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Conversion of plant biomass to furan derivatives and sustainable access to the new generation of polymers, functional materials and fuels

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5-Hydroxymethylfurfural (HMF) is an important versatile reagent, a so-called platform chemical, that can be produced from plant biomass compounds: hexose carbohydrates and lignocellulose. In the near future, HMF and its derivatives could become an alternative feedstock for the chemical industry and replace, to a great extent, non-renewable sources of hydrocarbons (oil, natural gas and coal). This review analyzes recent advances in the synthesis of HMF from plant feedstocks and considers the prospects for the use of HMF in the production of monomers and polymers, porous carbon materials, engine fuels, solvents, pharmaceuticals, pesticides and chemicals. The most important HMF derivatives considered in the review include 2,5-furandicarboxylic acid, 2,5-diformylfuran, 2,5-bis(hydroxymethyl)furan, 2,5-bis(aminomethyl)furan, 2,5-dimethylfuran, 2,5-dimethyltetrahydrofuran, 2,5-bis(methoxymethyl)furan, and 5-ethoxymethylfurfural. In the nearest future, a significant extension of the HMF application is expected, and this platform chemical may be considered a major source of carbon and hydrogen for the chemistry of the 21st century.
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I. Introduction

The continually increasing population on Earth results in an ~7% annual increase in the consumption of energy and organic matter.[1] Modern society is acutely dependent on non-renewable natural resources — crude oil, natural gas and coal, which currently provide ~80% of the energy and ~90% of the carbon-based chemicals for mankind.[1] However, the depletion of the reserves of fossil hydrocarbons has stimulated a search for new sources of energy and raw materials based on renewable resources. Currently, plant biomass is considered to be the main source of renewable carbon-based feedstocks that present a real alternative to crude oil and natural gas.[2–9] The Earth produces ~170 billion tons of plant biomass every year, although only 3% – 4% is now being used by mankind.[1] According to some estimates, the amount of energy that can be derived from biomass is almost 10 times as high as the annual world energy consumption.[10] It is believed that within 12 – 15 years, up to 30% of chemical feedstocks will be derived from plant biomass.[11,12] Russia occupies a top position in

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the world regarding the resources of plant biomass, especially wood (~23%).[13]

Approximately 75% of plant biomass is carbohydrates.[14] The key drawback that prevents the direct use of carbohydrates as feedstocks in the chemical industry and power engineering is too high an oxygen content. Furthermore, the main bulk of biomass carbohydrates (60%–80%) occur as cellulose, a poorly soluble biopolymer, which cannot be directly used for energy generation in modern chemical processes and devices.[15] This brings about the need to convert biomass to materials with lower oxygen content suitable for application in the chemical industry, power engineering and transport.[1,15–17] The development of effective methods for the processing of plant raw materials (cellulose and other carbohydrates) into valuable chemicals is a priority task of modern chemistry and chemical engineering.[6,7,15,18] A vigorously developing approach to biomass processing is based on the dehydration of carbohydrates to furan derivatives,[6,7,15,19] in particular, 5-hydroxymethylfurfural (HMF, Fig. 1), which is considered a key reagent, a so-called platform chemical,[20–23] for the synthesis of diverse practically valuable products, including polymers, pharmaceuticals, solvents and fuels. In 2014, the first industrial manufacture of HMF based on the acid-catalyzed dehydration of fructose was started to operate.[24] Last year, several large manufacturers of chemical products announced the construction of plants for the production of important HMF derivatives such as furan-2,5-dicarboxylic acid (FDCA) and dimethyl furan-2,5-dicarboxylate (FDME) (see Fig. 1).[25] In the short term, it is planned to use FDCA and FDME for the manufacture of polyethylene furanoate (PEF) and polypropylene furanoate (PPF) — biopolyesters meant for replacing polyethylene terephthalate as a packaging material in the foodstuff industry.[25]

Since the middle of the 2000s, the growth of the number of publications devoted to HMF and its derivatives has become explosive.[20] This review gives, relying on an analysis of the most important papers published mainly in the last three years, a brief evaluation of the state-of-the-art methods for the preparation of HMF and its key derivatives regarding the prospects for their industrial implementation and considers the main applications of these compounds.

The key abbreviations used in the text are listed below.

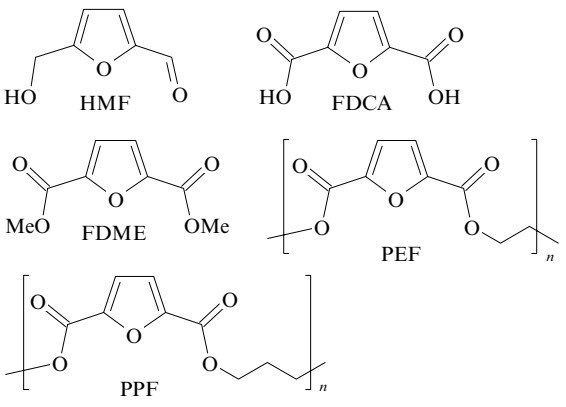


Figure 1. 5-Hydroxymethylfurfural (HMF) and the most important monomeric and polymeric HMF derivatives that are planned to be produced in industry in the coming years.

[BMIm]Cl —1-n-butyl-3-methylimidazolium chloride;
[EMIm]Cl —1-methyl-3-ethylimidazolium chloride;
AMF — 5-acetoxymethylfurfural;
BAMF — 2,5-bis(aminomethyl)furan;
BEMF — 2,5-bis(ethoxymethyl)furan;
BFF — 5,5′-oxydi(methylene)bis(furan-2-carbaldehyde);
BHMF — 2,5-bis(hydroxymethyl)furan;
BHMTHF — 2,5-bis(hydroxymethyl)tetrahydrofuran;
BMF — 5-bromomethylfurfural;
BMMF — 2,5-bis(methoxymethyl)furan;
CMF — 5-chloromethylfurfural;
DFF — 2,5-diformylfuran;
DMF — 2,5-dimethylfuran;
DMTHF — 2,5-dimethyltetrahydrofuran;
EMF — 5-ethoxymethylfurfural;
FA — fumaric acid;
FC — furfural;
FDCA — furan-2,5-dicarboxylic acid;
FDME —furan-2,5-dicarboxylic methyl ester;
FFCA — 5-formylfuran-2-carboxylic acid;
FMF — 5-formyloxymethylfurfural;
GVL — γ-valerolactone;
HAF — 2-hydroxyacetylfuran;
HDO — hexane-1,6-diol;
HMFCA — 5-hydroxymethylfuran-2-carboxylic acid;
HMF — 5-hydroxymethylfurfural;
HPA — 2-hydroxypropanoic acid;
LA — levulinic acid;
MA — maleic anhydride;
MAC — maleic acid;
MIBK — methyl isobutyl ketone;
OGA — 2-oxoglutaric acid;
PBF — poly(1,4-butylenefuran-2,5-dicarboxylate) (polybutylene furanoate);
PEF — poly(ethylenefuran-2,5-dicarboxylate) (polyethylene furanoate);
PPF — poly(1,3-propylenefuran-2,5-dicarboxylate) (polypropylene furanoate);
SA — succinic acid;
TEMPO — 2,2,6,6-tetramethylpiperidin-1-oxyl;
THFDCA — tetrahydrofuran-2,5-dicarboxylic acid.

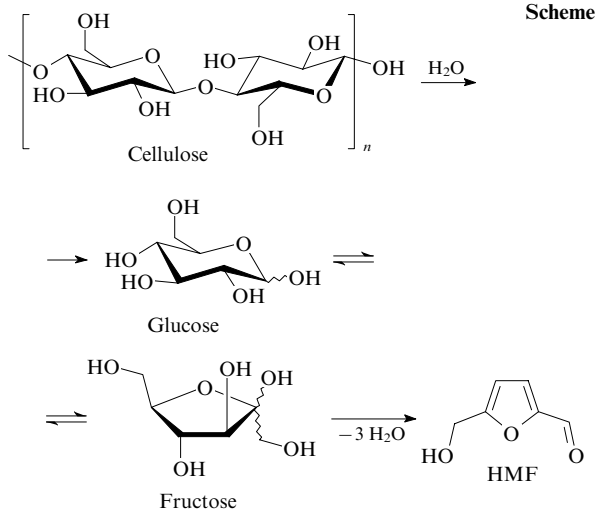
II. Synthesis of 5-hydroxymethylfurfural from renewable raw materials

II.1. Dehydration of carbohydrates to 5-hydroxymethylfurfural

The key synthetic pathways to HMF are based on the acid- or metal-catalyzed dehydration of hexoses.[6,11,19–23,26–31] Monosaccharides, disaccharides and polysaccharides, that is, fructose, glucose, saccharose, inulin, starch, cellulose and so on, are used as the hexose feedstock. In most publications, the synthesis of HMF from polysaccharides is started with the hydrolysis of polysaccharides to glucose and/or fructose.[6,11,19–21,23,26,28,29] Glucose reversibly isomerizes to fructose, which then loses three water molecules to give HMF (Scheme 1).

Thus, fructose is usually assumed to be the key precursor of HMF.[6,11,20,32] The dehydration of fructose gives HMF in a higher yield than the dehydration of glucose or other hexoses, which is taken, in some cases, as indirect evidence supporting this assumption.[20] It is noteworthy, however, that recent calculations of the transition state

Scheme 1

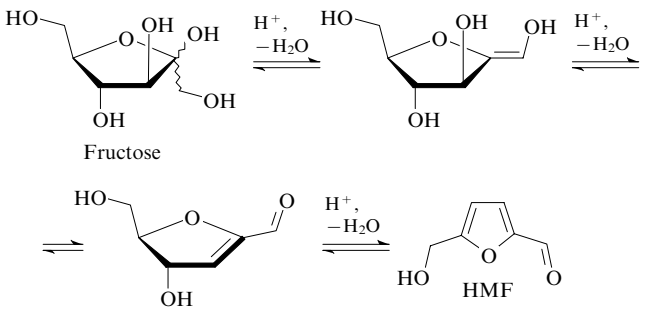


energies and kinetic experiments demonstrated the possibility of an alternative pathway comprising the dehydration of glucose to HMF in acidic aqueous solution, *i.e.*, synthesis without preliminary glucose isomerization to fructose *via* cyclic five-membered cations resulting from the elimination of a water molecule from the protonated glucose molecule.[21, 33] Density functional theory (DFT) calculations also provided the conclusion that glucose can be dehydrated to give HMF *via* the formation of acyclic 1,2-enediol in acidic ionic liquids without the formation of fructose.[34] Scheme 2 shows a simplified mechanism of this process.

Fructose dehydration can probably follow different mechanisms depending on the nature of the reaction medium and the catalyst used.[11, 20] Fructose dehydration mechanisms involving cyclic and acyclic intermediates have been considered in the literature.[20, 28] Although cyclic and acyclic forms of fructose occur in equilibrium in solutions,[35, 36] the dehydration *via* cyclic intermediates formed upon the successive elimination of water from D-fructofuranose is more likely (Scheme 3),[6, 11] especially for reactions in DMSO and in ionic liquids.[19, 20, 37, 38] A detailed analysis of the published data on the kinetics of dehydration of various hexoses to HMF has been presented in a review.[20]

The synthesis of HMF by the dehydration of carbohydrates is usually accompanied by the formation of by-products. Typical by-products are levulinic (LA) and formic acids, which are formed upon the rehydration of HMF; 2-hydroxypropanoic acid (HPA); polymeric compounds of a complex structure and variable composition (humins); furfural (FC); 2-hydroxyacetylfuran (HAF); HMF dimers, for example, BFF (Fig. 2); and some other products.[11, 20] The process selectivity depends appreciably on the raw

Scheme 3



material used and reaction conditions. Furthermore, since HMF is unstable, its yield follows a non-monotonic dependence on the duration of the synthesis.[20, 22, 23, 39]

Before the 1980s, most of the methods of HMF synthesis were based on the homogeneous acid-catalyzed dehydration of sugars in aqueous solution.[40] The modern methods for HMF preparation from carbohydrates are often classified depending on the solvent system used.[20, 40, 41] In single-phase systems, the reaction is conducted either in one

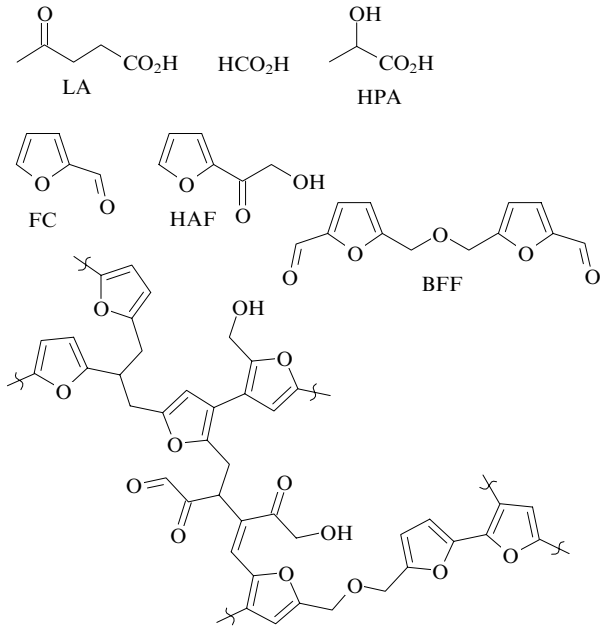
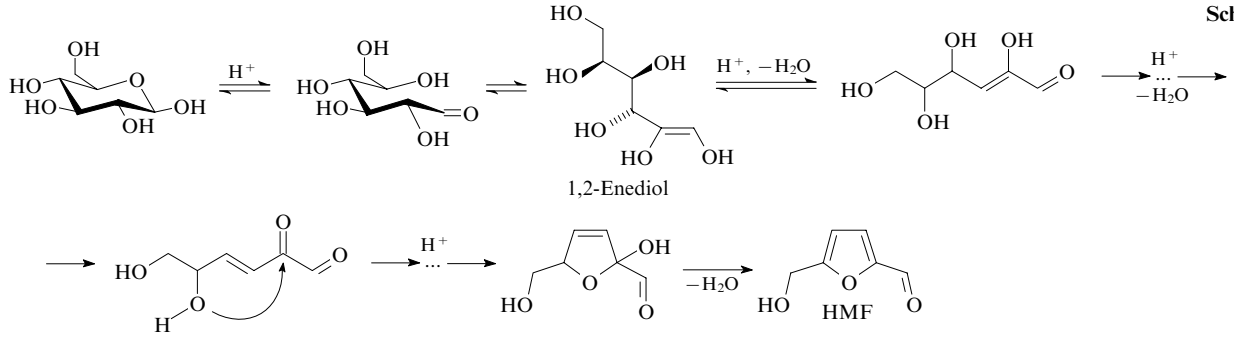


Figure 2. Typical by-products of the synthesis of 5-hydroxymethylfurfural.

Scheme 2



solvent [water, DMSO, DMF, *N*,*N*-dimethylacetamide (DMA), *N*-methylpyrrolidone, acetic acid, acetone, *etc.*] or in two or more completely miscible solvents (for example, acetone–DMSO). Two-phase systems usually include an aqueous solution and an organic solvent either immiscible or partly miscible with water, such as methyl isobutyl ketone (MIBK), butanone, dichloromethane, butan-2-ol, THF, or 2-methyltetrahydrofuran. Syntheses in ionic liquids are classified in a separate group.[20, 40, 41]

II.2. Methods for the synthesis of 5-hydroxymethylfurfural from fructose

Methods for the synthesis of HMF from fructose,[20] which serves as the feedstock in an operating plant,[24] have been developed most thoroughly. The dehydration of fructose in aqueous solution is usually catalyzed by mineral acids (HCl, H_2SO_4, H_3PO_4 and so on), soluble Zn, Nb, La, Fe or other metal salts, or various acidic heterogeneous catalysts such as cation exchangers, Ti, Zr, Fe and transition metal oxides and poorly soluble salts and zeolites.[6, 20, 22, 30, 31, 40, 41] Usually, the synthesis is performed either at temperatures of ~100 °C and atmospheric pressure or at 120–270 °C at elevated pressure. At temperatures of 140–200 °C, fructose dehydration proceeds at a high rate even without a catalyst.[20] Therefore, the process can be carried out in flow-type reactors with short residence times, which is convenient for commercial implementation. The yields of HMF reported in different publications vary over a broad range: from several percent to ~70%, even for similar conditions of synthesis.[6, 20, 22, 30, 40, 41] According to van Putten *et al.*,[20] this may be a consequence of improper analytical procedures used in some earlier works. The yield of HMF decreases with the increasing fructose concentration in the reaction medium, all other factors being the same.[20] In single-phase aqueous systems, the synthesis of HMF with a yield above 50% is hardly achievable because HMF is hydrolyzed to give levulinic and formic acids.

An efficient method for increasing the yield of HMF is the use of two-phase systems comprising an aqueous solution and an organic solvent for the dehydration of fructose and other carbohydrates.[20, 21, 31, 39, 42, 43] In these systems, the HMF being formed is continuously extracted with the organic solvent; therefore, its concentration in the aqueous phase remains relatively low, and hence the rate of HMF hydrolysis decreases and the process selectivity increases.[21] Most often, methyl isobutyl ketone serves as the organic extractant in these two-phase systems;[21, 39, 44, 45] more rarely used solvents include butanone, acetone, dichloromethane, butan-2-ol and other alcohols, and THF.[20, 40, 41] Both homogeneous and heterogeneous catalysts are used.[21, 22] As a rule, the yield of HMF increases with the increasing organic to aqueous phase volume ratio and in the presence of salting-out agents, such as sodium chloride or sulfate.[21, 46] The nature of the salting-out agent can have a considerable influence on the partition ratio of HMF. Sodium sulfate is one of the most efficient salting-out agents for aqueous solution–MIBK systems.[44] Recently, dimethyl carbonate was shown to be an efficient organic phase for HMF synthesis in a two-phase system in the presence of a heterogeneous $[(Ce(PO_4)_{1.5}(H_2O)(H_3O)_{0.5}(H_2O)_{0.5})]$ catalyst. Under these conditions, the product is readily separated together with the organic phase, and the evaporation of the extractant under vacuum affords crystalline HMF with 99% purity in ~70% yield.[47]

Quite a few studies have been devoted to the synthesis of HMF by the dehydration of fructose in organic solvents including DMSO, DMF, DMA and *N*-methylpyrrolidone; the solvents reduce the rate of HMF hydrolysis and increase the reaction selectivity.[20] Dimethyl sulfoxide is used most often.[22] The temperature of the synthesis can vary from 77 to 180 °C.[20] In the presence of acidic homogeneous catalysts [H_2SO_4, BF_3, $LaCl_3$, $Sc(OTf)_3$, acidic organic salts], the yields of HMF in DMSO can exceed 90% and even approach 100%.[20] Heterogeneous catalysts (cation exchangers; metal oxides, for example, ZrO_2, TiO_2, and WO_3/ZrO_2; zeolites; supported acids; metal salts, for example, zirconium phosphate; phosphotungstic acid; mesoporous carbons with grafted SO_2OH groups and so on) usually afford HMF in 60% to 100% yields.[20, 48–51] It is noteworthy that at temperatures above 150 °C, fructose dissolved in DMSO is converted to HMF in >90% yield without a catalyst.[22] The key drawback of DMSO and other high-boiling polar solvents is the complexity of isolating HMF from the reaction mixture;[20, 22] the separation of a high-boiling solvent by distillation is usually impossible because of the thermal instability of HMF, and extraction into less polar solvents immiscible with DMSO is of low efficiency. Therefore, attempts have been made to perform dehydration in relatively low-boiling solvents such as acetic acid and aliphatic alcohols (methanol, ethanol, butanol and so on). In acetic acid, 5-acetoxymethylfurfural (AMF) is formed as the major dehydration product, while in alcohols, O-alkyl ethers of HMF are usually formed, with yields ranging from 20% to 77%.[20] 5-Hydroxymethylfurfural ethers can be of interest as intermediates in the production of fuels, specific extractants and chemicals. It is notable that the dehydration of fructose in isopropyl alcohol in the presence of heterogeneous catalysts based on mesoporous carbons functionalized on the surface by arylsulfonyl groups may give HMF in a yield of up to 91%; however, the catalyst activity decreases after regeneration.[52] A heterogeneous catalyst based on polyvinyl alcohol sulfate in isopropyl alcohol produces HMF in a yield of 85% within 130 s under microwave heating to 130 °C; the catalyst is reusable many times without the loss of catalytic activity.[53]

Fairly high yields of HMF (up to ~100%) are attained if fructose dehydration is conducted in ionic liquids. As ionic liquids, organic salts are used, most often *N*-butyl-*N*′-methyl- and *N*-butyl-*N*′-ethylimidazolium chlorides and fluoroborates.[6, 20, 26, 29, 31, 36] Other suitable compounds are other dialkylimidazolium salts, protic salts of alkylimidazoles, pyridinium and other heterocycle salts, tetraalkylammonium and tetraalkylphosphonium salts and low-melting mixtures of various organic and inorganic salts.[20, 22, 30, 37, 40, 41, 54] Both homogeneous and heterogeneous catalysts of this type are used, including protic acids, Lewis acids (BF_3, $PtCl_2$, $SnCl_4$, $GeCl_4$, $CrCl_3$), cation exchangers, aluminosilicates and metal oxides.[20, 30, 37, 40, 41, 54] However, even without additional catalysts, the dehydration of fructose in many ionic liquids, especially acid salts, proceeds at 80–140 °C to give HMF in high yields.[20] The yield of HMF in ionic liquids is considerably affected by the concentration of water in the reaction mixture. In the presence of water, phase microheterogeneities can appear in ionic liquids and affect the fructose dehydration.[55] When only traces of water are present, the rate and the selectivity of the fructose dehydration to HMF are relatively high, but when the concentration of water is

above 10%, the product yield considerably decreases. To increase the yield of HMF and make the results reproducible, it has been proposed to carry out the dehydration of fructose in ionic liquids with the continuous removal of the water formed in the synthesis at a reduced pressure by means of a device such as a rotary evaporator, which enables intense mass exchange in viscous media.[56] A considerable problem faced in the preparation of HMF from fructose and other carbohydrates in ionic liquids is the isolation of the target product, which is usually accomplished by extraction into organic solvents (ethyl acetate, THF, MIBK and so on) that are immiscible with ionic liquids.[20, 31, 43, 57] As a rule, extraction is inefficient due to the formation of strong hydrogen bonds between the ionic liquid anion and the HMF hydroxy group. The addition of minor amounts of alcohols to the extractant leads to the competitive displacement of HMF from the ion pairs with ionic liquid halide anions and thus markedly increases the partition ratio and extraction efficiency.[57] Recently, supercritical CO_2 has been proposed for solving the problem of isolating HMF and recycling ionic liquids. The dehydration of fructose is conducted in a mixture of ionic liquid with acetone, and then supercritical CO_2 is added; this induces the separation of the homogeneous system into layers and the recovery of most of the HMF together with the acetone – supercritical CO_2 phase, while most of the catalyst and unreacted fructose remain in the ionic liquid.[58] A comparison of alternative procedures for HMF synthesis from fructose in ionic liquids and in water – MIBK two-phase systems demonstrates a higher efficiency of two-phase systems under industrial conditions, despite the lower yields of HMF, owing to the simpler isolation and purification of the target product and lower cost of extractant and catalyst regeneration.[43]

II.3. Methods for the synthesis of 5-hydroxymethylfurfural from glucose

Glucose is much more abundant in nature than fructose; furthermore, glucose can be produced on an industrial scale by the hydrolysis of cellulose.[19] Therefore, glucose is considered to be more economically promising than fructose as a feedstock for HMF production in the future.[19, 22, 32, 59]

Unfortunately, the dehydration of glucose to HMF is less selective, and the appropriate choice of the catalytic system is a crucial issue in this case.[19, 20, 22, 32, 33, 59] This is because the formation of HMF requires a preliminary isomerization of glucose to fructose (see Scheme 1).[20, 60] Glucose isomerization proceeds rather readily in basic media, whereas fructose dehydration occurs in acidic media.[60, 61] It is possible to design a consecutive isomerization – dehydration process in separate reactors loaded with basic and acid catalysts, but this design is currently considered to be less efficient for HMF production than one-pot processes.[59, 61]

Most one-pot methods for the synthesis of HMF from glucose are based on the use of catalytic systems combining Lewis and Brønsted acidity. Lewis acids catalyze the glucose isomerization to fructose according to a 1,2-hydride transfer mechanism, while Brønsted acids accelerate the dehydration of fructose to HMF.[60, 61] The isomerization is often the rate-limiting step for the whole process.[59, 62, 63] As the acidity increases, the rate of glucose isomerization to fructose usually decreases, whereas the rate of fructose dehydration to HMF increases.[59] If the isomerization step is too slow, HMF, which is rapidly formed from fructose, decomposes to a large extent to levulinic and formic acids and polymerizes to give humins.[32] In the synthesis of HMF from glucose in ionic liquids, the decomposition of HMF rather than glucose or fructose is believed to be the major cause for the decrease in the product yield.[36]

Catalysts often used for this purpose include mixtures of protic acids with Lewis acids, for example, $AlCl_3$ and HCl[64] or $AlCl_3$ and maleic acid;[65] chromium salts in the presence of Brønsted acids and bromide ions;[32, 66] and $TiO_2 - ZrO_2$ (1 : 1) mixed with the Amberlyst 70 cation exchanger.[67] Chromium and aluminum salts have proven to be especially efficient, although quite a few examples of the successful use of $GeCl_4$, H_3BO_3, B_2O_3, $SnCl_4$, $H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$, $Yb(OTf)_3$ and ZrO_2 as catalysts have also been reported.[20, 26, 40] Recently, sulfanilic acid,[68] which acts as a bifunctional catalyst combining nucleophilic (NH_2) and acid (SO_2OH) sites in one molecule, has been shown to be efficient. A promising trend in the synthesis of HMF from glucose is heterogeneous catalysis using bifunctional catalysts combining Lewis and Brønsted acid sites.[69 – 78] Examples of such catalysts are modified zeolites,[70, 79 – 82] aluminum- or boric acid-doped silica gel catalysts,[83, 84] chromium(III)-enriched montmorillonite[85] and bentonite,[86] sodium-modified Nb, Ti, Zr and Al phosphates,[87] porous organic polymers modified by sulfonic and phosphotungstic acids,[88] porous polydivinylbenzene containing NH-acid groups ($SONHSO_2C_4F_9$) and Cr^{3+} ions[89] and heteropolyacids such as $Cs_2[Cr_3O(EtCO_2)_6](H_2O)_3]_2[\alpha\text{-}SiW_{12}O_{40}]$ (Ref. 90) and $(n\text{-}C_{16}H_{33}NMe_3)H_4PW_{11}TiO_{40}$.[91] Most often, heterogeneous catalysts can be used repeatedly, although the adsorption of humic substances leads to a gradual decrease in their activity.[20]

The HMF synthesis from glucose can be performed in aqueous solutions, two-phase systems, organic solvents and ionic liquids.[20]

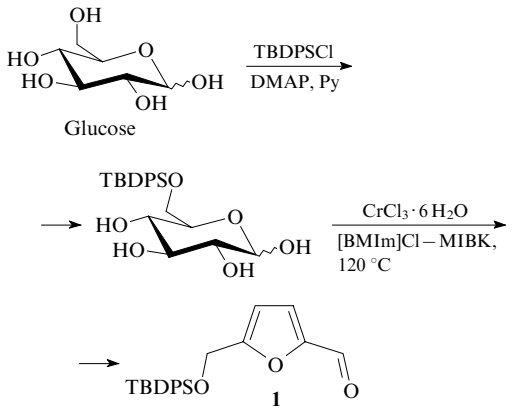
The product yields in aqueous solutions do not exceed 40%. In two-phase systems, the yield of HMF varies from 37% to 86%.[20, 22] For example, in the two-phase reaction system consisting of a 5% solution of glucose in saturated brine and dioxane (organic phase), the yield of HMF was 86% with a catalyst mixture of $TiO_2 - ZrO_2$ and Amberlyst 70.[67] The additional emulsification of the two-phase systems increases the yield of HMF by 10% – 20%, all other factors being the same.[64]

Many examples of HMF synthesis from glucose in organic solvents — DMSO, DMF, DMA, caprolactam, butanol, lactones and so on — have been described. The highest yields of HMF (40% – 80%) have been attained in aprotic polar solvents in the presence of chromium salts or bifunctional heterogeneous catalysts.[20, 22, 61, 69, 74, 90, 92] When chromium salts are used as catalysts, the reaction rate in DMSO is lower than those in DMA or butan-1-ol, because Cr^{3+} ions form strong low-activity complexes with DMSO molecules.[93] The key drawback of most aprotic polar solvents is the difficulty of isolating HMF from the reaction mixture.

In recent years, much attention has been paid to HMF preparation from glucose in ionic liquids as the methodological basis for the development of the one-pot syntheses of HMF from cellulose.[4, 6, 26, 94] Considerable progress in the HMF synthesis from plant raw materials was made by Zhao *et al.*,[95] who demonstrated in 2007 that catalysis by $CrCl_2$ in [EMIm]Cl at 100 °C results in almost equal yields of HMF

(~68%) when synthesized from glucose and from fructose. Later, it was found that the use of $CrCl_3$ in various ionic liquids gives similar results.[20,29,94] The key role of the chromium salts in ionic liquids, similar to in other systems, is to perform the selective isomerization of glucose to fructose, and, according to kinetic measurements, this is the rate-limiting step.[96] Apart from chromium salts, most other catalysts that are used in other solvent systems can also be employed in ionic liquids. Most often, the yield of HMF varies in the 40% to 80% range.[20,26,97] Some publications note the efficiency of microwave heating.[98] For example, in the microwave-assisted $CrCl_3$-catalyzed reaction in [BMIm]Cl, the yield of HMF reaches 85% within 2.5 min, whereas in the case of convective heating, the yield is only 57% within 3 h.[36] The key role in decreasing the yield is played by side oligomerization processes involving the hydroxymethyl groups of HMF and glucose. Protection of the hydroxymethyl group allows for a substantial increase in the selectivity; for example, with O(6)-protected glucose, the isolated yield of compound **1** is 81% (Scheme 4).[56] One more efficient approach to increasing the yield is the continuous removal of the HMF being formed from the ionic liquid. For instance, the reaction catalyzed by $CrCl_3$ in the [BMIm]Cl–1,2-dimethoxyethane system gave HMF in ~65% yield; the amount of glucose was 80 mass % with respect to the ionic liquid.[99]

Scheme 4



TBDPS = Bu^tPh_2Si, DMAP is 4-(*N*,*N*′-dimethylamino)pyridine, Py is pyridine

Deep eutectic solvents, similar in their properties to ionic liquids, are regarded as promising media for the conversion of glucose and hexose polysaccharides (see a review [100]). For example, in the two-phase system (choline chloride + $AlCl_3$ + H_2O)–MIBK, the yield of HMF from glucose was 70%.[101]

II.4. Methods for the synthesis of 5-hydroxymethylfurfural from disaccharides, cellulose and other polysaccharides

However, other important feedstocks for the synthesis of HMF are di- and polysaccharides such as saccharose, inulin and starch. The synthesis comprises the hydrolysis of the polysaccharide to a monosaccharide (glucose or fructose), the reversible isomerization of glucose to fructose and the dehydration of the latter to HMF.[22,28] The approaches to the synthesis of HMF from inulin are similar to the methods of synthesis from fructose, while the methods used for the synthesis from saccharose and starch are similar to those from glucose.[19,20,102]

Cellulose is considered the principal raw material for the preparation of HMF in the near future, because it is the most readily available inedible polysaccharide.[19,22,23,28,94] As in the case of monosaccharides, HMF synthesis from cellulose can be performed in traditional single-phase systems (water, organic solvents of water–organic mixtures), aqueous solution–organic solvent two-phase systems and ionic liquids.

When cellulose is heated in water, within a short period of time (several seconds to 5 min) at 250–350 °C, HMF is formed in 4%–12% yield, even without a catalyst.[20] In the presence of mineral acids, the yield can increase to ~21%.[20] The yield of HMF synthesized from cellulose in water substantially increases in the presence of heterogeneous catalysts combining Lewis and Brønsted acid sites.[20,28,94] For example, the use of a micellar heterogeneous catalyst, the heteropolyacid $Cr[(DS)H_2PW_{12}O_{40}]_3$ (DS is dodecyl sulfate), resulted in a 53% yield of HMF formed after 2 h at 150 °C, the conversion of cellulose being 77%; furthermore, the catalyst could be recycled without the loss of activity.[103] With the mesoporous zeolite H-ZSM-5 at 190 °C, the yield of HMF was 46% within 4 h.[104] In organic solvents, the yields of HMF obtained from cellulose are usually moderate. For example, the $CrCl_3$–HCl system in dimethylacetamide in the presence of 10% LiCl afforded HMF in a yield of 29%–33% within 2 h at 140 °C.[20,105]

Relatively high yields of HMF when prepared from cellulose are attained in two-phase systems comprising an aqueous solution and an organic extractant, especially in concentrated salt systems that dissolve cellulose.[20,22,106] For example, in the saturated aqueous solution ($NaHSO_4$ + $ZnSO_4$)–THF system, the yield of HMF was 53% within 60 min at 160 °C, the cellulose conversion being 96%.[107] The use of a ~72% solution of $ZnCl_2$ with the addition of HCl (0.2 mol liter^{-1}) and MIBK as the extractant provided an ~81% yield of HMF from microcrystalline cellulose within 40 min at 150 °C, and the catalytic system was reusable many times without a significant loss of the catalytic activity.[108] When sulfamic acid was used as the catalyst in the aqueous NaCl–THF system at 180 °C under microwave heating for 40 min, the yield of HMF was 52%.[109] Sulfanilic acid in the water–MIBK system at 150–180 °C provided the cellulose conversion to HMF in a yield of 37%–52%. The heteropolyacid $(n\text{-}C_{16}H_{33}NMe_3)H_4PW_{11}TiO_{40}$ in the water–butan-1-ol system at 160 °C furnished HMF in a yield of 40.6% within 8 h,[91] while in the presence of $(HOCH_2CH_2NMe_3)_xH_{3-x}PW_{12}O_{40}$ ($x = 1–3$) in the water–MIBK system at 140 °C, the yield of HMF was 75%.[110] In the reaction catalyzed by phosphated titania in a water–THF mixture containing *N*-methylpyrrolidone, mechanically preactivated cellulose pretreated with sulfuric acid was converted to HMF in 86% yield within 105 min at 180 °C.[111]

Ionic liquids, which dissolve cellulose by breaking the hydrogen bonds between its molecules, are effective media for the conversion of cellulose to HMF.[20,23,28,29,94,112] The conversion of cellulose in ionic liquids without a catalyst or catalyzed by acidic ionic liquids, for example, $[C_4H_8SO_3HMIm]X$ ($[C_4H_8SO_3HMIm]$ is 3-methyl-1-(4-sulfobutyl)imidazolium; X = Cl, HSO_4), at temperatures of 100–120 °C usually affords HMF in ~15%–20% yield;[20]

some publications using microcrystalline cellulose reported up to 33% yields.[113] The yield of HMF increases to 40% – 70% when chromium salts serve as catalysts;[20, 22, 114] furthermore, the use of 10 mol.% $CrCl_2$ in [EMIm]Cl (120 °C, 6 h) was reported[115] to provide an 89% yield of HMF. The heating of cellulose in [BMIm]Cl with chromium trichloride hexahydrate for 1 h at 130 °C followed by extraction into ethyl acetate afforded crystalline HMF with 98% purity in a yield of 50%.[56] The preparation of HMF in 30% – 70% yields in the presence of other Lewis acid catalysts such as H_3BO_3 and transition metal salts has also been reported.[22, 26, 116] For example, in the $CuCl_2$ – ([$C_4H_8SO_3$HMIm][$MeSO_3$]) system at 160 °C, the yield of HMF was 69.7%.[117]

Quite a number of recent studies address the use of ionic liquids for the direct preparation of HMF from various agricultural and wood industry wastes, *e.g.*, wheat and rice straw or corn stalks (see a review[27]). According to some publications, HMF yields of ~50% based on the carbohydrate content in the biomass have been attained.[27] The yield of HMF is considerably affected by the pretreatment of the plant raw material. For instance, the pretreatment of wood chips or rice stalks with a 3% aqueous solution of NaOH for 24 h at 60 °C followed by heating for 6 h at 120 °C in [BMIm]Cl containing 4% $CrCl_3 \cdot 6H_2O$ made it possible to obtain HMF in 76% – 79% yield based on the glucans present in the raw material.[118] The pretreatment of lignocellulose with an alkaline solution causes the partial destruction of the ether and glycosidic bonds and the removal of hemicellulose and lignin, resulting in fiber loosening. This probably reduces the diffusion restrictions for cellulose hydrolysis and hence increases the yield of HMF.[118]

Some papers report the application of various heterogeneous catalysts, modified minerals[119] and polymers[120 – 126] for a one-pot cellulose conversion to HMF in ionic liquids. However, the yield of HMF in these systems does not exceed ~50%.

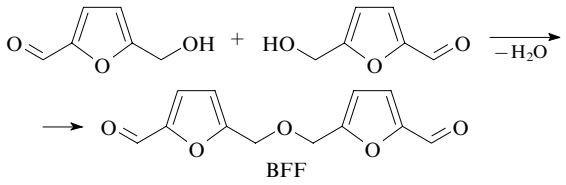
II.5. Chemical engineering aspects of the production of 5-hydroxymethylfurfural

For scaling-up the synthesis of HMF to an industrial level, the design of process equipment, the efficiency of the isolation and purification of the target product, the recycling of the catalyst system and the environmental safety of the production process become significant issues, along with the costs of the carbohydrate raw material and the catalytic system, the product yield and the reaction rate.[1] Although the first industrial production of HMF commenced in 2014,[24] the vast majority of studies have been performed using laboratory batch reactors — test tubes, ampoules, flasks, autoclaves and so on, which do not adequately model the industrial process.[20] Therefore, the choice of an efficient method of HMF synthesis and the optimization of the equipment design remain important tasks in plant raw material processing.

In the large-scale industrial production of HMF, the productivity of the reactor unit is largely determined by the residence time of the reaction mixture. The high-temperature (≥170 °C) methods for the dehydration of carbohydrates imply a short residence time (seconds or fractions of a second) and, despite the relatively low yield of HMF, they may prove to be quite promising for large-scale production. These processes would better be performed in continuous flow reactors, including tubular reactors or stirred flow reactors.[20, 127] Flow reactors can be used in both non-catalytic and catalytic HMF synthesis processes with homogeneous and heterogeneous catalysts.[20, 111, 128 – 130] Flow recirculating modes with a relatively low degree of conversion (20% – 30%) per pass and the continuous withdrawal of HMF by extraction were shown to be efficient for the dehydration of glucose to HMF.[131] A promising trend in the development of continuous high-temperature HMF production processes is the use of microreactors, which achieve a very fast heating of the reaction mixture to the desired temperature and subsequent fast cooling.[20, 132, 133] In these reactors, homogeneous catalysts can be supported on the microchannel surface; for example, sulfo groups can be attached *via* the sulfonation of the hydroxyl groups on the inner surface of the silica-fused capillaries.[133] A serious problem faced by the use of flow reactors, especially with heterogeneous catalysts, is the formation of insoluble polymers (humins), which are deposited on the reactor walls and catalyst surface, thus hampering the heat and mass transfer and deactivating the catalyst.[20] Additional problems of flow reactors are related to the use of poorly soluble cellulose and lignocellulose as the feedstock. When ionic liquids are used, their high viscosity can also complicate the synthesis in flow reactors.[134]

The efficiency of HMF synthesis largely depends on the product isolation and purification stages.[20, 22, 31, 43] Since the HMF stability is relatively low and decreases in the presence of acidic impurities, the isolation and purification may be accompanied by considerable loss of the product *via* hydrolysis and polymerization.[39] Furthermore, even minor impurities markedly affect the storage stability of HMF and the efficiency of its further processing.[56] The highest storage stability is inherent in crystalline HMF with at least a 99.9% content of the major compound, whereas the oily product of 97% – 99% purity decomposes at room temperature in as soon as two weeks to give mainly the dimer (BFF) (Scheme 5).[56]

Scheme 5



The isolation of HMF from aqueous solutions usually includes the separation of poorly soluble humic products by filtration or centrifugation followed by the extraction of HMF into an organic solvent.[20, 31] It is noteworthy that in aqueous solutions, ionic liquids or polar solvents such as DMSO, the HMF molecules are well solvated, and the HMF partition ratios in the reaction mixture – extractant systems are usually moderate.[42] Methyl isobutyl ketone, ethyl acetate, and butanol and other higher alcohols are used as extractants.[42] Although the extraction capacities of ethyl acetate,[45] butan-1-ol[135] and some other alcohols[20] are somewhat higher than that of MIBK, the latter is preferred for the extraction of HMF from acidic solutions, especially during the HMF synthesis in two-phase systems in the presence of acid catalysts, because ethyl acetate is prone to hydrolysis, while butan-1-ol and other primary alcohols form mixed ethers with HMF. Dimethyl carbonate

(DMC), which has a much higher extraction capacity than MIBK (the HMF partition ratio is 2.31 for DMC–water systems and only 0.9 for MIBK–water systems), was proposed as a new, highly efficient low-boiling extractant for HMF recovery from aqueous solutions.[47] The addition of inorganic salts to the aqueous solution usually results in HMF salting-out to the organic phase. For example, in the system comprising a 23% aqueous solution of NaCl and MIBK, the HMF partition ratio is ~2.5 times as high as that in the water–MIBK system.[45] The nature and concentration of the inorganic salt considerably influence the partition ratio of HMF.[44,135] For example, sulfates and acetates have a salting-out effect, whereas nitrates reduce the partition ratio, and lithium chloride either increases or decreases the HMF partition ratio in aqueous solution–MIBK systems, depending on the concentration.[44] According to experimental data, sodium sulfate is among the most efficient salting-out additives.[21,44] Anions have a similar effect on the partition ratio of HMF between aqueous solutions and butan-1-ol.[135] Owing to the salting-out effect of mineral salts, it is possible to extract HMF into other solvents that are miscible with pure water but form two-phase systems with aqueous solutions of salts, for example, THF, propan-2-ol, acetonitrile, and acetone.[21] The recovery of HMF from ionic liquids is promoted by the addition of low-molecular-weight alcohols. For instance, a minor amount of ethanol added suppresses the solvation of HMF by ionic liquids as a result of competing hydrogen bond formation between the hydroxyl groups of ethanol and the ionic liquid anions, thus increasing the partition ratio between MIBK and [BMIm]Cl by a factor of ~10.[57] A new technique for enhancing the HMF recovery from ionic liquids is the use of supercritical CO_2. The introduction of supercritical CO_2 into homogeneous mixtures of ionic liquids with acetone after the synthesis induces fast phase separation, which allows for efficient HMF extraction into a mixture of supercritical CO_2 with acetone.[58] 1,2-Dimethoxyethane was proposed as a new high-performance extractant, which efficiently dissolves HMF, has a reasonable boiling point (85 °C) and provides more intense mass exchange owing to its lower viscosity.[99]

A fairly efficient technique for increasing the yield of HMF is counter-current extraction during the synthesis.[20,39] For example, counter-current extraction with MIBK ensures a 98% recovery of HMF from aqueous solutions.[45] Extraction is also the principal method used to recover HMF from ionic liquids or high-boiling organic solvents (DMSO, DMA, DMF).[20,22,23,26,29,57,113] The efficiency of the HMF extraction from these systems is even lower than that from aqueous solutions.[20,43] Furthermore, because of their partial solubility in the extractant, aprotic solvents and ionic liquids contaminate the isolated HMF.[20,43,56] It is worth noting that many studies dealing with isolation of HMF recommend the preliminary neutralization of the reaction mixtures. This eliminates a considerable portion of the polymeric impurities, which are acidic, and retards the acid-catalyzed decomposition of HMF.[20,39] However, the neutralization of the reaction mixtures inevitably destroys the catalytic system and hence the system cannot be reused. It is more reasonable to neutralize the HMF extracts after they have been separated from the reaction mixture so that the catalytic system remains intact.[43,56]

A variety of adsorbents have been proposed for the recovery of HMF from water or aqueous-organic mixtures.[20] For example, highly hydrophobic commercial activated carbons produced by the carbonization of polymeric materials possess a considerable adsorption capacity towards HMF (up to 0.86 g g^{-1} at 20 °C) and can enable the selective recovery of HMF from aqueous solutions in the presence of fructose.[136] The highly selective adsorption of HMF from aqueous solutions in the presence of fructose and levulinic and formic acids has been found for organic sorbents based on nanoporous products of 4,4′-bis(chloromethyl)-1,1′-biphenyl polymerization.[137,138] Modified zeolites have demonstrated relatively high sorption capacity (up 0.46 g g^{-1}), selectivity (~100%) and regenerability in the recovery of HMF from aqueous solutions in the presence of fructose.[139] Zeolites coated by silicate membranes have been proposed for HMF isolation from ionic liquids.[134]

In some studies, HMF was isolated and purified by vacuum distillation at temperatures from 114 to 190 °C and pressures from 0.05 to 1 mm Hg.[20] However, in most studies, distillation was recognized as inefficient, as it is associated with a considerable loss of HMF due to decomposition at elevated temperature.[22,42,57,99]

The key method for the preparation of high-purity crystalline HMF is crystallization.[20,43,56] 5-Hydroxymethylfurfural can be crystallized from a saturated aqueous solution (~7% water in HMF),[20] from diethyl ether at approximately −20 °C,[56] from a mixture of diethyl ether and hexane at approximately −25 °C [43] and from methyl *tert*-butyl ether at ~5 °C.[20] Crystallization is usually performed after the isolation of HMF from the reaction mixture by extraction or adsorption.

II.6. Economic evaluation of the prospects for the industrial production of 5-hydroxymethylfurfural by various methods

The assessment of the feasibility of various methods for HMF production demonstrates that the major contribution to the commercial product's prime cost is made by the cost of the feedstock. According to some estimates, the prime cost of the HMF obtained from fructose is ~80% determined by the cost of the carbohydrate.[20,22] Other important factors are the yield of the HMF, the costs of the by-products (for example, levulinic acid), catalyst and other reagents and solvents, the energy expenditure and the cost of equipment.[20]

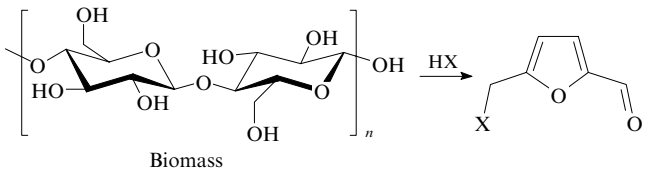
For HMF to become an alternative to the petroleum feedstock in the industrial production of monomers and agrochemical and pharmaceutical products, its world market price should not exceed, presumably, ~1 US dollar per kg.[20] This price level could be attained even by the use of a fructose feedstock if the HMF production output is at least 100 000 tons per year. However, the potential use of HMF in the production of fuels requires that its price be substantially lower; this is possible only if HMF is obtained in a good yield from cellulose or, more likely, from lignocellulose.[20]

Catalytic methods of synthesis are considered more beneficial, especially for the HMF production from glucose or its polymers (starch or cellulose).[20,22] Bifunctional heterogeneous catalysts are believed to have good prospects;[20,74,77,78] however, a serious problem is catalyst deactivation as a result of the adsorption of humic compounds on the surface.[20,74] Aqueous-organic systems and

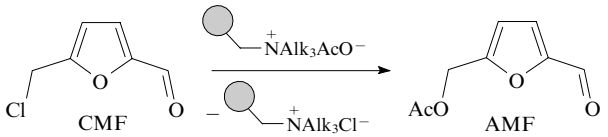
ionic liquids are the most promising reaction media.[20, 22, 43] Although the syntheses of HMF in aprotic polar solvents such as DMSO, DMF or *N*-methylpyrrolidone usually give high product yields, the use of these methods on an industrial scale is hardly practicable, because of the difficulty of HMF isolation.[20, 140] Ionic liquid processes also have some significant drawbacks: the difficulty of the isolation of HMF, the high cost and toxicity of ionic liquids, the high energy expenditure for regeneration, and the unstable catalytic properties of these systems in the presence of even minor impurities.[20, 26, 27] A comparative analysis of two alternative methods for the synthesis of high-purity crystalline HMF from fructose, namely, in ionic liquids and in the water – MIBK two-phase system, provided the conclusion that the latter method should be preferred for scaling up for industrial production.[43] Apparently, the industrial utilization of ionic liquids could be expedient for HMF production from a lignocellulose feedstock.[26, 27, 140]

As a possible way to reduce the expenses associated with the difficulty of HMF isolation from reaction mixtures, it was proposed to process the carbohydrate biomass to less hydrophilic and more stable HMF derivatives, which are much easier to isolate from the reaction mixture and to purify. Such HMF derivatives include 5-chloromethyl- (CMF), 5-bromomethyl- (BMF), 5-acetoxymethyl- (AMF) and 5-formyloxymethylfurfurals (FMF) (Scheme 6).

Scheme 6



X = Cl (CMF), Br (BMF), HC(O)O (FMF)



Of the most interest is CMF,[141 – 143] which is a more convenient reagent, in some cases, than HMF. 5-Chloromethylfurfural is formed in a 70% – 83% yield upon the direct conversion of cellulose in two-phase systems consisting of aqueous HCl and an organic extractant (dichloroethane, toluene, cyclohexane and so on) at 90 – 110 °C. It is relatively stable in acid medium and, owing to its rather high lipophilicity, is readily isolated from reaction mixtures by extraction and can be purified by vacuum distillation.[141] 5-Bromomethylfurfural can be prepared in a similar way in a 67% – 74% yield.[143] 5-Formyloxymethylfurfural is synthesized at a ~30% yield by heating biomass, for example, bamboo pulp, in formic acid at 150 °C in the presence of NaBr as a catalyst.[144] 5-Acetoxymethylfurfural is easily obtained in a >90% yield by treating CMF with anion exchangers or alkylammonium acetates.[145] Both AMF and FMF are less toxic than CMF and can serve as alternative stable substitutes for HMF.

A fairly promising way of decreasing the cost of HMF derivatives — monomers, fuels, pharmaceuticals and so on — is the one-pot synthesis of these compounds from a carbohydrate feedstock, that is, without the isolation and purification of the intermediate HMF.[14, 146]

III. 5-Hydroxymethylfurfural as a raw material for the chemical and energy industries

III.1. Most important monomers obtained from 5-hydroxymethylfurfural

After a large-scale production of HMF is developed, some of its derivatives (Fig. 3) would be able to substitute, at least partially, for the currently used monomers that are produced from petroleum products.[20, 147] The most important monomers that can be employed for polymer synthesis by polycondensation include furan-2,5-dicarboxylic acid (FDCA), 2,5-diformylfuran (DFF) and 2,5-bis(hydroxymethyl)furan (BHMF).[147, 148] Also of interest are 5-hydroxymethylfuran-2-carboxylic acid (HMFCA) and 2,5-bis(aminomethyl)furan (BAMF).[147] It is assumed that in the near future, these compounds may replace terephthalic and adipic acids, alkanediols and hexamethylenediamine in the industrial production of polymers.

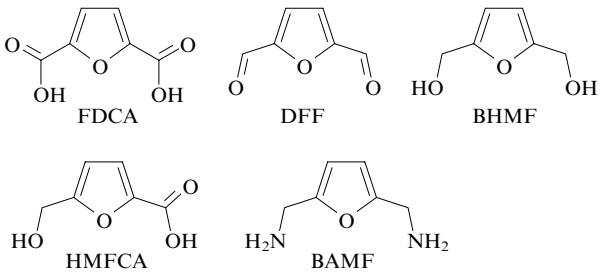


Figure 3. Most important HMF-derived furan monomers.

III.1.a. Furan-2,5-dicarboxylic acid and its derivatives

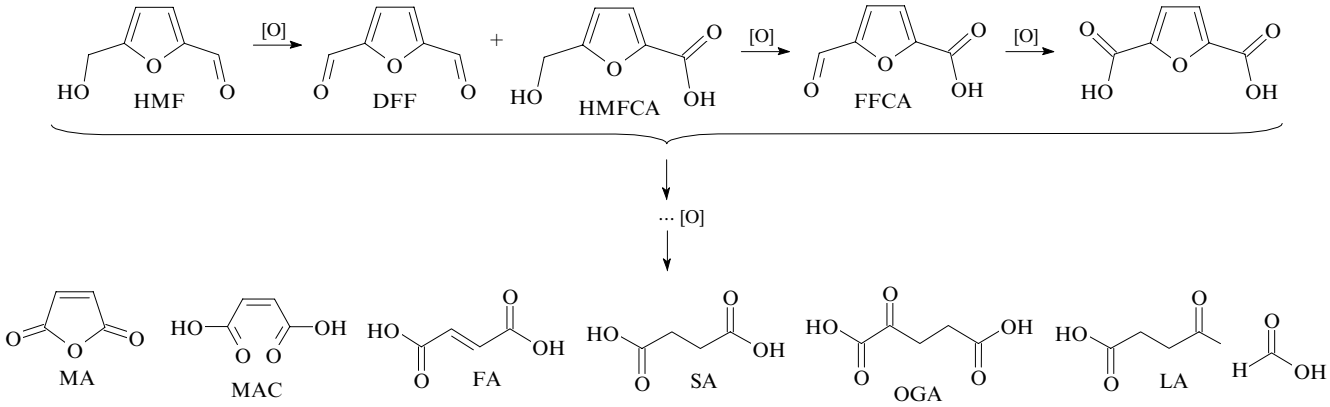
As noted above, furan-2,5-dicarboxylic acid is a very important monomer, a so-called platform chemical.[149 – 152] Presumably, in the near future, FDCA would replace terephthalic and isophthalic acids.[1, 18, 20, 147 – 149] According to the estimates of companies that develop polymer production processes based on renewable raw materials, the world output of FDCA may reach 300 000 tons per year by 2018.[153, 154] In March 2016, the large chemical company BASF and the innovative company Avantium announced a joint venture for the construction of the first FDCA industrial plant with a capacity of up to 50 000 tons per year in Antwerp.[25, 155]

Usually, FDCA is prepared by the direct oxidation of HMF. The oxidation can include the formation of various intermediates and by-products (Scheme 7).[152, 156, 157]

5-Hydroxymethylfurfural is oxidized rather easily by conventional inorganic oxidants such as N_2O_4, HNO_3, $KMnO_4$, with the FDCA yields being 24% – 70%.[20] The relatively low selectivity, high cost and large amounts of toxic by-products formed in reactions with these oxidants preclude the use of these methods in large-scale production.[152] Instead, catalytic processes of HMF oxidation with air, molecular oxygen or peroxides are more promising.

Homogeneously catalyzed HMF oxidation with air in acetic acid in the presence of Co^{II}, Mn^{II} or Zn^{II} acetate and

Scheme 7



HBr (~60% yield) and oxidation with *tert*-butyl peroxide in the presence of copper chlorides (43%–45% yields) have been reported.[151,152] A semi-continuous process has been developed for the homogeneous aerobic oxidation of HMF with oxygen in acetic acid, at a Co : Mn : Br molar ratio of 1 : 0.015 : 0.5, temperature of 180 °C, pressure of 30 atm and $CO_2 : O_2$ molar ratio of 1 : 1, giving FDCA in a 90% yield.[158] A pilot unit has been designed for the production of FDCA by this method, providing 5–6 kg of FDCA with 92% purity in a 75% yield over a period of 3 h.[149] A process of the homogeneous oxidation of HMF to FDCA with hydrogen peroxide has been proposed.[157] According to a chromatographic analysis, in the presence of the molybdenum complex catalyst $[EMIm]_4[Mo_8O_{26}]$ at 100 °C, the conversion of HMF is 99.6% within 2 h with a selectivity of ~100%.

Heterogeneously catalyzed processes of HMF oxidation with air or molecular oxygen are considered to be more promising for industrial implementation.[149,151,152] High activity and selectivity have been found for catalysts based on noble metals — Pt, Pd, Ru and Au.[159] For example, platinum supported on activated carbon, graphene oxide, TiO_2, ZrO_2 or γ-Al_2O_3 in alkaline aqueous solutions enables the oxidation of HMF to FDCA in a 69%–100% yield; particularly, high activity, selectivity and recycling stability are inherent in lead- or bismuth-modified bimetallic catalysts, Pt-Pb/C, Pt-Bi/C and Pt-Bi/TiO_2.[149,151,152] A magnetically recyclable catalyst composed of platinum nanoparticles supported on paramagnetic Fe_2O_3 spheres coated by a carbon layer has been developed. This catalyst can be readily separated from the reaction mixture in a magnetic field.[160] According to liquid chromatography data, this catalyst provides a ~100% yield of FDCA in water in the presence of Na_2CO_3 at 90 °C.

A shortcoming of most heterogeneously catalyzed processes of HMF oxidation to FDCA is the necessity to conduct the synthesis in alkaline solution, which then need to be neutralized to isolate the crystalline FDCA, which gives rise to mineral salt wastes.[152] Oxidation processes that do not require inorganic bases are more environmentally benign. For example, the oxidation of HMF in water on polyvinylpyrrolidone-stabilized platinum nanoparticles affords FDCA in an 84%–95% yield; however, the large amount of the catalyst required (5 mol.%) and the low concentration of HMF that can be handled were reported for this method.[161] Supported catalysts, namely, platinum nanoparticles supported on modified carbon nanotubes[162] or on synthetic C-O-Mg supports obtained by the thermolysis of a MgO mixture with resorcinol,[163] enable the oxidation of HMF in water without bases at 95 °C to give FDCA in 96%–99.5% yields, the catalysts being reusable many times.

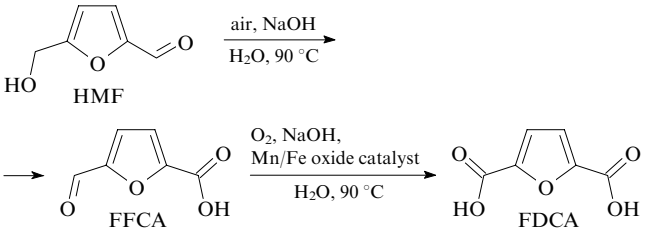
High yields of FDCA (70%–93%) are obtained upon HMF oxidation with oxygen in alkaline aqueous solutions in the presence of palladium catalysts (Pd/C, Pd/ZrO_2/La_2O_3, Pd/Al_2O_3, Pd/C/γ-Fe_2O_3/hydroxyapatite, Pd-polyvinylpyrrolidone and so on).[149,151,152] Ruthenium catalysts are also suitable, although they often give mixtures of FDCA with 2,5-diformylfuran.[151,152,164] However, with $[Ru(OH)_x]$-based catalysts supported on MgO, $MgO \cdot La_2O_3$ or hydrotalcite, the yields of FDCA formed in water in the presence of bases can reach 95% according to chromatographic data.[165] The use of a commercial Ru/C catalyst (Aldrich) for the oxidation of HMF with oxygen in water without alkali at 120 °C and 0.2 MPa results in FDCA in an 88% yield within 10 h (chromatographic analysis).[166] The isolated yield was 78%; furthermore, FDCA can be obtained by the oxidation of crude HMF synthesized by the dehydration of fructose in isopropyl alcohol in a 53% overall yield based on fructose.[166] Thus, ruthenium catalysts are also rather promising, especially considering the relatively low cost of ruthenium compared with that of other noble metals applied for HMF oxidation.[165]

Supported gold nanoparticles have been found to be highly efficient catalysts for the aerobic oxidation of HMF to FDCA in aqueous solutions.[149,151,152] For example, in the oxidation of HMF with air or molecular oxygen in alkaline aqueous solutions catalyzed by Au/CeO_2, Au/TiO_2, Au/$Ce_{0.9}Bi_{0.1}O_{2-\delta}$ or Au/HY zeolite, the yield of FDCA varies from 84% to ⩾99%. The selectivity of the Au/CeO_2 catalyst depends appreciably on the degree of removal of residual polyvinylpyrrolidone, which is used for gold nanoparticle stabilization during the preparation of the catalyst.[167] More stable catalytic properties were demonstrated by bimetallic catalysts, Au-Cu/TiO_2 and Au_8-Pd_2/C, which retain high activity and selectivity after repeated recycling.[152] Gold-based catalysts for the oxidation of HMF in the absence of bases have also been developed. Indeed, Au/hydrotalcite catalysts afford FDCA in a yield of 99% upon the oxidation of HMF in water, although the catalyst activity gradually decreases in the course of recycling.[152] Ardemani *et al.*[168] demonstrated that this is related to the irreversible adsorption of HMF and acidic oxidation inter-

mediates. The catalytic activity can be stabilized by either adding sodium hydroxide, which removes the adsorbed products by increasing their solubility, or increasing the gold concentration in the catalyst to ~10%. In addition, FDCA was prepared in high yields (94% – 96%) by the oxidation of HMF in water in the absence of bases catalyzed by Au-Pd alloy nanoparticles supported on carbon nanotubes.[169]

Attempts have been made to manufacture catalysts for FDCA synthesis using less expensive transition metals.[149, 151, 152] For example, HMF oxidation by treatment with Bu^tOOH in acetonitrile catalyzed by a Co^{II} complex with *meso*-tetra(4-pyridyl)porphyrin supported on a polymer affords FDCA in a yield of 90.4%.[170] When HMF was oxidized with molecular oxygen in 4-chlorotoluene at 110 °C in the presence of amino-modified SBA-15 silica gels containing immobilized VO^{2+} and Cu^{2+} ions, the yield of FDCA was 62.7%,[171] while the use of a spinel-type metal oxide catalyst ($Li_2CoMn_3O_8$) and NaBr as a co-catalyst in the aerobic oxidation of HMF in acetic acid at 150 °C provided an 80% isolated yield of FDCA in the synthesis on a gram scale.[172] Catalysts based on Fe^{3+} complexes with porphyrin can drive the aerobic oxidation of HMF in water to give FDCA in a 79% yield.[173] Neaţu *et al.*[174] proposed a two-step process, the first step being the non-catalyzed aerobic oxidation of HMF to FFCA in an alkaline aqueous solution followed by the separation of the formed humic impurities and the second step being the catalytic oxidation of FFCA to FDCA with oxygen at a pressure of 8 atm and a temperature of 90 °C for 24 h using catalysts based on mixed manganese and iron oxides (Scheme 8). The selectivity of the first step was ~80%, and the selectivity of the second step (according to HPLC data) approached 100%.

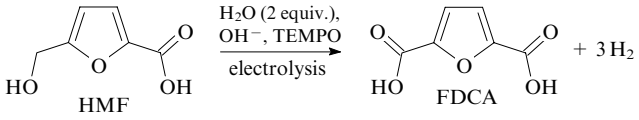
Scheme 8



It is noteworthy that FFCA can be obtained in a ~90% yield (according to HPLC) by the oxidation of HMF in water with oxygen or air without bases with a mixed copper and cerium oxide ($CuO \cdot CeO_2$) as the catalyst. Therefore, FFCA can become a new accessible reagent.[175] Generally, heterogeneous catalysts based on non-noble metals are less efficient than those based on Au, Pt, Pd or Ru.[149, 151, 152]

A number of electrocatalytic processes for the oxidation of HMF to FDCA in alkaline aqueous solutions have been proposed, using a variety of anodic materials, for example, $NiO/Ni(OH)_2$ (71% yield), $PdAu_2/C$ (83% yield, but the product is contaminated by a HMFCA impurity difficult to separate) and Pt/C (80% yield).[152] In recently developed electrochemical and photoelectrochemical processes, the HMF oxidation to FDCA occurs in a borate buffer at pH 9.2 and 40 °C (the FDCA yield is 98% based on HMF, and the faradaic efficiency is 93%) on gold, $BiVO_4$ or carbon felt anodes.[176] A key distinctive feature of this method is the use of 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) as an oxidation mediator (Scheme 9). However, the necessity of using a too large amount of the mediator [TEMPO : HMF = 1.5 (mol.)] calls for the further optimization of the method for the possibility of practical implementation.

Scheme 9



Several biocatalytic methods for the oxidation of HMF to FDCA by enzymes generated by microorganisms have also been reported.[152] These methods afford FDCA in yields of >95% at room temperature. Considerable drawbacks of the biocatalytic methods are too long a reaction time (usually, at least 24 h) and the necessity to use solutions with a low concentration of HMF ($10^{-1} – 10^{-3}$ mol liter^{-1}).

Although FDCA is formed from HMF in high yield, the cost of HMF as a feedstock is still rather high. The synthesis of FDCA and other monomers directly from carbohydrates without the isolation of HMF is considered to be a promising approach.[14, 146, 149, 152] However, carbohydrates are readily oxidized by the same oxidants as HMF is. Therefore, it is necessary to separate the dehydration of carbohydrates to HMF and the oxidation of HMF to FDCA either in space or in time. The former approach is usually implemented in heterogeneous systems. For example, Kröger *et al.*[177] demonstrated for the first time the possibility of the FDCA synthesis from fructose in a reactor consisting of two chambers separated by a membrane. In one chamber, the HMF synthesis occurs in a stirred aqueous solution of fructose with an acid-type heterogeneous catalyst, and in the second chamber, HMF that has penetrated through the membrane is oxidized to FDCA in a MIBK solution in the presence of a heterogeneous catalyst (PtBi/C). The yield of FDCA in this reactor is only 25%, with the HMF diffusion through the membrane being the rate-limiting step. An attempt was also made to encapsulate the heterogeneous catalyst into a silicone shell, which was then saturated with MIBK, and grains of this catalyst were used for the one-pot synthesis of HMF; however, the yield of FDCA was also only ~25%.[177] For the one-pot synthesis of FDCA, the use of cobalt acetylacetonate particles encapsulated into silica membranes has been proposed. Silica functions as an acidic catalyst and accelerates the dehydration of fructose, which diffuses towards the cobalt acetylacetonate surface on which the HMF formed is oxidized to FDCA.[152] Recently, a synthesis of FDCA from fructose in a three-phase reactor has been reported.[178] The principle of the reactor operation is illustrated in Fig. 4. In one compartment of the reactor, a carbohydrate is dehydrated in a system comprising a tetraethylammonium bromide melt and water with dispersed acidic cation exchanger and dissolved (in the case of synthesis from glucose) $CrCl_3$ (phase *1*). The resulting HMF is extracted with MIBK (phase *2*) and migrates *via* a special bridge filled with MIBK into the second compartment containing an aqueous solution of Na_2CO_3 and a suspended Au_8Pd_2/hydrotalcite catalyst (phase *3*). An air flow is passed through phase *3*. According to Yi, Teong and Zhang,[178] the yields of FDCA in this reactor are 78% and 50% for the syntheses from fructose and glucose, respec-

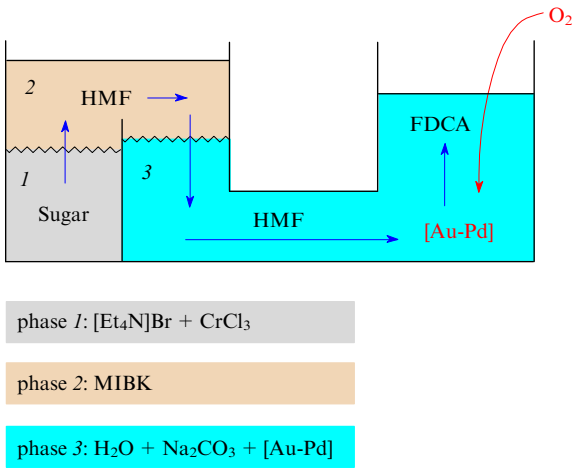


Figure 4. Synthesis of furan-2,5-dicarboxylic acid from carbohydrates in a three-phase reactor.[178]

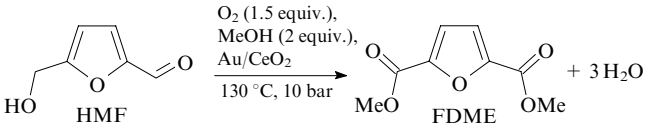
tively; however, the time required for the reaction is ~20 h. The process rate is limited by the mass transfer of HMF from phase *1* to phase *3*.

According to the latter approach, the acid-catalyzed dehydration of a carbohydrate in isopropyl alcohol is first carried out, and the solvent is then distilled off. Then, the HMF (formed in ~85% yield) is back-extracted into water to separate the humins and other impurities and then oxidized with oxygen in the presence of the Au/hydrotalcite catalyst, with the overall yield of the FDCA based on fructose being ~83%.[179] Wang *et al.*[180] reported the synthesis of FDCA including the dehydration of fructose in DMSO catalyzed by Fe_3O_4@SiO_2-SO_3H, which is then separated in a magnetic field, and oxidation with Bu^tOOH catalyzed by $Fe_3O_4-CoO_x$. This process gave FDCA in a 59.8% yield based on fructose.

Although one-pot processes of FDCA synthesis from carbohydrates without the isolation of crystalline HMF are still to be markedly improved, their further development seems quite promising for the industrial production of FDCA from plant raw materials, as they eliminate expenses for the purification, storage and transportation of unstable HMF.

An important FDCA derivative is the corresponding dimethyl ester (FDME), which is used for the synthesis of polyethylene furanoate.[147,150] This ester can be prepared in high yield by the oxidative esterification of HMF in methanol with the use of gold-based heterogeneous catalysts, for example, Au/CeO_2 or Au/TiO_2, in the presence of MeONa (Scheme 10).[152] Dimethyl furan-2,5-dicarboxylate is purified rather easily by vacuum sublimation.[152]

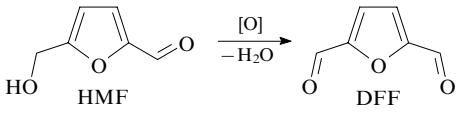
Scheme 10



III.1.b. 2,5-Diformylfuran

However, another important derivative of HMF that is promising for the manufacture of polymeric materials and pharmaceuticals is 2,5-diformylfuran (DFF).[20,147] Unlike HMF, DFF has a relatively high melting point (109–110 °C), is non-hygroscopic and can be readily isolated from aqueous solutions by extraction into organic solvents and purified by recrystallization from either organic solvents or water; it is quite stable in the crystalline state and can be stored and transported.[181] Numerous methods have been developed for the preparation of DFF by the oxidation of HMF (Scheme 11).[20,147]

Scheme 11



The oxidation of HMF to DFF can be accomplished by organic and inorganic oxidants: $K_2Cr_2O_7$–DMSO, $MnO_2-CH_2Cl_2$, NaOCl + Mn^{III}, 2-iodoxybenzamides supported on polymers, NaClO or halogens + TEMPO, H_2O_2 in the presence of chloroperoxidase (see reviews[20,30]), (diacetoxyiodo)benzene + TEMPO in acetic acid,[182] DMSO in the presence of HBr or NaBr,[183,184] 4-acetamido-2,2,6,6-tetramethyl-1-oxopiperidinium tetrafluoroborate in ionic liquids,[185] $NaNO_2$ in trifluoroacetic acid [186] and so on. These oxidants enable the formation of DFF in a 60%–100% yield and are convenient for laboratory synthesis; however, their use on an industrial scale is hampered by either the formation of large amounts of toxic wastes or the high cost of the oxidation systems.

Catalytic oxidation with molecular oxygen or air in the presence of homogeneous or heterogeneous catalysts is considered to be more suitable for industrial application. High yields of DFF can be attained in the presence of a variety of catalytic systems based on transition metal salts [Co, Mn, V, Cr,[20,147] $VOSO_4/Cu(NO_3)_2$ (Ref. 187)] or combinations of transition metal salts with nitroxides or their precursors [CuCl–TEMPO in the presence of chelating amines or pyridine derivatives,[188] $Cu(NO_3)_2$–NHPI (NHPI is *N*-hydroxyphthalimide),[189] $Cu(NO_3)_2$–1-hydroxybenzotriazole,[190] $Fe(NO_3)_3$–NHPI,[191] $Fe(NO_3)_3$–TEMPO [192]]. Two patents claim a homogeneously catalyzed process of HMF oxidation with oxygen in the AcOH–4-AcNH-TEMPO–HNO_3 system (4-AcNH-TEMPO is 4-acetamido-2,2,6,6-tetramethylpiperidin-1-oxyl) at temperatures of 50–80 °C to give DFF in a ~98% yield.[193,194] An enzymatic aerobic HMF oxidation process to give DFF in a yield of 92% has been developed recently; however, the oxidation requires too long a time (~96 h).[195]

Quite a few efficient heterogeneous catalysts for the aerobic oxidation of HMF to DFF have been devised.[147] High yields of DFF are attained when the reaction is catalyzed by various vanadium,[196–203] ruthenium [204–213] or manganese compounds,[214–216] gold nanoparticles supported on manganese oxide (Au/MnO_2),[217] Ag-OMS-2 (Ag-OMS-2 = $AgMn_8O_{16}\cdot n\,H_2O$),[218] $Mn_{0.70}Cu_{0.05}Al_{0.25}$ (Ref. 219) or molybdenum compounds $Cs_xH_{3-x}PMo_{12}O_{40}$ (x = 0.5, 1.5, 2.5).[220] Recently, copper nanoparticles supported on cellulose in solutions of $Bi(NO_3)_3\cdot 5\,H_2O$ in acetonitrile have been demonstrated to be efficient towards the aerobic oxidation of HMF [the yield of DFF is 82% (Ref. 221)]. However, the large amount of bismuth nitrate required for the process (0.75 mol per mol of HMF) is a

severe drawback of this method. An efficient catalyst based on carbon-supported partially reduced iron and cobalt oxides has been proposed. With this catalyst, the oxidation of HMF with oxygen in toluene at 1 MPa in the presence of Na_2CO_3 (1 : 1 relative to HMF) gives DFF in a quantitative yield; furthermore, the catalytic system can be reused many times without a significant decline of the activity.[222] Heterogeneous catalysts free from transition metals have also been proposed for the aerobic oxidation of HMF to DFF. These catalysts include graphene oxide in DMSO,[223] graphene oxide in the presence of dissolved TEMPO as a co-catalyst in organic solvents,[224, 225] and TEMPO derivatives immobilized on SiO_2 (Refs 226, 227) or $Fe_3O_4@SiO_2$.[228]

A preparative electrocatalytic method for the synthesis of DFF giving the product in 61% – 63% isolated yields has been reported.[181] The reaction is catalyzed by 4-AcNH-TEMPO in a two-phase system consisting of CH_2Cl_2 and an aqueous electrolyte ($KI + NaHCO_3 + Na_2SO_4$). The method is distinguished by the easy isolation and purification of DFF and the possibility of the repeated use of the electrolyte.[181]

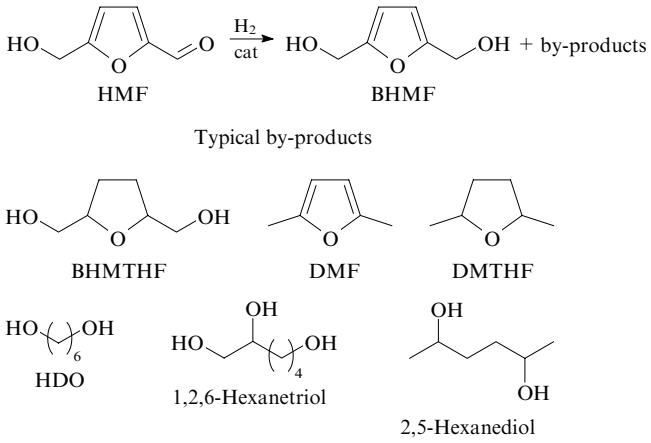
One-pot syntheses of DFF from carbohydrates have also been proposed.[146] For example, 4-acetamido-2,2,6,6-tetramethyl-1-oxopiperidine tetrafluoroborate was used as the oxidant in a one-pot synthesis of DFF (95% yield) from fructose in ionic liquids.[185] A one-pot synthesis of DFF from fructose (45% – 80% yield) or from glucose (26% – 28% yield) in DMSO, which serves as both a solvent and an oxidant, with NaBr, HBr or NaBr + HCOOH as the catalyst has been developed.[183] A one-pot process for the DFF synthesis from fructose that appears to be more suitable for scaling-up is based on the WO_3HO-VO(Salten)-$SiO_2@Fe_3O_4$ bifunctional catalyst [Salten is bis(3-salicylideneaminopropyl)amine] and hydrogen peroxide as the oxidant in propan-2-ol; this procedure gives DFF in 60% isolated yield.[229] Other developed one-pot syntheses of DFF from fructose employ air or oxygen as oxidants and heterogeneous catalysts based on vanadium compounds (60% – 71% yield),[200 – 202, 229] $Cs_{0.5}H_{2.5}PMo_{12}$ (69% yield)[220] or ruthenium compounds (49% – 79% yield),[206, 230] magnetic catalysts Fe_3O_4-SBA-SO_3H (SBA is mesoporous silica) or K-OMS-2 (K-OMS-2 = $KMn_8O_{16} \cdot n\,H_2O$) (80% yield)[214] and graphene oxide in a two-stage one-pot process (72% yield).[223]

III.1.c. 2,5-Bis(hydroxymethyl)furan and 2,5-bis(hydroxymethyl)tetrahydrofuran

2,5-Bis(hydroxymethyl)furan and 2,5-bis(hydroxymethyl)-tetrahydrofuran (BHMTHF) are considered highly promising monomers for the production of polyesters.[147]

The key method for the synthesis of BHMF is the hydrogenation of HMF (Scheme 12).[20, 147, 231] For preparative purposes, BHMF is convenient to obtain by reducing HMF with $NaBH_4$, whereas for industrial implementation, hydrogenation with hydrogen at elevated pressure with heterogeneous catalysts is preferred.[20, 147, 231] The key by-product formed in the heterogeneously catalyzed hydrogenation with hydrogen, especially at elevated temperatures, is BHMTHF, which has its own value as a monomer. Other typical by-products are 2,5-dimethylfuran (DMF) and 2,5-dimethyltetrahydrofuran (DMTHF), hexane-1,6-diol (HDO), hexane-1,2,6-triol and hexane-2,5-diol (see Scheme 12).[147, 159] As highly selective catalysts, various supported metals are used: Pt/C, Ru/C, Pt/Al_2O_3, Co/SiO_2, Cu/SiO_2, Cu/ZnO, Pd/C, Ir/TiO_2, Au/Al_2O_3, Ir-ReO_x/SiO_2, 2 $CuO \cdot Cr_2O_3$ and Pt_2O/C.[20, 147, 231 – 234] Often, water is the most appropriate solvent, although rather good results have also been obtained in ionic liquids, dioxane and THF. The hydrogen pressure is usually 8 – 80 atm, and the temperature is 35 – 120 °C. The yields of BHMF under optimal conditions vary from 80% to ~100%.[147, 235]

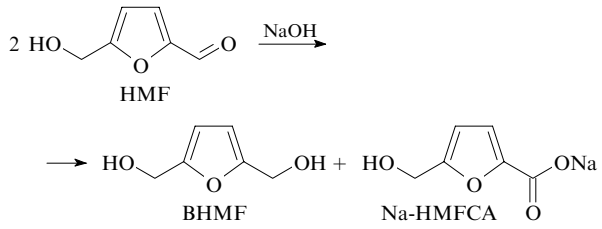
Scheme 12



One more convenient method for the preparation of BHMF is catalytic hydrogen transfer hydrogenation. The possible hydrogen donors are methanol with MgO as the catalyst at 160 °C (the yield is ~100% in 3 h)[236] and ethanol with $ZrO(OH)_2$ as the catalyst at 150 °C (the yield is ~83%),[237] whereas the use of propan-2-ol with Lewis acid catalysts (γ-Al_2O_3, ZrO_2, TiO_2, ZrO_2/SBA-15, TiO_2/SBA-15) results in the formation of the corresponding BHMF ethers.[238]

However, another possible pathway to BHMF is the Canizzaro reaction (Scheme 13). A simple method has been proposed recently for the joint preparation of BHMF (87% isolated yield) and sodium 5-hydroxymethylfuran-2-carboxylate (83% isolated yield) by the treatment of HMF in water with NaOH (0.9 equiv.) with the subsequent separation of the two products by the crystallization of the sodium salt from ethyl acetate.[239]

Scheme 13

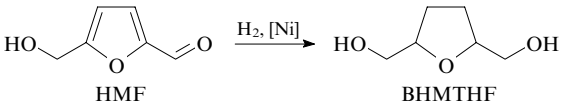


The electrocatalytic reduction of HMF to BHMF, which is the major HMF reduction product formed on a Ag, Fe, Ni, Zn, Cd or In cathode in an aqueous solution of sodium sulfate, may be of certain interest. The highest selectivity (> 85%) was attained on a silver cathode[240] or Fe, Ni, Cu or Pb cathode in 0.5 M H_2SO_4 (the highest activity was exhibited by Ni cathodes at a potential of −0.35 V *vs.* SHE and a current density of 20 mA cm^{-2}).[241] The recently developed photoelectrochemical synthesis of BHMF from HMF is conducted in aqueous solution at pH 9.2 (borate buffer) with silver cathodes and a $BiVO_4$ electrode function-

ing as the photoanode.[242] The HMF reduction gives BHMF with a selectivity and faradaic efficiency approaching 100%.

An efficient approach to the synthesis of BHMTHF is the hydrogenation of HMF with hydrogen catalyzed by heterogeneous nickel catalysts in the temperature range of 60–200 °C and an H_2 pressure range of 60–140 atm (Scheme 14).[20, 147, 159, 231, 243] The most efficient catalysts are Raney nickel, Ni/kieselguhr, Ni-Fe/CNT (CNT are carbon nanotubes), Ni/Al_2O_3 and $Ni\text{-}Pd/SiO_2$.[147, 244, 245] Other applicable catalysts are Pd/C and Ru/CeO_2.[147] Water, diethyl ether, ethanol and some other compounds have been tested as solvents. The yields of BHMTHF can be as high as 90%–100%.

Scheme 14



III.1.d. 2,5-Bis(aminomethyl)furan

2,5-Bis(aminomethyl)furan (BAMF) is of interest as a monomer for the synthesis of polyamides.[147] The key methods for the preparation of BAMF are the reductive amination of DFF and the ammonolysis of BHMF (Scheme 15).[147, 246]

The reductive amination of DFF can be catalyzed by Raney nickel, iridium complexes, Ni/CaO, Cu/Fe_2O_3 and Ru/ZrO_2. For the ammonolysis of BHMF, ruthenium complexes have also been used.[147, 246]

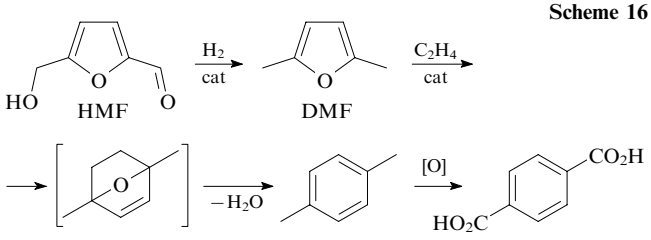
III.1.e. Monomer without a furan ring prepared from 5-hydroxymethylfurfural

The HMF furan ring is fairly reactive and can undergo various ring-opening transformations. Therefore, HMF and its derivatives can serve as feedstocks for the production of various monomers containing no furan ring in the molecule.[20, 147]

In this respect, most attention has been attracted by the synthesis of *p*-xylene, which can be used for the commercial production of terephthalic acid *via* oxidation. *p*-Xylene is synthesized by the Diels–Alder reaction of 2,5-dimethylfuran obtained by the hydrogenation of HMF (see Section III.4.a below) with ethylene (Scheme 16).[147, 247–251] The cycloaddition is usually catalyzed by Lewis acids; zirconium-containing zeolites are especially efficient and afford *p*-xylene in a yield of ~90%.[247]

Apart from DMF, other HMF derivatives such as 5-hydroxymethylfuran-2-carboxylic acid (HMFCA) are

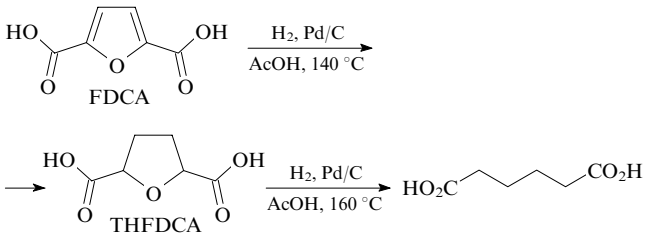
Scheme 16



also able to add ethylene according to the Diels–Alder reaction pattern to give 2,4-disubstituted benzenes, which can be oxidized to terephthalic acid.[252, 253] The synthesis of terephthalic acid from HMF oxidation products could become more economically feasible than the synthesis from DMF; however, the yields of the Diels–Alder adducts from HMFCA and its derivatives do not exceed 53%.[252, 253]

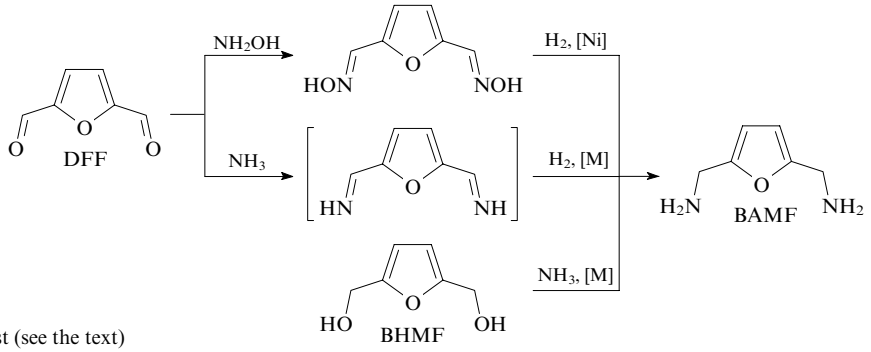
Upon hydrogenation with hydrogen on palladium catalysts in acetic acid, FDCA is converted to tetrahydrofuran-2,5-dicarboxylic acid (THFDCA), which is then converted to adipic acid (Scheme 17).[20, 254] An important compound obtained from HMF is hexane-1,6-diol (HDO).[255] Apart from its direct use in the synthesis of polyesters, HDO can also be used for the preparation of adipic acid or caprolactam (Scheme 18).[256, 257]

Scheme 17



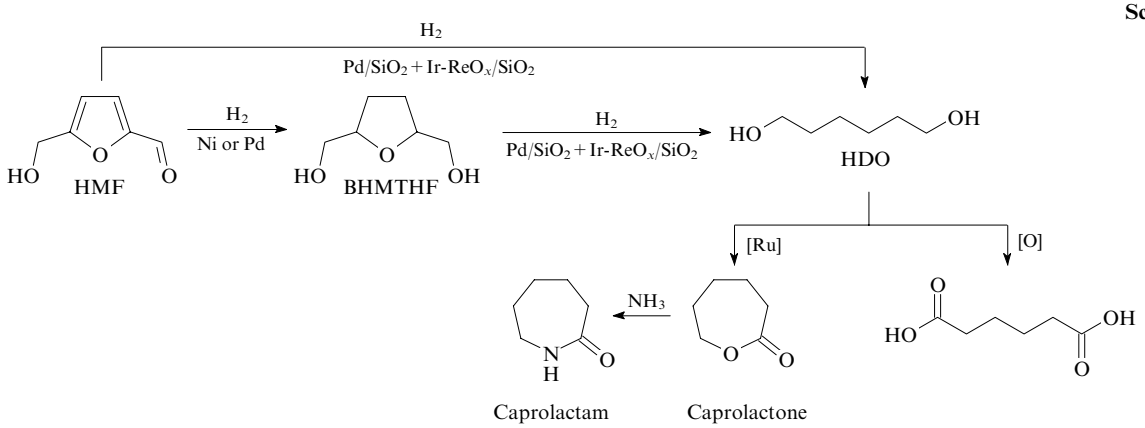
5-Hydroxymethylfurfural can serve as the feedstock for the production of maleic anhydride. For example, the oxidation of HMF with oxygen (at 10 atm) in acetic acid at 100 °C for 4 h in the presence of vanadium catalysts [V_2O_5, $VOHPO_4$, $(VO)_2P_2O_7$] gives 75%–79% yields of maleic anhydride (Scheme 19).[258] Maleic anhydride can be prepared in an overall yield of 44%–50% without the purification of the crude HMF (resulting from the dehydration of fructose in isopropyl alcohol) using vanadium oxide as the catalyst.[258] Quite similar results were obtained upon the oxidation of HMF with oxygen in mixtures of acetic acid with acetonitrile in the presence of the

Scheme 15



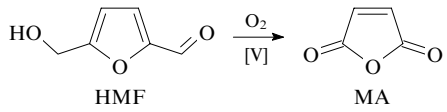
M is a metal-containing catalyst (see the text)

Scheme 18



$H_5PV_2Mo_{10}O_{40} \cdot x\,H_2O$ catalyst (90 °C) [259] or vanadium acetylacetonate.[260]

Scheme 19



III.2. Polymeric materials based on 5-hydroxymethylfurfural and its derivatives

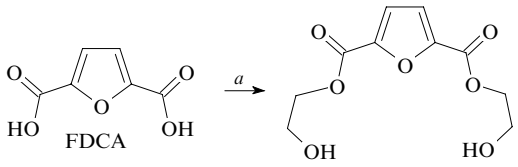
This section addresses polymeric materials based only on HMF derivatives that contain furan rings. Since HMF can also serve as the source of terephthalic and maleic acid derivatives and acyclic diols, the scope of the applicability of HMF as a feedstock for the polymer industry becomes much wider.

III.2.a. Polymers based on furan-2,5-dicarboxylic acid

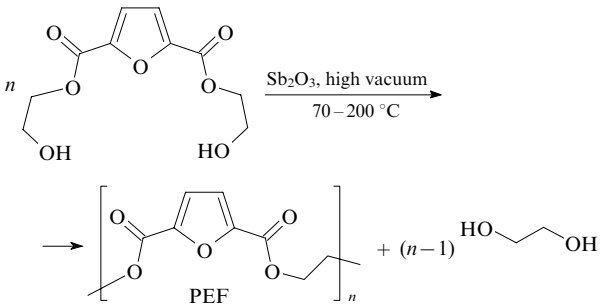
The most important polymeric derivatives of FDCA are polyesters. According to estimates of industry consulting companies, more than 60% of produced FDCA will be spent by 2020 for the manufacture of polyesters to replace the polyesters based on adipic and terephthalic acids and obtained from fossil raw materials.[149] Among the FDCA-based polyesters, the most attention has been attracted by polyethylene furanoate (PEF).[147–150, 154, 155, 261, 262] This polyester is a non-toxic, biocompatible polymer completely based on plant raw materials that could replace, in the near future,[155] polyethylene terephthalate (PET) — one of the most abundant polymers (with a world output of ~50 million tons per year).[263] Polyethylene furanoate has better physicomechanical characteristics (thermal plasticity, mechanical strength, *etc*.) than PET, and its gas permeability is substantially lower (10–11 times for O_2 and 2–19 times for CO_2, depending on the polyester preparation method).[149, 261] These properties make PEF a remarkable material for the manufacture of plastic packaging for carbonated beverages, the output volume of which on the basis of PET is now ~15 million tons per year (estimated [264] as of 2009). Furthermore, PEF could replace PET in the manufacture of textile fibers, packaging films, nanocomposite coating materials [265] and other articles.[149, 266] Recently, PEF was shown to be biodegraded under the action of enzymes produced by *Thermobifida cellulosilytica*.[153] The expenditure of non-renewable energy (generated from fossil or nuclear fuel) and the amounts of CO_2 emissions should be 43%–5% and 45%–70%, respectively, lower in the manufacture of PEF than in the manufacture of PET.[261, 264] The five world's largest consumers of polymeric materials — Coca-Cola, Ford Motor, Heinz, Nike and Procter & Gamble — announced in 2012 that by 2020 they were going to switch from PET produced from fossil raw materials to polymers completely produced from renewable plant sources, with expectations being mainly associated with PEF.[149] Since 2010, PEF has been industrially manufactured on a small scale by the Avantium company.[150, 266] A large-scale production of this polymer is planned for the near future.

Although PEF was obtained for the first time in the 1940s,[149, 150] broad interest in this material was aroused in 2009 after the publication of Gandini *et al*.,[267] who described the key physicomechanical properties and the two-step synthesis of this polymer (Scheme 20).

Scheme 20



(*a*) $HO(CH_2)_2OH$ (10 mol.), HCl (aq.), 75 °C, 6 h



Polyethylene furanoate with a molecular weight (M_n) of ~83 000 g mol^{-1} has a glass transition temperature of 75–80 °C and melting temperature of 210–215 °C; it is thermally stable up to 300 °C;[267] the Young's modulus is 2070–2450 MPa; the tensile yield stress is 35–67 MPa; and the elongation at break is only 3%–4%.[150, 268] Depending on the polymerization method and the degree of crystal-

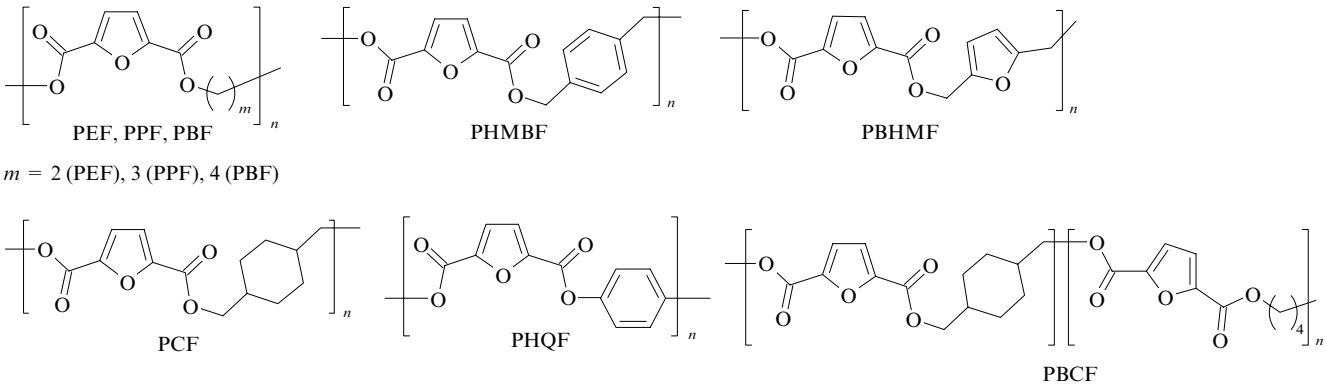


Figure 5. Most important polyesters derived from furan-2,5-dicarboxylic acid.

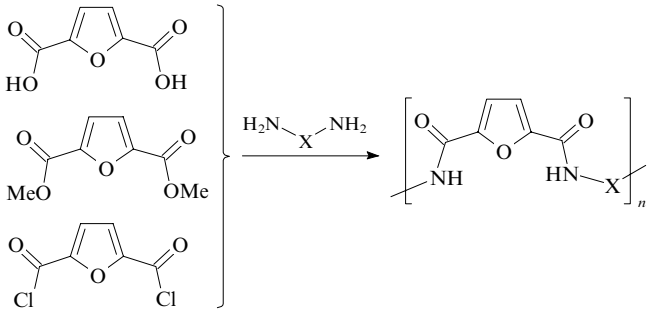
linity of the polyester, these parameters should substantially vary.[149, 268]

One more FDCA polyester that has prospects of industrial manufacture in the near future is polypropylene furanoate (PPF, $m = 3$, Fig. 5). This polymer, which would presumably be completely produced from renewable raw materials, could also be employed for the manufacture of packaging for carbonated beverages and food products.[269] In January 2016, DuPont and ADM announced the development of a PPF production process based on the reaction of dimethyl furandicarboxylate (FDME) with propane-1,3-diol and the planned construction of a pilot plant in Decatur (Illinois, USA).[25, 155] In its physicomechanical characteristics, polybutylene furanoate (PBF) is similar to polybutylene terephthalate and holds good promise as an alternative to this plastic in the future.[270] A variety of polyesters based on aliphatic diols with a greater number of methylene units; polyesters based on aromatic diols (PHMBF) and phenols (PHQF), FDCA and BHMF (PBHMF) and 1,4-cyclohexanedimethanol (PCF); and FDCA copolymers with lactic acid, various dicarboxylic acids and diols, *e.g.*, PBCF, have been developed (see Fig. 5).[149, 150, 261, 263, 271] According to *in vitro* tests, the FDCA copolymers with ethylene glycol and lactic acid are much more biodegradable, while their physicomechanical properties are close to those of PEF homopolymers.[272]

The key methods for the synthesis of these polyesters include the direct polycondensation of FDCA with diols and the high-temperature transesterification of FDME. These reactions are usually catalyzed by Lewis acids. The methods for the synthesis of various polyesters based on FDCA are discussed in detail in a number of dedicated reviews.[148–150, 261]

However, another important class of polymeric FDCA derivatives is the polyamides.[150, 273] Furandicarboxylic acid polyamides are usually obtained by the ammonolysis of FDME with aliphatic diamines at high temperatures, by the reaction of various diamines with FDCA dichloride in solutions or heterogeneous systems, or by heating FDCA salts at temperatures above 200 °C (Scheme 21).[150] Since the reactions of FDME with diamines are accompanied by the partial methylation of the amino groups, a two-step process for the polyamide synthesis has been proposed.[273] The first step is the preparation of oligoamides by the reaction of FDME with aliphatic diamines at ~50 °C, while the second step is the cross-linking of the oligoamides through treatment with a bifunctional linker, such as furan-2,5-dicarboxylic acid dichloride or phthalic acid dichlorides.[273] There are also methods for the preparation of polyamides by the reaction of FDME with terminal aliphatic diamines with different numbers of methylene units, catalyzed by the Novozym 435 enzyme produced by *Candida antarctica*.[274, 275] An advantage of the enzymatic synthesis is a higher molecular weight of the polymers achieved in this case compared with that using conventional methods. The physicomechanical properties of FDCA-based polyamides have not been adequately studied as of yet, especially those of arylene amides.[150] Polymers based on aliphatic diamines are comparable in some parameters with phthalic acid polyamides.[273–276]

Scheme 21



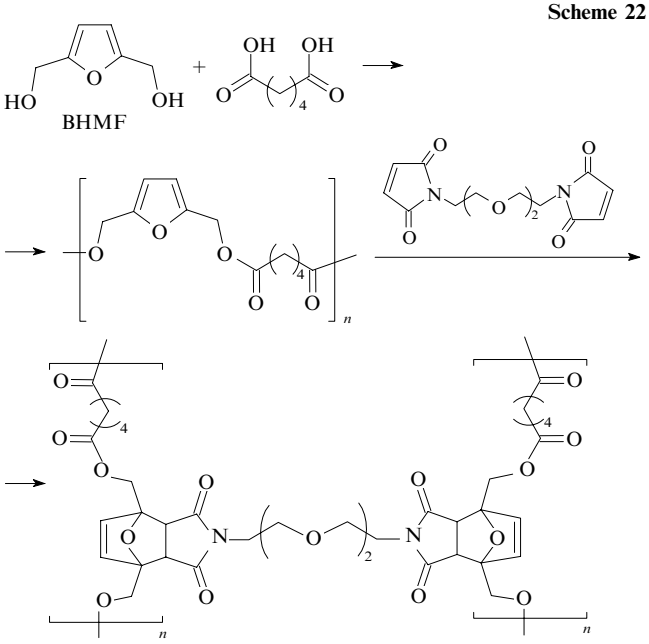
X = $(CH_2)_m$, cycloalkanediyl, arylene

Apart from polyesters and polyamides, other polymeric FDCA derivatives have also been reported. They include polyester ketones obtained by the Friedel–Crafts reaction of FDCA dichloride with aromatic esters;[277] polyester amides synthesized by the reaction of 2,5-bis(oxazolin-2-yl)furan with sebacic acid;[278] polyester urethanes,[279] polyepoxides[280] and other derivatives.[150]

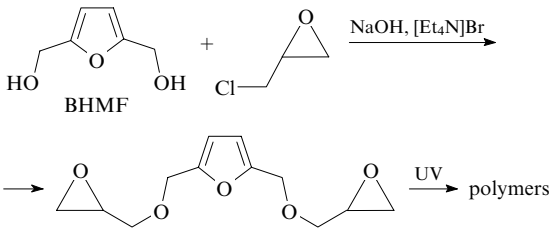
III.2.b. Polymers based on other 5-hydroxymethylfurfural derivatives

2,5-Bis(hydroxymethyl)furan and -tetrahydrofuran can be used for the preparation of polyesters and polyurethanes.[147, 148] BHMF polyesters can undergo a reversible Diels–Alder reaction with bis-maleimides (Scheme 22) to give polymers with physicomechanical properties varying over a broad range and with the capacity for self-recovery

Scheme 22



Scheme 23

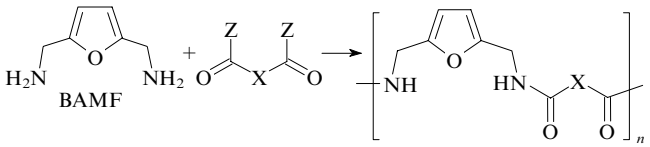


upon mechanical damage [281, 282] as well as a shape memory effect.[283] The reaction of BHMF with epichlorohydrins gives rise to epoxides (Scheme 23), which readily polymerize on exposure to UV radiation and can be used as photocurable polymeric materials.[284]

Difuran polyols obtained by the benzoin condensation of HMF with the subsequent reduction or oxidation of the adducts react with isocyanates to give polyurethanes (Scheme 24).[285]

A patent describes the application of 2,5-bis(aminomethyl)furan (BAMF) and 2,5-bis(aminomethyl)tetrahydrofuran for the synthesis of polyamides (Scheme 25) and polyurethanes and the curing of epoxy resins.[147]

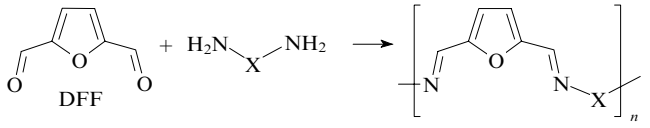
Scheme 25



X = $(CH_2)_m$, aryl, 2,5-furandiyl; Z = OH, Cl, *etc.*

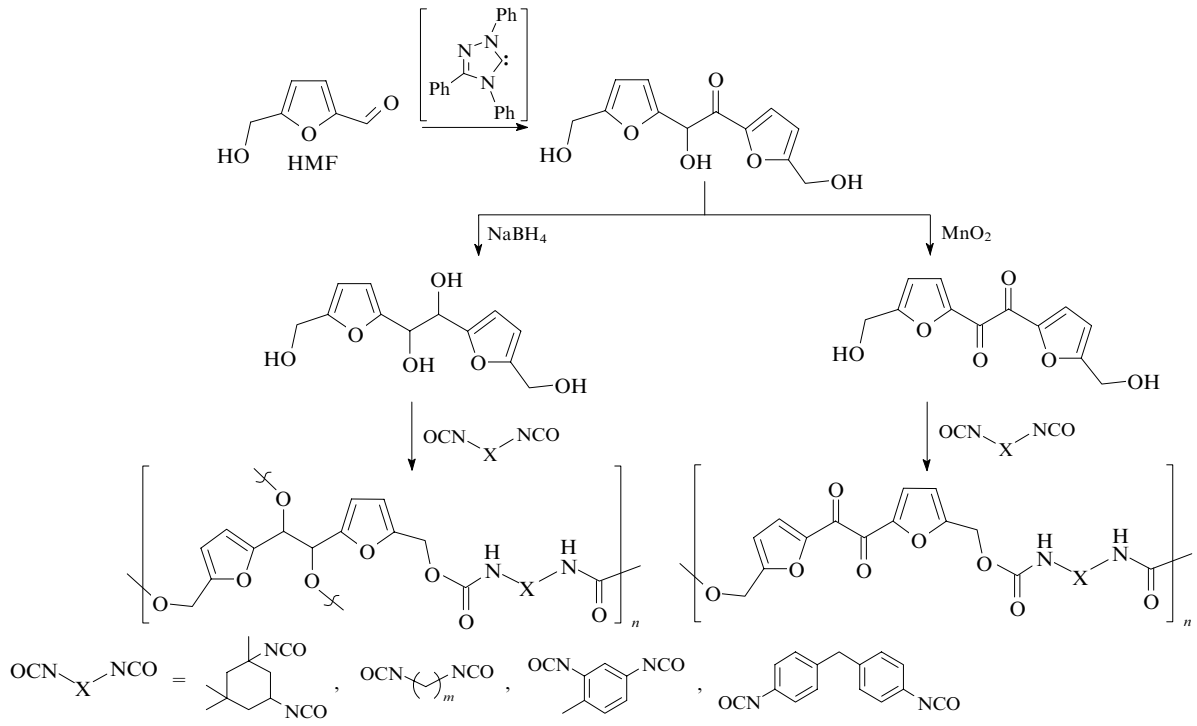
2,5-Diformylfuran and various diamines can also serve for the preparation of polyimines (Scheme 26), which can be used as liquid crystals in various optical devices.[147, 286] The reactions with dicarboxylic acid bis-hydrazides afford polymeric hydrazones with valuable optical properties.[147, 286] A number of resins based on the products of DFF condensa-

Scheme 26

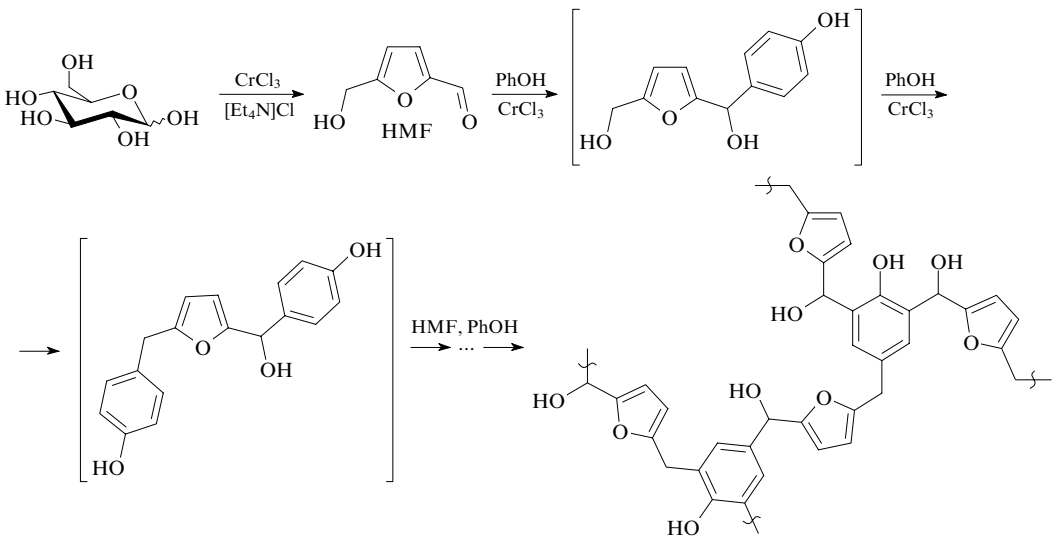


X = $(CH_2)_m$, aryl

Scheme 24



Scheme 27



tion with urea and phenols have been reported.[147] Porous polymeric materials obtained by DFF condensation with aromatic diamines have been studied as potential gas storage materials.[287] Polyarylvinylenes based on DFF can find use as semiconductor materials in organic transistors.[288]

5-Hydroxymethylfurfural, including that prepared *in situ* from carbohydrates, readily reacts with phenols to give complex polymers, analogues of the Novolac phenol formaldehyde resins. These polymers are applicable for the manufacture of composite plastics (Scheme 27).[289 – 292] The hydrolysis of lignin can serve as a renewable source of phenols for such polymers.[291, 293]

Other monomeric derivatives of HMF resulting from furan ring cleavage in various reactions such as hydrogenation (for example, hexane-1,6-diol), oxidation (maleic anhydride), hydrolysis (levulinic acid) and cycloaddition (terephthalic acid) markedly extend the scope of application of HMF in the synthesis of polymeric materials.

III.3. 5-Hydroxymethylfurfural in the synthesis of porous materials. Aerogels and other nanocarbon materials

5-Hydroxymethylfurfural serves for the manufacture of porous carbon materials, including carbon aerogels, electronically conducting materials with very low density and large specific surface area, that are used for the fabrication of electrodes in supercapacitors, storage batteries, fuel cells and other electrochemical devices and as sorbents, hydrogen storage materials, heat insulators and so on.[294, 295] Aerogels are usually obtained by the copolymerization of HMF with phenols followed by low-temperature (< 200 °C) carbonization.[294, 296 – 299] Often, HMF is formed in these processes from carbohydrates — fructose, glucose, cellulose and so on. The carbon materials produced by this method contain various polar groups on the pore surface and are hydrophilic, and hence they can be used as electrode materials[297] and sorbents for the extraction of cations and anions from aqueous solutions.[299]

5-Hydroxymethylfurfural formed *in situ* from carbohydrates also serves as the starting material for the production of supported graphenes by plasma pyrolysis[300] and graphene oxide by the oxidation of carbonized HMF-based polymers.[301]

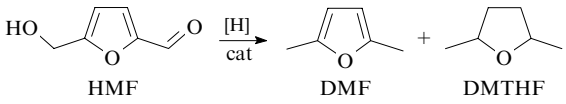
III.4. Motor fuels and solvents

III.4.a. 2,5-Dimethylfuran and 2,5-dimethyltetrahydrofuran

2,5-Dimethylfuran (DMF) is a most extensively investigated HMF derivative regarded as a promising component of motor fuels of the future.[10, 302 – 306] It has a high energy density (31.5 MJ liter^{-1}), an acceptable boiling point (92 – 94 °C) and a high research octane number (119).[6, 10, 146, 306, 307] In its kinematic parameters and combustion characteristics, DMF is comparable with motor petrol, and in some parameters, DMF is superior. It can be used as an efficient oxygenate additive to diesel fuel, reducing the soot formation.[308, 309] Furthermore, DMF is immiscible with water, thus favorably distinguishing it from ethanol and butanol, which are alternative renewable fuels.[302] Apart from its engine fuel application, DMF can serve as a feedstock for the production of *p*-xylene (see Section III.1.e) and 2,5-dimethyltetrahydrofuran (DMTHF). The latter is also a fairly promising motor fuel considered as an alternative to petrol and can also be used as a solvent. 2,5-Dimethyltetrahydrofuran possesses a high energy density (31 MJ liter^{-1}), is barely miscible with water, has a boiling point of 90 °C and is more stable during storage than DMF.[146, 310]

A key method for DMF synthesis is the hydrogenation of HMF in the presence of heterogeneous catalysts (Scheme 28).[6, 23, 74, 146, 231, 302, 306] The attention of the scientific community was drawn to DMF in 2007, after the publication of Dumesic and co-workers,[3] who proposed a two-step synthesis of DMF from fructose and discussed the key properties of DMF as a prospective fuel. The hydrogenation of HMF to DMF with hydrogen was performed in the presence of the copper ruthenium Cu-Ru/C catalyst [Cu : Ru = 3 : 1 (mol)] in butan-1-ol at 220 °C and 6.8 atm in a liquid-phase reactor (71% yield) and a flow vapor-phase reactor (76% – 79% yield).

Scheme 28



After the development of a synthetic route to DMF involving the copper ruthenium catalyst, quite a few other

catalysts based on noble metals have been tested.[6, 23, 231] 2,5-Dimethylfuran has been synthesized from HMF using a variety of ruthenium, palladium and platinum catalysts: Ru/C,[311 – 313] RuSn/C,[314] Ru-K-OMS-2 (2% Ru),[315] Ru/Co_3O_4,[316, 317] Ru-Cu-Fe_3O_4/N-rGO (N-rGo is nitrogen-doped graphene oxide),[133] Ru/hydrotalcite,[318] Ru-Sn/ZnO,[319] Ru/NaY-zeolite,[320] Pd/C,[321] Pd-$Cs_{2.5}H_{0.5}PW_{12}O_{40}$/ K-10 ($PW_{12}O_{40}$ is the dodecatungstophosphate anion, K-10 is montmorillonite),[322] Pd_xAu_y/C,[323] Pd-$ZnCl_2$/C,[324] Pd/Fe_2O_3,[325] Pt/C,[324] and Pt/rGO (rGO is reduced graphene oxide).[326] High activity was found for bimetallic catalysts: Pt_3Ni/C, Pt_2Zn/C and PtCu/C,[327] Pt_3Co_2/C,[328] PtCo@HCS (bimetallic PtCo nanoparticles surrounded by porous carbon spheres),[329] and PtNP@UiO-67 [platinum nanoparticles encapsulated in a metal-organic framework based on $Zr_6O_4(OH)_4(CO_2)_{12}$ and biphenyl-4,4′-dicarboxylic acid].[330] Most of the catalysts containing ruthenium, palladium or platinum are suitable for flow reactors and enable the synthesis of DMF in 70% to 98% yields.

There are efficient catalysts for the HMF hydrogenation to DMF based on non-noble metals, with nickel and copper being the most demanded.[307] Out of the nickel catalysts, worth noting are Raney nickel,[331] Ni/Al_2O_3,[243] Ni/perovskite,[307] Ni/OMD (OMD is mesoporous carbon-based supports enriched with nitrogen compounds resulting from the high-temperature decomposition of ethylenediamine),[332] silicate-supported nickel nanoparticles,[333] Ni/Co_3O_4 [334] and bimetallic Ni-Fe/CNT catalysts.[245] These catalysts afford DMF in yields of ~70% to 98%. Among the copper catalysts, noteworthy are Cu/ZnO,[233] ruthenium-doped Cu_{20}-Ru_2-PMO catalysts (PMO is a porous Mg and Al mixed oxide),[335] Cu/ZrO_2 [336] and CuZn alloy nano-sized particles.[337] Using copper catalysts, DMF can be prepared in an up to ~90% yield. The major by-product of HMF hydrogenation on copper and nickel catalysts is DMTHF.

Efficient methods have been developed for DMF synthesis by the hydrogen transfer hydrogenation of HMF. Propan-2-ol, methanol and formic acid are used as hydrogen sources, and Ru/C, Ru-RuO_2/C, Pd/Fe_2O_3 and Cu/PMO serve as catalysts.[302, 338 – 340]

In many cases, DMF can be obtained in good yields from carbohydrates without the isolation of the intermediate HMF or immediately after the extraction of HMF from the reaction mixture without further purification.[3, 146, 312, 313, 340]

An attempt has been made to perform the electrocatalytic reduction of HMF to DMF at various metal and graphite cathodes.[10, 240, 241, 302] The maximum selectivity to DMF (35.6%) was achieved in aqueous ethanol solutions of sulfuric acid at copper electrodes.[341]

2,5-Dimethyltetrahydrofuran is the product of the further hydrogenation of DMF; therefore, the yield of DMTHF usually increases with the increasing duration of synthesis and is accompanied by a parallel decrease in the yield of DMF.[243, 318] The selectivity of the HMF hydrogenation is considerably affected by not only the catalyst and the temperature but also the solvent, the fluid dynamic conditions in the vessel, the presence of impurities and so on.[74]

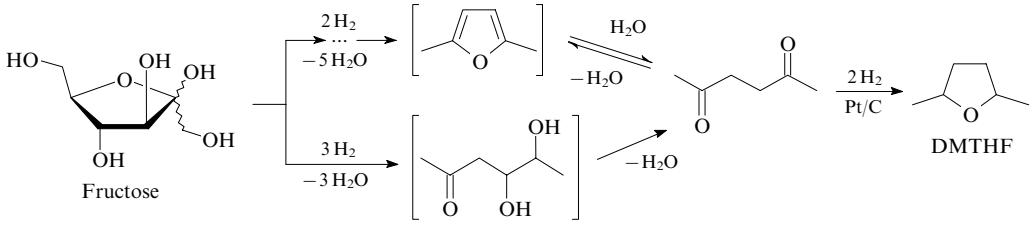
When HMF is hydrogenated to DMF and DMTHF in aqueous solutions in the presence of heterogeneous catalysts, the reaction system becomes three-phase (heterogeneous catalyst, aqueous solution, hydrogenation – hydrogenolysis organic products). Under these conditions, the process selectivity considerably depends on the fluid dynamics in the reactor.[342] In a study of transition metal-based catalysts (Pt/C, Ir/C, Pd/C, Ru/C, Ni/C, Co/C) in the three-phase system in a continuous flow reactor, the Pt/C and Ir/C catalysts showed low selectivity to DMTHF, whereas the highest selectivity was found for Pd/C.[342]

In organic solvents, a high selectivity to DMTHF was exhibited by Ni and Pd catalysts. Indeed, the hydrogenation of HMF with hydrogen in dioxane in a batch reactor with the $Ni/NiSiO_3$ catalyst at 150 °C and 1.5 MPa for 3 h gave DMTHF in a yield of 76.9% as a mixture with DMF (15.7% yield).[333] In a Ni/Al_2O_3-catalyzed reaction in dioxane at 180 °C and 1.2 MPa, the yield of DMTHF was 97.4% within 20 h,[243] while in the presence of the Pd/C catalyst, the reaction in dioxane containing some dimethyl dicarbonate [$(MeOC(O))_2O$ at a temperature of 120 °C and a pressure of ~2 atm resulted in an ~95% yield within 15 h.[321]

Several methods for the preparation of DMTHF from fructose have been developed.[146] For example, the one-pot hydrogenation of HMF with hydrogen in a [BMIm]Cl – THF two-phase system at 220 °C and 5 MPa on the Ru/C catalyst gave a mixture of DMF (47% yield) and DMTHF (20% yield).[312] Despite the fact that Pt catalysts demonstrate low selectivity in the three-phase system, in 90% ethanol, Pt/C catalysts poisoned by sulfur afford DMTHF from fructose in a 50% yield in a one-pot process at 175 °C and 10.3 MPa.[343] Presumably, the hydrogenation of fructose in this synthesis proceeds *via* hexane-2,5-dione without the intermediate formation of HMF (Scheme 29).

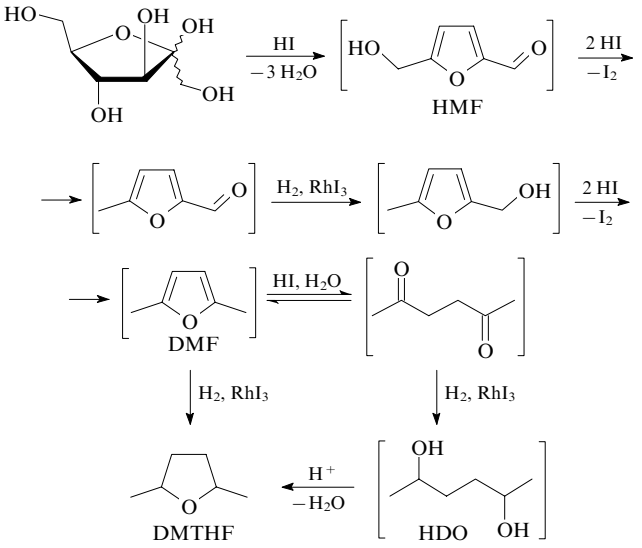
Of considerable interest is direct homogeneously catalyzed conversion of carbohydrates to DMTHF in two-phase systems comprising an aqueous solution (RhX_3 + HI) and an organic extractant (X = Cl, I).[344, 345] As the organic extractant, DMTHF can be used. The synthesis occurs at a hydrogen pressure of ~20 atm at 80 – 140 °C.[344] This process was studied in relation to fructose, glucose, saccharose, cellulose and lignocellulose. The yield of DMTHF varies from ~50% (from lignocellulose) to ~80% (from fructose). The catalytic system was found to be recyclable at least ten times without decreasing the yield of DMTHF from fructose. A detailed investigation of the reaction

Scheme 29



mechanism in relation to fructose demonstrated that HI plays a dual role: a catalyst of the fructose dehydration to HMF and a reducing agent for the hydroxymethyl groups (Scheme 30).[345] The I_2 thus formed is reduced with hydrogen in the presence of a Rh catalyst, which also catalyzes the hydrogenation of the C=O and C=C bonds. The process involves the parallel formation of acyclic intermediates, hexane-2,5-dione and hexane-2,5-diol.

Scheme 30



It is worth noting that DMTHF is also the key intermediate in the recently developed process for the direct cellulose conversion to liquid linear hydrocarbons *via* hydrogenation over ruthenium catalysts.[346, 347]

Recently, an alternative route to DMTHF has been proposed, involving the catalytic hydrogenation of hexane-2,5-dione over the Pt/C catalyst in the presence of a heterogeneous acidic catalyst, Amberlite IR-120H; the product yield is ~99%.[310] Hexane-2,5-dione can be obtained by the hydrolysis of DMF in the water–MIBK two-phase system[348] or by treating HMF in water with zinc.[349] The synthesis of DMTHF from DMF *via* hexane-2,5-dione can also be conducted as a one-pot process in 90% aqueous THF; the yield is 74%.[310]

III.4.b. 5-Ethoxymethylfurfural and other ethers and esters

The hydroxymethyl groups of HMF and BHMF are readily O-alkylated. The resulting ethers contain rather large numbers of carbon atoms and are considered promising motor fuel components.[2, 74, 304, 305] Most of the attention has been attracted by 5-ethoxymethylfurfural (EMF) and 2,5-bis(alkoxymethyl)furans (BMMF and BEMF) (Fig. 6).

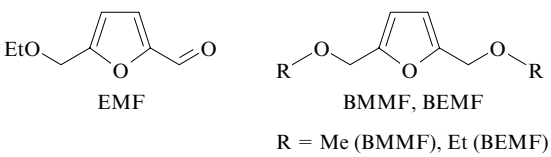
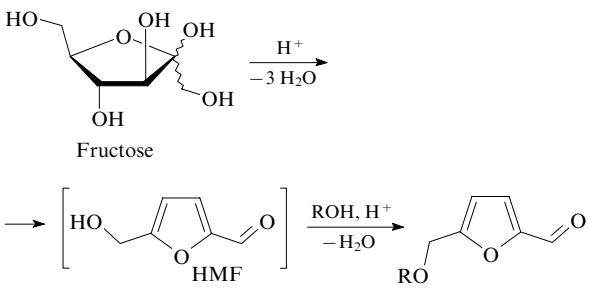


Figure 6. 5-Hydroxymethylfurfural- and 2,5-bis(hydroxymethyl)-furan-derived ethers.

5-Ethoxymethylfurfural can serve as a diesel fuel component (up to 20% of the total composition), decreasing the soot and scale formation and the sulfur oxide emissions. The energy density of EMF is 30.3 MJ liter^{-1}, which is close to the value for a typical diesel fuel (33.6 MJ liter^{-1}).[304] Apart from being used as a fuel, EMF is widely utilized as a flavoring agent for wine and beer.[304] Methods for the preparation of HMF ethers in 70%–92% yields by a reaction with ethanol in the presence of homogeneous[350] and heterogeneous acidic catalysts have been developed.[2, 74, 304, 350–354] An alternative synthetic route is the reaction of CMF with ethanol, resulting in EMF in a >90% yield.[143] From a practical standpoint, of most interest are one-pot processes giving EMF and other ethers from carbohydrates (Scheme 31). There have been methods developed for the conversion of fructose, glucose, saccharose and inulin in the presence of ethanol using various bifunctional catalysts, Brønsted and Lewis acids (H_2SO_4, $AlCl_3$), functionalized ionic liquids, heteropolyacids, zeolites, graphene oxide and so on.[2, 74, 146, 353–360] The EMF yield usually ranges from 40% to 83%. Unfortunately, the EMF yields upon the direct conversion of cellulose usually do not exceed 25%, which is attributable to the drastic conditions required for the cellulose depolymerization.[304, 361]

Scheme 31

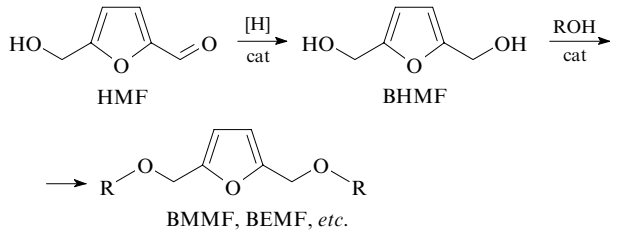


R = Et, Bu^n, *etc.*

2,5-Bis(alkoxymethyl)furans (BMMF, BEMF, *etc.*) are considered efficient diesel fuel components for increasing the cetane number.[2, 350, 362, 363] For example, BMMF has a boiling point of 190 °C, a freezing point below −37 °C and a cetane number of 80 (that for a conventional diesel fuel is ~45).[362] 2,5-Bis(alkoxymethyl)furans are obtained in 60%–80% yields by the reaction of BHMF with alcohols in the presence of acid-type catalysts.[2, 238, 362–365] An efficient approach to the synthesis of these compounds is to combine the steps of the HMF hydrogenation to BHMF and reaction of the latter with alcohols (Scheme 32). This is done using mixtures of hydrogenation catalysts with acid-type catalysts. For example, the hydrogenation of HMF with hydrogen in ethanol in the presence of Pt/Al_2O_3 and the Amberlyst-15 cation exchanger gives BEMF in a 59% yield over one step.[350] Processes have been developed in which ethanol serves simultaneously as a solvent, hydrogen source and O-alkylating agent.[238, 363, 364, 366]

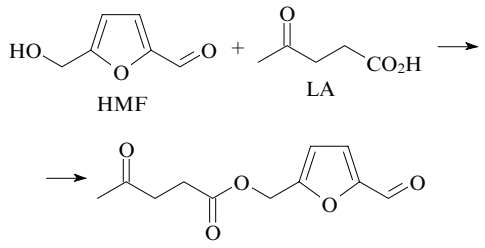
Of a certain interest as fuels are the products of the esterification of the hydroxymethyl group of HMF. For example, 5-acetoxymethylfurfural (AMF) approaches petrol in its energy density.[367] The levulinate resulting from the enzyme-catalyzed esterification of HMF with levulinic acid is considered a potential fuel additive (Scheme 33).[368]

Scheme 32



R = Me, Et, Pr^i, Bu^n, Bu^i

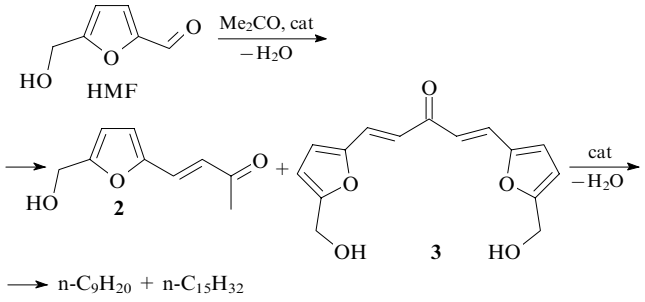
Scheme 33



III.4.c. Products of condensation of 5-hydroxymethylfurfural with CH acids and alcohols

The condensation of HMF with carbonyl compounds followed by hydrogenation can serve as a source of normal hydrocarbons, which can be used as diesel fuel or aviation kerosene components.[2, 303, 304, 367, 369, 370] The reaction with acetone (Scheme 34), giving rise to unsaturated ketones **2** and **3**, has been studied in the most detail. The subsequent hydrogenation of the ketones is accompanied by furan ring opening, resulting in normal C_9 and C_{15} hydrocarbons.[367, 370]

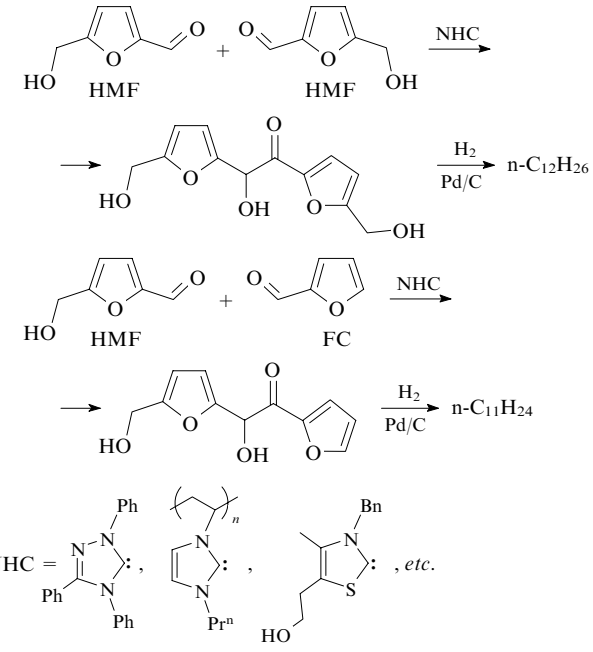
Scheme 34



The condensation and hydrogenation can be carried out in aqueous solution. The hydrocarbons formed in the final step are insoluble in water and are easily separated from the starting reactants and intermediates. The condensation can be catalyzed by homogeneous catalysts (NaOH, zinc and ytterbium salts),[2, 367, 369] heterogeneous catalysts (mixed oxides, for example, MgO-ZrO_2, hydroxides, zeolites)[74, 367, 371] and even CO_2 at a pressure of ~2.5 MPa and a temperature of ~200 °C.[372] Hydrogenation occurs with Pd- and Pt-based catalysts at temperatures of 100 – 300 °C and hydrogen pressures of 25 – 60 atm.[367] It is possible to use bifunctional catalysts, for example, Pd/MgO-ZrO_2, that catalyze both steps. The yields of hydrocarbons are 70% – 80% based on HMF. Cycloalkanes with n-alkyl substituents can be prepared using cyclopentanone and cyclohexanone.[373]

However, another important approach to the preparation of alkanes is the benzoin condensation of HMF or its derivatives (Scheme 35). The reaction proceeds with high

Scheme 35



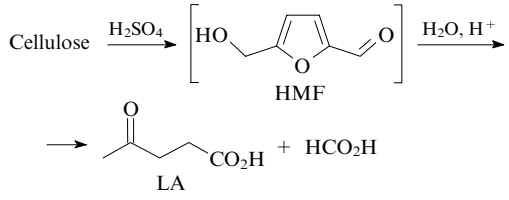
yields when catalyzed by N-heterocyclic carbenes, including those generated *in situ* in systems consisting of ionic liquids and highly basic amines such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or immobilized azolium salts and tertiary amines.[2, 304, 374 – 376] The cross-condensation of HMF with furfural was also implemented.[377] The hydrogenation of furoins in the presence of palladium catalysts affords linear C_{11} and C_{12} hydrocarbons (see Scheme 35).[304, 374]

The reactions of HMF with glycerol, butanol and other alcohols in the presence of acid-type catalysts give acetals mixed with the products of the O-alkylation of the hydroxymethyl group. These compounds are potential diesel fuel additives, improving the viscosity and decreasing the freezing point.[367, 378]

III.4.d. Levulinic acid derivatives

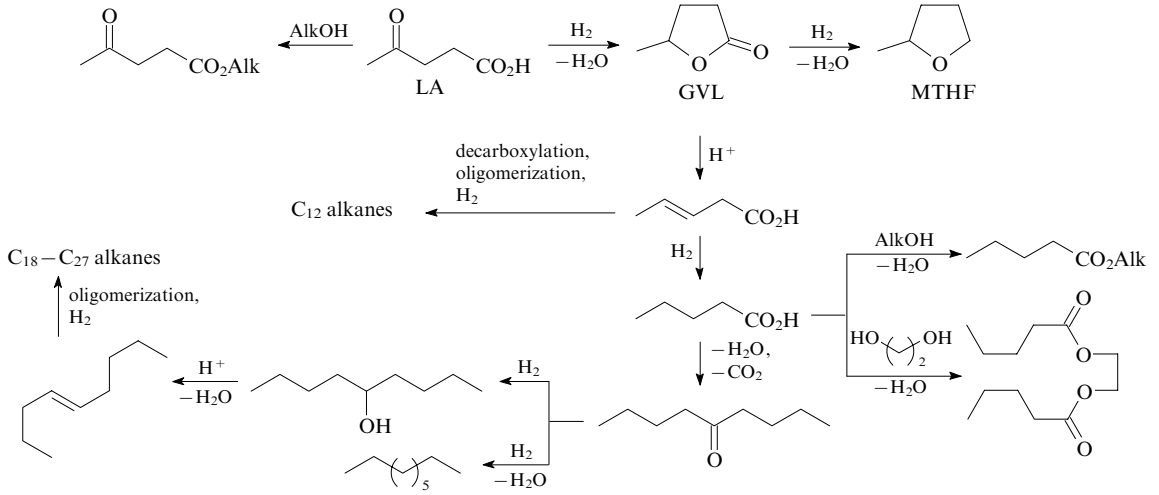
Levulinic acid is formed upon the hydrolysis of HMF with formic acid elimination (Scheme 36).[22] Like HMF, levulinic acid is a platform chemical applicable for the synthesis of diverse products, including motor fuels.[22, 305, 379] It is produced from lignocellulose, without the isolation of the intermediate HMF, in a yield of up to 50% based on the hexose content in the lignocellulose material.[367]

Scheme 36



Highly important levulinic acid derivatives suitable as solvents, plasticizers and engine fuel components are alkyl

Scheme 37



esters. For example, the addition of ethyl levulinate to diesel fuel (up to 20% of the total composition) decreases the freezing point, suppresses the soot formation and decreases the toxic emissions.[367]

One more important levulinic acid derivative is γ-valerolactone (GVL). This compound is used as a solvent in the perfume and food industries and as an efficient petrol additive (instead of ethanol) for increasing the octane number.[380, 381] γ-Valerolactone is obtained by either the hydrogenation of levulinic acid to γ-hydroxyvaleric acid followed by lactonization or the initial lactonization of LA followed by hydrogenation (Scheme 37).[381] The hydrogenation can be conducted in the presence of either homogeneous or heterogeneous catalysts based on metals (Ru, Pd, Pt, Ni, Rh, Ir, Au, Cu).[367, 380] As a source of hydrogen, formic acid, which is a by-product of LA synthesis, can be used apart from molecular H_2.[380, 382–384] One-pot processes for GVL preparation from carbohydrates (fructose, glucose or cellulose) with formic acid and alcohols as hydrogen sources have been developed.[380, 381, 385–388]

Levulinic acid and γ-valerolactone can serve as feedstocks for the production of other engine fuel components: esters of valeric acid, 2-methyltetrahydrofuran (MTHF) and various hydrocarbons (see Scheme 37).[2, 303, 304, 367, 389, 390]

III.5. 5-Hydroxymethylfurfural in the synthesis of pharmaceuticals, pesticides, nutrient additives and chemicals

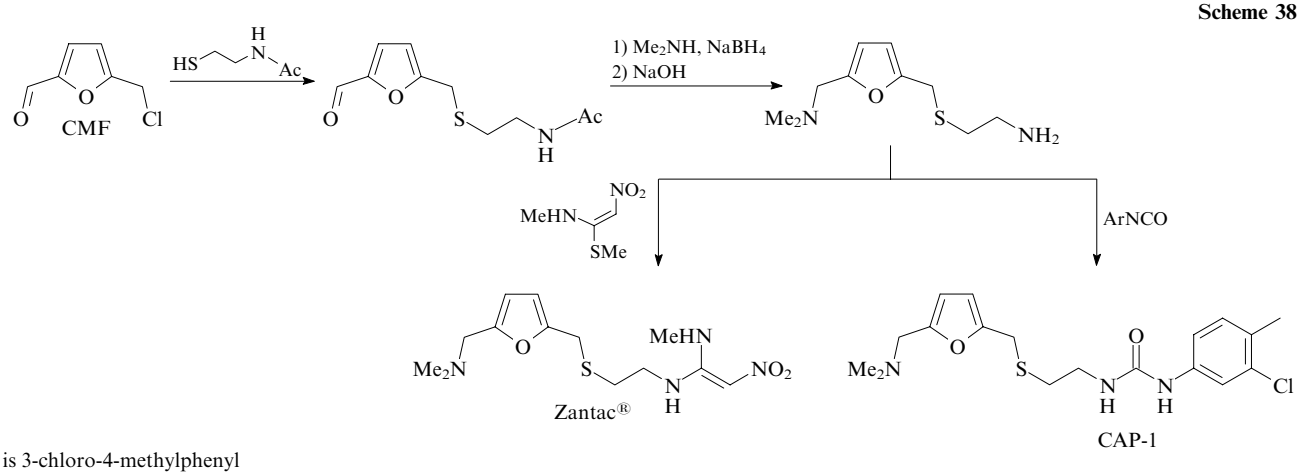
Since HMF is a polyfunctional reagent, it is also used for the preparation of biologically active compounds. In the review of van Putten *et al.*,[20] the key methods for the HMF structure modification are classified, and data on the application of HMF for the synthesis of pharmaceuticals, pesticides, nutrient additives and chemicals published before 2013 are analyzed. Here, we will consider only briefly the most important examples of HMF applications in these areas published in recent years.

The syntheses of the widely used antiulcer drug Ranitidine (Zantac®) from 5-chloromethylfurfural (CMF) in four steps[56, 391] and a promising anti-HIV agent CAP-1 have been reported (Scheme 38).[392]

5-Chloromethylfurfural also serves as the starting compound for the preparation of natural furyl-substituted fatty acids, for example, acid **4**, which possess anti-inflammatory and anti-atherosclerotic activities and are also used as food antioxidants (Scheme 39).[393]

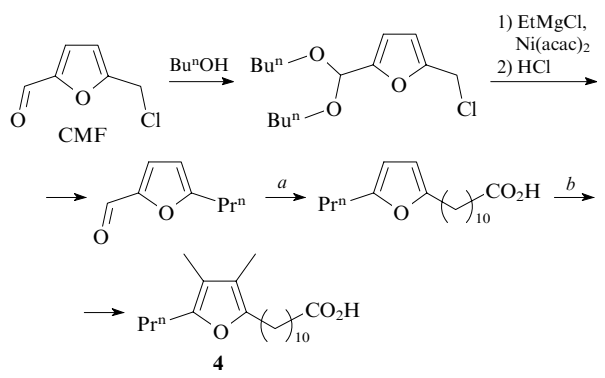
The condensation of HMF and 5-methoxymethylfurfural with acetone underlie the development of relatively simple methods for the synthesis of rehmanones, natural compounds produced by the plant *Rehmannia glutinosa*.

Scheme 38



Ar is 3-chloro-4-methylphenyl

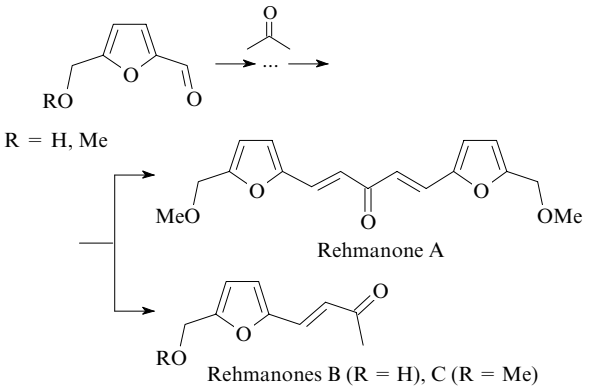
Scheme 39



(*a*) 1) $Ph_3P(CH_2)_9CO_2H$, LiHMDS (LiHMDS is lithium hexamethyldisilazide); 2) H_2, Pd/C; (*b*) 1) CH_2O, AcOH; 2) H_2, Pd/C; acac is acetylacetonate

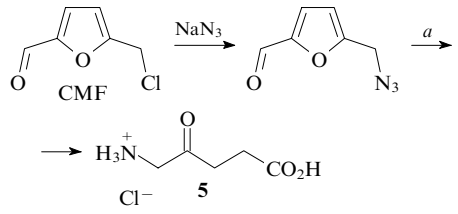
Rehmanones could find use as blood platelet aggregation inhibitors and immunostimulants (Scheme 40).[394]

Scheme 40



5-Aminolevulinic acid and its derivatives are herbicides. Methods for the synthesis of 5-aminolevulinic acid hydrochloride (**5**) based on HMF and CMF have been developed; one method is depicted in Scheme 41.[20, 395]

Scheme 41



(*a*) 1) O_2, Rose Bengal, *hv*, MeOH; 2) H_2, Pd/C, HCl, MeOH

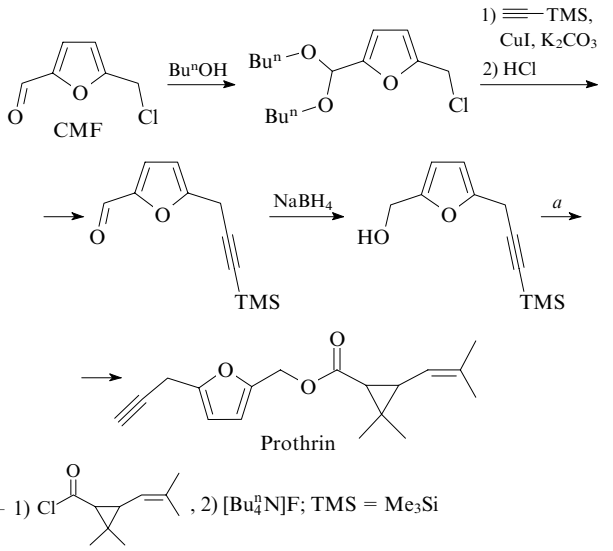
A synthetic route to the insecticide Prothrin based on CMF has been elaborated. The route includes the reaction of CMF dibutyl acetal with trimethylsilylacetylene, the reduction of the aldehyde group and acylation with chrysanthemic acid chloride (Scheme 42).[396]

5-Hydroxymethylfurfural serves as the starting compound for the preparation of diverse crown ethers (for example, compounds **6** – **9**) and macrocycles (**10**, **11**) (Fig. 7), which are applicable as analytical reagents.[20]

In an aqueous solution at 70 °C in the presence of Amberlyst-15 as the catalyst, BHMF gradually rearranges to α-6-hydroxy-6-methyl-2*H*-pyran-3(6*H*)-one (**12**) in a yield of up to 53% (Scheme 43).[397] Compound **12** is an important reagent for the preparation of sugar analogues and biologically active compounds.

The hydrogenation of HMF catalyzed by Au/Nb_2O_3 is accompanied by the ring transformation of the furan moiety to give 3-hydroxymethylcyclopentanone (**13**) — an impor-

Scheme 42



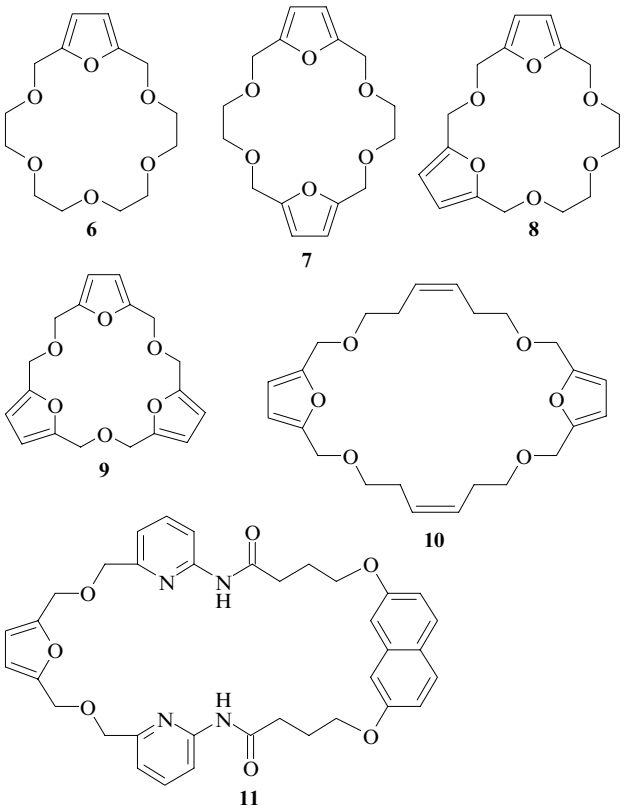
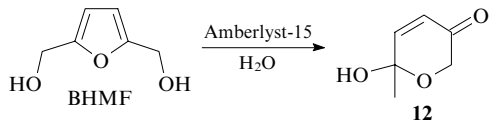


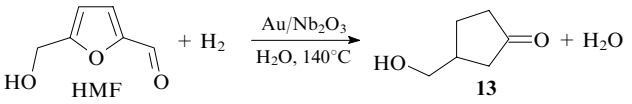
Figure 7. Crown ethers **6** – **9** and macrocycles **10** and **11** obtained from 5-hydroxymethylfurfural.

Scheme 43



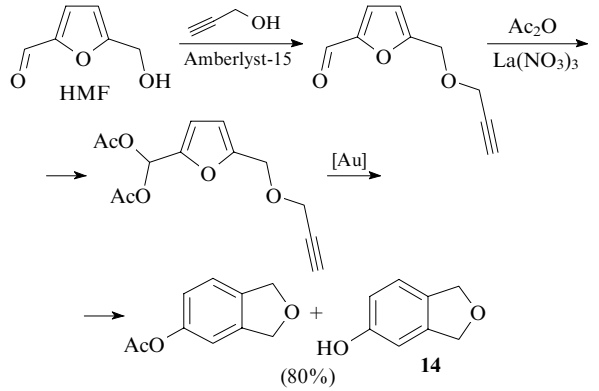
tant reagent for the production of flavoring agents, pesticides and polymers (Scheme 44).[398, 399]

Scheme 44



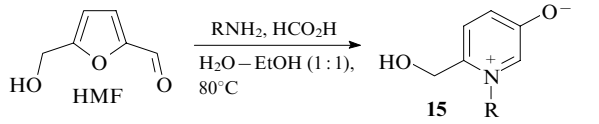
A method has been proposed for the preparation of biologically active phenols derived from 1,3-dihydroisobenzofuran (for example, compound **14**) by the reaction of HMF with propargyl alcohol (Scheme 45).[400]

Scheme 45



The ring transformation of HMF under the action of aliphatic amines underlies the method for the synthesis of mesoionic 6-hydroxymethylpyridines **15**, which could find various applications in the search for biologically active compounds (Scheme 46).[401]

Scheme 46



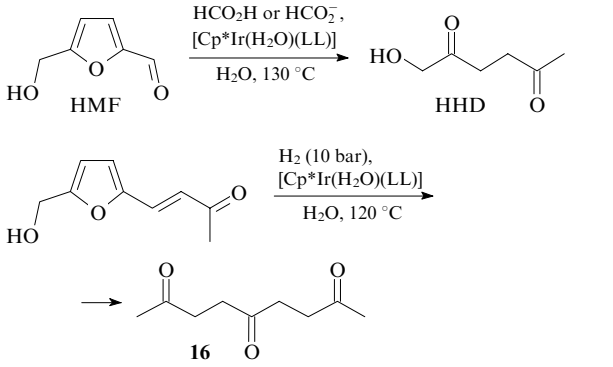
R = Alk, $(CH_2)_nNH_2$

The reduction of HMF with hydrogen or with an aqueous solution of formic acid or formate buffer (pH = 2.5), catalyzed by an iridium complex at 120 – 130 °C, affords 1-hydroxyhexane-2,5-dione (HHD) in a yield of up 85% (Scheme 47).[402–404] This dione is suitable as a polyfunctional reagent for the synthesis of diverse monomers, cycloalkanes, heterocycles and other chemicals. A similar hydrogenation of the product of the aldol condensation of HMF with acetone results in the formation of the symmetrical nonanetrione **16** in a yield of 72% (see Scheme 47).[404]

Oxidative ammonolysis has been proposed for the preparation of the bis-imidate **17** and the bis-amidine hydrochloride **18**, which are useful reagents for the synthesis of nitrogenous heterocycles (Scheme 48).[405]

5,5′-Oxydi(methylene)bis(furan-2-carbaldehyde) (BFF) is considered to be a promising reagent for the synthesis of

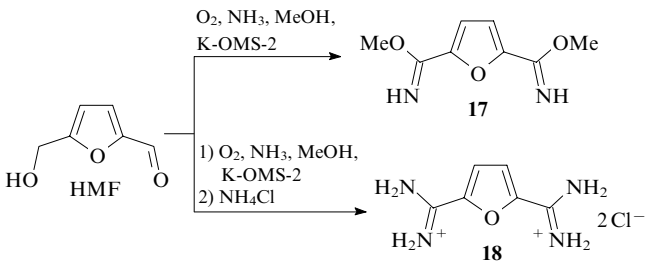
Scheme 47



Cp* = η^5-C_5Me_5, LL is 2,2′-bipyridine,1,10-phenanthroline, 2,2′-bipyrimidine, *etc.*

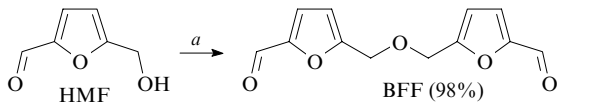
biologically active compounds and polymers. This compound is usually formed as a by-product in the synthesis of HMF.[56] Recently, BFF was synthesized in a 98% yield in

Scheme 48



the presence of Amberlyst-15 in dichloromethane with ultrasonic activation at a temperature of 25–35 °C (Scheme 49).[406] The authors note that ultrasonic activation increases the yield almost twofold compared with that under similar conditions (35 °C, 120 min) but without sonication.

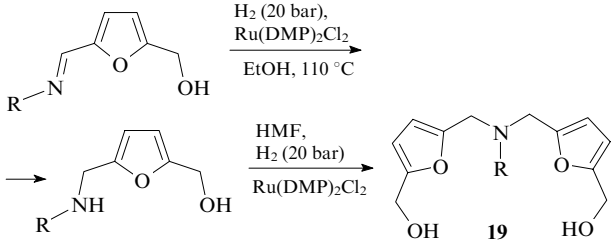
Scheme 49



(*a*) Amberlyst-15, CH_2Cl_2, ultrasound, 25–35 °C

Bis(hydroxymethylfurfuryl)amines **19** — promising reagents for the synthesis of polymers and macrocycles — have been prepared by the hydrogenation of the products of HMF condensation with amines (Scheme 50).[407]

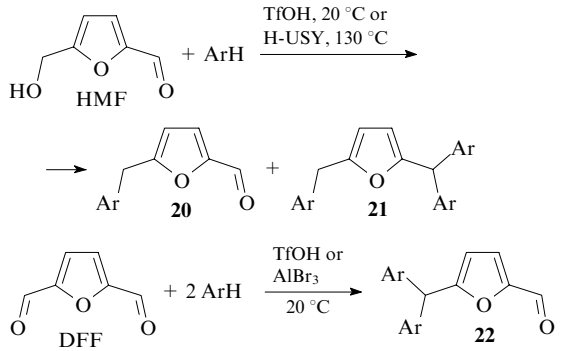
Scheme 50



R = Me, Et, Bu^n, Bu^t, Bn, *etc.*; DMP is 2,9-dimethyl-1,10-phenanthroline

5-Arylmethylfurfurals **20** were synthesized by the reaction of HMF with arenes in trifluoromethanesulfonic acid (TfOH) at room temperature or in the presence of H-USY acid zeolites at 130 °C (Scheme 51).[408] The yields of compounds **20** in TfOH vary from 17% to 91%, and with zeolite catalysts, the yields are 45% – 79%. The main by-products formed in reactions with highly nucleophilic arenes are compounds **21**. A similar reaction of DFF with arenes in TfOH or in the presence of the $AlBr_3$ catalyst affords 5-diarylmethylfurfurals **22** in 15% – 98% yields (see Scheme 51).[408] Derivatives **20** and **22** are of interest as starting compounds for the synthesis of biologically active products.

Scheme 51



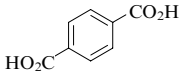
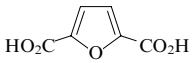
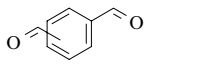
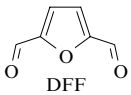
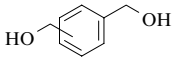
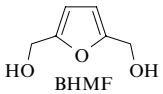
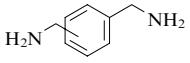
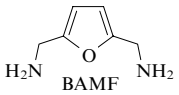
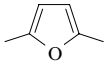
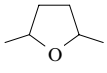
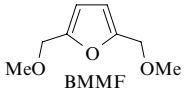
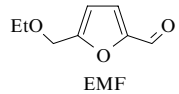
IV. Conclusion

The processing of plant biomass into valuable chemicals and fuels by dehydration of carbohydrates to HMF can be considered one of the most promising approaches to the solution of the raw material and energy problems of mankind in the near future. Therefore, the development of efficient methods for the synthesis of HMF and its important derivatives from plant sources, especially non-edible ones, is a topical issue of modern chemistry and chemical engineering. The HMF production processes based on lignocellulose, which is the most abundant renewable carbon raw material on Earth, will be most significant.

An important problem for HMF production, storage and transportation is its relatively low chemical and thermal stability in non-crystalline form.[56] The preparation of stable HMF derivatives with a protected hydroxyl group (see, for example, Scheme 4) makes it possible to considerably increase the product yield and simplify the isolation, although this requires introducing additional steps. Another possible solution to this problem may be to develop one-pot processes for the synthesis of practically valuable HMF derivatives — monomers, fuels and chemicals — from plant biomass. Highly promising are combined processes that employ by-products of the dehydration of carbohydrates, formic and levulinic acids, as reagents for HMF modification. For example, formic acid can serve as a source of hydrogen for HMF hydrogenation, and levulinic acid can be used as an acylating reagent for the preparation of HMF esters.

The range of practically important products obtained from HMF is extremely broad. Of the greatest interest for the industrial manufacture in the near future are monomers and polymers (Table 1) derived from furan-2,5-dicarboxylic acid and 2,5-bis(hydroxymethyl)furan and motor fuels based on 2,5-dimethylfuran, 2,5-dimethyltetrahydrofuran,

Table 1. Most important products obtained from crude oil and natural gas and their potential HMF-derived counterparts, the commercial production of which may be started in the near future.

No.	Existing industrial products	Applications	Future industrial products
1	 Terephthalic acid	Polyesters and polyamides	 FDCA
2	 tere-/iso-phthalaldehyde	Polyimines, phenol aldehyde resins	 DFF
3	 m-/p-benzenedimethanol	Polyesters, polyurethanes, epoxides	 BHMF
4	 m-/p-phenylenedimethanamine	Polyamides, polyurethanes, curing agents for epoxy resins	 BAMF
5	C_6-C_{15} hydrocarbons	Petrols and diesel fuel	 DMF
6		Petrols, solvents	 DMTHF
7	$C_{11}-C_{22}$ hydrocarbons	Diesel fuel	 BMMF
8		Diesel fuel, flavoring agents	 EMF

HMF esters and C_9-C_{15} hydrocarbons obtained by the hydrogenation of the products of HMF benzoin condensation or HMF aldol condensation with ketones.

As seen from Table 1, the most important existing monomers, disubstituted benzenes, may be replaced in the near future by 2,5-disubstituted furans containing similar functional groups (lines 1 – 4). Disubstituted furan derivatives such as 2,5-dimethylfuran and 2,5-dimethyltetrahydrofuran and 2,5-bis(alkoxymethyl)furans and 5-alkoxymethylfurfurals may become alternatives to the currently used motor fuels, which mainly consist of linear and branched C_6-C_{22} hydrocarbons (lines 5 – 8). In addition, many HMF derivatives such as 2,5-dimethylfuran and 2,5-dimethyltetrahydrofuran, 2,5-bis(hydroxymethyl)furan and the products of aldol and benzoin condensations can serve as feedstocks for the production of compounds of other classes: terephthalic acid, aliphatic hydrocarbons, diols, diamines and dicarboxylic acids applied as monomers and fuels in the state-of-the-art infrastructure of the chemical industry, transport and power engineering.

An analysis of the modern trends of the HMF chemistry shows that this platform chemical should be considered not only a furan derivative. A considerable extension of the target application of HMF as a source of hydrogen and carbon for the chemistry of the 21st century can be expected in the nearest future.

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