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5-Hydroxymethylfurfural (HMF). A Review Focussing on its Manufacture*

B. F. M. Kuster,
Eindhoven (The Netherlands)

The acid-catalysed dehydration of hexoses results in the formation of 5-hydroxymethylfurfural (HMF). Fructose and inulin are especially good starting materials. A review is given of the many methods to produce HMF. The reaction kinetics are dealt with in the sections: raw material, hydrolysis and reversion, catalysts, reaction temperature and time, the concentration and the risk of polymerization and the solvent and HMF stability. Manufacturing processes are illustrated for fructose as the starting material: aqueous systems with homogeneous acid catalysis or those using ion-exchangers as catalyst, systems using dimethyl sulfoxide as the solvent and those using other organic solvents. A short treatment is given on processes starting with glucose, work up procedures and the formation of levulinic acid and other *in situ*-formed HMF-derivatives.

5-Hydroxymethylfurfural. Ein Überblick über seine Herstellung. Die säurekatalysierte Dehydratisierung von Hexosen resultiert in der Bildung von 5%-Hydroxymethylfurfural (HMF). Fructose und Inulin sind besonders gute Ausgangsmaterialien. Es wird ein Überblick über die zahlreichen Methoden zur Herstellung von HMF gegeben. Die Reaktionskinetik ist eingeteilt in die Abschnitte „Rohmaterial, Hydrolyse und Reversion, Katalysatoren, Reaktionstemperatur und -zeit, Konzentration und das Risiko der Polymerisierung und das Lösungsmittel und die Stabilität“. Die Herstellungsverfahren werden für Fructose als Ausgangsmaterial illustriert: Wäßrige Systeme mit homogener Säurekatalyse oder unter Verwendung von Ionenaustauschern als Katalysatoren, Systeme unter Verwendung von Dimethylsulfoxid als Lösungsmittel und solche, die andere Lösungsmittel verwenden. Ein kurzer Hinweis wird auf Verfahren gegeben, die mit Glucose beginnen, Aufarbeitungsverfahren sowie auf die Bildung von Levulinsäure und andere *in situ* gebildeten HMF-Derivaten.

1 Introduction

Earlier reviews on HMF include that of Moye [3] in 1964 (161 ref.), which covers preparation procedures as well as physical and chemical properties and industrial uses. In the series *Advances in Carbohydrate Chemistry* two reviews have appeared, one by Newth [4] in 1951 and the other by Feather and Harris [5] in 1973. Two French reviews appeared in 1981: one by Gaset [6] on HMF manufacture (88 ref.) and the other by Faury [7] on further HMF chemistry (150 ref.). Furan polymers have been reviewed in 1986 by Gandini [8] (209 ref.). There is an abundant amount of literature available on HMF (over 1000 references), but this review will focus on HMF manufacture covering most of the relevant data of the last thirty years. Some overlap with Gaset's review cannot be avoided, but the data are treated in a different way and the most recent data are included.

1.1 The dehydration reaction

HMF, shown in Fig. 1, originates from hexoses by the loss of three molecules of water in an acid catalysed reaction. In aqueous mixtures HMF enters into a consecutive reaction taking up two molecules of water, to yield levulinic and formic acid. In non-aqueous systems HMF hydrolysis can be suppressed. Under all circumstances cross-polymerization reactions occur leading to coloured soluble polymers and insoluble, brown to black, humins.

The dehydration passes at least through two intermediate stages: $C_6H_{10}O_5$ and $C_6H_8O_4$. Mechanisms that involve either cyclic or acyclic intermediates have been proposed as shown in

Fig. 1. Products from the acid catalysed dehydration and rehydration, of hexoses.

Fig. 2. Although the acyclic route seems to be most favoured nowadays, real evidence is still lacking. Mechanistic studies are difficult because of the lability of the intermediates which, therefore, occur in tiny amounts only.

During reaction the hexoses form reversion products by self-condensation. From aldoses, e.g. glucose, oligosaccharides are formed, whereas ketoses, e.g. fructose, give rise chiefly to the tricyclic dianhydrides. These compounds can be hydrolysed back to hexoses. Some of the possibilities are given in Fig. 3.

2 Kinetics

Kinetic studies have been carried out by Teunissen (1930) [9, 10], Mc Kibbins et al. (1958) [11, 12] Breen (1964) [13], Kuster et al. (1975) [14–20], Mercadier et al. (1981) [21–23] and Van Dam et al. (1986) [24]. Maximalisation of HMF yield has been the main objective of these and many other studies. It appears from Fig. 4, showing the overall reaction network, that it is not obvious to obtain high yields. In addition to a solvent and a catalyst the reaction mixture consists of hexoses and reversion products (raw materials), HMF, levulinic- and formic acid (hydrolysis products), intermediates, hydroxyacetyl furan (HAF, see Fig. 2), other side products, soluble brown polymers and insoluble

*) This is a short version. Additional material including a more comprehensive reference list, can be obtained from the author.

This review has been written on the occasion of the third symposium of "Lawine", (Dutch Working Group on Inulin), and the renewed activities on HMF in the Netherlands in general. Dutch work on HMF, partly financed by the IOP-k (Dutch National Innovation Oriented Program on Carbohydrates) is going on at Delft University of Technology [1], TNO Zeist [2] and in the Eindhoven group of the author.

Fig. 2. Possible mechanisms for the dehydration reaction.
 a) acyclic route, see e.g. Feather and Harris [5] and references cited therein.
 b) cyclic route, see e.g. Newth [4] and references cited therein.
 c) such route could also be envisaged.

Fig. 3. Some reversion products.

Fig. 4. The dehydration reaction network.
 (HAF = hydroxyacetylfructose, see also Fig. 2).

black humins. Due to the ratio of formation and disappearance rates for the intermediates and HAF, these occur in very low concentrations only and do generally not show up in the analysis.

The kinetics will be treated in the following subsections:

- raw material, hydrolysis and reversion.
- catalyst
- reaction temperature and time,
- the concentration and polymer formation,
- the solvent and HMF stability.

2.1 Raw material, hydrolysis and reversion

HMF can be produced from all hexoses, and also from those oligo- and polysaccharides which can yield hexoses on hydrolysis, as well as from waste materials containing such compounds. However, it appears to be more selectively produced from keto-hexoses. The cheapest source

nowadays amply available is fructose, obtained from sucrose hydrolysis or glucose isomerisation processes. However inulin, a fructan, shows promising [25].

In aqueous systems hydrolysis of sucrose and inulin is generally much faster than dehydration. Using sucrose the glucose unit often can be recovered unchanged [26].

Two reasons can be mentioned for the higher yields of HMF from fructose when compared to glucose.

Glucose forms a very stable ring structure, the fraction of open chain forms in solution and the enolisation rate are consequently low. Fructose on the other hand forms less stable ring structures, there is more of the open chain form in solution and the enolisation rate is comparatively high. Because enolisation is believed to be the rate determining step HMF yields will be higher starting from fructose than from glucose.

Fructose forms di-fructose-di-anhydrides [27–29] in an equilibrium reaction in such a way that the most reactive groups for cross-polymerisation are internally blocked, with a consequently positive effect on selectivity. Glucose on the other hand forms true oligo-saccharides which still contain reactive reducing groups, leaving more risk for cross-polymerisation with reactive intermediates and HMF. The importance of reversion during the dehydration reaction has been pointed out by Van Dam et al. [24] (see Fig. 3).

Because glucose is cheaper than fructose, the use of glucose as a raw material will get some special attention in the section on manufacturing processes. Most of the further data will refer to fructose dehydration.

2.2 Catalysts

In Table 1 the catalysts mentioned in the literature are summarized. All reactions presented in Fig. 4 are catalysed by acids, proton as well as Lewis acids. In the first preparations oxalic acid has been used. (The

Table 1.
Catalysts Used in the Dehydration Reaction.

Catalyst	References
Oxalic acid	e.g. [13, 26, 30]
None	[31–34]
H ₂ SO ₄ , H ₃ PO ₄ , HCl	e.g. [11, 14, 28, 35–43]
Levulinic acid	[74]
p-Toluene sulfonic acid	[24, 41]
"I ₂ "	[44–46]
NH ₄ ⁺ sulfate/sulfite	[47]
Pyridinium phosphate	[48–50]
Pyridinium HCl	[51]
ZnCl ₂ , AlCl ₃	[52]
Al salts	[53–55]
Th, Zr-ions	[56]
Zr-phosphate	[57]
Cr, Al, Ti, Ga, In-ions	[58]
ZrOCl ₂ , VO (SO ₄), TiO ₂	[59, 60]
V-porphyrin	[61]
Zr, Cr, Ti-porphyrin	[62, 63]
BF ₃	[64]
Ion-exchangers	e.g. [1, 21, 65–72]
Zeolite	[73]

reaction can also be carried out catalysed by in situ formed acidity, but this generally does not lead to optimal yields). Most commonly used cheap acids are H₂SO₄, H₃PO₄ and HCl. Iodine also has been mentioned as a catalyst but the catalytic action appeared to be due to hydroiodic acid formed [39]. The use of Zn, Al, Cr, Ti, Th, Zr and V, as ion, as salt or as complex, in soluble as well as in insoluble form, is mentioned in literature. However, it does not result in significant improvement in yield although sometimes a higher activity is observed. In DMSO, BF₃-etherate has been used.

Except for some metal salts most of the above mentioned catalysts are in dissolved form and are difficult to regenerate, the cheaper acids are just neutralized and disposed off as salt after reaction. To avoid

regeneration and disposal problems use can be made of acidic ion-exchangers. Using ion-exchangers the reaction temperature is generally limited to below 130°C, resulting in a limited rate per amount of catalyst. Furthermore, for a long lifetime, the formation of insoluble humins should strictly be avoided. Therefore, ion exchangers have only been used in DMSO or in aqueous systems with continuous HMF removal by extraction or adsorption.

2.3 Reaction temperature and time

Within the practical limits for catalyst concentration, there is a reciprocal relationship between the reaction temperature and the time needed for proper conversion. Working in water around 150°C reaction times are usual 1 to 5 h [26, 43]. Increasing the temperature to 270°C brings reaction time back to 10 s [74]. Working in DMSO with ion-exchangers as catalyst at 80°C, 8 h are needed [57]. Because catalyst activity is higher in certain non-aqueous systems shorter reaction times and lower temperatures suffice in such systems, e.g. working in polyethyleneglycol at 160°C, 30 s are usual [17, 20].

It appears that the activation energy for HMF formation is higher than for HMF disappearance with the result that the maximum obtainable concentration increases with increasing temperature [11, 14, 35]. Formation rate of HMF is increased by a higher enolisation rate as well as by a higher proportion of acyclic and furanose forms of fructose at higher temperature.

2.4 The concentration and the risk of polymerization

For economical reasons the reaction mixtures should be as concentrated as possible. However, apart from handling problems, the main disadvantage of concentrated solutions is the resulting low selectivity. The higher the chance that reactive compounds collide with each other, the higher is the rate of cross-polymerization and humin formation [14, 23, 24].

In aqueous systems losses due to humin formation amount up to 35% for 1M fructose solutions going down to 20% for 0.25 M. It is not clear if polymerization losses can be completely avoided by working in very dilute solutions. In this respect it is interesting to know that a large portion of certain humins isolated from sorbose have been stated to consist of HAF-polymers [75]. If this would also be true for fructose humin, apparently humin also forms via a parallel reaction which cannot be avoided by dilution.

In certain non-aqueous systems less problems occur with polymerization using high concentrations. In mixtures of e.g. DMSO or polyethyleneglycol containing up to 50% by weight fructose, yields around 70% can be obtained [20, 42, 64]. Heating an equimolar mixture of crystalline fructose with pyridinium hydrochloride for 30 min at 120°C, has been reported to yield 70% HMF [51].

2.5 The solvent and HMF stability

The solvent appears to have a very pronounced effect on the course of the reaction. The primary task of the solvent is to induce fluidity and enable contact of reactant and catalyst. Good solvation properties for the solutes are needed if working in concentrated mixtures is preferred and solute interactions leading to humin formation must be prevented. Water has been most frequently used. It is an excellent solvent for as well fructose as HMF. However, water is also a reactant: it plays a role in the reversion equilibrium and in the hydrolysis of HMF. Decreasing water concentration by mixing in organic solvents, shifts the reversion equilibrium to the dianhydrides thereby diminishing the risk of humin formation [24] and suppresses HMF hydrolysis resulting in high yields [9–11, 17].

The use of aqueous solvent mixtures has been the subject of several patents, Peniston [35] added butanol, Hales et al. [38] dioxane. If solubilities are high enough also completely anhydrous systems can be used: dimethylformamide [44, 45], acetonitrile [71], quinoline [46] and most favourite, dimethyl sulfoxide (DMSO) [33, 57, 64, 68]. However, these solvents have several drawbacks: they are high-boiling and therefore product removal and purification give some additional problems. Apart from being rather expensive they also have some risk for health and environment.

Smythe and Moya [42] gave an extensive treatment on non-aqueous sugar solvents, several of which, e.g. polyglycol-ethers, also were suitable for the dehydration reaction.

A special position have the free glycols. Mixing in ethylene glycol in water, Van DM et al. [24] showed that this had a strong destabilizing effect on HMF: apparently by acetal formation, the hydrolysis rate of HMF is speeded up. That also the initial sugar can have a similar effect has been shown by Kuster and Van der Baan [14, 16] who found that rate constants for HMF hydrolysis are substantially higher in the presence than in the absence of sugars.

Where compounds containing free α -diol groups induce instability of HMF by acetalisation of the aldehyde group, compounds with isolated hydroxyls generally form stable HMF ethers with the hydroxymethyl group. If no solvent hydroxyls are available, HMF can easily form the di-HMF-ether.

The solvent system also influences the formation and appearance of polymeric materials and humins. Non-aqueous polar solvents generally give no problems with solid humin formation.

When working in aqueous systems the solvation of the acid protons highly diminishes the catalytic acidity. Changing to partly anhydrous systems the acids are generally much more able to protonate the reactants. Fructose dehydration is speeded up at least 10 times going from water to an aqueous mixture with 70% polyethyleneglycol. In spite of this effect on the catalytic activity, the hydrolysis rate of HMF decreases upon reducing the water content [14, 17].

3 Manufacturing Processes

The first preparations of HMF used sucrose as feedstock [26, 30, 31, 37], and while the glucose part stayed largely unconverted, molar yields of only 25% (50% based on the fructose part) were obtained. Yields could be improved using high temperatures [53, 74], aqueous solvent mixtures [35] or aluminium sulfate catalyst [54, 55], but especially by continuous removal of HMF from the reaction mixture by extraction [32]. Methyl isobutyl ketone (MIBK) appeared to be an ideal extraction solvent and has been used in many studies.

This section will focus on procedures which may have good prospects for economical HMF production. For that reason we will not treat any further the procedures using "special" catalysts as mentioned in Table 1, but only those using cheap acids or ion-exchangers. The use of glucose or fructose as a feedstock demands different conditions and will be treated separately. The use of sucrose resulting in an equimolar mixture of glucose

and fructose will probably never lead to interesting yields and will therefore not be treated further. This process section will be concluded by giving some details on work-up procedures.

3.1 Processes starting from fructose

The best raw material for HMF manufacture is fructose, crystalline fructose, fructose rich syrups or inulin hydrolysate. The presence of glucose and other carbohydrate compounds as well as protein impurities will lower the yield.

Processes can be subdivided into aqueous and non- or mixed-aqueous systems, into those using simultaneous product removal or not and into those using homogeneous acids or acid ion-exchangers. Furthermore processes can be carried out batch-wise or in a continuous mode. In order to obtain reasonable yields, in aqueous systems simultaneous product removal is always necessary.

In Table 2 the most interesting processes are presented. They will be shortly commented on in the following sections. An important parameter is the HMF load in the final solution which will be given as an average weight percentage.

3.1.1 Aqueous systems, homogeneous acid

Using aqueous sucrose solutions, Cope [32] introduced the method of simultaneous extraction with MIBK, in order to increase HMF yield. With a similar method Kuster et al. [19] obtained selectivities up to 75% at reasonable HMF concentrations, 10% in MIBK, using a continuously operated stirred tank reactor. The aqueous phase could be further extracted and recycled with the unreacted fructose.

The patent of Rapp [43] gives the only procedure solely using water which obviously is an advantage. The reaction mixture is separated on calcium loaded ion-exchanger columns. Unreacted fructose can be reused. The HMF-fraction is pure enough to be concentrated and crystallized. Disadvantages are the high dilution with water resulting in 1% aqueous HMF solution and a low selectivity of 55%.

3.1.2 Aqueous systems, ion-exchangers

The Toulouse group together with Roquette Frères [23, 67, 69] did extensive studies using ion-exchangers and continuous

Table 2.
Processes Starting from Fructose.

Solvent	Catalyst	°C	Time	Batch continuous	Yield** selectivity	Remarks*	Ref.
H ₂ O	H ₃ PO ₄	170–220	1–10 min	c	76 (s)	A	19
H ₂ O	H ₂ SO ₄	140	2 h	b	55 (s)	B	43
H ₂ O	I.E.	78–88	8–24 h	b/c	78 (s)	A	23, 67, 69
H ₂ O	I.E.	90	15 h	b	"90"	A	72
H ₂ O	I.E.	90	48 h	b	70 (s)	C	1
DMSO	none	150	2 h	b	92		33
DMSO	none	100	16 h	b	100		71
DMSO	I.E.	60–130	2–8 h	b/c	80–96		66, 70
DMSO	I.E.	76	5 h	c	97	A	68
H ₂ O/butanol	H ₂ SO ₄	170	8 min	b	68		35
H ₂ O/dioxane	HCl	180	4 min	b	69 (s)		38
THFA/glycolethers	misc.	boiling point	2.5 s	b	"82"		42
PG-600	HCl	120–200	1–10 min	c	65		20
acetone	H ₂ SO ₄	210	28 s	c	81		107

* A: simultaneous extraction with MIBK B: fractionation of reaction mixture using column chromatography C: continuous HMF removal by selective adsorption.

** (s) selectivity, " " method of analysis, e.g. UV-absorption, questionable.

extraction with MIBK. Disadvantages are rather low yields, low catalyst activity and a high dilution with MIBK resulting in 2% solutions. *El Hajj* et al. [72], trying out a similar procedure, reported a high selectivity (90%).

Recent work in Delft has been carried out by *Vinke* et al. [1] on a process with simultaneous product removal by selective adsorption on activated carbon. The carbon can adsorb as much as 0.3 g HMF/g in equilibrium with a 0.5% aqueous HMF solution. Up to now a selectivity of 70% has been obtained. HMF could be removed from the carbon by extraction with ethanol. Selective adsorption would especially be interesting if good recovery without excessive dilution is guaranteed.

3.1.3 Systems using dimethyl sulfoxide (DMSO)

The use of DMSO for the dehydration reaction is especially known from the work at the Noguchi Institute [66]. High HMF yields are reported using ion-exchanger catalysts. *Brown* et al. [71] and later *Museau* et al. [33] mentioned almost quantitative yields of HMF by just heating fructose in DMSO solution without any catalyst. *Gaset* et al. [68] studied the combination of DMSO as a solvent, ion-exchanger as the catalyst and simultaneous extraction with MIBK. These investigators reported a yield of 97% but the final MIBK solution had only a 2% HMF content and contained all the DMSO used (over 10% of total weight).

Main disadvantage of processes using DMSO is that this solvent is difficult to separate from HMF. (See also work-up procedures).

3.1.4 Other organic-solvent systems

Good examples of the early work, demonstrating the beneficial effect of the addition of organic solvents to aqueous fructose solutions, are given by *Peniston* [35] adding butanol and by *Hales* et al [38] adding dioxane. Similar trials were repeated recently by *Stenzenberger* et al. [49, 50]. *Smythe* and *Moye* [42] tested a range of anhydrous solvents for the dehydration reaction, especially solvents containing the grouping R-O-C-C-OH e.g. tetrahydrofurfuryl alcohol and mono-methyl ethers of (di-)ethyleneglycol. They demonstrated that reasonable yields (up to 80% according to UV-absorption) could be obtained, HMF-ethers being formed as by-products. *Kuster* [20] tested polyethyleneglycol-600, which can be used as a flow agent in the vacuum distillation of HMF [76], as a solvent for the dehydration reaction. He found that a 1/1 w/w mixture of fructose and PG-600 became homogeneous on adding a small amount of acid and heating for a few minutes at 85°C. While fructose itself hardly dissolves in PG-600 it apparently did so by the formation of soluble dianhydrides (see Fig. 3). On passing this mixture through a tube reactor reasonable HMF yields are obtained at high temperatures and short reaction times. Also some ethers are formed.

Recent work in our laboratory [107] has shown that it is also possible to use acetone as a solvent and a crude mixture of fructoseacetones as the feedstock for a continuous high pressure tube reactor. However, up to now high yields only have been obtained at relatively low concentration (1–2%).

3.2 Processes starting from glucose

To valorize ligno-cellulosic waste materials, it often has been tried to use these materials for the production of HMF. However, due to the low enolization rate of glucose, low yields are obtained. Therefore, these processes will be given a short treatment only. An extensive kinetic study on glucose dehydration has been carried out by *McKibbins* et al. [11, 12]. In the

older patents several data can be found on the use of glucose. Aluminium salts were used as catalyst in wood hydrolysate conversion by *Bolcs* [52] and *Garber* and *Jones* [53, 74], H_2SO_4 , short reaction times and temperatures up to 290°C in wood chips and glucose conversion by *Snyder* [36] and *Tokarev* and *Sharkov* [77], while *Hales* [38] used mixed-aqueous solvents. Sometimes yields up to 80% have been mentioned but in view of later results, yields probably will never have been higher than 50%.

With the purpose to increase yields, acid-base mixtures have been tried as the catalyst; the base supposed to catalyze the enolization or intermediate formation of fructose. *Smith* [47] used ammonium sulfate or sulfite and *Mednick* [48] a mixture of pyridinium and phosphoric acid, the latter procedure being repeated recently by *Stenzenberger* et al. [49, 50]. The highest yield obtained was 50%. The combined action of amines and acids results in complicated product mixtures containing furans, together with phenols, pyrroles and pyridines [78, 79].

Recent studies on HMF production from celluloses by combined hydrolysis and dehydration are given by *Dadgar* and *Foutch* [80] using MIBK-extraction, *Garves* [81, 83] using mixed aqueous solvent systems and *Durand-Pinchart* [84] using a mixture of solids and acidified MIBK. Again yields did not exceed 50%. *Szmant* and *Chundury* [64] dehydrated starch and glucose using DMSO and BF_3 -catalyst. *Simkovic* et al. [34] obtained a 31% yield in supercritical water.

3.3 Work-up procedures

In order to make proper cost estimates for HMF not only data must be available on reaction conditions and yields but also full details should be known about how to isolate HMF in a more or less pure form.

To obtain pure HMF from a reaction mixture the following procedure has been given by *Middendorp* [30] and later by *Haworth* and *Jones* [26]:

- filtration of humin, – neutralization with CaCO_3 ,
- addition of $\text{Pb}(\text{OAc})_2$ and filtration, -extraction of the filtrate with EtOAc , -drying the extract with Na_2SO_4 ,
- evaporation of EtOAc and – high vacuum distillation of the dark brown syrup obtained.

The high-vacuum distillation has been the subject of two patents. For a good distillation yield the feed should be free of acid and moisture, be degassed and have a minimum contact time at high temperature [85]. High-vacuum film evaporation is most suitable and a non-volatile flowing agent, e.g. Polyethyleneglycol-600, should be added for proper handling [76]. Recoveries of over 90% can be realized. Using vacuum distillation it is also possible to separate HAF from HMF, HAF being slightly more volatile, and to further purify a crude distillate to over 99% purity [37].

While distillation is the oldest procedure in use, chromatographic methods are the latest development. Many systems common in laboratory practice can be applied, e.g. fractionation on silica or alumina columns, but the materials used are expensive and probably difficult to regenerate. However, the use of ion-exchangers and activated carbon, common techniques in sugar industry practice, offer some interesting possibilities. Fractionation of reaction mixtures is possible using ion-exchanger columns in the Ca-form, yielding HMF fractions pure enough for direct crystallization [43]. Also selective adsorption/desorption on activated carbon could offer good possibilities [1]. The generally high dilution of the resulting HMF solutions is a disadvantage, while up to now it is not yet clear if the reusability of the materials suffices.

The procedures given so far all have been in use to work up aqueous reaction mixtures. While volatile solvents easily can be removed by distillation, the use of high-boiling solvents posses-

ses some special problems, e.g. it is difficult to use vacuum distillation to separate HMF from DMSO [71, 72]. As yet it is impossible to make proper cost evaluations because too little is known about efficient work-up procedures for such mixtures. Final purification of crude HMF can be done by vacuum distillation, by fractional melting and washing, and by recrystallization from miscellaneous solvents e.g. water, diethyl ether, petroleum ether [37, 43].

4 In situ Formed Derivatives

HMF is generally rather unstable under the conditions of its formation. It often also is not used as such but in a derivatised form. Therefore, it is equally well interesting to consider manufacture of HMF-derivatives, especially if those derivatives can easily be formed *in situ*, are more stable, can easier be worked up or are even more useful compounds than HMF itself.

We will shortly deal with the following derivatives: levulinic acid, HMF-ethers, esters and halogen derivatives, and also with *in situ* oxidation and hydrogenation. All the compounds mentioned are often as useful as HMF itself.

4.1 Levulinic acid

Carrying the acid catalyzed dehydration in aqueous systems to completion results in an equimolar mixture of levulinic and formic acid along with a certain amount of insoluble humins. The kinetics of HMF hydrolysis have been studied [9, 10, 14]. Because levulinic acid is a stable product, yields up to 70% can be obtained from fructose as well as from glucose if not too high concentrations are used. An extensive kinetic study on the formation of levulinic acid from glucose has been given by McKibbens et al. [11, 12] and most recent mechanistic studies by Horvat et al. [86, 87]. Schraufnagel and Rase [65] used ion-exchangers as catalyst and sucrose as the raw material; Jow et al. [73] obtained a 67% yield from molten fructose using a zeolite catalyst. Because of its stability, levulinic acid can also be prepared from hexose containing wastes. Reviews on levulinic acid have been written by Leonard (1956) [88], Kitano et al. (1975) [89] and Thomas and Barile (1984) [90, 91]. The latter authors mention the use of levulinic acid derivatives as liquid fuel extenders.

4.2 HMF ethers

In anhydrous systems HMF forms the di-HMF-ether or in the presence of alcohols 5-alkoxymethylfurfurals [40, 92]. The ethers are more stable than HMF [71] and can often more easily be isolated, the lower alkyl ethers by distillation, the di-HMF-ether by crystallization. Early data on di-HMF-ether are given by Middendorp [30] and Aso [93]. High yields of this compound also can be obtained from DMSO solutions [33, 94]. Garves [83] obtained a low yield of methoxymethylfurfural, upon heating starch, cellulose or lignocelluloses with acidic methanol.

4.3 HMF esters

HMF can easily be esterified *in situ* and, although esters are less stable than ethers, doing so can be very helpful in the isolation and purification. *In situ* procedures in DMSO are given in two patents [70, 95].

4.4 Halomethylfurfurals

The halomethylfurfurals are most popular amongst the HMF-derivatives, probably because of their usefulness in further

organic synthesis. If the dehydration reaction is carried out in non- or mixed-aqueous systems containing at least an equimolar amount of transferable halogen, the compounds are formed in high yield. It has even been suggested to prepare HMF by hydrolysis of the chloromethyl compound [96]. Early preparations are given by Haworth and Jones [26]. More recently much work has been done by Hamada et al. [97, 98]. These authors obtained 5-chloromethylfurfural by heating a mixture of hydrochloric acid, a surface active agent and aromatic or halogenated solvents with sugars for 1 h at 70 to 80°C applying high speed stirring. The reported yields, as a brown syrup, were 60% from glucose, 62% from sucrose and 77% from fructose. Using $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (one equivalent per mol of sugar) instead of the acid and a surface active agent did increase the yield from fructose up to 92%. Similar procedures have been given by Szmant et al. [99]. Fayet and Gelas [51] also obtained the chloro-derivative by heating solid mixtures of fructose with pyridinium-HCl.

4.5 In situ hydrogenation and oxidation

Although no descriptions of *in situ* hydrogenation procedures for HMF were found, there should exist good possibilities and much can be learned from the literature on furfural hydrogenation. For stabilization purposes especially the ring has to be saturated, leading to tetrahydrofuran derivatives. HMF can be hydrogenated also to bis-hydroxymethylfuran, which is a useful compound to make resins [84]. It is also possible to produce 5-methylfurfuryl alcohol and 2,5-dimethylfuran [100], the latter compound being an excellent fuel extender.

Oxidations carried out with the dehydration reaction mixtures result in 2,5-diformylfuran, 5-hydroxymethylfuroic acid, 5-formylfuroic acid or 2,5-furan-dicarboxylic acid. Especially the acid groups stabilize the compound and offer new possibilities for product isolation and purification. Depending on the process conditions high selectivities can be obtained for each of the compounds. Oxidation procedures have been given by Morikawa [46, 101, 102], Krupenskii [103], Bernasconi et al. [104] and El Hajj et al. [72]. Especially noble metal catalysts give high yields [105].

5 Conclusion

In view of the many potential applications, HMF manufacture could be a potential outlet for carbohydrate containing agricultural products towards the chemical industry. Up to now, however, commercial realization has proven to be difficult and several pilot-plant trials apparently failed.

At the moment a reasonable, totally aqueous procedure, yielding crystalline HMF, is available [43]. If fructose can be obtained at 0.50 DM/kg, a cost price has been estimated of 6 DM/kg HMF [2]. Agricultural business is especially interested in converting large quantities, and, at the price mentioned, producing some polymers and resins would be the highest volume application feasible [8]. Once such an operation has got started, certainly the lower volume, higher value applications will follow. However, in order to valorize quantities which will have some effect on agricultural surpluses, more efficient processes resulting in a lower HMF price are required.

As described in this review there are many such possibilities. Attention should be given to the relation between reaction system and work-up procedure. While e.g. high yields have been mentioned using DMSO, it appeared to be difficult to isolate HMF from such mixtures. On the other hand one should not only focus on HMF: *in situ* formed derivatives could be equally well interesting, depending on the solvent and catalyst and the application that is in mind.

It is likely that maximum yields of HMF from fructose are around 80% of theoretical and due to the loss of water the best mass yield would be 1 kg HMF from 2 kg fructose. It is also interesting to develop integrated procedures starting from inulin. Although up to now low yields have been obtained from glucose it cannot be excluded that good yields can be obtained using unconventional catalyst and solvent systems. The main problem in obtaining high yields in the dehydration reaction is that losses due to polymerization increase considerably at the more economical, high concentrations. The overcome this problem is a major challenge for future research [106].

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Address of author: Dr. Ben F. M. Kuster, Laboratorium voor Chemische Technologie, Technische Universiteit Eindhoven, Postbus 513, 5600 MB Eindhoven, The Netherlands.

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Patents/Patente**

Courtauld PLC, GB-London: **Production of cellulose acetate**. EP 0359116 A2 (Int. Cl. C08F-210/06), angem. 07.09.89, offengel. 21.03.90.

A process for the production of cellulose acetate from wood pulp which comprises forming a slurry of the wood pulp in water, passing the slurry through a press to remove water, drying the pressed slurry to form dried cellulose material and subsequently esterifying the dried cellulose material with an acetylating agent after activation with acetic acid to form cellulose acetate, characterised in that the pressed slurry of wood pulp is dried in a pin mill through which a hot drying gas is passed under conditions which produce an exit temperature of the drying gas in the range 80°C to 95°C and a moisture content of the dried cellulose material in the range 4 to 15% by weight (based on the dry weight of the material) to provide a dried cellulose material in the form of a cellulose flock which does not require reactivation prior to acetylation additional to the normal activation with acetic acid. lg

Teepack Inc., Oakbrook Illinois, USA: **Nichteßbare Nahrungsmittelhülle aus verstärkter Amylose oder Amylosestärke**. EP 0185927 B1 (Int. Cl. A22C-13/00), angem. 19.11.85, offengel. 02.07.86, erteilt 14.03.90.

Nahrungsmittelumhüllung oder -hülle mit einem amylosehaltigen Material, dadurch gekennzeichnet, daß das amylosehaltige Material eine zusammenhängende, vernetzte Polymermatrix bildet, mit welcher eine Faserverstärkung imprägniert ist. lg

Braunschweigische Maschinenbauanstalt AG, D-3300 Braunschweig: **Kontinuierlich arbeitende Zuckerzentrifuge**. EP 0257270 B1 (Int. Cl. B04B-3/00), angem. 14.07.87, offengel. 02.03.88, erteilt 14.03.90.

Kontinuierlich arbeitende Zuckerzentrifuge mit einer um eine zentrische Drehachse antreibbaren, sich kegelförmig vom Boden zum Abwurfrand öffnenden Siebtrommel mit einem Siebbelag, der sich vom Boden der Trommel oder dem oberen Rand eines bodenseitigen Beschleunigungstopfes für die Aufgabe der Füllmasse bis in den Bereich des Abwurfrandes erstreckt, wobei die Trommel und/oder der Siebbelag in Richtung der zentrischen Drehachse gesehen mit dieser

abschnittsweise einen unterschiedlichen Winkel bildet und eine Einrichtung zur Zuführung von Deckwasser in dem querschnittsweisen Bereich der Trommel vorgesehen ist, indem ein erster, vom Abwurfrand der Trommel (I) ausgehender Abschnitt der Trommel und/oder des Siebbelages mit der Drehachse einen solchen Winkel α bildet, daß während des Betriebes bei Unterbrechung der Füllmassezufuhr und Aufrechterhaltung der betriebsmäßigen Deckwasserzufuhr die Gutschicht auf diesem Siebabschnitt verharrt, daß sich ein anschließender zweiter Abschnitt (II) über den mittleren Höhenbereich der Trommel erstreckt und einen etwa 3 bis 7° größeren Winkel mit der Drehachse bildet und ein von diesem mittleren Abschnitt bis zum Boden der Trommel bzw. dem oberen Rand eines bodenseitigen Beschleunigungstopfes reichender dritter Abschnitt (III) vorgesehen ist, welcher etwa den gleichen Winkel mit der zentrischen Drehachse bildet wie der erste Abschnitt. lg

ESPE Stiftung & Co. Produktions- und Vertriebs-KG, D-8031 Seefeld: **Alginate-Abformmaterial, Verfahren zu seiner Herstellung und Verwendung einer Calcium- und/oder Strontiumsalzlösung**. EP 0359189 A2 (Int. Cl. A61K-6/10), angem. 12.09.89, offengel. 21.03.90, identisch mit DOS 3831043.

Alginate-Abformmaterial, enthaltend drei räumlich voneinander getrennte Bestandteile (a), (b) und (c), nämlich, bezogen auf die Gesamtmasse von a) + b) + c),

- 10 bis 49,999 Gewichts-% alginathaltiges Pulver,
- 50 bis 89,999 Gewichts-% Wasser und
- 0,001 bis 10 Gewichts-% flüssige Zusammensetzung, enthaltend 1 bis 90 Gewichts-%, bezogen auf die Gesamtmasse von c), gelöste Calcium- und/oder Strontiumsalze.

wobei die Calcium- und/oder Strontiumionen-Konzentration in der Gesamtmasse von b) + c) 5 bis 100 mmol/l beträgt. lg

Chemische Fabrik Grünau GmbH, D-7918 Illertissen: **Verfahren zur Herstellung pulverförmiger, wasserauswaschbarer, enzymatisch abgebauter Heteropolysaccharide**. EP 0359075 A1 (Int. Cl. C12P-19/04), angem. 02.09.89, offengel. 21.03.90.

Verfahren zur Herstellung pulverförmiger, wasserauswaschbarer, enzymatisch abgebauter Heteropolysaccharide dadurch gekennzeichnet, daß man Heteropolysaccharide mit 0,5 bis 3,0 Gew.-% Enzymen und 20 bis 60 Gew.-% Wasser, jeweils bezogen auf Heteropolysaccharid-Menge, bei Temperaturen zwischen 15 und 30°C vermischt, die

** DAS = Deutsche Auslegeschrift; DOS = Deutsche Offenlegungsschrift; DPS = Deutsche Patentschrift; EP = Europäisches Patent.