Preparation of 5-hydroxymethylfurfural via fructose acetonides in ethylene glycol dimethyl ether

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.
[Link to publication](#)

PREPARATION OF 5-HYDROXYMETHYLFURFURAL VIA FRUCTOSE ACETONIDES IN ETHYLENE GLYCOL DIMETHYL ETHER

JI-DONG CHEN,† BEN F. M. KUSTER* and KEES VAN DER WIELE
Technische Universiteit Eindhoven, Laboratorium voor Chemische Technologie, P.O. Box 513, 5600 MB
Eindhoven, The Netherlands

Abstract—A new procedure for the preparation of 5-hydroxymethylfurfural (HMF) has been studied, in which 1,2:4,5-di-*o*-isopropylidene-*β*-D-fructopyranose is dissolved in ethylene glycol dimethyl ether (EGDE) containing an appropriate amount of water and sulfuric acid as a catalyst. HMF yields were greater than 70 mol%. Data were obtained for several combinations of temperature and concentrations of acid and water at a reactant concentration of 0.5 M. Temperature and acid concentration influenced the catalytic activity, but had little effect on the yield of HMF. EGDE is a cheap and easily regenerable solvent which, in the acidic medium, does not generate by-products whilst HMF remains stable in it up to a temperature of 453 K. The reaction can be carried out in a continuous tubular reactor without the problem of plugging by insoluble solid humins.

1. INTRODUCTION

The acid-catalyzed conversion of hexoses (e.g. fructose) into HMF has been known for a long time.[1] Based on renewable resources, HMF is suggested to be a very interesting and versatile intermediary product. Due to its wide range of diverse industrial applications, many suggestions have been made to utilize this dehydration reaction in a commercially practical manner for the manufacture of HMF. Up to now, however, commercial realization has proven to be difficult. Recently,[2] more attention has been paid to the development of cheap and efficient processes for the production of HMF on a large scale.

In this dehydration reaction, the most commonly used catalysts are mineral acids[3-12] such as H_2SO_4, H_3PO_4, HCl and organic acids such as oxalic acid,[13-15] levulinic acid[16] or *p*-toluene sulfonic acid.[10,17] Boron trifluoride etherate[18] can also be used. The use of Zn, Al, Cr, Ti, Th, Zr and V as ions, as salts or as complexes, as catalysts[19-24] has not brought much improve-

ment in the yield of HMF. Using ion exchangers[25-30] as catalysts the turnover number is generally small and the reaction temperature is limited to below 130°C

The temperature has a strong influence on the reaction. Higher temperatures generally lead to higher yields of HMF. It was demonstrated that the activation energy for HMF formation is higher than that for HMF disappearance with the result that the maximum obtainable concentration increases with increasing temperature.[3,5,12] However, high yields of HMF can also be obtained working in dimethyl sulfoxide (DMSO) with ion exchangers as catalysts at low temperatures (e.g. 80°C[22]).

Apparently the solvent has a very pronounced effect on the course of the dehydration. Previously, water was most commonly employed as a solvent. Water is an excellent solvent for both fructose and HMF. However, the solvation of protons in water highly reduces the catalytic activity for the dehydration. Furthermore, in such aqueous systems the rehydration of HMF to levulinic and formic acid becomes an important subsequent reaction. It is obvious that the manufacture of HMF by simple dehydration in acidic aqueous solutions will not result in high HMF yields.

Several methods to increase yields have been described in the literature. In aqueous systems, the yield can be improved by a simultaneous

---

*To whom correspondence should be addressed.
†Present address: Technische Universiteit Delft, Laboratorium voor Organische Chemie, P.O. Box 5045, 2600 GA Delft, The Netherlands.

List of symbols: DIpF-1—1,2:4,5-di-*o*-isopropylidene-*β*-D-fructopyranose; DIpF-2—2,3:4,5-di-*o*-isopropylidene-*β*-D-fructopyranose; DMSO—dimethyl sulfoxide; FID—flame ionization detector; HMF—5-hydroxymethylfurfural.

extraction of HMF[31-34] or adsorption of HMF on activated carbon.[35] The key factor in these processes is a rapid removal of HMF from the acidic medium in which it is formed. However, these systems generally suffer from high dilution or partially irreversible adsorption of HMF.

Another method is the addition of an organic solvent to the aqueous solution, e.g. adding butanol[3] or dioxane.[7] Disadvantages of such systems are the difficulty of preventing rehydration and ether formation of HMF with the solvent if alcohols are employed. Moye et al.[9,11,36] carried out extensive studies using a new series of alcoholic sugar solvents which contained the grouping R–O–C–C–OH in their structures. High HMF yields (up to 80%) were obtained, but the formation of HMF ethers could not be avoided. Moreover, fructose concentration in these solvents was limited to 1.53%.

More recently, many studies have been carried out using DMSO as a solvent.[18,22,26,37] Excellent yields of HMF can be reached with ion exchangers or boron trifluoride etherate as a catalyst and even without any catalyst.[30,38] The problem is, however, the difficulty of recovering HMF from this polar aprotic solvent. An interesting continuous process was developed by Kuster et al.,[39] who used polyethylene glycol 600 as solvent. A 1/1 w/w mixture of fructose and polyethylene glycol 600 became homogeneous on adding a small amount of acid and heating for a few minutes at 85°C. On passing this mixture through a tubular reactor, reasonable HMF yields were obtained at high temperatures and short reaction times. However, some HMF ethers were also formed and the feasibility of product removal and purification by vacuum film evaporation has still to be proven.

Recently, Rapp[2] has reported a totally aqueous process, in which the reaction mixture is separated by ion exchanger columns whereby crystalline HMF is obtained. However, the selectivity is rather low (55%) and a high dilution of reaction solution with water is caused by the separation procedure.

A comprehensive review focussing on HMF manufacture has recently been presented by Kuster.[40]

Up to now, it has been known that solvents which are able to dissolve fructose are water, pyridine, quinoline and a series of polar aprotic solvents. The solubility of fructose in alcohols is limited. Recently, a new procedure has been developed in our laboratory. As shown in Fig. 1, fructose is first converted to 1,2:4,5-di-o-isopropylidene-β-D-fructopyranose (DIpF-I). As soon as fructose and some fructose-like intermediates have been produced by hydrolysis of the fructose acetonide a rapid dehydration of the fructose to HMF occurs simultaneously at an elevated temperature. In this way, high reactant concentrations can be achieved using cheap and easily regenerable solvents, and the reactive hydroxyl groups of fructose which induce HMF instability are blocked at an earlier stage of the dehydration.

This paper reports a new procedure for the preparation of HMF. The use of ethylene glycol dimethyl ether as a volatile solvent provides an advantage for HMF separation and solvent reusability. Good HMF yields have been obtained at a full conversion of fructose, even employing high reactant concentrations.

2. EXPERIMENTAL

2.1. Equipment, procedure and reaction conditions

Fructose acetonides were prepared in accordance with the literature.[41] All experiments concerning hydrolysis and the dehydration were carried out with degassed and argon protected solutions in a series of glass ampoules with a volume of 0.35 ml. These ampoules with an internal diameter of 1.5 mm and a wall thickness of 0.38 mm allow an isothermal state of the reaction solution to be reached at temperatures

Fructose   1, 2 : 4,5 – di – o – isopropyli –   5 – hydroxymethylfurfural
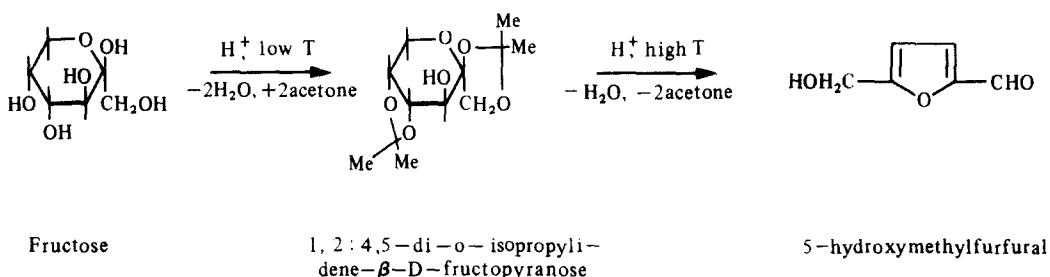   dene – β – D – fructopyranose

Fig. 1. Dehydration of fructose to HMF via 1,2:4,5-di-o-isopropylidene-β-D-fructopyranose.

around 483 K within 5 s, so that actual performance times are normally 5 s longer than the reaction times given herein. Those ampoules were placed in a polyalkylene glycol bath (453 ± 0.5 K) and quenched in water (20°C) at different time intervals.

Because high temperature and high internal pressure are involved, one must be very careful preparing the reaction ampoules. After sealing one side of an ampoule, the reaction solution was introduced with a syringe leaving 33% of the volume empty so as to allow liquid expansion at high temperatures. These ampoules were put in a vacuum desiccator and degassed before argon gas was introduced. This procedure was repeated three times within 10 min so that air in the ampoule was completely replaced by argon gas. Finally, the open side of the ampoule was sealed by melting the ampoule top.

Standard reaction conditions were used as follows unless otherwise stated: $[DIpF-1]_0$ 0.5 M, $[H_2SO_4]_0$ 0.005 M, $[H_2O]_0$ 7.5 M, T 453 K, solvent is ethylene glycol dimethyl ether.

2.2 Analysis

Gas–liquid chromatography (g.l.c.) analysis was performed with a Packard Model 438A g.l.c. apparatus. Column: capillary column (WCOT fused silica), 10 m × 0.22 mm (i.d.); liquid phase, CP.Sil-5-CB; film thickness,

0.12 μm. The operating conditions: programmed temperatures, 50°C to 230°C: 0–2 min, 0°C/min; 2–5.5 min, 20°C/min; 5.5–8 min, 0°C/min; 8–17 min, 20°C/min. Injection temperature, 250°C; detector (FID) temperature, 300°C; injection amount, 0.5 μl; attenuation, 2^2; H_2 flow rate, 25–30 ml/min; air flow rate, 250–300 ml/min.

HMF and fructose have to be silylated before g.l.c. analysis. The routine analysis of the silylated compounds is as follows: 20 μl sample is diluted with 1000 μl acetone containing $0.6 g \cdot l^{-1}$ pentadecane (as internal standard) and this solution is silylated with 300 μl TRI-SIL Concentrate (a 2:1 mixture of hexamethyldisilazane and trimethylchlorosilane, Pierce Chem. Co.) for at least 30 min at an ambient temperature before being injected.

3. RESULTS AND DISCUSSION

3.1. Production of HMF from fructose via different fructose acetonides

It has been shown[41] that 1,2:4,5-di-o-isopropylidene-β-D-fructopyranose is the product of the kinetically controlled condensation of fructose with acetone. It is thermodynamically less stable than 2,3:4,5-di-o-isopropylidene-β-D-fructopyranose (DIpF-2). Figure 2 shows differences in the kinetics of HMF production from the different isomers of fructose acetonides. Since the hydrolysis rate constant of fructose acetonides to fructose is higher than the dehydration rate constant of fructose to HMF, significant fructose concentrations appeared during the reactions. The fructose concentrations shown in Fig. 2 represent only the maximum solubilities of fructose in the system at ambient temperatures, real fructose concentrations at reaction temperatures being higher than these. Because the hydrolysis rate constant of 2,3:4,5-di-o-isopropylidene-β-D-fructopyranose to fructose is lower than that of 1,2:4,5-di-o-isopropylidene-β-D-fructopyranose which is comparable with the results presented by Tipson et al.,[42] the HMF formation rate from 2,3:4,5-di-o-isopropylidene-β-D-fructopyranose was somewhat lower than that from 1,2:4,5-di-o-isopropylidene-β-D-fructopyranose. However, the maximum yields obtained from the different isomers were almost the same. 1,2:4,5-di-o-isopropylidene-β-D-fructopyranose was chosen as reactant for further studies because it can be easily prepared and formation of mesityloxide, which is a by-product produced
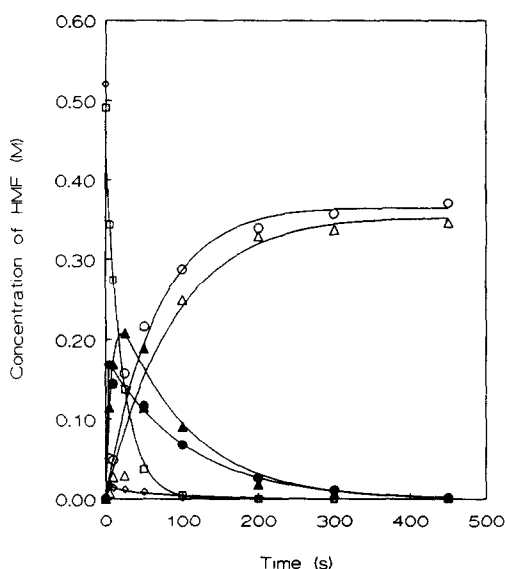

Fig. 2. Production of HMF from fructose via different fructose acetonides. (◇ DIpF-1, □ DIpF-2, ● fructose from DIpF-1, ▲ fructose from DIpF-2, ○ HMF from DIpF-1, △ HMF from DIpF-2. Reaction conditions: $[DIpF-1]_0$ 0.520 M, $[DIpF-2]_0$ 0.491 M, $[H_2SO_4]_0$ 0.005 M, $[H_2O]_0$ 7.5 M, T 453 K, ethylene glycol dimethyl ether.)
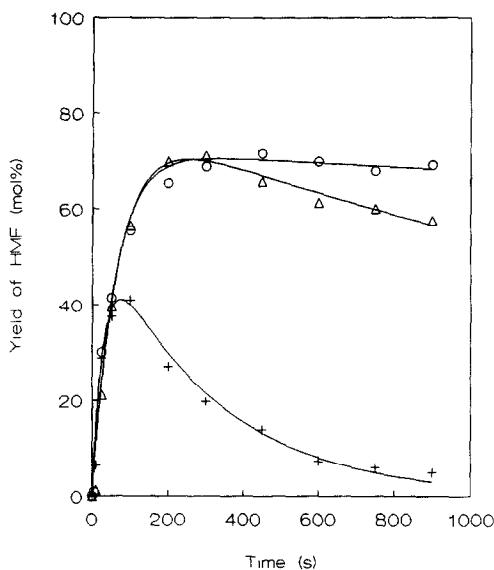
Fig. 3. Solvent effect on HMF yield. (Ethylene glycol dimethyl ether + 50 v% cosolvent: ○ none, △ 2-methoxyethanol, +ethylene glycol. Reaction conditions: [DIpF-1]$_0$ 0.5 M, [H$_2$SO$_4$]$_0$ 0.005 M, [H$_2$O]$_0$ 7.5 M, T 453 K.)

by condensation of acetone itself in the course of preparation of fructose acetonides in acetone, is much less than that resulting from the preparation of 2,3:4,5-di-o-isopropylidene-β-D-fructopyranose.

3.2. Solvent effect

Figure 3 shows the effect of solvent on HMF yield. Moye[36] pointed out that fructose in solvents containing R–O–C–C–OH groups is rather stable. It can be seen in Fig. 3 that reasonably high HMF yields could be obtained from the use of either ethylene glycol dimethyl ether alone or mixed with 2-methoxyethanol, but HMF in the presence of 2-methoxyethanol was less stable than in its absence. According to g.l.c.–m.s. analysis, 5-methoxyethoxymethylfurfural was produced, which is an ether of HMF and 2-methoxyethanol. Brown et al.[30] reported that hydroxymethylfurfural ethers and levulinate esters resulted from fructose dehydration using a series of alcohols as solvent. Ethylene glycol alone is a poor solvent for 1,2:4,5-di-o-isopropylidene-β-D-fructopyranose; however, it could be used as a cosolvent with ethylene glycol dimethyl ether (1/1 v/v). As displayed in Fig. 3, a strong destabilizing effect of ethylene glycol on HMF occurred, which has also been found by van Dam et al.[17] using a 1/1 v/v mixture of water and ethylene glycol as solvent.

Using ethylene glycol dimethyl ether as solvent, HMF has been shown to be stable and no by-product is formed from the solvent iself. The

solvent containing some water can dissolve not only fructose and HMF, but also some reversion products such as 2,1':1,2'-di-o-fructopyranose dianhydride at high temperatures. The polymers produced as by-products during the reaction remained dissolved and no insoluble solid humins were observed. These phenomena are similar to working in DMSO systems.

3.3. Effect of water concentration on HMF yield

Previously, Kuster[43] found that the replacement of water by polyethylene glycol 600 in the dehydration reaction was very beneficial to the formation of HMF because it accelerated its formation and retarded its rehydration. In our new system, certain amounts of water are needed to reach good HMF yields, as can be concluded from Fig. 4.

As HMF is an unstable intermediate product, its yield results from a balance between its formation and disappearance. The hydrolysis rate of fructose acetonides to fructose can be strongly influenced by the water concentration. For example, using a water concentration of 0.5 M as additive and 0.25 M 2,3:4,5-di-o-isopropylidene-β-D-fructopyranose as reactant, the free fructose concentration was very low in the course of the dehydration, even lower than the g.l.c. detection limit. The slow hydrolysis caused by the shortage of water most likely became the rate limiting step for the overall reaction. Consequently, the rate of HMF formation apparently became too low compared to
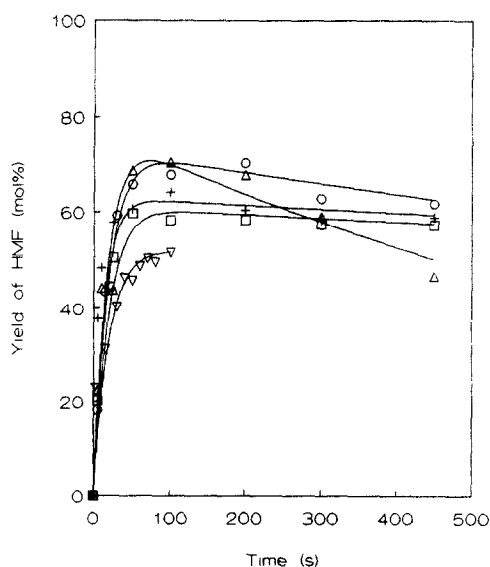

Fig. 4. Effect of water concentration on HMF yield. ([H$_2$O]$_0$: ▽ 0 M, □ 1.0 M, +2.5 M, ○ 7.5 M, △ 13.0 M. Reaction conditions: [DIpF-1]$_0$ 0.5 M, [H$_2$SO$_4$]$_0$ 0.005 M, T 483 K, ethylene glycol dimethyl ether.)

its rate of degradation. Therefore low HMF yields were obtained using either 1,2:4,5-di-*o*-isopropylidene-β-D-fructopyranose or 2,3:4,5-di-*o*-isopropylidene-β-D-fructopyranose as the starting material at low concentrations of water.

The solvation of the acid proton by adding water diminishes its acidity, which can reduce the catalytic activity. However, water increases the hydrolysis rate of 1,2:4,5-di-*o*-isopropylidene-β-D-fructopyranose to fructose and the solubilities of both fructose and its reversion products. Although the equilibrium between fructose and its reversion products can be shifted towads fructose by adding more water in an organic solution,[17] it was identified by g.l.c. that some complicated reversion products of fructose existed when using a water concentration of 7.5 M, especially at higher reactant concentrations (0.75 and 1.0 M). These reversion products could also be found in systems using DMSO as solvent. Figure 4 shows that the disappearance of HMF was speeded up using a water concentration of 13 M. This could be attributed to the formation of levulinic and formic acid. Fructose could also be dissolved directly in a mixture of water (13 M)/ethylene glycol dimethyl ether up to 0.5 M, but a HMF yield of only 61.4 mol% could be obtained compared to a 70.4 mol% from 1,2:4,5-di-*o*-isopropylidene-β-D-fructopyranose under the same reaction conditions.
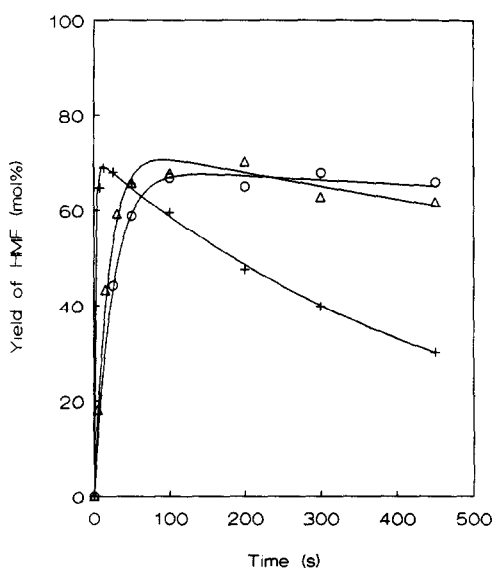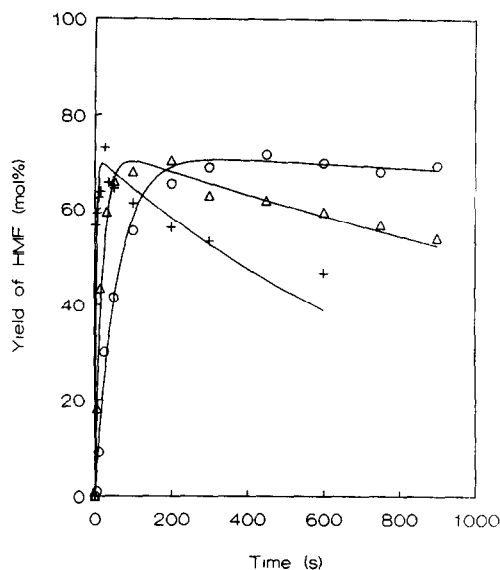

Fig. 6. Influence of temperature on HMF yield. (Temperature: O 453 K, △ 483 K, + 513 K. Reaction conditions: $[DIpF-1]_0$ 0.5 M, $[H_2SO_4]_0$ 0.005 M, $[H_2O]_0$ 7.5 M, ethylene glycol dimethyl ether.)

3.4. Influence of sulfuric acid concentration and temperature on HMF yield

Figures 5 and 6 show that sulfuric acid concentration and temperature apparently influences the HMF formation rate, but bring about little difference in HMF yield. HMF in ethylene glycol dimethyl ether has shown to be stable up to a temperature of 453 K.

Recently, Urashima *et al.*[44] investigated the condensation of HMF with some aldoses on heating, by means of [1]H-n.m.r., g.l.c.-m.s. and thin-layer chromatography and provided some evidence that polymerization can be caused by condensation of HMF with sugars. As can be seen in Figs 5 and 6, side reactions mainly occur at an early stage prior to reaching a maximum HMF yield, which seems to indicate that the polymerization in the organic solvent is mainly caused by the interaction of HMF with fructose or intermediates.

3.5. Influence of reactant concentration on HMF yield

For economic reasons fructose concentrations should be as high as possible. Figure 7 shows the dependence of HMF yield on initial reactant concentration. It can be seen that HMF yields amounted to 71.4, 68.4 and 64 mol% when using high reactant concentrations of 0.5, 0.75 and 1.0 M respectively.

Using diluted aqueous solutions (0.01 to 0.1 M), Antal and Mok[45] demonstrated that low
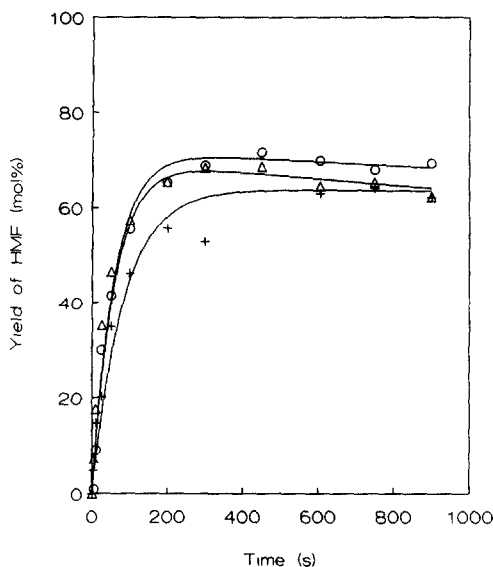

Fig. 5. Influence of sulfuric acid concentration on HMF yield. ($[H_2SO_4]_0$: O 0.0013 M, △ 0.005 M, + 0.020 M. Reaction conditions: $[DIpF-1]_0$ 0.5 M, $[H_2O]_0$ 7.5 M, T 483 K, ethylene glycol dimethyl ether.)

Fig. 7. Influence of initial 1,2:4,5-di-o-isopropylidene-β-D-fructopyranose concentration on HMF yield. ([DIpF-I]$_0$: $\bigcirc$ 0.50 M, $\ominus$ 0.75 M, $+$ 1.00 M. Reaction conditions: [H$_2$SO$_4$]$_0$ 0.005 M, [H$_2$O]$_0$ 7.5 M, T 453 K, ethylene glycol dimethyl ether.)

ene glycol dimethyl ether containing some water and sulfuric acid as a catalyst for the preparation of HMF has been found to be a feasible process. HMF yields amounted to more than 70 mol% at a full conversion of fructose. These results were obtained for several combinations of temperature, concentrations of both acid and water, using a reactant concentration of 0.5 M. The organic solvent mixed with an appropriate amount of water provides good reaction conditions. Temperature and acid concentration strikingly influence the catalytic activity, but have little effect on the yield of HMF.

Ethylene glycol dimethyl ether is a cheap and easily regenerable solvent. In the acidic medium no by-product is produced from the solvent itself and HMF has shown to be stable in it up to a temperature of 453 K. Polymers as by-products remain dissolved in this system, therefore this reaction can be carried out in a continuous tubular reactor without the problem of plugging.

fructose concentrations also resulted in low HMF yields. We also observed that even if DMSO was applied as a solvent, a very dilute fructose solution (e.g. 0.02 M) led to a relatively low yield. Other side reactions such as oxidation of HMF in the presence of a strong acid and oxygen or reactions of HMF with some impurities probably arise more significantly in these cases. In contrast, in aqueous systems with high fructose concentrations, generally higher fructose concentrations lead to lower HMF yields and selectivities, due to higher order polymerization reactions and a possible destabilizing effect of carbohydrate on HMF.[12,17]

Although a higher reactant concentration gives rise to a decrease in HMF yield, as can be seen in Fig. 7, this effect appears much less pronounced as compared to aqueous systems. This is probably attributed to the solvent properties of ethylene glycol dimethyl ether. In the new system, the fructose produced from the hydrolysis of 1,2:4,5-di-o-isopropylidene-β-D-fructopyranose and HMF might be stabilized by the solvent to prevent further side reactions, thus minimizing the humin formation and giving reasonably high yields of HMF even employing high reactant concentrations.

4. CONCLUSIONS

The use of 1,2:4,5-di-o-isopropylidene-β-D-fructopyranose as a reactant dissolved in ethyl-

REFERENCES

1. G. Dull, Chem. Ztg 19, 166–216 (1895).
2. K. M. Rapp, Ger. Offen. DE 3,601,281 (1987); Chem. Abstr. 107, 154,231r (1987).
3. Q. P. Peniston, U.S. Pat. 2,750,394 (1956); 52, 1,284b (1958).
4. F. H. Snyder, U.S. Pat. 2,851,468 (1958); 53, 5,673d (1959).
5. S. W. Mckibbins, Ph.D. Thesis, University of Wisconsin, USA (1958).
6. J. F. Harris, J. F. Saeman and L. L. Zoch, For. Prod. J. 10, 125–128 (1960).
7. R. A. Hales, J. W. Le Maistre and G. O. Orth, U.S. Pat. 3,071,599 (1963); 59, 576a (1963).
8. C. J. Moye and Z. S. Krzeminski, Aust. J. Chem. 16, 258–269 (1963).
9. C. J. Moye and R. J. Goldsack, J. Appl. Chem. 16, 206–208 (1966).
10. C. J. Moye, Aust. J. Chem. 19, 2317–2320 (1966).
11. B. M. Smythe and C. J. Moye, U.S. Pt. 3,219,484 (1965); 64 8,468g (1966).
12. B. F. M. Kuster, Ph.D. Thesis, Eindhoven University of Technology, The Netherlands, June (1975).
13. J. A. Middendorp, Recl. Trav. Chim. 38, 1–71 (1919).
14. W. N. Haworth and W. G. M. Jones, J. Chem. Soc. 667–670 (1944).
15. J. J. Breen, Ph.D. Thesis, Delft University of Technology, The Netherlands, July (1964).
16. J. D. Garber and R. E. Jones, U.S. Pat. 2,929,823 (1960); 54, 17,416i (1960).
17. H. E. van Dam, A. P. G. Kieboom and H. van Bekkum, Stärke 38, 95–101 (1986).
18. H. H. Szmant and D. D. Chundury, J. Chem. Technol. Biotechnol. 31, 135–145 (1981).

19. R. E. Jones and H. B. Lange, U.S. Pat. 3,066,150 (1962); 58, 4,723b (1963).
20. R. E. Jones and H. B. Lange, U.S. Re. 25,745 (1965); 62, 13,366b (1965).
21. J. D. Garber and R. E. Jones, U.S. Pat. 3,483,228 (1969); 72, 90,257c (1970).
22. Y. Nakamura, Jpn. Kokai Tokkyo Koho 80,13,243 (1980); 93, 26,260c (1980).
23. G. P. Potapov, V. I. Krupenskii and M. I. Alieva, *React. Kinet. Catal. Lett.* **28**, 331–337 (1985).
24. G. P. Potapov, V. I. Krupenskii and M. I. Alieva, *Kinet. Katal.* **28**, 205–207 (1987).
25. R. A. Schraufnagal and H. F. Rase, *Ind. Eng. Chem. Prod. Res. Dev.* **14**, 40–44 (1975).
26. Y. Nakamura and S. Morikawa, Jpn. Kokai Tokkyo Koho 79,154,757 (1979); 92 215,264z (1980).
27. D. Mercadier, L. Rigal, A. Gaset and J. P. Gorrichon, *J. Chem. Technol. Biotechnol.* **31**, 489–496 (1981).
28. D. Mercadier, L. Rigal, A. Gaset and J. P. Gorrichon, *J. Chem. Technol. Biotechnol.* **31**, 503–508 (1981).
29. L. Rigal, A. Gaset and J. P. Gorrichon, *Ind. Eng. Chem. Prod. Res. Dev.* **20**, 719–721 (1981).
30. D. W. Brown, A. J. Floyd, R. G. Kinsmann and Y. Roshan-Ali, *J. Chem. Technol. Biotechnol.* **32**, 920–924 (1982).
31. T. El Hajj, A. Maroua, J. C. Martin and G. Descotes, *Bull. Soc. Chim. Fr.* **5**, 855–860 (1987).
32. A. C. Cope, U.S. Pat. 2,917,520 (1959); 54, 8,851d (1960).
33. B. F. M. Kuster and H. J. C. van der Steen, *Stärke* **29**, 99–103 (1977).
34. L. Rigal and A. Gaset, *Biomass* **3**, 151–163 (1983).
35. P. Vinke and H. van Bekkum, Proceedings 3rd Symposium on Inulin, Wageningen 1. 3. 1989, to be published.
36. C. J. Moye, *Rev. Pure Appl. Chem.* **14**, 161–170 (1964).
37. Y. Nakamura and S. Morikawa, *Bull. Chem. Soc. Jpn* **53**, 3705–3706 (1980).
38. R. M. Musau and R. M. Munavu, *Biomass* **13**, 67–74 (1987).
39. B. F. M. Kuster and J. Laurens, *Stärke* **29**, 172–176 (1977).
40. B. F. M. Kuster, *Stärke* **42**, 314–321 (1990).
41. R. F. Brady, Jr., *Carbohydr. Res.* **15**, 35–40 (1970).
42. R. S. Tipson, B. F. West and R. F. Brady, Jr., *Carbohydr. Res.* **10**, 181–183 (1969).
43. B. F. M. Kuster, *Carbohydr. Res.* **54**, 177–183 (1977).
44. T. Urashima, K. Suyama and S. Adachi, *Food Chem.* **29**, 7–17 (1988).
45. M. J. Antal, Jr. and W. S. L. Mok, *Carbohydr. Res.* **199**, 91–109 (1990).