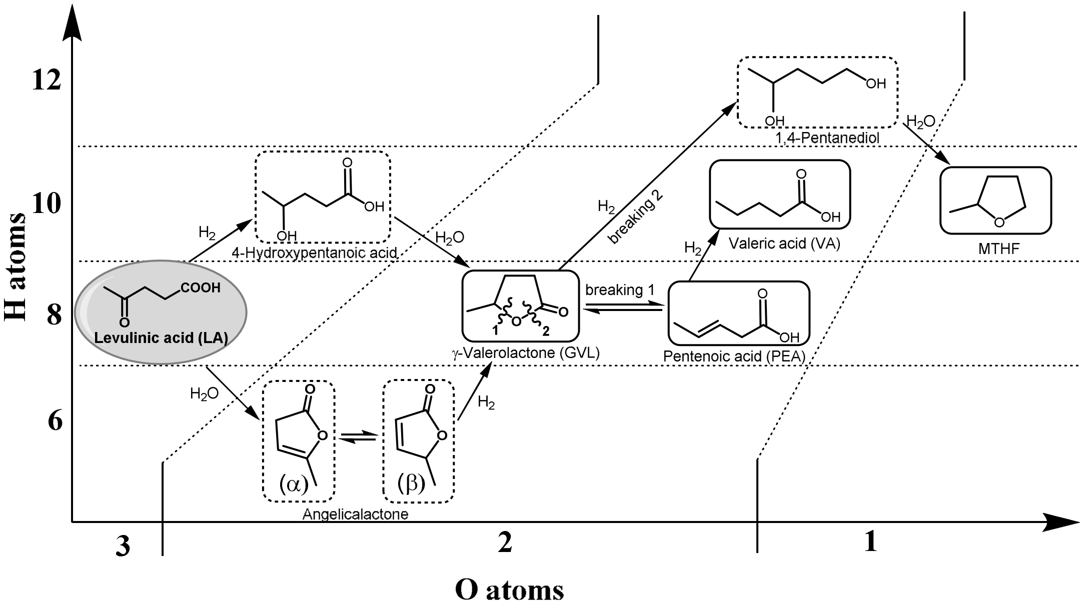

Figure 11. Levulinic acid (LA) hydrogenation pathways to different 5-carbon-atom biofuels. Adapted from Reference [149].

Compared with levulinic acid esters, valeric acid esters (VE) have a higher energy density due to their higher C/O and H/C ratios. The hydrogenation of LA to VA/VE in a one-pot approach requires not only hydrogenating sites but also acid functionalities, as the latter centres are required both for the conversion of LA to GVL and for the subsequent ring-opening step of GVL to VA, which is the rate-determining step. Thus, Ru/H-ZSM5, Ru/SBA-SO_3H, and Co embedded in ZSM-5 catalysts have been shown to generate good yields of the targeted products (46%, 94%, and 97%, respectively) at 3–5 MPa H_2 and 473–523 K.[149-151] The presence of alcohols is required, otherwise the yield of VA and its esters is lower. Deactivation is a major reported problem for Ru catalysts, where coke deposition, dealumination of zeolites,[149] and leaching of the sulfonic sites of the SBA-SO_3H catalyst[150] were identified as the main sources of deactivation. In contrast, embedding Co nanoparticles within the HZSM-5 cages prevents Co leaching, resulting in a very stable catalyst with consequent maintenance of the yield of VA and its esters above 90% for eight cycles.[151]

2-Methyltetrahydrofuran (MTHF) has been approved for use as a component of P-Series type fuels by the US DOE[152] since certain properties of MTHF make it suitable for gasoline blending without engine modifications. These include the octane number of 74, better miscibility with common hydrocarbon-based fuels than alcoholic additives, less susceptibility to polymerisation, low volatility, and lower emission of contaminants.[153] MTHF is currently produced *via* hydrogenation of MF, as discussed in Section 2.1.4. However, an alternative method for producing MTHF is *via* the hydrogenation of LA through a multistep sequence of reactions in which GVL is first produced; a deeper reduction gives rise to 1,4-pentanediol, and finally, ring closure by dehydration affords MTHF (Figure 11).

The liquid phase hydrogenation of LA to MTHF in one-pot was first demonstrated using a bimetallic Re-Pd/C catalyst. Yields close to 70% were achieved in a continuous process (6 h, 523 K, 100 MPa H_2).[154] Leitner *et al.* proposed an efficient and flexible process capable of tuning the selectivity for GVL, 1,4-PDO, and MTHF[155] by selecting the composition of the catalytic system (i.e., by using a Ru-containing precursor complex, a set of mono-, bi-, and tri-dentate phosphine ligands, and ionic and/or acidic additives). Thus, by adding an acidic ionic liquid, the selectivity to MTHF was greatly improved to furnish a yield of 92% upon complete conversion of LA (18 h, 433 K, 10 MPa H_2). The catalyst was reutilised in four consecutive batches without any loss of the catalytic activity. Catalytic transfer hydrogenation (CTH) has also been explored. This approach is particularly interesting because it involves the use of formic acid, which can be obtained during the production of LA from C_6 sugars. Bermúdez *et al.* recently reported selective CTH using Cu-based nanocatalysts and a commercial Pd/C system in microwave-assisted reactions.[156] The yield of MTHF achieved with this Cu catalyst was approximately 70% at 323 K after 0.5 h of microwave irradiation (300 W). The Cu-based catalysts exhibited significant deactivation compared to the more stable Pd/C catalyst. Interestingly, the gas phase hydrogenation has also been demonstrated by using inexpensive Ni-Cu/SiO_2 catalysts. A high yield of MTHF (89%) and high stability for more than 300 h was reported at 538 K and 2.5 MPa H_2.[157]

Electrochemical hydrogenation to n-octane. The electrochemical transformation of LA into *n*-octane at room temperature has been demonstrated.[158] Overall, the process is a net reduction, but in practice, the process requires two electrochemical reactions, namely, electrochemical reduction of keto compounds and electrochemical oxidative decarboxylation-dimerisation of a carboxylic acid (known as the Kolbe reaction). Interestingly, this process can be conducted in aqueous solutions, and therefore, the *n*-octane spontaneously separates from the medium without any separation and purification steps. Admittedly, there is still considerable room for improvement and optimisation of the electrochemical process in terms of the energy efficiency of the electrochemical process in comparison to the existing chemical/catalytic routes.

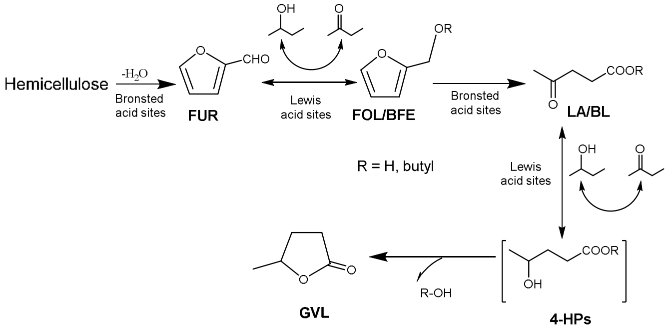

Figure 12. Domino reaction for the synthesis of γ-valerolactone (GVL) from cellulose with a combination of Lewis and Brönsted acid sites (adapted from Reference 159).

Thermal deoxygenation to liquid aromatic fuels. Thermal deoxygenation (TDO) of LA into a mixture of aromatic liquids has been proposed as an alternative pathway for producing biofuels. Specifically, the TDO procedure involves neutralising LA with $Ca(OH)_2$ to obtain the corresponding salt. This salt is subjected to high temperatures (623–723 K) to form cyclic and aromatic products with a low oxygen-carbon ratio, thereby improving the energy density. These TDO products can be enhanced by hydrogenation and dehydration using Ru and Pt catalysts and can then be used as hydrocarbon fuels.[160] Later, these authors also reported achieving high yields of deoxygenated hydrocarbons when mixtures of levulinic and formic acid were used; a molar ratio of 1 provided the highest yield.[161]

2.1.3. γ-Valerolactone: Derived chemicals and biofuels

Synthesis. GVL is chemically stable under normal conditions and possesses low toxicity. GVL is completely soluble in H_2O, and its high boiling point (480 K) facilitates its separation or purification through distillation.[162] GVL has recently been proposed as an excellent solvent for processing lignocellulosic biomass into valuable platforms such as HMF, LA, and GVL itself.[162,163] The use of GVL as a platform for the production of biofuels and chemicals has been exhaustively reviewed elsewhere.[162,164] However, the commercial use of GVL is still limited, primarily because of its high production costs.

Extensive research has been conducted on the transformation of LA into GVL involving the use of Ru, Pt, and inexpensive Cu-based catalysts and relatively moderate H_2 pressure (1–5.5 MPa) and temperature (403–473 K). This route has been the subject of excellent reviews and interested readers are directed to these reviews and references therein for further details as this is not a direct synthesis from FUR.[114,162,165,166]

GVL can also be synthesised from FOL, but this involves an additional step for production and subsequent isolation of FOL from FUR.[147] Remarkably, the direct conversion of FUR into GVL has been reported by Román-Leshkov *et al.*[159] *via* one-pot conversion of FUR into GVL through a cascade scheme with 3 steps (Figure 12) as follows: *i*) a Meerwein–Ponndorf–Verley (MPV) hydrogenation of FUR to FOL, in which butanol is used as the solvent and hydrogen as the donor; butyl furfuryl ether can also be formed (in Figure 12, R = *n*-butyl); *ii*) ring-opening hydration of FOL (or butyl furfuryl ether, BFE) in levulinic acid (or butyl levulinate, BL); and finally, *iii*) the MPV hydrogenation of LA (or butyl levulinate, BL) into GVL (through 4-hydroxypentanoic acid or its butyl ester intermediate). A GVL yield as high as 68% was obtained with 5 wt.% FUR in butanol containing H_2O, at 393 K over 24 h using Zr-Beta zeolite (with Lewis acid sites) as the hydrogen transfer catalyst and Al-MFI zeolite (with nanosheet morphology an Brønsted acid sites) as the ring-opening hydration catalyst. This domino-like reaction involving the use of a hydrogen donor alcohol, which precludes the need for H_2 at high pressure, does not use a non-precious metal catalyst but rather utilizes considerably less expensive zeolites. Unfortunately, the GVL yield declined progressively over successive cycles (3 cycles), and more investigation is required to make this direct synthesis possible. The initial yield was substantially (but not completely) recovered when the catalysts were calcined at 823 K for 10 h in air. This result suggests that fouling or poisoning by coke deposits has a great impact on the catalyst deactivation. No information was provided regarding which specific reaction is involved in the deactivation.

Derived chemicals and biofuels

GVL has been proposed as a feedstock for producing chemicals, particularly monomers for polymers that are either currently derived from oil or that possess specific chemical properties and excellent acceptance by consumers. Figure 13 summarises the major routes described for the synthesis of these chemicals; these multiple possibilities are the topic of earlier reviews,[114,162,164] where further details can be found.

GVL can be used for gasoline additive (extender) admixing.[167] GVL exhibits a lower vapour pressure and higher energy density than ethanol. However, there are limitations to its direct application in the present infrastructure, such as its low energy density, blending limits, and high solubility in H_2O.[2] Deoxygenation and the consequent increase of the H/C ratio and/or increase of the carbon chain length (either by esterification with alcohols or by some C-C coupling reactions) are required to increase the energy density.

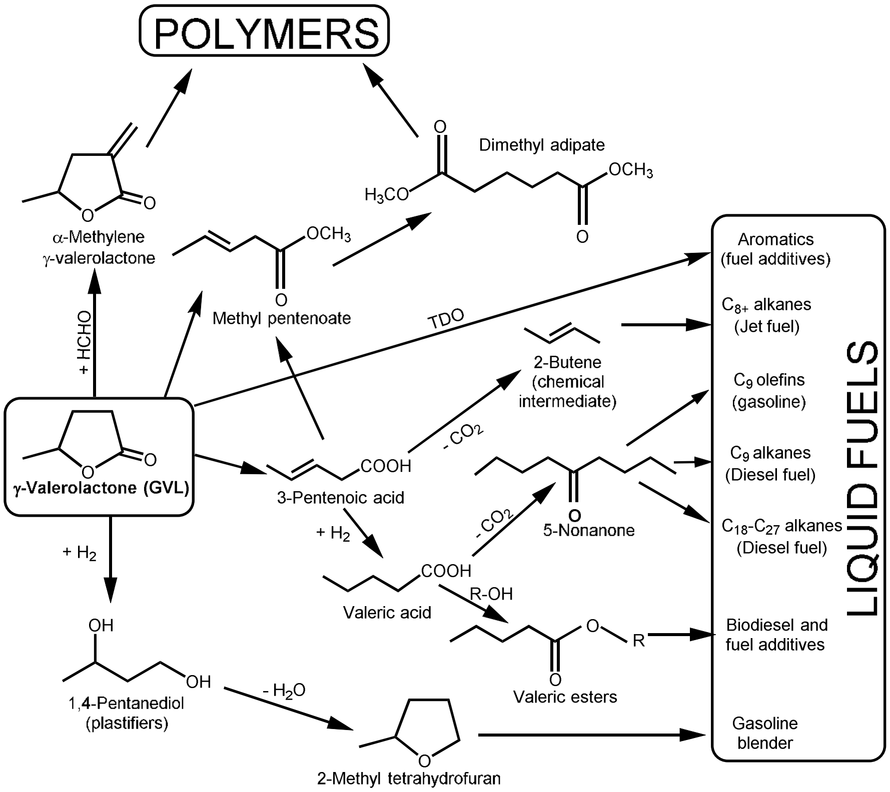

Figure 13. γ-Valerolactone (GVL) as a chemical platform for the production of fuels and chemicals (from Reference 162).

With regard to the production of liquid fuels from GVL (Figure 13), one of the alternatives is the *hydrogenation of GVL to MTHF*, which was in fact indirectly mentioned during the discussion of the direct conversion of LA to MTHF because GVL is an intermediate in the reaction. However, specific investigations on the hydrogenation of isolated GVL are much rarer. In this context, the evaluation of a Cu/ZrO_2 catalyst by Cao *et al.* must be noted.[168] Through proper selection of the conditions for activation of the catalyst (calcination at 673 K) and the reaction conditions (6 MPa H_2, 513 K), a yield of MTHF close to 95% was obtained (at nearly full GVL conversion).

A second route (Figure 13) involves production of *aromatic hydrocarbons from GVL through thermal deoxygenation* (TDO). Benzene, toluene, and xylene are predominantly formed by pyrolysis at 773 K with ZSM-5.[169] The catalysts were slightly deactivated, but could be regenerated up to 4 times by calcination at 773 K.

Finally, the other possibilities illustrated in Figure 13 are based on two deoxygenated molecules derived from GVL: pentenoic acid and valeric acid. Pentenoic acid can be further deoxygenated by decarboxylation and oligomerised to a mixture of C_{8+} alkanes in the range of jet fuels. Valeric acid also presents two simultaneous possibilities: esterification to alkyl esters (biodiesel) or deoxygenation and oligomerisation *via* 5-nonanone to C_9 alkanes/olefins (diesel/gasoline fuels) or to a mixture of C_{18}–C_{27} alkanes (diesel fuel). Further and more detailed information can be obtained elsewhere.[114,162,164]

2.1.4. Tetrahydrofurfuryl alcohol and derivatives

Tetrahydrofurfuryl alcohol (THFA) is a water-miscible, biodegradable chemical derived from FUR by hydrogenation. THFA is useful in many different applications, extending from high-boiling solvents for printing inks to the pharmaceutical industry. However, the primary application of THFA (Figure 14) is the synthesis of specialty chemicals such as 3,4-dihydro-2H-pyran (dihydropyran). Dihydropyran is used as a reagent for protecting alcohols in organic synthesis,[170,171] and in the synthesis of important agrochemicals and pharmaceuticals because it contains a double bond that is able to react with H_2, H_2O, Cl_2, alcohols, glycols, and organic acids.[172,173]

THFA has also been proposed for use as a biofuel or as a fuel additive based on the similarity of some of its physical and chemical properties to those of kerosene (octane number of 83).[153,174] Moreover, oxygenated compounds derived from the etherification of THFA with different alcohols or acetals such as tetrahydrofurfuryl tert-butyl ether and ditetrahydrofurfuryl polyacetal have also been proposed for use as diesel additives due to the significant decrease of particle emissions.[175] These reactions are performed under batch conditions in the presence of Amberlyst 15 as an acid catalyst by placing THFA in contact with isobutene or dioxane, respectively, at temperatures lower than 373 K.

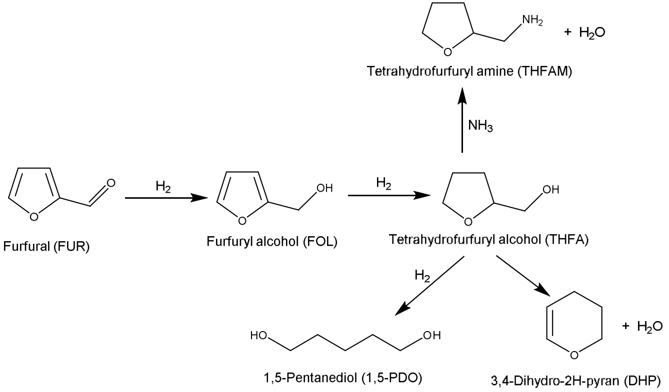

Figure 14. Hydrogenation of furfural to tetrahydrofurfuryl alcohol (THFA) and its main commercial derivatives.

THFA is industrially produced by the hydrogenation of FOL using a supported Ni catalyst under moderate temperatures (323–373 K) in gas- or liquid-phase operation,[48] but it has also been widely demonstrated that direct hydrogenation of FUR can also be used to obtain THFA. Other catalysts based on expensive metals such as Pt, Ru, and Pd have also been tested, resulting in good THFA yields. Tables 4a, 4b, and 4c summarise the most relevant results reported in the scientific literature for both the direct hydrogenation of FUR and for the hydrogenation of FOL under liquid- and gas-phase conditions. Gas-phase hydrogenation processes in a fixed-bed reactor are more amenable to scale-up, enhanced productivity, handling, and preventing leaching compared those in the liquid-phase.[176]

Comparison of the data concerning the direct one-step liquid-phase hydrogenation of FUR to THFA and for reactions starting from FOL reveals that the best catalytic results were attained in the absence of solvent,[177,178] or in the presence of methanol,[179] although TFHA yields close to 100% have been reached by using very dilute FOL solution in ethanol over Pt[180] and Ru[87] complexes. In general, the H_2 pressures were lower than 6 MPa, whereas the reduction of FOL appeared to require lower reaction temperatures. On the other hand, there are few studies devoted to the gas-phase hydrogenation, although TFFA yields close to 100% can be reached with Ni-based catalysts using FOL or FUR as starting materials, but with the use of very high H_2/substrate molar ratios.

THFA can present two different stereoisomers. Wei *et al.* reported the selective asymmetric hydrogenation of FOL to (S)-(+)-THFA (84.4% THFA yield, 98.3% ee optical yield), catalysed by a

Table 4a. Catalyst performance in the direct one-step liquid-phase hydrogenation of furfural (FUR) to tetrahydrofurfuryl alcohol (THFA)

Catalyst	Reaction conditions						Conv. (%)	Yield (%)	Ref.
	FUR (wt.%)	Solvent	H_2 (MPa)	Temp. (K)	Time (h)	cat./FUR (wt.)			
$NiCrO_4$	87	water	0.7	413	5	0.075	100	70	183
Ni-Cr	100	none	4.6	408	2.25	0.1	100	90	184
Supported Ni and Cu	100	none	4	403	3	0.026	100	97	177
NiCu/SBA15+Na_2CO_3	5	water	4	433	4	0.4	>99	40	185
Ru/MgO	49	ethanol	15	383	n/a	0.042	100	78	186
RuO_2	59	methanol	5	393	2.5	0.035	100	43	177
RuO_2+Cu	59	methanol	5	393	1.5	0.069	100	86	177
Pd/C	2.4	water	8	448	0.5	0.32	98	62	187
Pd/MFI	11.5	isopropanol	3.4	493	5	0.086	84	83	188
Pd-Ir-ReO_x/SiO_2	10	water	6	323	2	0.1	100	78	104
Pd-Ru/MFI	11.5	isopropanol	3.4	493	5	0.086	98	48	188

Table 4b. Catalyst performance in the liquid-phase hydrogenation of furfuryl alcohol (FOL) to tetrahydrofurfuryl alcohol (THFA)

Catalyst	Reaction conditions						Conv. (%)	Yield (%)	Ref.
	FOL (wt.%)	Solvent	H_2 (MPa)	Temp. (K)	Time (h)	cat./FOL (wt.)			
Supported Ni	100	none	4	403	3.8	0.03	99	96	177
Supported Ni	100	none	4	453	1.7	0.04	100	98	178
$NiPd/SiO_2$	5	water	8	313	2	0.21	99	96	189
Pd/C	59	methanol	5	393	1.6	0.04	81	64	177
Pd/MnO_x	10	water	3	393	4	0.05	46	46	190
Pd/TiO_2	7.8	methanol	0.1	298	1	0.10	82	69	191
RuO_2	59	methanol	5	393	1.6	0.04	99	89	177
Ru/TiO_2	3.1	2-propanol	2.7	363	2	0.06	90	83	192
Ru/hectorite	1.6	methanol	2	313	1	0.22	100	99	179
$Ru/MgAl_2O_4$	10	water	6	393	4	0.05	100	84	190
Ru/MnO_x	10	water	3	333	12	0.05	91	91	190
Ru/NaY	10	water	6	393	4	0.05	100	77	190
cis-$[Ru(6,6'\text{-}Cl_2bpy)_2(OH)_2]((3,5\text{-}(CF_3)_2C_6H_3)_4B)_2$	1.5	ethanol	5.1	403	4	0.10	100	>99	87
Rh/MnO_x	10	water	3	393	4	0.05	32	31	190
SiO_2-alginic acid-amino acid-Pt complex	2.8	ethanol	0.1	303	24	0.44	100	100	180
Pt/C	6	2-propanol	3	433	1	0.10	100	46	187

Table 4c. Catalyst performance in the gas-phase hydrogenation of furfural (FUR) or furfuryl alcohol (FOL) to tetrahydrofurfuryl alcohol (THFA)

Catalyst	Substrate	Reaction conditions				Conv. (%)	Yield (%)	Ref.
		Contact time	H_2/substrate (mol ratio)	Temp. (K)	Time (h)			
Ni/kieselguhr	FOL	0.025 h^{-1} WHSV	105	355	n/a	100	99	193
Ni/SiO_2	FUR	0.1-3 $g_{cat}/h/mol_{total}$	n/a	473	n/a	15	15	69
Ni/SiO_2	FUR	0.884 $g_{cat}/h/mol_{total}$	36	413	0.5	100	94	176

n/a: not available

silica-supported alginic acid-amino-Pt complex at 303 K and 0.1 MPa H_2 pressure using FOL and ethanol as the solvent.[180] The catalyst was only slightly deactivated during reuse for 4 runs.

Finally, as described earlier for FOL synthesis, supercritical CO_2 has been demonstrated to be an excellent medium for the hydrogenation of FUR. By selecting the temperature in each of the two catalytic reactors, the first loaded with copper chromite and the second with Pd/C, different furanic compounds can be synthesised.[119] Thus, a THFA yield of 96% could be obtained by using both reactors in series at 393 and 473 K, respectively, under conditions of 15 MPa H_2, 1 mL/min CO_2, and 0.05 mL/min FUR.

On the other hand, the direct one-pot synthesis of THFA from xylose has also been explored, in which the dehydration of xylose to FUR was combined with subsequent hydrogenation processes using a single biphasic (water-organic) solvent.[181] Two catalysts were used, Amberlyst-15 as the dehydration catalyst (aqueous phase) and a hydrophobic Ru/C catalyst (organic phase) for the hydrogenation reaction. The hydrophobic solvents disfavoured the competitive hydrogenation of xylose to xylitol due to the low solubility of xylose in the organic phase (where the Ru/C catalyst is soluble). In contrast, the FUR formed *via* the dehydration of xylose was hydrogenated both in the organic phase and at the organic/water interface. The highest selectivity to THFA (50%) was achieved under conditions of 408 K, 2.5 MPa H_2, and using a biphasic H_2O-cyclohexane system, but with a modest xylose conversion of 32%. Along with THFA, other products like GVL, LA, pentanediols, and minor amounts of cyclopentanone (CPONE), 1-hydroxy-4-pentanone and 1,4-pentanedione, were also detected. This same research group also developed a multilevel rotating foam biphasic reactor based on the use of Ru-impregnated carbon foam as a hydrogenation catalyst and a mordenite-coated Al foam in the aqueous phase as a dehydration catalyst.[182] This system eliminates the contribution of the interface to the overall catalytic activity and also eliminates interaction between both catalysts. The benefits of this system lie in the easy catalyst recovery and reutilisation, but it is necessary to enhance the catalyst-reactant contact because the THFA yield was still low. Regarding the reaction mechanism, in the case of liquid-phase reactions, the data achieved with the Ru/TiO_2 catalyst best fit to the single-site Langmuir-Hinshelwood model.[192] In this reaction, hydrogen is molecularly adsorbed (non-dissociative adsorption), and the surface reaction between adsorbed H_2 and FOL is the rate-controlling step. Competitive adsorption of TFHA with both reactants (H_2 and FOL) was also observed. Similar conclusions were obtained by Tomishige *et al.* for the gas-phase hydrogenation of FOL to THFA, but on Ni/SiO_2 catalysts.[176] The attack of adsorbed hydrogen species on the furan ring is the rate-determining step, thus producing THFA without prior formation of free dihydrofurfuryl alcohol. This latter step is the only one that is sensitive to the structure of the catalyst as smaller Ni particles give rise to high TOF values; the hydroxyl group of the FOL molecule outside the furan ring favours the adsorption of FOL on the edges or corners of the metal particles. In the same study, the authors also evaluated the direct gas-phase hydrogenation of FUR to THFA and concluded that complete hydrogenation proceeds in two consecutive steps, where the first step is the hydrogenation of FUR to FOL.[176] They proposed the existence of a strongly adsorbed FUR molecule, which then reacts with two adsorbed H atoms. The second step is the hydrogenation of FOL to THFA; FUR hydrogenation is favoured over FOL hydrogenation because FUR molecules are strongly adsorbed on the nickel surface.

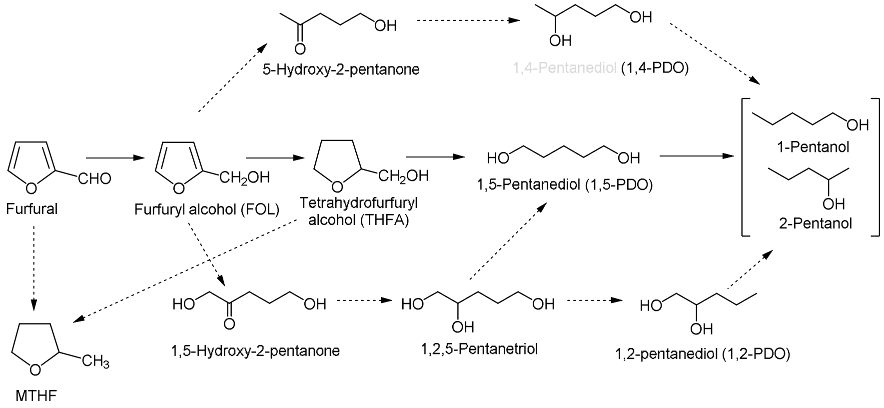

Figure 15. Products and reaction pathways in the hydrogenolysis of furfural (FUR) to 1,5-pentanediol (1,5-PDO) (adapted from Reference 194).

Extensive research concerning the reusability of the catalyst is lacking, but Merat *et al*. found that in the liquid-phase hydrogenation of FOL, the best catalyst could be used for thirty catalytic runs, although the time-on-stream was increased from run-to-run to compensate for deactivation and maintain a THFA yield greater than 96%.[177] The Ru/TiO_2 catalyst was slightly deactivated when used in this reaction, but could be recycled by washing with 2-propanol to remove the by-products present on the active sites responsible for the deactivation.[192] No leaching of Ru was observed. Biradar *et al.* confirmed the recyclability and stability of a Pd/MFI catalyst, even when FUR was used as the feedstock.[188]

2.1.5. 1,5-Pentanediol and derived biofuels

This section reports the technical feasibility of using FUR for production of di-alcohols with a linear 5 carbon atom chain (1,5-pentanediol) and with OH groups at both ends (these terminal diols are generally called α,ω-diols or terminal diols). Lange *et al.* proposed that 1,5-PDO can be converted to valuable biofuels by esterification (e.g., to pentyl valerate or pentanediol divalerate) or by etherification (e.g., to dipentyl ether).[7] Interestingly, terminal diols like 1,3-propanediol and 1,4-butanediol are used in industry as monomers in the manufacture of polyesters and polyurethanes; if these amines are aminated to diamines for the synthesis of polyamides,[195] subsequent synthesis of 1,5-PDO from FUR also enables the production of monomers for the production of polyesters, polyurethanes, and polyamides from biomass.

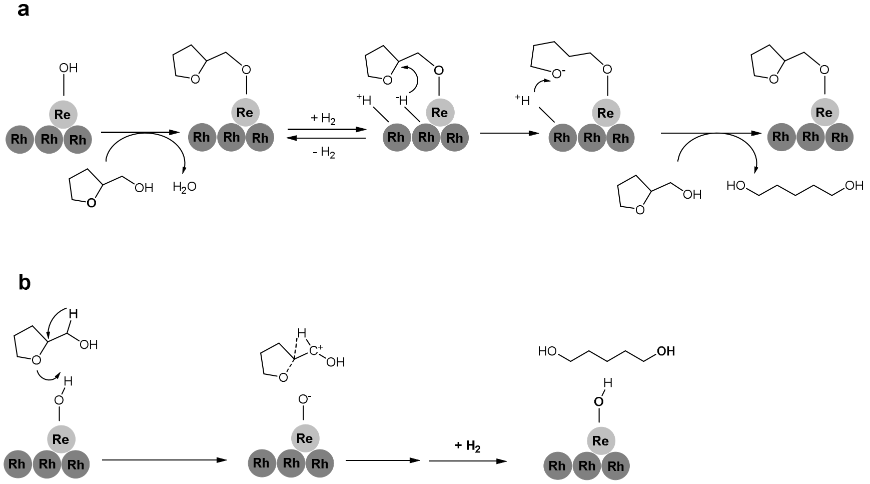

Figure 16. Mechanisms of tetrahydrofurfuryl alcohol (THFA) hydrogenolysis: a) *via* hydride-mediated carbanion formation;[197,205] and b) oxocarbenium formation by concerted protonation/hydride transfer steps.[207] Schemes adapted from Reference 202.

Most of the research conducted on the production of 1,5-PDO focused on the hydrogenolysis of THFA and not on the direct route from FUR;[176,196-208] therefore, this approach requires initial isolation of THFA. Tomishige *et al.* recently reviewed the latest advances in the hydrogenolysis of THFA and the state-of-the-art on this topic. Further details can be found in the above-mentioned review and the references therein.[202] A selectivity of 95% to 1,5-PDO at 99% conversion was achieved under batchwise operation with a 5 wt.% aqueous solution of THFA using a substrate/catalyst wt. ratio of 10, at 373 K and 8 MPa H_2 over 24 h of reaction using a Rh-ReO_x/C catalyst (see Figure 15 for all possible products and reaction pathways of this reaction). Continuous operation has also been explored, but in this case, the catalyst must be reduced under a H_2 flow prior to operation to obtain a high 1,5-PDO yield.[207,209] Other non-conventional reaction media have been explored, but only for the second step. Chatterjie *et al.* demonstrated that supercritical CO_2 (12 MPa) results in a THFA conversion of >80% with a 1,5-PDO selectivity >90% (4 MPa H_2, 24 h, 333 K, Rh/MCM-41 catalyst).[208]

Another route, first described in 1946, is also initiated in THFA but proceeds *via* rearrangement to dihydropyran with subsequent hydrolysis to δ-hydroxyvaleraldehyde and hydrogenation to 1,5-PDO.[171] This three-step route yields only 70% 1,5-PDO and also requires further distillation steps for purification of the intermediates.[195]

Higher yields have been obtained in the direct synthesis of 1,5-PDO from FUR by using Rh- or Pd-modified Ir-ReO_x/SiO_2 catalysts [104,194,210] and conducting the reaction in a one-pot two step approach by combining hydrogenation of FUR to THFA followed by hydrogenolysis of the latter. The hydrogenation of FUR to THFA was conducted at low temperature (313 K) using 6 MPa H_2; hydrogenolysis of the formed THFA was later accomplished in a second step by increasing the temperature to 373 K. Under these conditions, the highest yield of 1,5-PDO (78%) was achieved at complete FUR conversion with the Rh-Ir-ReO_x/SiO_2 system prepared by sequential impregnation (the catalyst required prior *in situ* reduction at 473 K). The selectivity to 1,5-PDO was less than that achieved by starting directly from THFA because other secondary reactions can also occur (see Figure 15; in addition to the main reaction route indicated by continuous arrows, other pathways are observed and indicated by dotted arrows): 1,4-PDO, 1,2-PDO, 1-PDO, 2-PDO, THFA, MTHF, and 1,2,5-pentanetriol were also detected.[194]

Characterisation of the Rh-Ir-ReO_x/SiO_2 catalysts showed that an Ir–Rh alloy was formed and that two-dimensional ReO_x clusters with Re in a low valence state partially covered the alloy particles. The interesting point is that the low valence Re atoms were in intimate contact and interacted with Rh-Ir atoms at the surface of the alloy particles. The hydrogenation of FUR to tetrahydrofurfuryl alcohol (THFA) occurs on the Ir–Rh alloy sites, where the ReO_x species enhance the hydrogenation rate. The second step, which requires a higher temperature, is the hydrogenolysis of THFA to 1,5-pentanediol that also involves the ReOx-modified Ir–Rh alloy particles.[194] In the case of Pd-Ir-ReO_x/SiO_2, no Pd-Ir alloy is formed, and the hydrogenation step occurs on ReO_x-promoted Pd particles, whereas Ir particles covered by ReO_x species are responsible for the hydrogenolysis step.

The Rh-Ir-ReO_x/SiO_2 catalyst undergoes deactivation, possibly by leaching and sintering of the metal particles.[194] The Pd-Ir-ReO_x/SiO_2 catalyst is slightly less active and but more stable than the Rh counterpart, although sintering of the metal particles occurred. More research on the deactivation process appears to be needed.[104] Thus, the mode of catalyst deactivation is a matter of controversy for single hydrogenolysis of THFA to 1,5 PDO. It appears that the extent of deactivation may depend on the reaction conditions and type of catalyst.[203,205,207]

The reaction mechanism involves conversion of FUR to THFA as the first step, same as that mentioned previously, but the second step involving hydrogenolysis of THFA to 1,5-PDO remains controversial. Consequently, this step requires further clarification. Two different mechanisms have been proposed (Figure 16).[197,207] Tomishige *et al.* proposed a hydride-mediated carbanion mechanism in which THFA is initially chemisorbed on ReO_x species to form a terminal alkoxide adspecies. The hydride adspecies present on the vicinal Rh atom and formed by the dissociative adsorption of H_2 that generates a hydride and proton, attacks the 2-position of the ring, breaking the ether bond *via* a S_N2 reaction. Subsequent hydrolysis of the adsorbed 1,5-PDO (represented in the scheme in only one step) releases the product and heals the catalytic sites for a new cycle.[197,205] On the other hand, Dumesic *et al.* proposed a concerted acid-mediated mechanism: the Re-OH acid sites present in the vicinity of the Rh atoms transfer a proton to the O ring, and the ring is then opened while the H atom in the -CH_2OH group (α position) concertedly migrates to the β position (2-position of the furan ring). Thus, 1,5-PDO is formed by hydrogenation of the eventually formed protonated aldehyde. A similar mechanism was also proposed by Melián-Cabrera *et al*.[211]

2.1.6. 2-Methyl furan and derived biofuels

2-Methyl furan (MF), which is also known as sylvan, is a flammable and water-insoluble liquid. MF is used as a solvent and as a feedstock for the production of antimalarial drugs (chloroquine), pesticides (like chrysanthemate), methyltetrahydrofuran (MTHF), perfume intermediates, nitrogen and sulfur heterocycles, as well as functionally substituted aliphatic compounds. Further details of the properties of MF as a solvent can be found elsewhere.[14] Moreover, as discussed below, a new route for the production of liquid fuels with high alkane and low oxygenate content from MF has recently been proposed.[212,213]

MF can also be used directly as a motor biofuel because of its octane number of 74.[153] In this context, Wang *et al.* found that MF has a thermal efficiency that is greater than that of gasoline and 2,5-DMF due to its fast burning rate and notably better knock-suppression ability.[214] The potential of MF as a biofuel has been substantiated by Lange e*t al*.[7] in terms of investment costs, capital index, and fuel economy during a road trip by comparing MF with MTHF, trimer hydrocarbons (described in Section 2.1.6.1), and ethyl furfuryl ether (EFE).

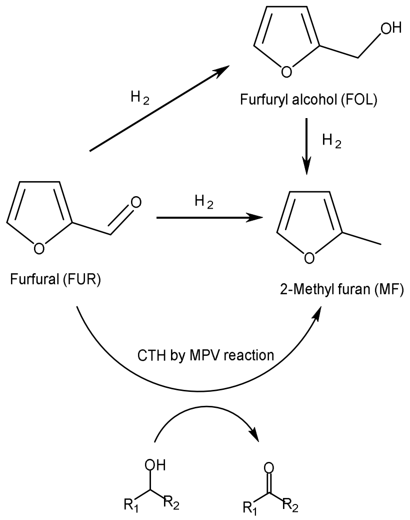

Figure 17. Different routes for the synthesis of 2-methyl furan (MF) from furfural (FUR).

MF is currently produced as a by-product of the synthesis of FOL from FUR.[48] Strictly speaking, the formation of MF requires hydrogenolysis (hydrogenation in most of the scientific literature) of the C-O bond in the FOL molecules.

Attempts have been made to produce MF in high yields from pure FOL *via* liquid- or gas-phase hydrogenation reactions. Liquid phase yields higher than 90% have been achieved by using copper-supported asbestos, silica, and pumice, [215] a CaO-promoted copper chromite catalyst,[216] and a Pd/TiO_2 catalyst.[191] In the gas-phase reactions, an 80% yield of MF was achieved with bimetallic Fe-Cu catalysts,[217] and 93% yield was obtained with a commercial Cu:Zn:Al:Ca:Na catalyst.[52] No relevant information regarding the stability and reusability of the catalysts was provided in these reports.

Nevertheless, most research has been focused on producing MF directly from FUR, either by gas-phase or liquid-phase hydrogenation (Figure 17). Liquid-phase catalytic transfer hydrogenation (CTH) has also received significant attention. The most relevant results conducted to date from FUR are summarised in Table 5. Attempts to perform hydrogenation reactions in supercritical CO_2, as well as the electrocatalytic hydrogenation of FUR to MF, are not included in Table 5 but are discussed later in this section.

The main drawback to commercial implementation of the direct hydrogenation of FUR to MF is related to the selectivity since undesired reactions, leading to other reaction products, are inevitable, including the decarbonylation of FUR to furan and further hydrogenation of MF to MTHF, 2-pentanone, and 2-pentanol.

The highest yields of MF from gas-phase hydrogenation have been obtained with Cu-containing catalysts, primarily those based on reduced copper chromite supported on different substrates; other systems gave rise to poorer selectivities to MF (Table 5). Catalyst deactivation is a major issue in gas-phase hydrogenation, as confirmed in several studies,[32,218-220] although it has also been reported that copper chromite dispersed on activated lump charcoal could be used intermittently over a period of 3 months with an overall MF yield of 91%.[221] The principal cause of catalyst deactivation is coke deposition, and therefore, a regeneration step to remove these coke deposits and to reduce the CuO_x species is required.

Liquid-phase hydrogenation reactions have also been explored in attempts to overcome the deactivation problems associated with the use of higher temperatures in the gas-phase process. Early studies employed Ni supported on a kieselguhr catalyst.[81] Other systems based on Cu, Ru, and Pt have also been explored, but furnished lower MF yields compared to the gas-phase reaction (Table 5).

Interestingly, the simultaneous production of FUR and HMF from biomass and the subsequent upgrading of these chemicals to MF and dimethyl furan, respectively, have recently been attempted.[222] FUR has been extracted in conjunction with HMF from the reaction medium using THF, and was converted into MF (93% yield) using Ru/Co_3O_4 as the catalyst (Table 5).[222] However, there is an evident lack of information regarding the stability and reusability of this catalyst in the liquid phase. In contrast, the activity of a $CuNiMgAlO_y$ catalyst remained almost unchanged after 3 cycles and the catalyst exhibited only a 10% loss of conversion after 6 catalytic cycles.[65] Remarkably, similar stability was observed when this catalyst was tested in the gas-phase hydrogenation of FUR after 36 h of time-on-stream.

An interesting approach to enhance the MF selectivity in the liquid phase is the reactive distillation of MF under stripping conditions (H_2 flow) to prevent consecutive hydrogenation reactions.[7,223] Thus, a 31% MF yield was obtained at 443 K using a commercial CuCrBa catalyst and γ-valerolactone as the solvent. A yield of only ~17% was achieved in the absence of H_2 stripping.

The investigations conducted by coupling alcohol dehydrogenation with FUR hydrogenation (CTH by MPV reaction) are also compiled in Table 5. Different alcohols have been explored as reducing agents. Both gas- and liquid-phase conditions were explored.[224-230] The use of 1,4-BDO or cyclohexanol as alcohols results in the parallel production of γ-butyrolactone or cyclohexanone, respectively, both products being of industrial interest.[224-227] The CTH process offsets the limitations of the conventional individual alcohol dehydrogenation and FUR hydrogenation (that suffer primarily from difficulties in controlling the temperature of the process and the poor hydrogen utilisation and conversion, constrained by the thermodynamic equilibrium). Gas-phase CTH using Cu-based catalysts resulted in higher MF yields than liquid-phase CTH using noble metals such as Pt or Ru. The preference for the gas phase over the liquid phase, however, cannot be considered definitive because the type of alcohol is a key factor. Stability studies have been performed using a Ru/C catalyst, showing that the decrease in the FUR conversion and MF yield obtained after a catalytic cycle is accompanied by an increase in the FOL yield.[230] This deactivation is not caused by carbon deposition but is due to Ru oxide reduction during the CTH of FUR. The synergy between both Lewis acid sites (associated with the RuO_x species and the metallic Ru sites) resulted in a higher MF yield. The initial activity was completely recovered after catalyst regeneration.

Investigation of the reaction mechanisms has only been conducted for Ni and Pd systems, but in the context of the synthesis of FOL from FUR under gas-phase conditions (unfortunately no information is available on Cu catalysts to date). Thus, Sitthisa *et al.* studied Ni/SiO_2 and $Ni\text{-}Fe/SiO_2$ catalysts and observed that only FOL and furan were formed on the monometallic nickel catalyst; these species were respectively transformed into MF (*via* C-O hydrogenolysis) and C_4 products (butanal, butanol, and butane *via* ring opening).[71] Ni preferentially catalyses FUR decarbonylation to furan rather than hydrogenation.[231] In contrast, the presence of Fe in the bimetallic Fe-Ni alloy suppresses the decarbonylation activity of Ni. DFT calculations suggested that the differences in selectivity could be related to the stability of η^2(C,O) surface species on the oxyphilic Fe species, with significant lengthening of the C-O bond, which can be readily hydrogenated to generate FOL, which is then converted into MF *via* hydrogenolysis, thereby inhibiting the formation of acyl species, the precursor of furan. In this reaction scheme, the hydrogenolysis step is proposed to occur prior to any atomic-H addition to the molecule, although this was not substantiated.

DFT calculations, as already mentioned in Section 2.1.1, have been conducted to investigate the adsorption modes and the energy barriers for interconversion of FUR, FOL, MF, and furan on Pd(111) surfaces.[74] These studies indicated that thermodynamics clearly favour the decarbonylation of FUR to furan and CO *vs.* the hydrogenation to FOL, although hydrogenation to FOL is kinetically preferred. The subsequent formation of MF occurs either in a 2-step process (hydrogenation of FUR to FOL followed by the H-assisted transformation of FOL to MF) or by initial dehydrogenation to form a methoxy intermediate, which is then directly deoxygenated to MF. The occurrence of a particular pathway primarily depends on the surface hydrogen coverage.

Finally, two alternative processes will be revised: hydrogenation in supercritical CO_2 and electrocatalytic hydrogenation. Supercritical CO_2 has been used in the synthesis of MF from FUR with a copper chromite catalyst. A MF yield of 90% was obtained using a CO_2 flow of 1 mL min^{-1} (pumphead at 263 K and 5.8 MPa), a FUR flow of 0.05 mL min^{-1}, and an operating pressure of 15 MPa, using a temperature of 513 K (not compiled in Table 5).[119]

Table 5a. Summary of catalyst performance in the gas-phase catalytic hydrogenation of furfural (FUR) to 2-Methyl furan (MF)

Catalyst	Reaction conditions				Conv. (%)	Yield (%)	Ref.
	Space velocity (h^{-1})	H_2/FUR	Temp. (K)	Time (h)			
$Cu_2Cr_2O_5$	0.15-0.3 (LHSV)	5-8	523	n/a	100	95	220
Supported Cu	n/a	-	413	n/a	10–20% of FOL formed	-	218
Cu/SiO_2	0.5 (WHSV)	17	493	10	100	90	61
$Cu_2Cr_2O_5$/charcoal	10 s contact time	15	498	n/a	100	99.5	219
$Cu_2Cr_2O_5$/activated charcoal	n/a	5	493	n/a	n/a	95	221
Metallic Cu	n/a	n/a	443	n/a	100	40	215
$CuO\text{-}Cr_2O_3\text{-}MnO_2\text{-}BaCrO_4$	n/a	2	448	5	100	85	232
Commercial Cu:Zn:Al:Ca	0.3 (LHSV)	25	523	n/a	n/a	87	52
$CuNiMgAlO_y$	4000 (GHSV)	10	493	36	87	44	65
$Cu\text{-}Fe/SiO_2$	48 (GHSV)	5	525	n/a	99	98	32
$Ni\text{-}Fe/SiO_2$	10 (WHSV)	25	523	n/a	n/a	40	71
$Pt/V_2O_5\text{-}TiO_2/MgO$	2 (WHSV)	2	523	0.5	98	38	56
Mo_2C	0.07-2.4 g_{cat} h mol^{-1}	405	423	3	12	7	233

Table 5b. Summary of catalyst performance in the liquid-phase catalytic hydrogenation of furfural (FUR) to 2-Methyl furan (MF)

Catalyst	Reaction conditions						Conv. (%)	Yield (%)	Ref.
	FUR conc. (wt.%)	Solvent	H_2 (MPa)	Temp. (K)	Time (h)	Cat/FUR (wt.)			
Cu-Fe	41	n-octane	9	493	14	0.08	99	51	110
Pt/C	5.82	n-butanol	8	448	0.5	0.10	99	40	234
$CuNiMgAlO_y$	33	ethanol	1	473	2	2.90	82	11	65
Ru-bis(diamine) complexes	1.45	ethanol	5	403	4	0.10	100	20	87
Ru/Co_3O_4	0.29	THF	1	443	24	5.99	100	93	222

Table 5c. Summary of catalyst performance in the catalytic transfer hydrogenation (CTH) of furfural (FUR) to 2-Methyl furan (MF)

Catalyst	Reaction conditions						Conv. (%)	Yield (%)	Ref.
	Alcohol	FUR/Alc (mol)	LHSV (h^{-1})	Temp. (K)	P (MPa)	Time (h)			
Cu-Zn	1,4-butanediol (gas phase)	1	0.2	483	0.1	4.7	100	97	227
Copper chromite	1,4-butanediol (gas phase)	1	0.7	478	0.1	100	100	96	226
Cu/Zn/Al	1,4-butanediol (gas phase)	1	0.7	498	0.1	4.7	100	93	235
Cu/Zn/Al	cyclohexanol (gas phase)	0.3	0.9	543	0.1	200	98	88	225
Cu/Mn/Si	cyclohexanol (gas phase)	0.3	0.49	552	0.1	8	100	94	224
Pd/Fe_2O_3	2-propanol (liquid phase)	0.03	-b	453	2.5	7.5	100	13	228
Ru/C	2-propanol (liquid phase)	0.0063	-b	453	2.04	10	95	61	230
$Ru/RuO_2/C$	2-butanol (liquid phase)	0.0078	-b	453	2.04	10	100	76	229

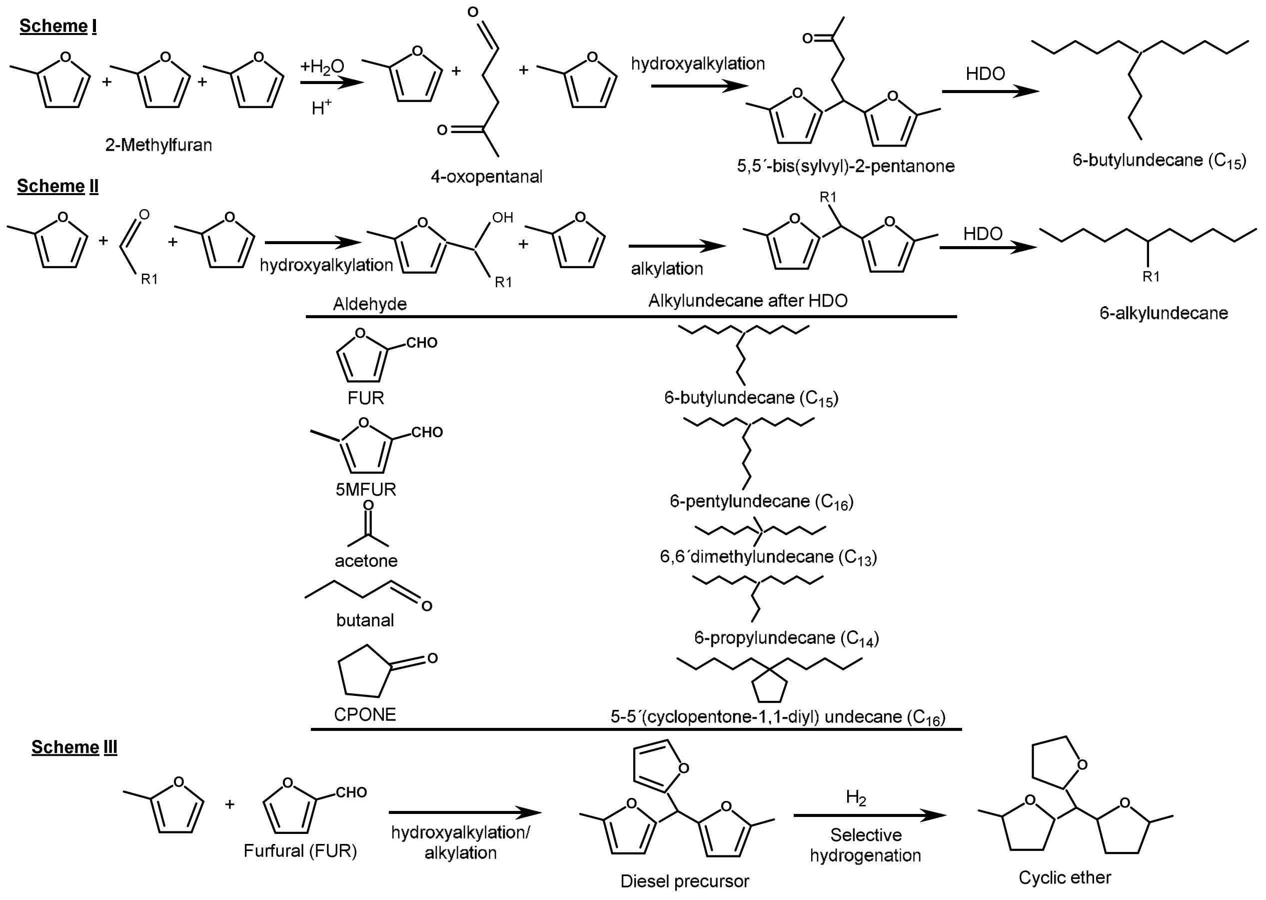

Figure 18. Synthesis of branched alkanes (diesel range) through the hydroxyalkylation of 2-methyl furan (MF) with different substrates and subsequent hydrodeoxygenation of the intermediate oxygenates.

The other strategy is the aqueous electrocatalytic hydrogenation of FUR using a sacrificial anode, where atomic hydrogen is generated *in situ* through the reduction of hydronium ions. Among the metals evaluated as cathode materials, Ni and Fe provided the best results. MF formation was favoured at very low pH (1.0), although the yields were consistently less than 10%.[120] Green *et al.* also detected the formation of MF, but with a selectivity of less than 10%, in the electrocatalytic hydrogenation of an aqueous solution of FUR in a continuous membrane reactor using a Pd/C cathode.[121] Remarkably, Nilges and Shröder obtained complete conversion of FUR with a MF selectivity of 80% on solid copper and electrochemically deposited copper as the electrode, and no electrode deterioration was detected.

Table 6. Hydroxyalkylation/alkylation of 2-methyl furan (MF) with different aldehydes and ketones to different diesel precursors

Substrates (mol. ratio)	Catalyst	Cat. (wt.%)[b]	Temp. (K)	Time (h)	Yield (%)	Ref.
MF	H_2SO_4	12	333	16	74	[236]
MF/MFUR (5:1)	p-TSA	1.8	323	6	93	[237]
MF/FUR (2:1)	Nafion-212	2.9	323	2	70	[238]
MF/FUR (2.2:1)	R-SO_3H-SiO_2	1.6 mol%	338	2	88	[239]
MF/HA (2:1)	Nafion-212	3.1	338	2	>65	[240]
MF/acetone (2:1)	Nafion-212	3.4	323	25	76	[241]
MF/butanal (2:1)	Nafion-212	3.2	323	4	90	[241]
MF/CPONE (2:1)	Nafion-212	3.0	338	12	91	[242]
MF/Mesityl oxide (1:1)	Nafion-212	4.2	333	2	~65	[243]

[a] Conversion of reactant in defect

[b] Percentage with respect to total reactants

5-MFUR: 5-Methyl furfural

HA: Hydroxyacetone

p-TSA: p-Toluenesulfonic acid

2.1.6.1. 2-Methyl furan trimer-derived biofuels

Corma *et al.* first demonstrated the synthesis of diesel-range branched alkanes from MF by a 2-step process.[212,213,236,237] The first step (Figure 18) is the formation of the diesel precursor *via* the hydroxyalkylation/alkylation of MF with an aldehyde or ketone. These precursors were subsequently subjected to hydrodeoxygenation (HDO) to afford diesel-range alkanes. Originally, Corma *et al.* utilized the trimerisation of MF (Scheme I in Figure 18). Trimerisation is initiated by the hydrolysis of MF to 4-oxopentanal (*via* ring opening and keto-enol tautomerism), and subsequently proceeds through two consecutive hydroxyalkylation and alkylation steps (also described as aromatic substitution of the ring with the electrophile 4-oxopentanal). The yield of the oxygenated trimer with 15 carbon atoms, 5,5-bis(sylvyl)-2-pentanone, was approximately 74% (12 wt.% aqueous H_2SO_4, 16 h, 333 K). One important feature of the reaction is the spontaneous separation of the diesel precursor from the aqueous phase, which also facilitates the recovery and the reusability of the catalyst.[236] Subsequent HDO treatment of the C_{15} diesel precursor was demonstrated in continuous mode with a fixed catalytic bed reactor using a composite 3 wt.% Pt/C-TiO_2 catalyst, 5 MPa H_2, and a space velocity of 1.12 h^{-1}. A temperature gradient along the reactor was recommended to prevent cracking of the trimer (393 K top zone, 623 K middle zone).[236] Ideally, HDO should afford the branched 6-butylundecane, but in practice, side reactions (cracking, oligomerisation, etc.) occur and a mixture of alkanes is produced. A molar yield of the diesel range fraction (C_9–C_{24}) exceeding 93% was obtained under these conditions.[236] This diesel pool exhibited an excellent cetane number and flow properties at low temperature. HDO continuous operation for more than 140 h was successfully conducted.[212] Again, the diesel fraction spontaneously separated from the aqueous phase, thus facilitating separation of the fuel without distillation.

The hydroxyalkylation/alkylation steps can also be conducted with other aldehydes or ketones (Scheme II in Figure 18) such as 5-methyl furfural (MFUR),[212,213,236,237] dihydroxyacetone,[240] butanal,[241] acetone,[241] mesityl oxide,[243] cyclopentanone,[242] FUR,[238,239] and methyl levulinate.[238]. Although all of the mentioned carbonylic compounds can be derived from lignocellulosic biomass, the utilisation of FUR must be stressed. MF is derived from FUR *via* hydrogenation; therefore, the use of FUR reduces the need for MF. In these cases, different solid acid catalysts have been employed; Table 6 summarises the results achieved with the most effective catalysts. Although H_2SO_4 was reported to be successfully separated and recycled in several runs for the hydroxyalkylation/alkylation step,[236] replacement of H_2SO_4 with a solid catalyst prevents corrosion problems and facilitates handling and the recovery of the catalyst. Reutilisation of the solid catalysts was tested for a number of catalytic runs, and no important deactivation was observed in successive runs in the investigations summarised in Table 6.

The diesel precursors obtained with the aldehydes and ketones mentioned in Table 6 have successfully been used in the HDO step with high yields of different alkylundecane molecules. Different catalysts have been explored in the HDO step and these catalysts afforded high yields of diesel fraction liquids, where the catalysts include Pt/Zr phosphate,[238] Pd/C,[240,241] Ni-W_xC/C,[241] Ni supported on different acid supports (SiO_2/Al_2O_3 and Hβ, ZSM-5 and USY zeolites),[242,244] and Ni-W_2C/SiO_2 and Mo_2C/SiO_2.[243]

Bell *et al.* recently proposed replacing HDO of the diesel precursor with selective hydrogenation of the double bonds without proceeding to hydrogenolysis of the alcohol and ether C-O bonds. The resulting product has been proposed as a diesel blending agent.[245] Scheme III in Figure 18 summarises this approach where MF and FUR are used as furanic molecules. Pd nanoparticles supported on ionic liquid-modified SiO_2 were used as catalysts, and in the specific case described in this figure, a 92% yield of the cyclic ether was achieved (30 h, 333 K, 2.1 MPa H_2). The six additional molecules of H_2 needed to obtain the corresponding 6-butylundecane are saved with this approach, which represents a 38% H_2 saving (including the H_2 needed to produce MF from FUR). Remarkably, the cyclic ether presents excellent fuel properties exemplified by the high cetane number (60.4), low freezing point (<233 K), high volumetric energy density (32.6 MJ/L), and good lubricity.[245]

2.1.7. 2-Methyl tetrahydrofuran (2-MTHF)

As stated above in the section devoted to the synthesis of 2-methyl tetrahydrofuran from LA, MTHF has also been proposed as an eco-friendly solvent,[246] and has been approved as a component of P-Series type fuel due to its appealing properties as a biofuel,[152,153] notwithstanding the fact that it also presents some drawbacks such as its high polarity, high vapour pressure, and the formation of peroxides.[166]

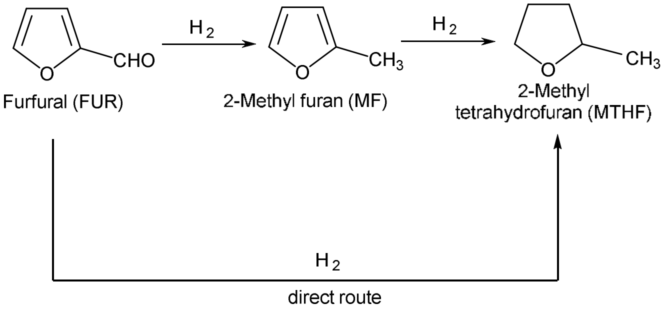

Figure 19. Different routes for the synthesis of 2-methyl tetrahydrofuran (MTHF) from furfural (FUR).

The synthesis of MTHF from either LA or GVL has been mentioned above, but MTHF is currently produced by either the liquid-phase (2 MPa) or gas-phase (atmospheric pressure) hydrogenation of MF using supported Ni catalysts.[48] Biswas *et al.* also reported a high MTHF yield (close to 100%) in this reaction using Pd/C catalysts at low reaction temperatures (<473 K) and low H_2/MF molar ratios (10–25).[247]

However, a more appealing route involves direct production of MTHF from FUR and not from pure MF (Figure 19). A number of investigations have been conducted on this route, exploring either the use of one or two reactors. For instance, Ahmed *et al.* demonstrated a continuous gas-phase process using two commercial catalysts in two different reactors. In the first reactor, FUR is hydrogenated to MF over a Ba/Mn-promoted copper chromite catalyst at 0.1 MPa and 448 K using a H_2/FUR molar ratio of 2, and in the second reactor, MF is transformed into MTHF using a Ni/Al_2O_3-SiO_2 catalyst with a H_2/MF molar ratio of 2 at 388 K.[232]. This system allows a chievement of a MF yield close to 50%, and the generated MF is further hydrogenated to MTHF in 87% yield in the second reactor. FOL and THFA are also formed in the corresponding reactors. Unreacted FUR and MF can be recycled.

The challenging one-step direct synthesis from FUR has also been attempted through one-stage hydrogenation of FUR in the presence of a double catalytic bed, where the first bed consists of a commercial copper-based catalyst (copper chromite) and the second bed is based on noble metals (Pd supported on activated carbon).[248] The process was conducted at 473 K using a H_2/FUR mole ratio of 11 to produce a yield of 91 wt.% MTHF.

Notably, the direct synthesis of MTHF from pentose sugars and lignocellulosic biomass has also been explored. Sen and co-workers,[249,250] using a soluble rhodium catalyst and HI/HCl + NaI additive in the presence of H_2, obtained a maximum yield of MTHF of 63% from corn stover (40% glucan, 24% xylan).[249,250] However, the economic and environmental viability of this process requires further investigation because an expensive catalyst and non-environmentally friendly reaction medium were used.

Supercritical CO_2 has also been employed for producing MTHF from FUR by combining copper chromite (first reactor at 513 K) and Pd/C (second reactor at 573 K) as catalysts. As previously indicated in other sections, the main advantage of this process is its flexibility because by modifying the temperature of each reactor, FOL, THFA, MF, MTHF, and furan can be produced.[119] Thus, it is feasible to obtain MTHF from FUR in ca. 80% yield operating at 15 MPa.

2.1.8. Cyclopentanone and derived biofuels

Cyclopentanone, hereinafter referred to as CPONE, is currently a speciality chemical that can be utilised in the synthesis of pharmaceuticals, fungicides, rubber chemicals, flavours, and fragrances. Due to its chemical similarity to cyclohexanone, CPONE has also been proposed as a feedstock for the synthesis of polyamides *via* δ-valerolactam.[187,234,251-253]

Currently, CPONE can be obtained *via* several petrochemical routes.[187,234,251-253] But recently, two different groups have demonstrated the possibility of obtaining cyclopentanone from liquid-phase hydrogenation of FUR.[185,187,234,254,255] This is an unexpected observation because the hydrogenation of FUR commonly proceeds through the reduction of the carbonyl and double bonds. Hronec *et al.*, using an aqueous FUR solution (5 wt.%), obtained a yield of 76 mol.% CPONE at full FUR conversion with a Pt/C catalyst at 433 K and 8 MPa H_2. The other minor products were cyclopentanol (5 wt.%), MF, and MTHF (overall yield less than 4%). Other reaction conditions such as lower H_2 pressure, higher temperatures, other catalysts such as supported Pd, Ru, Ni, and Cu-Ni systems or Cu-Mg-Al hydrotalcites, basicity or high acidity in the liquid medium, or acid and basic supports resulted in lower CPONE yields at the expense of other products.[185,187] When organic solvents (1-butanol or 1-decanol) were used instead of H_2O, carbonyl and ring hydrogenation derived products became predominant such as FOL, tetrahydrofurfuryl alcohol, MF, and MTHF. No significant catalyst deactivation was observed in a second reutilisation test;[234] unfortunately, longer term deactivation studies were not provided.

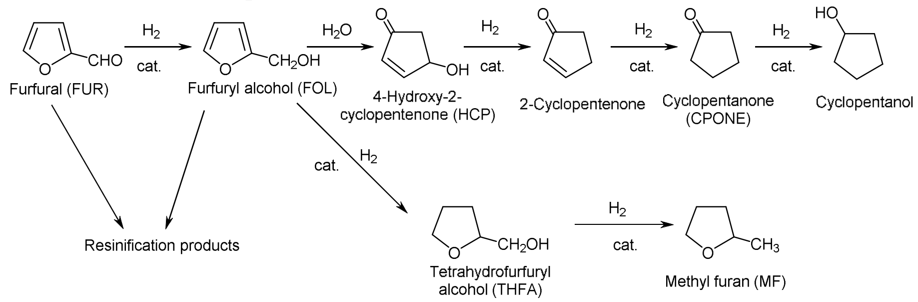

Figure 20. Reaction network involved in the hydrogenation of furfural (FUR) to cyclopentanone (CPONE).

Yang *et al.* proposed that the reaction is initiated with the reduction to FOL (Figure 20), which reorganises to 4-hydroxy-2-cyclopentenone (HCP) by a Piancatelli-type rearrangement. HCP is then successively hydrogenated to 2-cyclopentenone and then to CPONE. There is no clear consensus as to why the hydrogenation stops at CPONE and does not fully proceed to cyclopentanol. Hronec *et al.* claimed that a furfuryl alcohol-derived resin deposited at the surface of the catalyst inhibits this step,[254] whereas Yang *et al.* proposed that the presence of cyclopentenone is responsible for the inhibition.[185] FOL can also be hydrogenated to THFA, but Piancatelli rearrangement is favoured in the presence H_2O by an attack of a H_2O molecule at the 5-position of the FOL ring. Heavy products were also formed by resinification of FUR and FOL, which explains the observed C imbalance.

Based on the experiments conducted under different reaction conditions with different catalytic systems, Hronec *et al.* proposed that the following surface phenomena and species are involved in the mechanism: *i*) formation of an hydroxyalkyl species (*via* di-coordinated η^2(C-O) species) when FUR is adsorbed on the surface of the metal particles under H_2 pressure, *ii*) formation of a carbocation by the C-O scission of the hydroxyalkyl species, and *iii*) electrophilic attack of water on this carbocation at the 5-position to yield a surface intermediate that subsequently reorganises to yield the cyclopentanone.[187]

A remarkable advantage of this reaction is that it must be conducted in aqueous medium. The first step for the production of FUR from hemicellulose is the formation of a dilute aqueous solution of FUR. This means that this primary FUR-water solution is a good candidate for obtaining cyclopentanone. Consequently, the expensive and energy-demanding distillation step to produce purer FUR would not be required for this reaction, thus making this route very attractive.

2.1.8.1. Biofuels derived from cyclopentenone

A novel route for producing liquid biofuels from CPONE has already been technically demonstrated. The first route consists of a two-step procedure that first involves the self aldol condensation of CPONE to afford 2-cyclopentylidene-cyclopentanone, which is hydrodeoxygenated (HDO) to finally produce bi-(cyclopentane) (BCP) (Figure 21).[185,256] BCP has been proposed to be a good candidate for renewable high-density fuel application as an additive to increase the volumetric heating value of conventional bio-based jet fuels and for blending with conventional biodiesel to increase its mileage per litre.[256]

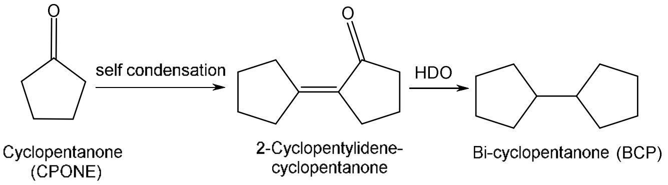

Figure 21. Simplified reaction scheme for the synthesis of bi-cyclopentane (BCP) from cyclopentanone (CPONE).

Basic catalysts are required for the self aldol condensation of CPONE. Homogeneous[185] as well as heterogeneous catalysts have been tested in batch reactors for this purpose. Among the different solid catalysts evaluated (MgAl and LiAl hydrotalcites, CaO, $CaO-CeO_2$, MgO, and KF/Al_2O_3), MgAl hydrotalcites gave rise to the highest yield of 2-cyclopentylidene-cyclopentanone, where 86% yield was achieved after 8 h at 423 K using 10 wt.% of catalyst (higher than that obtained with NaOH).[256] The second step of the process (HDO) has also been investigated by feeding the self-condensation product into a fixed-bed continuous flow reactor and performing the reaction at 503 K with 6 MPa of H_2. Ni/SiO_2 is as active as other Pd- and Ru-based catalysts,[185,256] wherein 93% yield was obtained with residual formation of cracking products (C_1-C_5 alkanes) and C_{10} oxygenates (partially hydrodeoxygenated products). Ni/SiO_2 did not undergo significant deactivation or Ni leaching after 24 h on stream.

A variation of the first step of this route has also been proposed, where rather than self aldol condensation, the process is initiated with FUR-CPONE aldol condensation.[257] More details are provided in Section 2.5 (Claisen-Schmidt condensation).

2.2. Amination reactions

Other important chemicals derived from FUR include furfurylamine (FAM) and tetrahydrofurfurylamine (THFAM). These chemicals have a broad range of applications such as the synthesis of herbicides, pesticides, fibres, piperidine derivatives, and pharmaceuticals (as a key intermediate for the production of the diuretic furosemide).[48] Piperidine is used as a solvent and in the pharmaceutical industry,[258] and optically active FAM derivatives have attracted the interest of organic chemists as building blocks for the preparation of a large spectrum of N-containing natural products. FAM has also been found to possess unique properties for use in engine cleaning formulations.[259,260] THFAM has been proposed as an agent to protect and recover plant tissues subjected to damage upon exposure to cold temperatures[261,262] and as an environmentally friendly composition for removing photosensitive etching-resistant polymer residue.[263] Substituted THFAM has been found to possess potent antidepressant activity in animals.[264]

FAM can be produced *via* the hydrogenation of furfural phenylhydrazone, furfural oxime, and the furfuryl azide of furonitrile, but these methods require expensive reagents for the preparation of such derivatives from FUR, and complicated reaction steps are involved in these preparations in most cases.[258] For this reason, the reductive amination of FUR over metal catalysts is a more economical process, which allows for conversion of the carbonyl functionality to an amine. The pathway proposed in the literature involves contact between FUR and NH_3, leading to the formation of furfurylimine, which is unstable and readily condenses to furnish the trimeric hydrofuramide (Figure 22). The hydrogenation of this trimeric compound affords difurfurylamine, which is subsequently aminated to FAM. The formation of furfurine through decomposition of the hydrofuramide, which occurs at temperatures greater than 388 K, must be avoided.[48,258] The main drawback in the synthesis of FAM is associated with the undesired formation of difurfurylamine and the stable furfurine, as well as the necessity to circumvent the use of primary amines as co-solvents; as such, an excess of ammonia or gradual admission of FUR during the reaction have been proposed.

FAM has been prepared by the direct hydrogenation of FUR in the presence of ammonia-saturated cold ethanol over a Raney nickel catalyst.[265] However, the FAM yield was below 80%, and difurfurylamine was formed as a by-product. Nickel supported on diatomite has also been tested as a catalyst, and by using ethanol along with ammonia and butyl amine as auxiliary primary amines, FAM yields exceeding 90% were obtained at

388–93 K and 2.5 MPa H_2.[266] In the absence of butyl amine, the yield was only 70%. The use of hydrogenating metal catalysts (Co and Ni) and high H_2 pressure have also been reported in the patent literature, although in some cases, hydrofuramide was used instead of FUR.[267-269] Other catalytic systems not based on Ni have also been investigated, such as a Co:Re:Mo catalyst.[258] The reaction was performed in the liquid phase using dioxane as the solvent and by employing moderate temperatures in a batch reactor at 348 K and 9 MPa. A FAM yield of 97% was achieved after 3 h of reaction time.

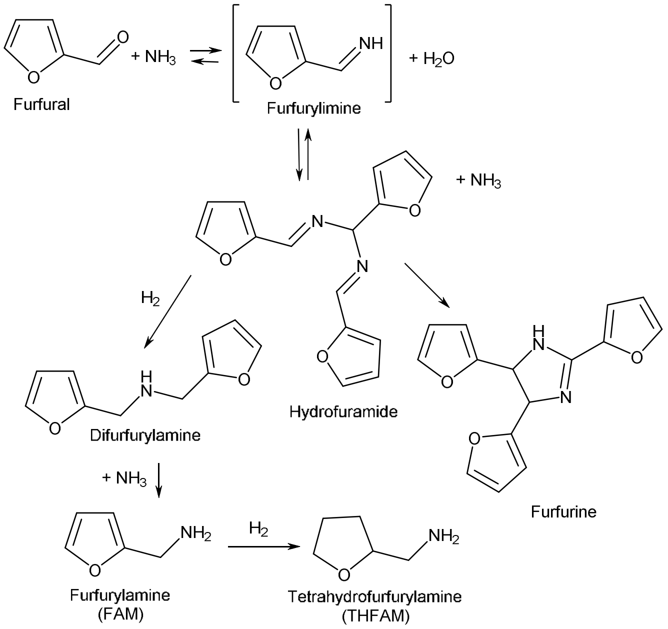

Figure 22. Furfural conversion to furfuryl amine (FAM) and tetrahydrofurfuryl amine (THFAM) (adapted from Reference 48).

No information regarding the kinetics and the mechanism for the reductive amination of FUR on the active sites of catalysts is available in the literature. Similarly, deactivation and reutilisation studies are lacking.

2.3. Oxidation of the aldehyde group: Furoic acid

Furoic acid (furan-2-carboxylic acid) has applications in the pharmaceutical, agrochemical, flavour, and fragrance industries.[14,270,271] Furoic acid is industrially produced by the Cannizaro disproportionation reaction of FUR in aqueous NaOH solution;[14,272] furfuryl alcohol and sodium furoate are formed as a result of this disproportionation reaction (Figure 23). The addition of sulfuric acid is required to neutralise the solution and to yield furoic acid; consequently, sodium bisulfate is formed. The temperature must be controlled because the Cannizaro reaction is highly exothermic. Other oxidation processes use strong oxidative reactants such as $KMnO_4$, MnO_2, or NaOCl. None of the former syntheses can be considered green syntheses. Investigations have been directed at achieving selective oxidation to furoic acid with cheaper and less polluting and toxic oxidative reactants such as O_2.

The initial strategy employs catalytic selective oxidation of aqueous FUR to furoic acid with O_2. A number of catalysts based on noble metals (Ag, Au, Pt, or Pd) supported on different metal oxides (CuO, Fe_2O_3, Co_2O_3, NiO, TiO_2, CeO_2, ThO_2, Bi_2O_3, or Sb_2O_5) have been explored, and the highest selectivity (96%) was achieved with the use of a Ag/CuO-CeO_2 catalyst (323–328 K).[273]. This catalyst could be reused for an unlimited number of runs, but accidental (sic) deactivation of the catalyst was possible, requiring rejuvenation by transfer of the catalyst to an alkaline medium and passing O_2 through the medium. Apparently, the formation of Cu_2O and Cu (reduction of CuO) and the deposition of organic molecules were the causes of the deactivation of the catalyst.[274]

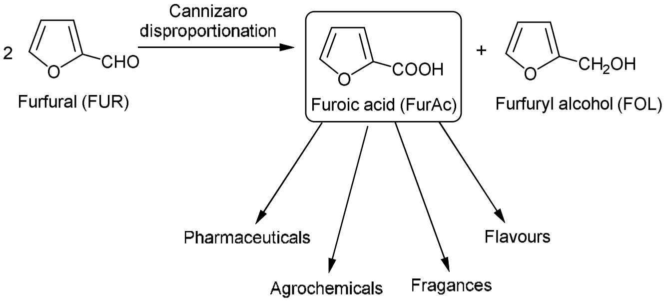

Figure 23. Synthesis of furoic acid (FurAc) from furfural (FUR), as well as main industrial applications of furoic acid.

The incorporation of Pb has been shown to significantly promote the activity of C-supported Pt catalysts.[275,276] Thus complete conversion of FUR to furoic acid was achieved using a Pb-Pt/C catalyst in the aqueous phase under conditions of 338 K, 1 h, and 0.36 M FUR concentration. The catalyst could be reused 10 times without deactivation. A mechanism for the reaction was proposed (Figure 24). First, the aldehyde is hydrated, and the Pb^{2+} ions act as adsorption sites for the hydrated aldehyde species. The π-electrons of the furanic ring are involved in the chemisorption. Reorganisation of the adsorbed hydrate results in the formation of furoic acid chemisorbed on the Pb sites; the Pt atoms act as a sink for the hydride ions liberated during rearrangement. FurAc desorption is facilitated at basic pH through the formation of the Na furoate. The chemisorbed hydride reacts with O_2, giving rise to OH^-, which liberates the Pt site; the latter along with the H^+ released during the rearrangement of the hydrated aldehyde yields water.

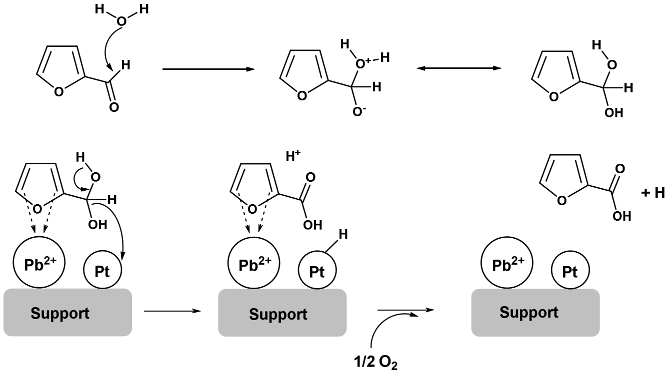

Figure 24. Mechanism of furfural oxidation to furoic acid with a Pb-Pt/C catalyst (adapted from Reference 275).

To prevent catalyst deactivation by furoate chemisorption, all of the latter alternatives require the co-feeding of a strong base to maintain a high pH that results in the formation of soluble furoate species. The addition of base is a serious drawback for the environmental sustainability of the process. In this context, very remarkable results have recently been obtained by Signoretto *et al.* using Au-based catalysts and air at low pressure (0.05 MPa) as an oxidant.[270,271,277,278] The addition of base was not required.[277] Among the various supports tested, the Au/ZrO_2 catalyst exhibited the best performance because it provides the proper trade-off between gold dispersion and the required acid–base properties.[278] A 90% conversion of FUR with a selectivity higher than 97% for methyl furoate was achieved in 1.5 h. They tuned the size of the Au particles by modifying the calcination temperature of the catalyst precursor. The presence of very basic O species on the Au clusters with a size close to 2 nm was claimed to be responsible for the high activity and selectivity. Larger Au nanoparticles cannot dissociate O_2 as efficiently and the activity decreases. On the other hand, the interaction of O atoms with the Au atoms in smaller clusters (<0.7 nm) is so strong that it has an adverse effect on the catalyst activity. The drawbacks of this approximation are that a very dilute FUR concentration (close to 0.15 wt.%) and a high reaction temperature (393 K) were needed, and the catalyst was deactivated as a result of deposition of organic molecules and carbonates on the Au particles as well as the support.[279] Calcination at high temperatures (<723 K) is required to completely remove the deposits.[270,271]

A second strategy involves the oxidative esterification to methyl furoate in the presence of O_2 and methanol. This process requires the addition of a base ($NaOCH_3$), but in a considerably smaller concentration than that used for the previously described conventional oxidation (no esterification). Methyl furoate can provide furoic acid through further hydrolysis of the ester. The ester also finds application in the fine chemicals industry (flavour and fragrances). Christensen *et al.* reported achieving almost 100% selectivity and a conversion close to 100% at room temperature using 0.1 MPa O_2 with a Au/TiO_2 catalyst.[279] The reaction proceeds through the formation of the hemiacetal *via* the reaction between methanol and FUR, and this intermediate is further oxidised to methyl furoate. A base is required to maintain a basic pH because an acidic pH would result in the formation of acetal species, which are much less prone to oxidation.[280] Regrettably, no reutilisation tests were performed to assess the deactivation of the catalysts.

Alternatives to chemo-oxidation

Photo-oxidation to furoic acid at room temperature in the presence of H_2O_2 has also been explored in methanolic solutions using a photogenerated Fe catalyst derived from iron organometallic complexes. The catalyst could be recovered from the reaction mixture by a precipitation and recrystallization protocol, and could be reused three times without deactivation. No structural analysis of the used catalytic species was provided.[281]

Another alternative to chemoxidation is electrochemical oxidation to furoic acid. Belgsir and co-workers demonstrated the simultaneous electrosynthesis of furoic acid and furfuryl alcohol from aqueous FUR by performing cyclic voltammetry and long-term preparative electrolysis experiments on noble (Au and Pt) and non-noble (Pb, Cu and Ni) metal electrodes.[282,283] According to the authors, an 80% yield of furoic acid was achieved through the electrooxidation of FUR, and a 55% yield of furfuryl alcohol was obtained by electroreduction.

2.4. Furfural acetalisation with glycerol: Fuel additives

The remarkable increase in the production of biodiesel has brought about worldwide availability of considerable amounts of glycerol at a low price but also with the serious problem of managing this surplus of glycerol. This has motivated the search for applications for the crude glycerol produced in the biodiesel process that cannot be consumed by the conventional routes due to the presence of impurities formed in the biodiesel synthesis process. Among the many reactions proposed (reforming, hydrogenolysis, oxidation, dehydration, etherification, carboxylation, chlorination, and so on),[284] glycerol acetalisation has been identified as a promising route for producing additives for diesel and biodiesel. Reductions in the emissions of hydrocarbons, carbon monoxide, unregulated aldehyde, and particulates of additivated fuels when compared with conventional diesel have been demonstrated.[285,286] Improvements in the flash point, oxidative stability, and cold flow-related properties such as the cloud point, pour point, and viscosity have also been demonstrated when glycerol is incorporated into biodiesel.[287-290] Moreover, the conversion of glycerol into additives improves the economic balance of the biodiesel process because it implies the complete transformation of the oil into biofuels because glycerol, approximately 10 wt.% of the oil phase, is also incorporated into the biofuel.

Much of the investigation has been dedicated to the acetalisation of glycerol with acetone[286,288,291] or alkyl and aryl aldehydes such as formaldehyde, butyraldehyde, or benzaldehyde,[284,289] but the acetalisation with FUR has also been demonstrated either in the presence of acid catalysts[292-296] or in the absence of a catalyst (using microwave irradiation by heating).[297] Figure 25 presents a schematic of glycerol acetalisation with FUR, resulting in the formation of a complex mixture of *cis* and *trans* isomers of each of the dioxane and dioxolane regioisomers.[292] Table 7 summarises the results reported to date. Soluble $ZnCl_2$ salt (with potential Lewis acid sites) presented a good yield, but could not be reused. Al-MCM-41 also presented very good yields of the acetals and reutilisation was demonstrated for 4 cycles. This yield was further improved by preventing the backward reaction by stripping the water produced during the course of the reaction with dry N_2. These authors also evaluated the utilisation of crude glycerol from the biodiesel reaction and found that NaCl must be extensively removed from crude glycerol. Initially, the reaction is catalysed by the protons released through the exchange between Na^+ with the acid sites in Al-MCM-41, but this exchange also deactivates the catalyst for further use. For other catalysts, reutilisation has not been explored or, as in the case of S- and Mo-promoted SnO_2 catalysts, deactivation of the catalysts was reported.

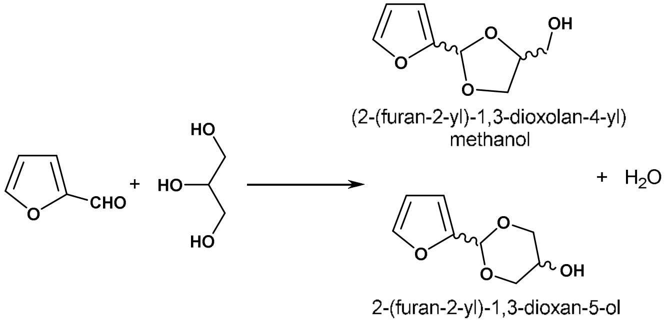

Figure 25. Simplified scheme for glycerol acetalisation reaction with furfural (FUR).

The data in Table 7 also raises the question of whether the catalyst is actually required because microwave heating drives the reaction in a fast and selective manner (75% FUR conversion and 45 and 55% selectivity to dioxolane and dioxane isomers, respectively) in 15 min under 600 W of microwave power, which is equivalent to 313 K.

Hydrogenating the furan ring of dioxolane and dioxane acetals to yield the corresponding tetrahydrofuryl-1,3-dioxane and dioxolane isomers has also been proposed.[296] The effects of incorporating up to 5 wt.% of a mixture of these hydrogenated acetals into biodiesel on the cloud point, density, and flash point has been investigated, and no significant negative effects were found. Higher concentrations could not be evaluated due to insolubility problems. To improve the solubility of these hydrogenated additives, subsequent acetylation of the dioxane and dioxolane derivatives with acetic anhydride was performed, resulting in the corresponding acetates. Thus, incorporation of up to 10 wt.% of derivatives was possible, and no negative effect on the tested properties was observed. These experiments demonstrate that glycerol-FUR acetals can be incorporated into biodiesel without adverse effects.

Table 7. Acetalisation of glycerol with furfural

Catalyst	Temp (K)	Gly/FUR (mol)	Time (h)	Cat.[a]	Conv. (%)	Yield (%)[b]	Ref.
PTSA[c]	b.p.[d]	1:1	3	0.06	n/a[e]	75	292
Re complex	373	1:5	4	0.2	100	77	295
$ZnCl_2$	373	1:5	0.7	1	n.r.	91	296
Al-MCM41	373	1:5	0.7	10	n.r	90[f]	296
MoO_3-SnO_2	298	1:1	2	5	100	100	293,29
SO_4^{2-}-SnO_2	298	1:1	2	5	100	100	4
Amberlyst	343	1:1	3	6	n/a	80	290
Microwave	413	2:1	0.3	-	75	75	297

[a] Weight or mole percentage with respect to glycerol
[b] Yield of all isomers (mol.%)
[c] PTSA: p-Toluenesulfonic acid
[d] Boiling point of the mixture (benzene, furfural and glycerol)
[e] n/a: Not available
[f] Stripping with N_2

2.5. Furfural condensation reactions

These reactions result in the formation of C-C bonds and consequently in heavier molecules. Three different condensation reactions between FUR and other molecules have been investigated: Claisen-Schmidt condensation with ketones, reductive condensation with itself, and condensation with furan.

2.5.1. Claisen-Schmidt condensation and derived biofuels

The aldol condensation reaction is widely employed in numerous fine chemical processes to form C-C bonds.[298] In the case of FUR, the condensation with acetone (Figure 26) that forms an aldol adduct (4-(2-furyl)-3-hydroxy-2-butanone) that undergoes dehydration to yield furfurylidene acetone (4-(2-furanyl)-3-buten-2-one, FAc) is of particular importance. These C8 monomers can further condense with another FUR molecule to form the C_{13} dimer, difurfurylidene acetone (1,5-bis-(2-furanyl)-1,4-pentadien-3-one, DFAc). Since FUR does not possess an α-H (Claisen-Schmidt condensation), the self-condensation of FUR is not possible. The final products of the reaction have interesting applications in the preparation of polymers with high thermal and chemical resistance, as well as organo-mineral concretes.[299,300] Furfurylidene acetone (FAc) is a flavouring agent used in the food industry.[301,302] This reaction was initially geared towards increasing the number of carbon atoms.[11,303-308]

Early studies focused on the condensation of FUR and acetone in H_2O with NaOH as a catalyst.[299,309-315] In summary, FAc is favoured in an excess of acetone and H_2O solvent (60–70% selectivity at 348–358 K), whereas DFAc (the C_{13} compound) is more readily formed in alcohol at low acetone/FUR ratios (80% selectivity at 348–358 K).[311] Notably, FUR and the condensation products can further react to form low polymers. However, the use of solid catalysts is preferred due to the facile catalyst recovery by filtration. In a pioneering study, Dumesic evaluated several solid base catalysts (hydrotalcites, MgO, CaO, La-ZrO_2, Y-ZrO_2, MgO-ZrO_2, MgO-TiO_2, ion-exchange resins, and NH_3-functionalised SiO_2) and MgO-ZrO_2 was found to be the most active.[306] Other authors have explored other catalysts including N-substituted Na-Y;[316] Co-Al spinels;[317,318] mixed oxides such as Mg-Al,[319-321] Ca-Zr,[322] WO_3-ZrO_2,[323] other MgO-ZrO_2 species,[322,324-327] supported Mg-Zr oxides on graphite[328] or MgO/Na-Y,[329] dolomites[330], chitosan,[331] and zeolites.[332,333] Table 8 compares the performance of selected solid catalysts. The results presented in this table clearly demonstrate that most of the catalysts present low activity under the evaluated conditions. Very long reaction times (>1000 min) or very high catalyst loadings (Fur/cat ratio <3) are generally required to achieve conversions of over 90%, except in the case of Co-Al spinel, Mg-Al hydrotalcite, and dolomite.

For prospective industrial applications of these catalysts, it is of paramount importance to address the stability of the solids in the reaction medium along with the activity. Most of the studies compiled in Table 8 refer to the deposition of heavy species as the main cause of deactivation.[322,324] This effect and a possible way to minimise the deactivation will be further discussed in the following section. Leaching of the active species is another main deactivation mechanism in this reaction. Some authors have proposed that batch reaction can prevent the leaching problem in the case of the MgO-ZrO_2 catalyst, because a decrease in the reaction temperature causes reprecipitation of the solubilised species, and consequently, the reutilisation of the catalyst is improved.[316] Finally, H_2O can deactivate the catalyst by reacting with active species to form less active phases, such as the conversion of MgO to $Mg(OH)_2$.[325,326] Two of the most active catalysts, hydrotalcite and dolomite, also presented serious difficulties in terms of reutilization due to leaching and deposition of carbonaceous deposits. Based on the presented results, the Co-Al spinel is the most promising catalyst, although no evaluation of possible leaching of the active species was performed.

The condensation of FUR with other ketones such as dihydroxyacetone, hydroxyacetone, and glyceraldehyde,[334,335] LA,[7,136,336] methyl isobutyl ketone (MIBK),[337] 2-pentanone and 2-heptanone,[338] and CPONE[257] has also been studied. The aldol condensation of FUR with CPONE is of particular interest since this can be selectively produced by hydrogenation of FUR; therefore, this approach utilises only FUR as the source of carbon. The use of other ketones offers the advantage of leading to branched alkanes with supposedly improved properties for use as jet fuels.

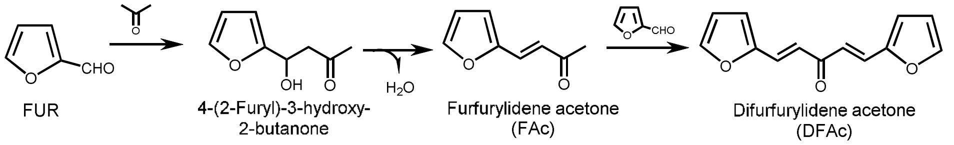

Figure 26. Aldol condensation of furfural (FUR) with acetone.

Further hydrogenation and dehydrodeoxygenation of the condensation products affords molecules in the range of diesel or jet fuels. Two steps are required to obtain liquid alkanes from the aldol products: first, hydrogenation to produce alcohols, followed by a dehydration/hydrogenation reaction (also called hydrodeoxygenation) that forms the final alkanes.[339] It has long been established that hydrogenation of the different functionalities in the aldol products proceeds according to the following sequence: first, C=C bonds in the side chain, then the C=O bond, C=C bonds in the furan ring, followed by hydrogenolysis of the C-O bond in the furan ring, and finally, the hydrogenolysis of other C-C bonds.[340-343]

Table 8. Comparison of the catalytic activity of different solid catalysts for the furfural (FUR)-acetone aldol condensation reaction

Catalyst	Reaction conditions				FUR conv. (%)	Select. FAc and DFAc (%)	Ref.
	FUR/cat. (wt)	Pressure (MPa)	Temp. (K)	Time (min)			
$MgO-ZrO_2$ [a]	3.7	0.1	393	1560	98	78	305
$MgO-ZrO_2$ [a,b]	1.25	5 (He)	393	1440	57	95	316
Co-Al spinel	6	0.1	413	300	96	99	317
WO_3-ZrO_2	1	1 (He)	353	1800	85	n/a	323
$MgO-ZrO_2$ [c]	1	1 (He)	353	1800	85	n/a	323
Chitosan [d]	0.96	0.1	423	240	97	~100	331
$MgO-ZrO_2$ [a]	1.5	1 (N_2)	323	1440	80	~100	324
Mg-Zr aerogels	13	0.1	333	180	70	90	327
MgO/NaY	0.8	0.1	358	480	99	98	344
Mg-Al hydrotalcite	3.25	0.1	373	120	95	90	320
$MgO-ZrO_2$/graphite	1.5	1 (N_2)	323	1440	97	85	328
Dolomite [e]	11	0.1	413	60	90	~100	330
MCM-22	6.5	Aut. P	373	120	60	89	333
HBEA	3.25	Aut. P	373	480	50	~ 100	332

[a] Preparation method according to Reference 345.
[b] Reaction in the presence of methanol.
[c] Same result with both catalysts prepared *via* co-precipitation.
[d] Catalyst dried under supercritical CO_2 conditions. Reaction in microwave reactor.
[e] Reaction in water and methanol mixture (1:1.5).

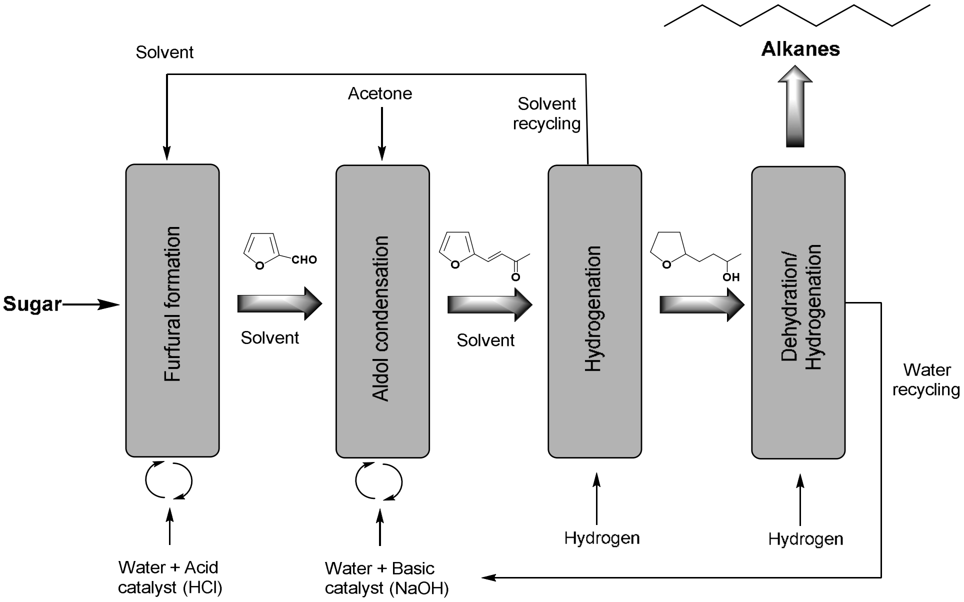

Figure 27. Industrial process for producing liquid fuels from sugars *via* furfural-acetone aldol condensation (adapted from Reference 307).

In Dumesic's first approach, the previously formed acetone aldol products were hydrogenated and the saturated molecules were finally transformed into alkanes in a 4-phase dehydration and hydrogenation (4-PD/H) reactor.[346,347] Following this latter reaction, the spontaneous separation of the alkanes from the aqueous phase avoids the need for a distillation step to separate the products of interest, thus favouring the energy balance of this process compared to the production of other water-soluble biofuels such as bioethanol. Based on the previous results, an industrial process for producing liquid alkanes from sugars has been envisaged and tested by Dumesic and co-workers.[307] This process consists of four reactors connected in series (Figure 27).

Other authors have proposed a similar process but using a by-product stream from wood-processing industries containing aqueous carbohydrate as the feedstock. A preliminary economic analysis suggested that the alkane production cost lies in the range of 2.0–4.4 USD per gallon.[348] The factors that can most significantly affect the price are the costs of the raw materials, the amount of organic phase used, and the concentration of xylose in the hemicellulose extract feed. The main challenge is to increase the yield in all of the steps such that the actual yield can be closer to the theoretical yield for this process (0.61 kg of alkanes per kg of xylose).[348]

The possibility of combining all or some of these steps has been demonstrated. Thus, a bifunctional Pd-based basic catalyst has been tested for the combined condensation and first hydrogenation step to form H_2O-soluble molecules.[305,306,318,322,349] Interestingly, the hydrolysis-dehydration-aldol condensation-hydrogenation of lignocellulosic-biomass to fuel precursors in one-pot has been also attempted with a Pd/WO_3-ZrO_2 catalyst.[323,350] One important advantage of this one-pot strategy is its stability. The deposition of heavy insoluble products was identified as one of the main causes of deactivation when conducting the aldol condensation. However, the heavy molecules deposited on the surface of the catalyst can also be hydrogenated to form more soluble alcohols, and in practice, minimise this source of deactivation.[351]

2.5.2. Biofuels by reductive self-coupling of furfural

Fu *et al.* recently proposed a 2-step route for the synthesis of biofuels in the range of linear C_8–C_{10} alkanes.[344] The key step is the initial formation of a C-C bond between two FUR molecules *via* reductive self-condensation (Figure 28). Metals such as Al, Zn, or Mg (in the form of powders) were used as stoichiometric reductants. Dimer yields as high as 95% were achieved with Zn (metal/FUR molar ratio = 1) at room temperature after 1 h of reaction with a 10% NaOH aqueous solution of FUR (~6 wt.%). A subsequent dehydration/hydrogenation step was required to obtain alkanes; some C-C scission may occur to generate lower alkanes. An 84% molar yield was obtained from aqueous solutions of the dimer using a $TaOPO_4$ catalyst at 4 MPa H_2, 573 K, and 3 h of reaction. A mixture of Pd/C and $NbOPO_4$ gave similar yields.

This reductive condensation route was also demonstrated with other chemical platforms derived from cellulose (methyl furfural from hydroxymethyl furfural) and lignin (anisaldehyde, vanillin, and veratraldehyde), yielding C_{11}–C_{12} and branched C_{13}–C_{14} alkanes, respectively. Therefore, this route can potentially produce biofuels from all of the components of lignocellulose.

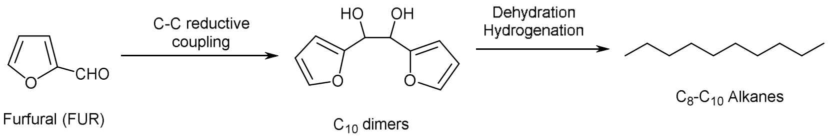

Figure 28. Formation of C_8–C_{10} alkanes *via* C-C reductive coupling of furfural.

This pathway still requires additional efforts to overcome some of the limitations of the process. For instance, the metal powders used in the first self-condensation step should be substituted by less expensive and more sustainable reductive reactants. Additional investigation on the reutilisation of the catalysts in the second step is also required.

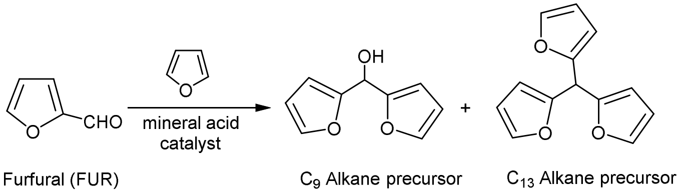

Figure 29. Formation of C_9 and C_{13} alkane precursors *via* furfural-furan condensation reactions.

2.5.3. Biofuels from condensation of furfural with furan

Huber *et al.* established another elegant route for creating diesel and jet fuel alkanes by forming a C-C bond between FUR and furan (a biomass-derived nucleophile).[335] They demonstrated that FUR can be condensed with furan, affording C_9 and C_{13} molecules (Figure 29). The latter can be subsequently hydrodeoxygenated to linear and branched diesel and jet fuels (C_9–C_{13} alkanes). A 79% yield to the C_{13} dimer was obtained by refluxing a solution of FUR in furan for 1 h in the presence of *catalytic amounts* (sic) of sulfuric acid. Hydroxymethyl furfural and other FUR-derived products were also successfully condensed with furan in high yields. Information is lacking regarding other relevant aspects of the reaction, such as the amount of catalyst used, kinetic studies, and the possibility of using other solid acids that can be separated from the reaction mixture and reused for a number of runs.

3. Chemicals and biofuels *via* reactions involving the removal of the aldehyde group

The products that will be described in this section require the removal of the aldehyde group as they all possess 4 carbon atoms. The first family of compounds is related to furan, which is obtained by decarbonylation. The two other families include compounds derived from oxidation of FUR either by O_2, H_2O_2, or by photooxidation.

3.1. Decarbonylation of furfural to furan and derivatives

Furan is primarily used as a solvent[14] and finds applications in the synthesis of pharmaceuticals, agrochemicals (i.e., Endothall), and pyrrole (Figure 30).[14,47,352-358] Interestingly, the synthesis of tetrahydrofuran (THF) and thiophene from furan has also been technically demonstrated.[14,47,359-371] The latter two compounds are currently petrochemicals[366,369] and are the starting point for a number of other applications. [364,372,373] Thus, polytetrahydrofuran (PTHF), also known as polyTHF or poly(tetramethylene ether) (PTME) is currently produced by THF polymerisation.[374,375] PolyTHF is amenable to a wide range of important applications, including the manufacture of polyurethanes and polyesters by reaction with diisocyanates or organic acids to form elastomers. Typical end-uses of the latter include coating materials, adhesives, textiles, automotive, and other industrial applications.

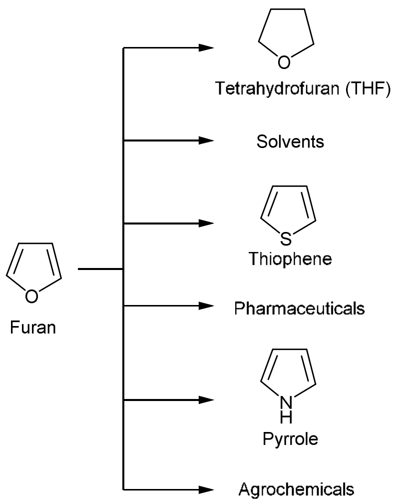

Figure 30. Main industrial applications of furan.

Furan is industrially produced through either the gas-phase or liquid-phase decarbonylation of FUR at 423–473 K with a supported Pd catalyst.[14,376-379] Unfortunately, the catalyst is continuously deactivated by fouling with coke, poisoning, and Pd sintering. Srivastava *et al.* deduced that two vicinal adsorbed FUR molecules react to form dimer species, which are subsequently transformed into the largest coke species[380] and are deposited over the surface, thus blocking the active sites.[381] Since fouling by coke is the most relevant deactivation mechanism, the catalyst can be regenerated to a large extent by burning the coke deposited over the course of the reaction. The coke removal step is critical because of its very exothermic nature, which can create overheated zones in the catalyst and consequently induce sintering of the Pd particles, which also detrimentally affects the catalyst lifetime. It has been proposed that co-feeding air and steam during the regeneration step minimizes metal sintering because H_2O helps to dissipate the heat generated during burning of the coke deposits.[378,382]

Research has primarily been devoted to overcoming deactivation of the catalyst by finding very stable catalytic formulations and by co-feeding H_2 with FUR. The latter strategy improves the catalyst durability because H_2 gasifies the coke deposits *in situ*. A H_2:FUR ratio between 0.5–10 has generally been used, where lower ratios result in faster deactivation and higher ratios are detrimental to the selectivity as other products can be produced, such as THF, FOL, THFA, MF, and MTHF.

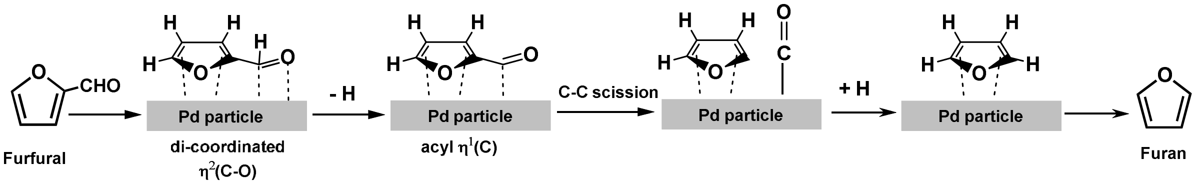

Figure 31. Mechanism of furfural decarbonylation on Pd from DFT calculations.[383]

Liquid-phase decarbonylation

Conducting the reaction in the liquid phase results in less intense deactivation processes and in a more viable process.[381,384-386] Furan has a low boiling point (304 K), and therefore, furan is continuously distilled at the reaction temperature. A Pd/C catalyst promoted by K_2CO_3 was identified as the best catalyst. Remarkably, a substantial improvement in the yield was obtained when the K_2CO_3-Pd/C catalyst was activated by UV irradiation; the mechanism underlying the activation was not disclosed. A productivity of 13 kg/g_{Pd} was reported after *ca.* 280 h of reaction time in semi-continuous mode at 432 K using 0.15 L_{FUR}/g_{cat} and a catalyst/promoter ratio (wt.) of 1. A higher productivity (36 kg/g_{Pd}) was obtained by operating in continuous mode.

Another alternative route for decarbonylating furanic aldehydes in the liquid phase under high CO_2 pressure using an Ir phosphine catalyst and dioxane and MTHF as solvents has recently been reported.[387] The investigated reaction involved decarbonylation of HMF to furfuryl alcohol (~95% yield); this approach could be applied to the FUR decarbonylation to furan.

Gas-phase decarbonylation

Different catalyst formulations based on Group VIII metals promoted by basic additives have been explored for the gas phase decarbonylation of FUR.[377,378,382,388,389] Comparison of the different systems is difficult due to progressive deactivation of the catalysts. Few reports provide the productivity values. Using a H_2/Fur ratio of 0.74 and temperature of 573–623 K, a 0.7 wt.% Pt/γ-Al_2O_3 catalyst promoted with Cs_2O (2 wt.% as $CsCO_3$) exhibited a productivity of 131 kg/g_{Pt} provided that once the catalyst was deactivated to 70% conversion, the temperature was increased up to 623 K to compensate for the deactivation.[377] Metal aluminates such as alkaline, alkaline-earths, and La, Ga, and Y aluminates have also exhibited good productivity and long catalyst lifetimes and stability.[390-392]

Gas-phase decarbonylation has also been tested in the absence of H_2, but with the use of mixed metal oxide-based catalysts; in this case, water was co-fed with FUR.[393,394] Among the various mixed oxide catalysts tested, alumina-supported MnO-ZnO-SrO-CdO or MnO-CdO-K_2O mixed oxide reportedly presented catalytic behaviour comparable to that of Pd/C and Pd/alumina systems. Reactivation of the catalyst *via* calcination of the coke deposits was not attempted.

Decarbonylation to furan on Pt catalysts has been shown to be a structure-sensitive reaction.[70,395] A remarkable change in the turnover rate (TOR) and selectivity to either furan or FOL was observed by changing the Pt particle size and shape. The highest selectivity to furan (>95%) was achieved with a Pt particle size of 1.5 nm, and the selectivity decreased to ~30% for Pt particle sizes of >3.6 nm (the FOL selectivity increased to ~70%).

Several aspects of the reaction mechanism in the gas phase have been disclosed. The decarbonylation of FUR, which is the rate-determining step, requires two surface active sites.[380] Furthermore, DFT calculations continue to provide further clues about the mechanism of this reaction on Pd surfaces;[74,75,383] as previously discussed in Section 2.1.1, FUR is preferentially chemisorbed on Pd surfaces as planar di-coordinated η^2-(C,O) and acyl η^1-(C) species (Figure 31). At low temperatures, the di-coordinated η^2-(C,O) mode predominates, undergoing transformation to the acyl η^1-(C) species upon heating, which decomposes into furan and CO. Furan eventually desorbs. In the presence of H_2, the di-coordinated η^2-(C,O) species can be hydrogenated to generate a hydroxyalkyl intermediate, which can be further hydrogenated to furfuryl alcohol, a non-desired product of the decarbonylation of FUR. The highest kinetic barrier corresponds to the endothermal dehydrogenation of the adsorbed flat FUR to an acyl intermediate (92 kJ/mol). The subsequent decarbonylation of the acyl intermediate is exothermic and possesses a lower energy barrier (66 kJ/mol). The formation of furfuryl alcohol is not thermodynamically preferred because of the higher potential energy of furfuryl alcohol relative to furan. However, the energy of the step with the highest kinetic barrier for the transformation of FUR to furfuryl alcohol (hydrogenation of the hydroxyalkyl intermediate) is 77 $kJ\cdot mol^{-1}$, which is therefore 15 $kJ\cdot mol^{-1}$ smaller than that of furan formation. This relatively low difference between the energy barriers indicates that the formation of furfuryl alcohol is kinetically favoured *versus* that of furan, particularly with the use of a high H_2/FUR ratio.

The role of the alkaline promoters has been proposed to involve inhibition of the route for hydrogenation of the carbonyl group at the expense of the decarbonylation pathway, thereby improving the selectivity to furan.[389] Alkaline promoters transfer electron density to the Pd particles, consequently increasing the electron density of the noble metal; thus, the FUR adsorption modes are modified with respect to the undoped situation, suppressing the di-coordinated η^2-(C,O) species (the precursor species of the hydrogenation route) and favouring the direct formation of a new acyl η^1-(C) species (precursor of the decarbonylation route).

Finally, it must be mentioned that supercritical CO_2 has also been used as a reaction medium for the decarbonylation of FUR to furan. As explained earlier, supercritical CO_2 can be used for hydrogenating FUR to different furanic compounds.[119] These authors attempted the decarbonylation of FUR in supercritical CO_2 in the absence of H_2. A yield as high as 98% was achieved from pure FUR by using a Pd (5 wt.%)/C catalyst at 523 K and 15 MPa.[119] The activity remained constant for a few hours; unfortunately, catalytic tests for longer periods of time were not reported.

3.2. Oxidation to maleic anhydride, C_4 dicarboxylic acids, and furanones

Furfural can be selectively oxidised to a number of C_4 oxygenated products, namely, maleic anhydride, C_4 dicarboxylic acids (like succinic, malic, and fumaric acids) and furanones. All of these products are of industrial interest. Thus, maleic anhydride (MA) is currently a petrochemical with a market volume of greater than 1,600 kTon/year.[396-399] MA is a commodity chemical with multiple applications (Figure 32), including the production of pharmaceuticals, agrochemicals, unsaturated polyester resins, vinyl copolymers, tetra- and hexa-hydrophthalic anhydrides (used as curing agents for epoxy resins), and polyalkenyl succinic anhydrides (like polyisobutylene succinic anhydride, used as a lubricant additive).[397,398]

Maleic acid (MAc), currently obtained through the hydration of maleic anhydride and with a market volume of approximately 25 kTon/year, is used as an acidulant in certain beverages and in the production of succinic acid, fumaric acid, and malic acid (the latter, a food and beverage additive, is also used in the pharmaceutical industry). Fumaric acid, a non-toxic reactant with fewer environmental restrictions and with a market volume close to 12 kTon·year^{-1}, is used as an acidulant in baking powders and beverages, as an additive in animal food, and in the synthesis of aspartic acid. It replaces maleic anhydride as a monomer for manufacturing unsaturated polyester resins and copolymers (for certain resins, substitution with fumaric acid results in improved hardness).[396,398,399] Succinic acid (SAc) is industrially obtained (20–30 kTon/year) through the hydrogenation of MA or Mac and by fermentation of biomass sugars (a renewable route). Figure 32 highlights the main industrial applications of SAc; more detailed reviews are available elsewhere.[400-402] Succinic acid-derived salts, esters, and imides have applications in the pharmaceutical, food, and agrochemical industries and as solvents and cooling and de-icing compounds. Hydrogenation and dehydration of SAc are involved in one of the current petrochemical routes utilised to produce the -butyrolactone (GBL), 1,4-butanediol, and tetrahydrofuran family. These compounds currently find numerous applications as solvents and as intermediates in the synthesis of pharmaceuticals, agrochemicals, and polymers. For example, GBL is an intermediate in the synthesis of 2-pyrrolidone, *N*-alkyl or *N*-vinyl pyrrolidones and the corresponding succinimides. Polymerisation of SAc with diamines or with diols has also been demonstrated to afford polyamides or polyesters with interesting properties, such as commercially available Bionolle® (a polybutylene succinate-based polymer).

The aforementioned C_4 anhydrides and dicarboxylic acids can be obtained through the partial oxidation of FUR. Gas-phase and liquid-phase oxidations have been demonstrated on the laboratory scale. O_2 from air has been proposed as an oxidant for the gas-phase oxidation, whereas in the liquid phase, both O_2 and H_2O_2 have been reported as oxidants. It is worthy to stress that the catalytic dehydrogenation of SAc to MA has also been demonstrated.[400] This means that the interconversion of MA, FumAc, and SAc can in practice be accomplished, and therefore, the synthesis of one of these compounds from FUR implies the synthesis of the others.

Gas-phase oxidation of furfural with O_2

The gas-phase oxidation of FUR is well known as inceptive studies date back to the first decades of the last century.[403-408] Vanadium oxide based catalysts (V oxide, V-Mo, and V-Bi mixed oxides) have furnished the best MA yield at temperatures between 473 and 573 K using air, fixed bed reactors, and short contact times (a few seconds).[403-408] As a result of the high temperature and the low H_2O concentration, MA is produced and MA yields from 15% to 90% were reported.

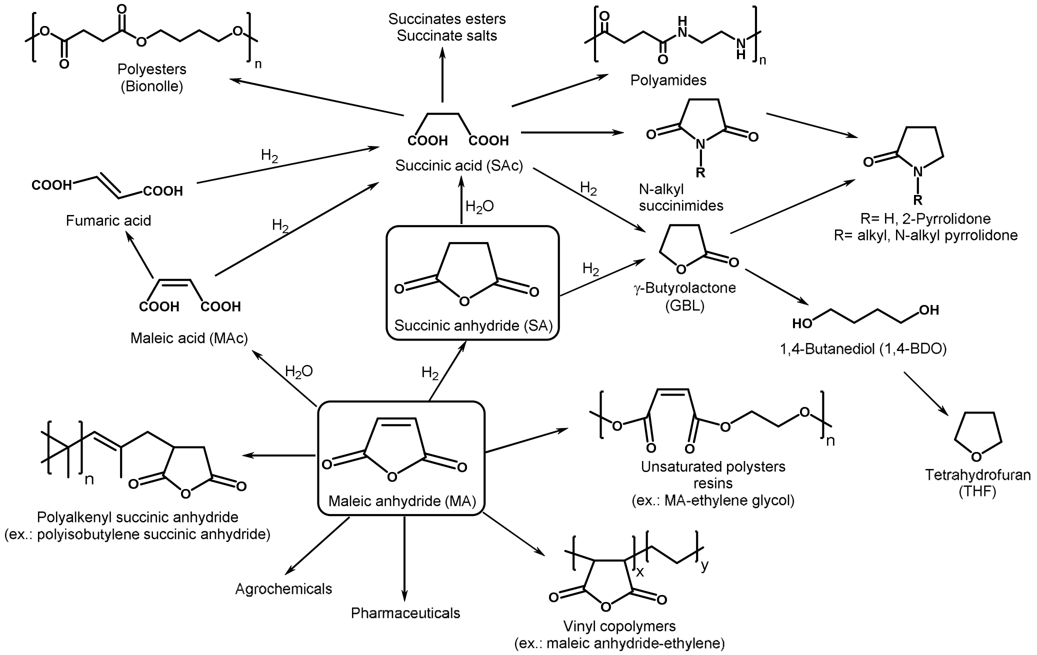

Figure 32. Summary of the most important uses of maleic anhydride/acid and succinic anhydride/acid.

Furfural resins are unavoidably formed during the gas-phase oxidation of FUR, appearing at the bottom end of the flow reactor and decreasing the selectivity to MA.[405] The resinous heavy products can be formed *via* the homogeneous oxidation of FUR and *via* both homogeneous and surface-catalysed reactions between FUR and intermediates or by-products.[409,410]

Furfural selectivity is improved by increasing the reaction temperature (re-oxidation of the reduced vanadium oxide active sites is then accelerated), the O_2 concentration (decreases the surface FUR coverage and therefore the formation of heavy molecules by condensation is inhibited), and by the addition of water (water displaces FUR from surface sites, thus preventing condensation and additionally inhibiting the homogeneous auto-oxidation of FUR with gaseous O_2). The formation of the heavy products has a kinetic effect, whereby the reaction rate declines due to deposition of these non-volatile compounds on the active catalyst sites.[410]

Structure-activity studies recently employed VO_x/γ-alumina catalysts to demonstrate that surface polyvanadate species present higher intrinsic reaction rates for MA formation than highly dispersed isolated vanadates or crystalline V_2O_5 species.[411] Furan and 2(5H)-furanone are also formed in minor amounts, indicating that these compounds must be considered in the reaction mechanism.

Kinetic analyses indicated that FUR oxidation proceeds in a parallel mode, in which FUR is oxidised to either MA or to CO_x in the temperature range of 493–753 K.[412-414] Higher temperatures are required to consecutively oxidise MA to carbon oxides. The reaction rates were better fitted by assuming a redox Mars-van Krevelen mechanism. The active site is reduced by FUR and reoxidised by gaseous O_2 to regenerate the catalyst. The reoxidation of the reduced catalyst was found to be the rate-determining step. The reaction order was found to be unity for the consumption of FUR and O_2.

Two mechanisms have been proposed and are summarised in Figure 33; both mechanisms are initiated by oxidation to furoic acid (FurAc) with subsequent decarboxylation. Milas *et al.* proposed that once decarboxylated, the as-formed furan (mechanism I) undergoes addition of an oxygen atom in the 1,4 position of the ring.[405] Subsequent ring opening affords maleic dialdehyde, and successive oxidation affords maleic anhydride. On the other hand Slavisnkaya *et al.*[409,410] proposed a different mode (i.e., mechanism II), in which furan is also formed from FUR, but furan is oxidised to 5-hydroxy-2(5H)-furanone by successive insertions of O atoms in positions 2 and 5 of the furan ring (2(5H)-furanone is proposed as an intermediate). Neither of these proposed mechanisms has been supported by any experimental evidence, either kinetic or spectrometric, or by theoretical studies.

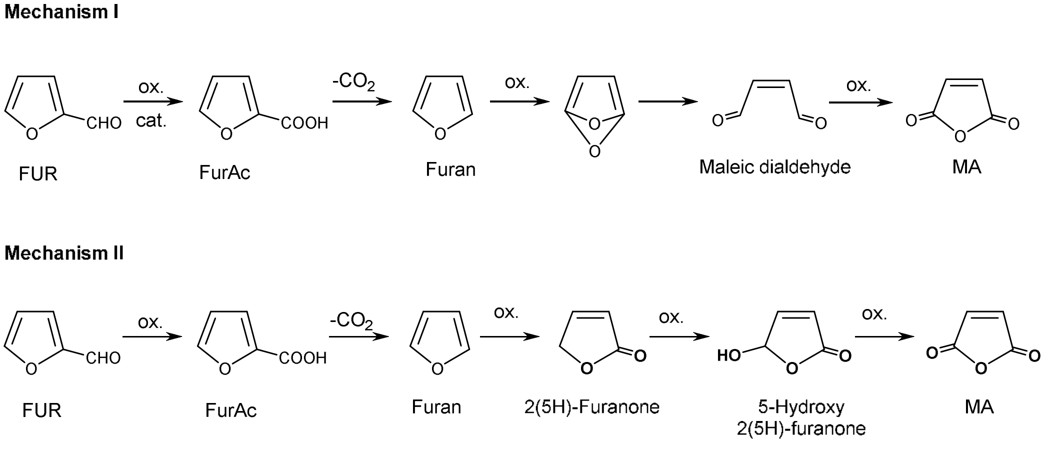

Figure 33. Mechanisms of the gas-phase oxidation of furfural (FUR) with O_2.[405,410]

Aqueous-phase oxidation with O_2

Investigation of this oxidation route was performed under batchwise operation using high O_2 pressure. Due to the presence of water and the low reaction temperature, MAc was formed. The combination of phosphomolybdic acid and $Cu(NO_3)_2$ as co-catalysts resulted in a MAc yield of 49% at ~100% conversion (368 K, 2 MPa O_2).[415] No reutilisation tests were conducted. The oxidative polymerisation of FUR to resins was a major challenge, and the use of a biphasic organic solvent/water system was proposed to overcome this problem.[416] Organic solvents with high affinities to FUR (tetrachloromethane, nitrobenzene, toluene, cyclohexane, and others) were evaluated. The concentration of FUR in the aqueous phase, where phosphomolybdic acid is located and oxidation occurs, was low. The organic solvent acted as a reservoir for FUR, thus preventing the polymerisation reaction. The authors also claimed that product separation and reutilisation were feasible. Furfural is concentrated in the organic phase, while maleic acid is essentially localized in the aqueous phase. The extraction of maleic acid from the aqueous phase would allow reutilisation of the catalyst. The organic solvent containing unconverted FUR could also be recycled for further reaction runs. The authors did not experimentally test this reutilization protocol. More recently, Yin *et al.* also conducted this reaction with vanadium phosphomolibdic acid in acetonitrile/acetic acid mixtures (2/1.3 v/v).[417] Since H_2O was not initially present, maleic anhydride (MA) (54% yield), not maleic acid (MAc), was preferentially formed. Interestingly, 5-acetoxyl-2(5H)-furanone, a high added-value biological product with important pharmaceutical applications, was also detected (7.5% yield).

Liquid-phase oxidation with hydrogen peroxide

The oxidation of FUR in the liquid phase can also be conducted using H_2O_2. In this case, a mixture of C_4 diacids, mainly maleic acid and succinic acid, is obtained.[418-439] Other diacids such as fumaric acid (FAc), malic acid, tartaric acid, and formic acid, as well as other oxygenated products such as 2(5H)-furanone, 2(3H)-furanone, and 5-hydroxy-2(5H)-furanone, are also formed in lower yields. The selectivity to the different acids and furanones is strongly affected by variables such as the reaction temperature, type of solvent, H_2O_2 concentration, and type of catalyst.

The reaction can be catalysed by either strong (H_2SO_4 or HCl) or weak acids (acetic acid, formic acid, and others). In fact, the reaction also proceeds without the addition of a catalyst, although at a slower rate; once the organic acids are formed, the reaction rate accelerates. Metal oxides have also been utilised as oxidation catalysts, and different transition metal compounds have been tested, including vanadyl sulfate ($VOSO_4$),[429,430] sodium vanadate ($NaVO_4$),[422] sodium molybdate (Na_2MoO_4),[428] potassium dichromate ($K_2Cr_2O_7$),[426] and Nb oxides.[440] Among the different catalysts tested, the highest yields of C_4 diacids has been achieved with those catalysts containing a tolyl group, namely, Amberlyst-15 and *p*-toluenesulfonic acid.[437-439,441] For instance, Amberlyst-15 resulted in SAc and MAc yields of 72% and 14%, respectively, using dilute FUR solutions (close to 2.5 wt.%) at 353 K, a H_2O_2/FUR mole ratio of 4, and 24 h of reaction time. The MAc yield can be improved (46%) by working at H_2O_2/FUR mole ratios higher than 7.5, but SAc is unavoidably formed, albeit in lower yields.[441] Solid Amberlyst-

15 presented the advantages of facile separation from the reaction medium by decantation and reusability for three runs without detectable deactivation.[437-439]

The use of methyltrioxorhenium, either in solution or supported on a variety of polymers, has also been tested.[442] A 70% MAc yield was achieved in the first run after 24 h at 293 K using 5 wt.% catalyst, 1% HBF_4 as a co-catalyst, and 5 equivalents H_2O_2 for polystyrene-supported methyltrioxorhenium. Succinic and furoic acids were also formed as minor products. The catalyst was reused for four additional runs under the same reaction conditions, and the yield of MAc did not decrease in successive runs (in fact, MAc yields from 77–90% were reported).

There is a strong consensus that the first step of the reaction consists of the Baeyer-Villiger oxidation of FUR to the corresponding 2-formyloxyfuran ester, which is unstable and undergoes hydrolysis in aqueous solution to form the corresponding 2-hydroxyfuran and formic acid. The 2-hydroxyfuran alcohol exists in keto-enol-like equilibrium with either furan-2(3H)-one or with the furan-2(5H)-one isomer giving rise, after several more steps, to SAc and MAc, respectively. More details can be found elsewhere.[418-439]

More recently, a MAc yield of *ca.* 80% was reported at 323 K after 24 h using titanium silicalite (TS-1), a 5 wt.% aqueous solution of FUR, and a H_2O_2/FUR mole ratio of 7.5.[443] Only minor yields of hydroxyfuranone (<10%), HCOOH (<5%), malic acid (<2%), furanones (<2%), and SA (<2%) were observed. Evidence was provided to indicate that by using this type of catalyst, the reaction does not follow the above-described mechanism, but rather follows a different pathway that involves the initial epoxidation of one of the heterocycle double bonds.

3.3. Oxidation to 5-hydroxy-furan-2(5H)-one

5-Hydroxy-furan-2(5H)-one is used in the synthesis of a number of products with applications in pharmaceuticals, insecticides, and fungicides.[14,444] The synthesis of surfactants has also been proposed.[445] As shown in the previous section, 5-hydroxy-furan-2(5H)-one can be produced as a sub-product during the oxidation of FUR with H_2O_2. However, it can also be obtained by the photochemical oxidation of FUR in the presence of photosensitiser dyes such as rose Bengal or methylene blue that absorb in the visible light region.[14,444-446]

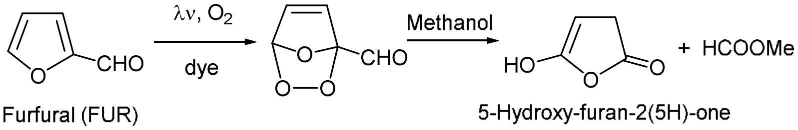

Figure 34. Simplified scheme of the photo-oxidation of furfural to 5-hydroxy-furan-2(5H)-one.

It has been proposed that an endo-peroxide is initially formed by the reaction of FUR with the singlet oxygen generated during the photochemical sensitisation of O_2 (Figure 34). This endo-peroxide is decarbonylated to afford the hydroxyfuranone. The reaction is conducted using methanol as the solvent, where methanol is partly transformed to methyl formate with the formic acid derived from the decarbonylation.[445] Synthesis with sunlight in solar photoreactors has been demonstrated,[444] paving the way for an economical and green synthesis of this fine chemical. Long-term operation assays to test the reutilisation of the very expensive sensitizer dyes were not presented.

4 Polymerisation of furfural and furfural-derived products

This section deals with the two most important resins derived directly from FUR, i.e., resins formed by FUR and by furfuryl alcohol polymerization. PolyTHF elastomer, obtained by THF polymerisation, is currently a commercial polymer and will not be revised in this review as it is not directly obtained from FUR.[374,375]

4.1 Synthesis of resins by furfural polymerisation

Furfural is very sensitive to resinification induced by acids and bases and, to a lower extent, by high temperatures.[447] FUR forms a black, insoluble solid with limited applications based on the carbon structure, for example, in adsorption applications. The majority of the industrially relevant resins are obtained through the polymerisation of FUR with other monomers, as will be explained later.

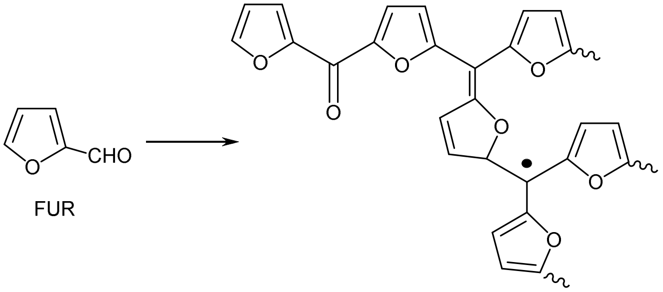

Figure 35. Formation of radical intermediates for the thermal resinification of furfural (FUR) under anhydrous conditions.

The resinification of FUR has been known for decades.[448] Many different catalysts have been used, including zeolites,[449] and thermal polymerisation under neutral conditions has also been performed.[14,450] Note that when forming solid resins as products, the separation of the catalyst following the reaction is not possible, and in this section, most of the presented examples are based on homogenous catalysts.

Due to the complexity of the polymerisation and the insoluble character of the formed solids, numerous interpretations of the mechanism have been proposed.[47] When the resinification occurs in aqueous acidic media, the mechanism consists of hydrolytic ring opening, which generates aliphatic open-chain products.[447] In contrast, anhydrous conditions and thermal treatment at 373–523 K favour the formation of a cross-linked product that preserves FUR as a monomer. The intermediates in this reaction have been determined to be formed by the condensation of three FUR monomers, leading to the formation of tertiary carbons. The hydrogen atoms of the tertiary carbons are very mobile and favour the generation of radicals that are very prone to resinification (Figure 35). This series of events is expected to occur under acidic or basic conditions, where the tertiary hydrogen atom can be abstracted as H^- (acidic media) or H^+ (basic media).[447,450,451]

The most common industrial furan resins are those obtained by cross-polymerisation of FUR with other reagents such as phenol, pyrrole, bisphenol, urea, formaldehyde, or acetone.[14,47] Some examples are presented in Figure 36. When phenol is used to copolymerise FUR, interesting materials can be obtained, such as thermosetting resins, resin-bonded grinding wheels, and coating abrasives.[14,452] Compared to the phenol-formaldehyde resins, the use of FUR presents the advantage of superior electrical properties and considerably lower toxicity because formaldehyde-based resins can produce hazardous formaldehyde emissions due to thermal degradation.[452,453] The initiation of the condensation reaction between phenol and FUR to form the resin can be both acid and base catalysed. Large interlinked systems are formed, in which the hydroxyl group of the phenol does not participate, as shown in Figure 36a.[14] Commonly, NaOH, KOH, or K_2CO_3 are used as basic catalysts for this reaction, although acids such as HCl can also be used to accelerate the gelation process.[453-455] In a typical process, liquid phenol is mixed with the catalyst and the mixture is heated to 400 K. Furfural is then added dropwise, and the reaction is maintained for 4 h.[453] The reaction mixture is subsequently evacuated under reduced pressure and cooled down to obtain a solid product.

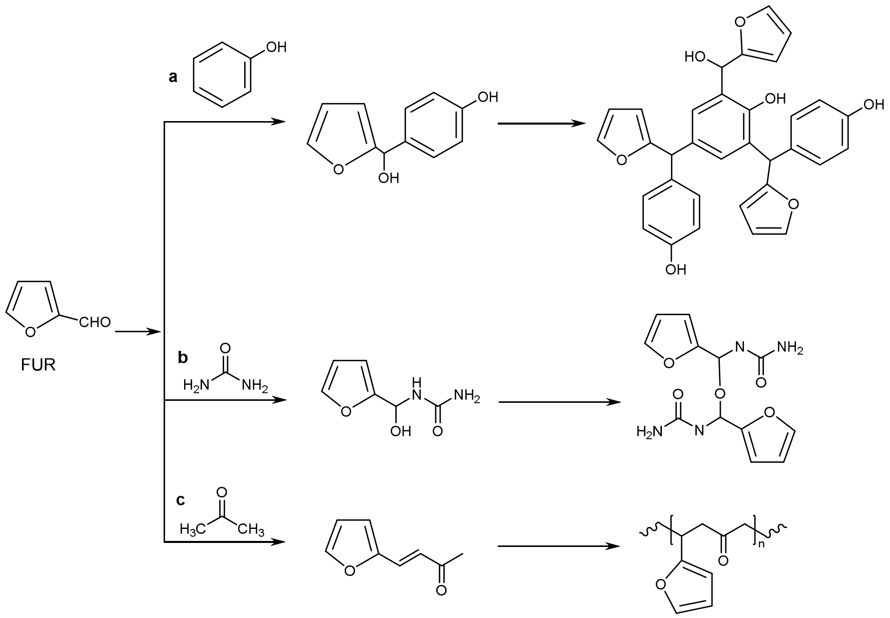

Figure 36. Co-polymerization of furfural (FUR) with selected monomers.

Urea has also been used as a monomer to produce resins for an extensive variety of applications, such as binders for sand core, manufacturing of foams, adhesives, or even agricultural fertilisers.[456,457] Acid catalysts (HCl, H_2SO_4, $FeCl_3$, and $SbCl_3$ HCl, H_2SO_4, $FeCl_3$, and $SbCl_3$) have been tested for this reaction.[458] Figure 36b depicts the formation of the intermediate oligomer.[14] The reaction can occur by dissolving FUR in a solution of urea in H_2O and adding HCl. After several minutes, a white precipitate is formed.[457] In the absence of a catalyst, the resin can be formed by mixing FUR and urea and maintaining the mixture for several weeks.[457]

For the polymerisation of FUR and acetone, aldol condensation is performed in a previous step, as described in Section 2.5.1, to produce FAc and DFAc. These molecules are then further subjected to acid catalysis to obtain black insoluble resins (Figure 36c).[459] The resulting polymers have been used as adhesives and corrosion-resistant coatings in foundries.[299,300,447]

As shown, FUR possesses strong potential as a monomer for producing many different interesting materials, and other FUR-derived monomers have been widely used to obtain polymeric products. A wide range of polymers such as furan polyamides, polyesters, polyurethanes, poly-Schiff, and polyhydrazides have been prepared using different monomers derived from FUR.[460]

Here, we briefly review the resins derived from furfuryl alcohol, which is currently one of the most important furanic polymers commercially available. Additional information is provided in other reviews that more extensively and deeply cover the different FUR-derived monomers and the possible polymers obtained from them.[447,460]

4.2. Synthesis of resins by furfuryl alcohol polymerisation

The main uses of furfuryl alcohol are related to the manufacture of furfuryl alcohol resins. Strictly speaking, FOL resins cannot be directly formed from FUR, but since a considerable fraction of the FUR produced worldwide is consumed in the production of furfuryl alcohol resins, we have included this type of resin in the review. The cross-linked resins possess exceptional chemical, thermal, and mechanical properties. These resins are used mainly in metal-casting cores and moulds. However, the low viscosity and high reactivity of FOL, together with the optimal chemical, mechanical, and thermal properties of its polymers, have allowed it to find applications in fields other than the foundry industry, such as in coatings with high resistance to corrosion, concretes, mortars, in wood protection, fibre-reinforced plastics, adhesives and binders, low flammability materials, and other carbonaceous products such as carbonaceous electrodes, capacitors, or even in the preparation of desalination membranes.[447,461-463]

Two other indirect applications of FOL resins are as follows: as mentioned in the previous section, when solid catalysts are used to catalyse the polymerisation reaction, they are incorporated into the structure of the final resin, forming matrix nanocomposites called polymer-based nanocomposites (PNCs).[464] In these materials, the nanoparticle fillers are immobilised within the polyfurfuryl alcohol matrix.[464,465] Compared to the normal polymer, the PNCs present increased glass transition temperatures and higher heat deflection temperatures and a higher onset of degradation.[464] Another interesting application lies in the effectiveness of FOL resins in producing carbonaceous materials with high carbon yield *via* pyrolysis. The addition of a pore-forming agent such as glycol during the resinification allows the formation of porous carbons with different morphologies[466] or the incorporation of nanoscale particles in the polymer matrix, leading to polymer-nanocomposites with improved properties.[465]

Furfuryl alcohol condenses in the presence of small quantities of aqueous acid solution in an exothermic reaction. Two possibilities can occur during the condensation of furfuryl alcohol (Figure 37). The first is alkylation at the C_5 position of the furan heterocycle (head-to-tail structure), forming a methylene bridge. The second is the condensation of two OH groups (etherification head-to-head structure);[460] nonetheless, the ether linkages can undergo loss of a formaldehyde molecule to yield the same head-to-tail structure.

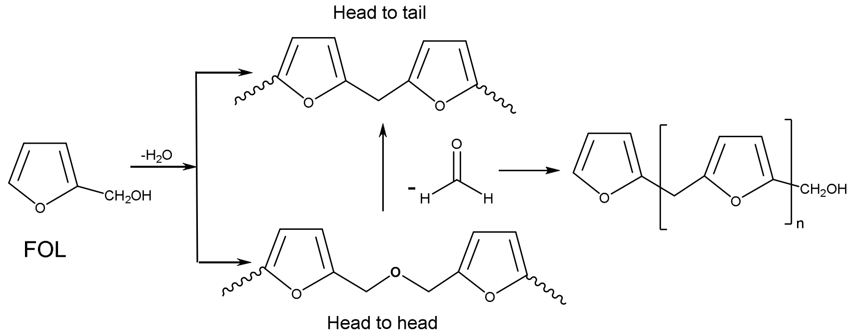

Figure 37. Acid-catalysed self-condensation of furfuryl alcohol (FOL).[460]

The resinification of FOL is autocatalytic and can be performed by manipulating the temperature, although inorganic acids (H_2SO_4, HCl, and HNO_3) have been traditionally employed as catalysts in this reaction.[14,467] In this case, the reaction is extremely exothermic and can potentially be explosive. It is thus imperative to control the temperature by cooling and accurately setting the proper pH value. The reaction can be neutralised and stopped at the desired viscosity.[14] Organic acids have been used, including *p*-toluenesulfonic in aqueous solution, dodecyl benzene sulfonic, formic, lactic, maleic and oxalic acids, among others.[468,469] Other evaluated Lewis-acid catalysts include $SnCl_4$, $TiCl_4$,[470] iodine,[471] and CuCl/*N,N,N',N'',N''*-pentamethyl diethylene triamine.[472]

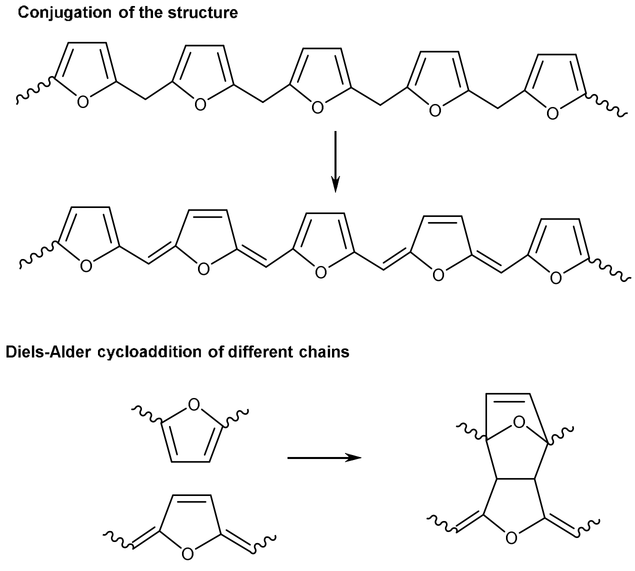

Figure 38. Mechanism of the cross-linking (heat-hardening) of furfuryl alcohol resins.[470]

After the first condensation step, once the desired viscosity has been obtained, a thermoplastic resin is obtained. Subsequently, a second step is performed at elevated temperature to induce the so-called ‘heat hardening’ or curing.[14] The double bonds of the furan rings in one chain condense with the double bonds in another chain and produce a tight cross-linked solid. Gandini and co-workers suggested the polycondensation mechanism depicted in Figure 38.[470] First, conjugated sequences are formed in the polyfurfuryl chains by hydride ion loss and deprotonation of the carbenium ions. Once the conjugated, unsaturated sites are formed, interchain Diels-Alder cycloaddition reactions occur between unconjugated and conjugated chains. The main advantage of cross-linking *via* the Diels-Alder reaction is the reversibility because it enhances the recycling of the materials by reversing the reaction towards the thermoplastic precursors.[473]

Therefore, the manufacture of resins involves two steps: production of the liquid resin and the final polymerisation leading to cross-linking.[47] Generally, the liquid intermediates are prepared industrially in batch mode. The furan derivatives are mixed with the catalyst in a reactor. The temperature is first increased to initiate the polymerisation reaction and then cooled to avoid excessive heat formation due to the exothermic nature of the reaction. The temperature must be maintained below 523 K; otherwise, furfuryl alcohol undergoes a strong exothermic reaction.[47] A neutralising agent is added when the desired degree of polymerisation is obtained. Excess water is removed by distillation, and the final resin is recovered.[14] The resins are hardened *in situ* by mixing with acidic substances. The curing process can occur at room or elevated temperature, typically from 398 to 548 K, depending on the desired application. Other possibilities consider supercritical drying of the resins to form aerogels with multiple applications.[474] The use of furfuryl alcohol resins is preferred over phenol/formaldehyde in foundry applications due to the hazards associated with formaldehyde emissions in the latter case.

Similar to FUR, other co-monomers have been used in addition to furfuryl alcohol to produce a variety of different commercial resins; these include formaldehyde, glyoxal, resorcinol, and phenolic compounds, among others.[47,475] Other dienophiles such as maleimides have also been employed as copolymers to induce the cross-linking of furan-based polymers.

5. Outlook and Challenges

This review describes the most relevant catalytic transformations of FUR to chemicals and biofuels. We have restricted our analysis to the routes with the highest potential, as the list of all the possible chemicals from FUR is enormous. Figure 39 summarises the chemicals and biofuels described in this review. As a consequence of the criteria selected in the Introduction section, in practice, these chemical compounds can be categorised into five groups:

a) Biofuels or additives that can be produced directly from FUR

b) Intermediate products that can be produced from FUR and transformed to biofuels or additives

c) Chemicals directly produced from FUR with current industrial applications

d) FUR-derived chemicals with high potential for important industrial applications, although their synthesis route from FUR has not yet been fully demonstrated (in terms of economic, technical, and/or environmental viability). Levulinic acid and γ-valerolactone are included in this group. These two chemicals can potentially be produced from both hemicellulose (*via* FUR and furfuryl alcohol) and cellulose (acid-catalysed dehydration), which results in the utilization and valorisation of all sugars present in lignocellulose.[2,50,162]

e) oil-derived chemicals that could also potentially be obtained directly from FUR.

The assignment of a given product to one of these 5 groups is not fixed and corresponds to the current situation; this could be revisited in the near future based on the implementation of new technologies.

The wide variety of present and future applications presented in this review demonstrates why FUR has been named one of the top added-value chemicals from biomass,[3] and why it is identified as one of the key chemicals in the so-called lignocellulosic biorefineries. However, the main bottleneck to FUR becoming an industrially relevant bio-based commodity is its price. A representative example is the production of maleic anhydride, which is currently a commercial petrochemical. The price of MA is in the range of the price of FUR (approximately 1,500 €/tonne).[401] The synthesis of MA from FUR requires a decrease in the price of FUR to become competitive *versus* the petrochemical route for MA production. Moreover, as it currently stands, the FUR market is unstable and volatile. For example, there was a shortage of FUR in 2011 that caused its price to peak at approximately 2,000 USD/tonne. In the near future, this situation is not expected to change significantly, meaning that the price of FUR will likely remain around 1,500 USD/tonne.[49] In principle, the development of new and larger FUR production facilities is part of the strategy to decrease (or at least maintain) the production costs of FUR and to accelerate the development of FUR-based biorefineries. Significant technological breakthroughs (some were mentioned in the Introduction section) are also needed to further decrease the current price of FUR.

In addition to these breakthroughs, other developments are also required to implement the use of FUR on the industrial scale. The current technologies for transforming FUR into chemicals are based on the use of high-grade FUR (~99%; the most common impurities are methylfuran and furfural methyl ketone). The production of such high purity FUR requires two energy-intensive distillation steps.[14] A reduction in the cost of the FUR-derived chemicals can be achieved if any of these distillation steps is avoided. A first approach could be the direct use of dilute aqueous FUR solution (*ca.* 5 wt.%) obtained primarily from lignocellulosic biomass. However, these raw solutions typically contain some carboxylic acids, and therefore, the development of robust technologies tolerant to H_2O and contaminants is required.

A problem related to the use of very dilute FUR streams is the corresponding low volumetric yields, which requires the construction of very large commercial plants, thus increasing the capital expenditure costs. A second possibility would be to use the concentrated FUR stream (~95% FUR) obtained after the first distillation step. The development of appropriate technologies for this approach appears to be more favourable because of the reduced presence of contaminants (such as carboxylic acids and resins), and therefore, a less harsh feedstock is managed.[14] The utilisation of either of these two solutions is indicated only for those products that can be easily and affordably purified from aqueous solutions.

Other advances needed for the competitive production of FUR on the industrial scale include the development of technologies capable of efficiently and consistently transforming lignocellulosic biomass from different origins and presenting significant differences in terms of composition, contaminants, etc. This is indeed necessary to ensure a constant supply of biomass feedstock throughout the year and to add flexibility to the production process, which ultimately lies in the overall FUR production costs.

Although FUR-based industries are not new, they are clearly underdeveloped at the moment. There is still a long way to go, many discoveries to be made, and some challenges that must be overcome for FUR biorefineries to become more prominent. We have already briefly mentioned some of these in the course of the review, but here we stress some investigations that need to be conducted in the near future to accelerate the deployment of FUR biorefineries. This description is not intended to be exhaustive but to provide, in our opinion, the most relevant directions.

Complete understanding of the fundamental aspects, including the reaction mechanisms at the molecular level, kinetic modelling, and identification of the active sites involved in the catalytic cycle, is far from being reasonably accomplished for most of the chemicals shown in Figure 39. This knowledge is essential for designing more active, selective, and durable technologies. More research efforts are required to cover this lack of information; this is evident not only for the transformation routes recently proposed in the literature but is also the case for other well-established reactions. Within this context, theoretical calculations (quantum chemical or density functional theory) have already been demonstrated as useful for revealing the reaction pathway. For example, the theoretical studies conducted on the hydrogenation of FUR to FOL, decarbonylation of FUR to furan, and hydrogenation of furan to THF should and must inspire future investigations for many other reactions.[74,75,383,476]

Substantial technical progress in the chemical technologies described in this review is also needed to improve the economics of these processes. Improvements of the current catalyst formulations, replacement of catalysts based on very expensive noble metals (Ru, Rh, Ir, Pd, Pt, etc.) by less expensive metals, co-feeding of gases (such as H_2 or water vapour) to modify the selectivity or to prevent catalyst deactivation are prospective approaches to this end. Another field of great importance is the development of new and/or advanced separation technologies (pervaporation, ultrafiltration, ceramic membranes, etc.) to purify the reaction products at a competitive cost. This is a very important field as many of the processes described here require substantial purification processes to separate the product from the reaction products, especially when dealing with processes that are not very selective.

Exploration of new reaction environments (supercritical fluids, new green solvents, ionic liquids, etc.), as well as novel and distinct approaches, is also urgently needed. Within this context, the transformation of FUR *via* electrochemical or photochemical processes may provide important breakthroughs. Both approaches are excellent examples of environmentally friendly methodologies that fulfil the principles of green chemistry, especially if sunlight or renewable electricity (e.g., produced by wind turbines) is used.[121,444] Some examples of photo-oxidation and electrochemical hydrogenation and oxidation of FUR to different products have been presented in this review.

Electrochemical hydrogenation of FUR is particularly attractive because H_2 is generated *in situ* in the reaction cell; hence, no external supply of expensive H_2 is required. This reaction is typically conducted at atmospheric pressure and near ambient temperatures. Furthermore, the scale-up of a continuous electrochemical process could be, in principle, much simpler than scale-up of the conventional catalytic process. Another interesting feature is related to the fact that the energy (electricity) is stored in the form of biofuels or chemicals.[121] A very appealing approach for electrochemical synthesis is presented when the oxidation and hydrogenation reactions can be coupled within the same cell, resulting in the simultaneous production of two valuable products and in the improvement of the overall efficiency of the process. An example of the coupling of the oxidation and hydrogenation reactions (FUR oxidation to furoic acid in the anode, and FUR hydrogenation to furfuryl alcohol in the cathode) is presented in Section 2.3.

For these alternative methodologies (photochemical and electrochemical processes), further advances to enhance the time yield productivity and detailed assessments of the economic viability are still needed. Presumably, the costs of the photosensitisers required for the photoxidation process or of the electricity in the case of the electrochemical processes may threat their practical application.

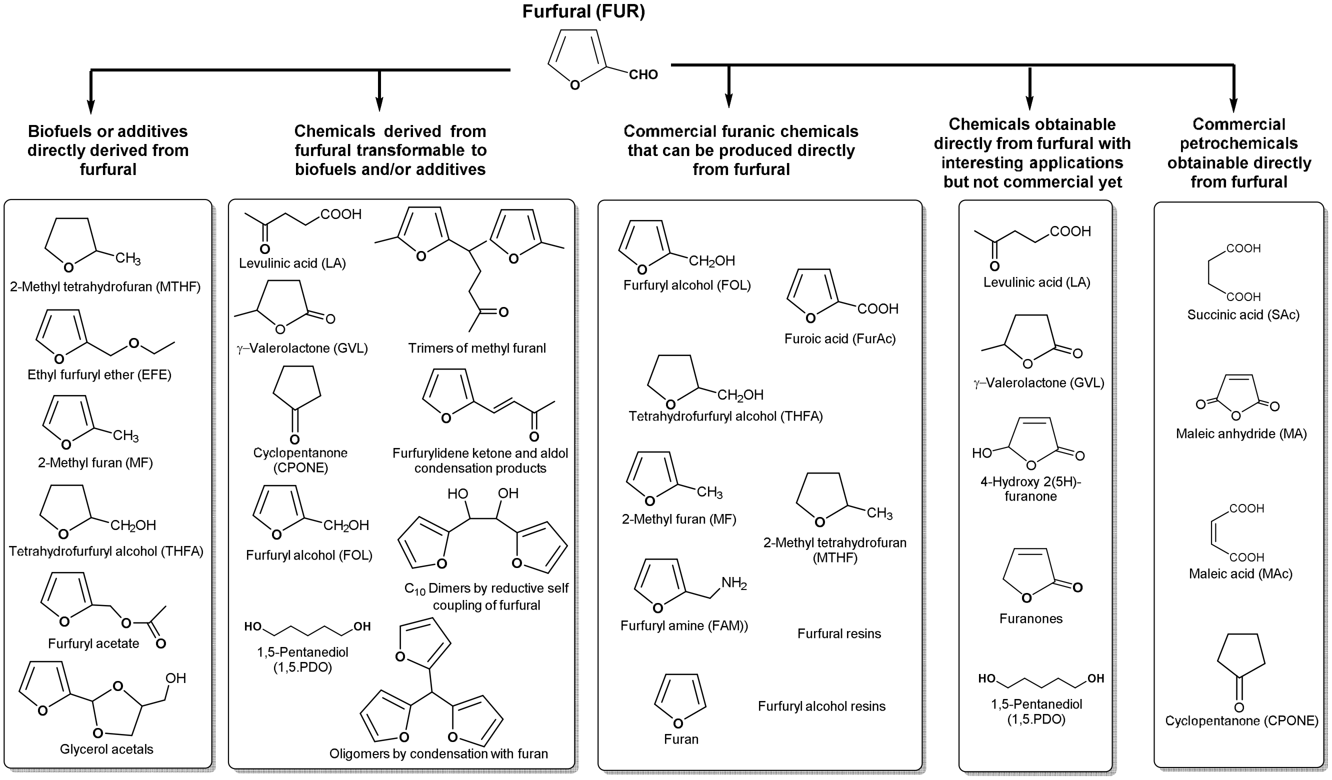

Figure 39. Family of chemicals, biofuels and fuel additives presented in this review.

The causes of catalyst deactivation for some of the processes described herein are well identified and understood, and catalyst regeneration procedures have been already developed and demonstrated. However, for many other reactions, the processes underlying the deterioration of the catalysts are not fully understood or are even unknown. This information is essential not only for designing more stable and resistant catalysts, but also for developing strategies to prevent/reduce the occurrence of deactivation phenomena and for finding appropriate reactivation protocols. In this context, it must be stressed that long-term operation research under real reaction conditions is also lacking for many of the processes reported herein. Most of the investigations conducted to date utilize FUR with a purity grade that is considerably higher and far from those of real industrial feedstocks. Investigations of the stability of the catalysts with real FUR solutions directly derived from biomass will be more informative; the presence of real impurities may seriously affect the long-term stability of the catalyst, particularly if undistilled FUR is used.

In addition to the fundamental scientific and technical knowledge, the commercial viability (economics, environmental issues, etc.) of many of the processes described in this review also needs to be assessed. In this context, the techno-economic analyses conducted for the production of 5-nonanone from levulinic acid,[477] conversion of lignocellulosic biomass to liquid hydrocarbon *via* decarboxylation of GVL to butenes,[478] and production of alkanes in the range of jet and diesel fuel *via* aldol condensation of FUR with acetone[348] constitute excellent examples to stimulate other similar evaluations of other processes discussed in this review. This type of analysis must be carefully conducted because many factors are difficult to account for and can be missed, such as the logistics involved in supplying the raw materials and shipping the products, the quality and quantity of competitors, the predictions of the price evolution, and fluctuations in the future and potential synergy effects with other industries, among others.

In this context, an important drawback of most of the biomass-based processes, particularly those for production of biofuels, is related to the use of large amounts of H_2 (in the reduction, hydrogenation, and hydrodeoxygenation steps). The non-renewable origin of the H_2 may seriously threaten the economic and environmental viability of these processes. The utilisation of catalytic hydrogenation transfer reactions (for instance, Meerwein-Ponndorf-Verley) or other molecules as H_2 sources (for instance, HCOOH) may be optional routes to overcome/minimise these problems.

Furfural-based biorefineries require very large investments, still present high technological risks, and their future viability is very much dependent on present and future incentives. Stable and long-term policies and mandates regarding the use of biomass-based chemicals and fuels are clearly required to ensure the economic viability of such biorefineries. In addition, FUR-based biorefineries should be competitive against the corresponding oil-derived chemicals and fuels. Although the oil market is very unstable and volatile, it uses relatively low-risk, very well-demonstrated technologies for producing the fuels and chemicals that our society demands. However, it is conceivable that in the very long term, biorefineries will clearly be a competitive option due to the depleting oil reserves and inherently high prices. However, in the near and midterms, environmental issues and energy/chemical supply security rather than economic advantages should encourage the development of FUR-based biorefineries.

6. List of Abbreviations

1,2-PDO	1,2-Pentanediol
1,4-BDO	1,4-Butanediol
1,4-PDO	1,4-Pentanediol
1,5-PDO	1,5-Pentanediol
4-HPs	4-Hydroxypentanoic acid or its esters
5MFUR	5-Methylfurfural
BCP	Bi-(cyclopentane)
BFE	Butyl furfuryl ether
BL	Butyl levulinate
CPONE	Cyclopentanone
CPOL	Cyclopentanol
CTH	Catalytic transfer hydrogenation
DALA	δ-Aminolevulinic acid
DFAc	Difurfurylidene acetone
DHP	3,4-Dihydro-2H-pyran (3,4-2H-dihydropyran)
DPA	Diphenolic acid
EL	Ethyl levulinate
EFE	Ethyl furfuryl ether
EMF	5-Ethoxymethyl-furfural
FumAc	Fumaric acid
FAc	Furfurylidene acetone
FAM	Furfuryl amine
FUR	Furfural
FurAc	Furoic acid
FOL	Furfuryl alcohol
GVL	γ-Valerolactone
GBL	γ-Butyrolactone
HCP	4-Hydroxy-2-cyclopentenone
HMF	5-(Hydroxymethyl)-furfural
LA	Levulinic acid
LAE	Levulinic acid esters
MA	Maleic anhydride
MAc	Maleic acid
MF	2-Methylfuran
MIBK	Methyl isobutyl ketone
MMF	5-Ethoxymethyl-2-furfural
MPV	Meerwein-Ponndorf-Verley
MTHF	2-Methyltetrahydrofuran
PA	Pentanoic/valeric acid
PAE	Pentanoic/valeric acid esters
PEA	Pentenoic acid
PEE	Pentenoic acid esters
PNC	Polymer-based nanocomposites
PTHF	Polytetrahydrofuran
PTME	Poly(tetramethylene ether)
PTMEG	Poly(tetramethylene ether) glycol
SAc	Succinic acid
THF	Tetrahydrofuran
THFA	Tetrahydrofurfuryl alcohol
THFAM	Tetrahydrofurfuryl amine
VA	Valeric acid
VE	Valeric esters

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8. Notes and references

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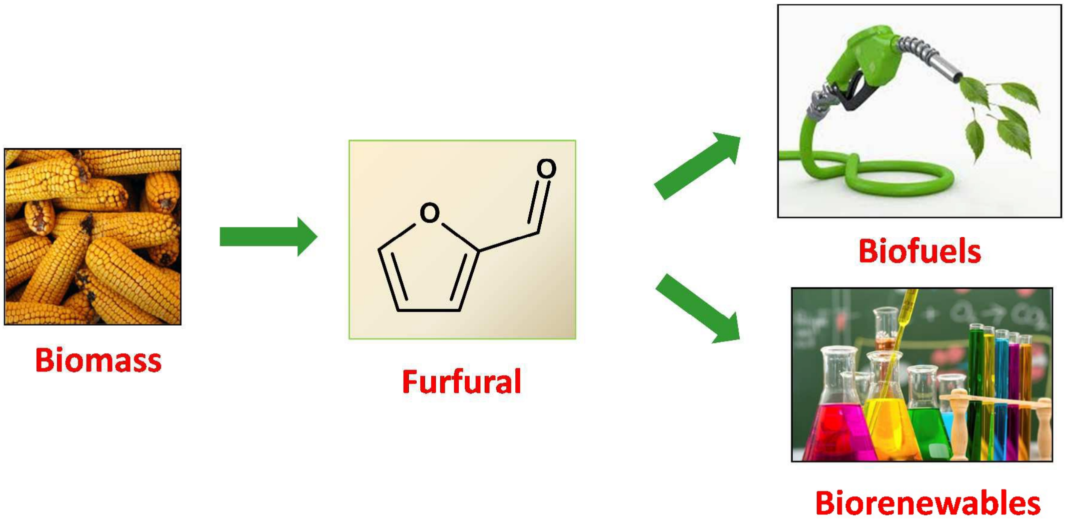

The aim of this review is to discuss the most relevant chemical routes for converting furfural to chemicals and to biofuels and additives.