

1 (Manuscript for *Separation and Purification Technology*)

2

3 Production of 5-hydroxymethylfurfural in a eutectic mixture of
4 citric acid and choline chloride and its extractive recovery

5

6 Takashi Kobayashi*, Masashi Yoshino, Yayoi Miyagawa, Shuji Adachi

7

8 Division of Food Science and Biotechnology, Graduate School of Agriculture, Kyoto

9 University, Sakyo-ku, Kyoto 606-8502, Japan

10

11

12

13

14

15

16

17

18

19

20

21 *Corresponding author: Tel: +81-75-753-6288; Fax: +81-75-753-6285.

22 E-mail address: tkoba@kais.kyoto-u.ac.jp (T. Kobayashi)

23

1 **Abstract**

2 Synthesis of 5-hydroxymethylfurfural (HMF¹) from D-fructose was analyzed from the
3 kinetic and equilibrium points of view in a eutectic mixture of citric acid and choline
4 chloride (CA/CC) or in [Bmim]Cl to achieve an efficient production of HMF in a biphasic
5 reaction system. The partition coefficient of HMF between an organic solvent and the
6 ionic liquid phases was measured using various organic solvents. Among these solvents,
7 ethyl acetate was found to exhibit the best performance for the extractive recovery of
8 HMF. The stability of HMF was also evaluated in CA/CC at 70–120 °C, and HMF was
9 found to be stable below 80 °C. Kinetic analysis of the formation of HMF was performed
10 under the assumption that the fructose was converted into HMF through parallel and
11 consecutive reactions. The kinetically calculated results matched well with the
12 experimental ones. The reaction behaviors were different at low and high (over 20%
13 (kg/kg of IL)) initial fructose concentrations. At high initial fructose concentrations, the
14 equilibrium yield of HMF decreased with increasing initial fructose concentration. The
15 addition of ethyl acetate to the CA/CC phase (biphasic reaction) was effective in
16 improving the HMF yield, especially when the fructose concentration was high.

17

18 **Keywords:** Biphasic reaction, 5-hydroxymethylfurfural, ionic liquid, kinetics, partition
19 coefficient

20

¹ **Abbreviations:** HMF, 5-hydroxymethylfurfural; CA/CC, eutectic mixture of citric acid and choline chloride; DMSO, dimethyl sulfoxide; IL, ionic liquid; THF, tetrahydrofuran; MIBK, methyl isobutyl ketone; HPLC, high-performance liquid chromatography.

1 **Highlights**

2

- 3 • 5-Hydroxymethyl furfural (HMF) was produced in a eutectic mixture.
- 4 • Kinetic analysis of HMF formation represented the experimental results well.
- 5 • Equilibrium yield of HMF decreased with increasing fructose concentration.
- 6 • Extractive recovery of HMF by ethyl acetate was effective in the biphasic
7 reaction.

8

9

1. Introduction

5-Hydroxymethylfurfural (HMF) is a useful material in the preparation of biofuels such as 2,5-dimethylfuran and is a precursor for polymers such as 2,5-furandicarboxylic acid. HMF can be obtained by the decomposition of saccharides such as glucose or fructose. In recent years, there has been a considerable focus on environmental problems related with the depletion of fossil fuels and achieving carbon neutrality. Therefore, HMF derived from biomass is attractive as a substitute for oil products, and many studies aimed at its industrial use have been performed.

HMF can be synthesized using catalysts such as a metal cation, an acid catalyst, zeolite, or an ion exchange resin in water [1], a mixture of water and organic solvent [2–8], or in subcritical fluids [9,10]. However, the yield of HMF is relatively low in water. The use of dimethyl sulfoxide (DMSO) in water has also been studied [5]. However, there are difficulties in the recovery of HMF, despite improvements in the yield. Although HMF is mainly produced in the aqueous reaction media at present, it is easily decomposed into byproducts such as levulinic and formic acids by rehydration [10]. As a result, the production cost is high.

In recent years, ionic liquids (ILs) have emerged as a new reaction media. A eutectic mixture consisting of choline and various carboxylic acids or urea also shows properties similar to those of ILs [11]. Hu et al. added carboxylic acids to choline chloride to synthesize HMF from fructose [12]. They clarified that a eutectic mixture of citric acid monohydrate and choline chloride (CA/CC) was the most suitable reaction medium for maximizing HMF yield.

There are many reports focusing on the optimization of the conditions such as the

1 type of ILs and catalysts for HMF preparation in order to obtain high yields and high
2 concentrations of HMF [12–22]. However, the number of studies primarily focusing on
3 the kinetics of the formation of HMF in ILs is limited [13,14,18,19], and knowledge of
4 the kinetics is presently insufficient to adequately predict the formation of HMF.

5 Moreover, the extractive recovery of HMF from an IL has been performed using
6 organic solvents such as ethyl acetate [13–16,23], tetrahydrofuran (THF) [24,25],
7 methyl isobutyl ketone (MIBK) [26], and diethyl ether [27,28]. In the extraction process,
8 water is often added to the reaction mixture prior to extraction to improve the
9 extraction efficiency [14–16]. Subsequently, an organic solvent is added to recover HMF.
10 It is necessary to remove the added water from the ILs in order to reuse them, but the
11 process of water removal involves high energy consumption.

12 Therefore, the continuous extraction of HMF from a biphasic reaction system
13 containing an IL and an organic solvent has been tried. Young et al. recovered HMF
14 with 72% yield from a biphasic system consisting of 1-butyl-3-methylimidazolium
15 chloride ([Bmim]Cl) and THF [25]; Hu et al. succeeded in achieving 66% recovery in a
16 biphasic system consisting of CA/CC and ethyl acetate [12]. However, the extraction
17 conditions such as the types of organic solvents and ILs used and the ratio of the two
18 phases were different in these reports. Therefore, there is still a limited systematic
19 understanding of the partition behavior of HMF between the two phases.

20 In this study, the partition coefficient of HMF was measured using ILs ([Bmim]Cl and
21 CA/CC) and various organic solvents. In addition, kinetic and equilibrium analyses
22 were performed to understand the conversion of fructose to HMF in the CA/CC medium.
23 The formation and extraction behaviors of HMF were also analyzed in the biphasic

1 system.

2

3

4 **2. Materials and methods**

5 2.1. Materials

6 Choline chloride, citric acid monohydrate, and D-fructose were purchased from Wako
7 Pure Chemical Industries (Osaka, Japan) or Nacalai Tesque (Kyoto, Japan). [Bmim]Cl
8 and HMF were obtained from Tokyo Chemical Industry (Tokyo, Japan) and
9 Sigma-Aldrich (St. Louis, MO, USA), respectively. All the other chemicals were
10 purchased from Wako.

11 The CA/CC eutectic mixture was prepared by mixing CA and CC in a molar ratio of
12 70:30 [29]. The mixture was subsequently heated at 125 °C for 1 h with stirring.
13 Hereafter, the term 'IL' refers to CA/CC, unless otherwise specified.

14

15 2.2. Partition coefficient of HMF between IL and organic phases

16 The partition of HMF between the IL (CA/CC or [Bmim]Cl) and organic phases was
17 measured using THF, 2-butanol, ethyl acetate, MIBK, and toluene as the organic phase.
18 The organic solvent (ca. 100 mL) was vigorously mixed with the IL (ca. 100 g) at 70 °C
19 for ca. 10 min. After phase separation, both the phases were used (as an organic
20 solvent-saturated IL and IL-saturated organic solvent) to study the partitioning
21 behavior of HMF. In order to evaluate the effect of HMF concentration on the partition
22 coefficient, HMF (5–20 mg) was dissolved in the organic solvent-saturated IL (0.5–2 g),
23 and the solution was mixed with 2–10 g of the IL-saturated organic solvent. The final

1 mixture was heated in an oil bath at 60–80 °C with stirring for 2 h. After separation of
2 the IL and the organic phases, aliquots of the organic phase (ca. 10 µL) and the IL phase
3 (ca. 20 mg) were sampled, and their HMF contents were measured by high-performance
4 liquid chromatography (HPLC) after dilution with an HPLC eluent.

5 HPLC analysis was performed using an LC-10ATVP HPLC pump (Shimadzu, Kyoto,
6 Japan) connected to a Cosmosil HILIC HPLC column (3.0 I.D. × 150 mm, Nacalai). The
7 eluent was 95% acetonitrile with a flow rate of 0.4 mL/min. HMF was detected using a
8 Shimadzu SPD-10AVVP UV detector with a wavelength of 280 nm.

9

10 2.3. Stability of HMF in IL

11 HMF (20 mg) was added to 2 g of the IL (CA/CC), and the mixture was heated at
12 70–120 °C with stirring. Periodically, an aliquot (ca. 20 mg) of the mixture was sampled
13 and diluted 250 times with water. The conditions for the HPLC analyses were the same
14 as those described in 2.2.

15 To evaluate the byproducts formed such as levulinic acid and formic acid, the sample
16 solutions were also analyzed for these compounds by HPLC. The HPLC conditions were
17 almost the same as that for the HMF analysis, except that RID-10A refractometer
18 (Shimadzu) and UV detector (210 nm) were used.

19

20 2.4. Conversion of fructose to HMF

21 The IL (CA/CC, 2 g) and D-fructose were placed in a 20 mL glass vial with a final
22 fructose concentration of 1–50% (kg/kg of IL). The mixture was heated at 60–100 °C
23 with vigorous stirring. At appropriate intervals, an aliquot (ca. 20 mg) of the reaction

1 mixture was sampled, and its HMF and fructose contents were measured by HPLC. The
2 HMF yield was defined as the molar amount of HMF formed per initial molar amount of
3 fructose.

4 The fructose concentration was measured using the HPLC system described above
5 with a Cosmosil Sugar-D HPLC column (3.0 I.D. × 150 mm, Nacalai) and an RID-10A
6 refractometer. The eluent was 90% acetonitrile with a flow rate of 0.4 mL/min.

7

8 2.5. Formation and extractive recovery of HMF in a biphasic system

9 The IL (CA/CC; 2 g) saturated with ethyl acetate was mixed with 20 g of IL-saturated
10 ethyl acetate in a 50 mL glass vial. D-Fructose was added to the vial at the final fructose
11 concentration of 1–50% (kg/kg of IL). The mixture was heated at 70 °C with vigorous
12 stirring. The organic and IL phases were sampled at appropriate intervals and their
13 HMF contents were measured by HPLC. The conditions for the HPLC analyses were
14 the same as those described in 2.2.

15

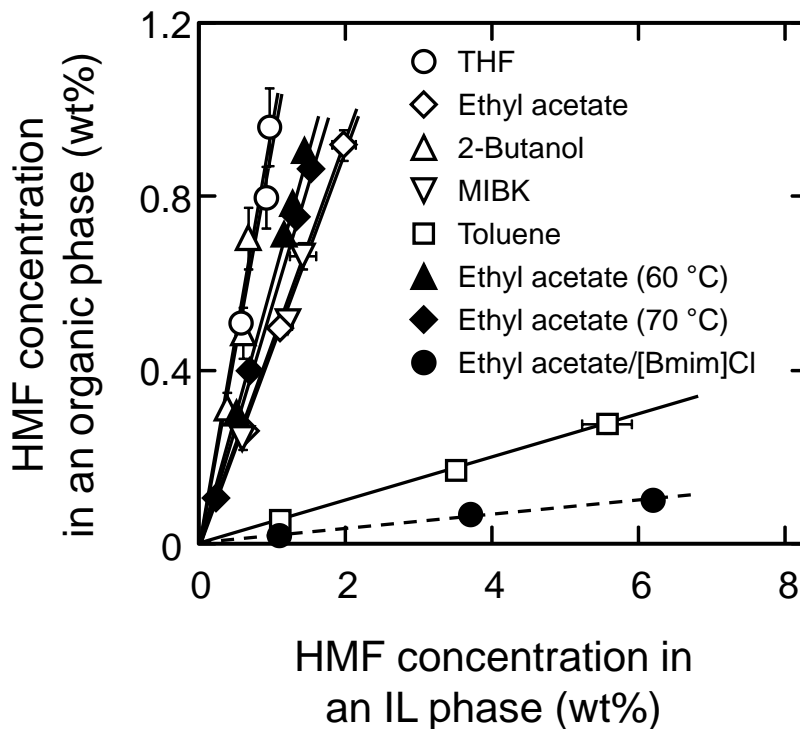
16 3. Results and discussion

17 3.1. Partition coefficient of HMF in a biphasic system

18 In these experiments, CA/CC or [Bmim]Cl was used as the IL to evaluate the
19 partition coefficient of HMF. Fig. 1 shows the HMF concentration in the organic phase
20 plotted against that in the IL phase for different combinations of organic solvents and
21 ILs with various HMF concentrations. The slope of each line provides the partition
22 coefficient of HMF between the organic and the IL phases. As seen in the figure, a
23 straight line was obtained in each case, indicating that the partition coefficient did not

1 depend on the HMF concentration, within the range of concentrations tested.

2



3

4 Fig. 1. Estimation of the partition coefficient of HMF in the organic phase versus the IL
5 phase at 60–80 °C. Open symbols refer to the data obtained using various organic
6 solvents and CA/CC at 80 °C. The closed symbols represent the data obtained using
7 ethyl acetate (organic phase) and CA/CC (IL phase) at 60 °C and 70 °C, respectively.
8 The closed circle represents the data obtained using ethyl acetate and [Bmim]Cl as
9 the organic phase and IL phase, respectively, at 80 °C.

10

11 When CA/CC was used as the IL phase, and THF was used as the organic phase, the
12 highest partition coefficient of 0.93 was obtained. In addition, when 2-butanol, ethyl
13 acetate, MIBK, and toluene were used as the organic solvent with CA/CC as the IL,
14 partition coefficients of 0.91, 0.46, 0.45, and 0.05, respectively, were obtained. Although

1 THF and 2-butanol gave higher partition coefficients compared to the other solvents,
2 these solvents exhibit some problems. THF often forms peroxides that would cause
3 explosion during the concentration and reuse of the solvent. In the case of 2-butanol, it
4 easily mixed with CA/CC, which would cause a loss of the IL and would complicate
5 operations during the purification of HMF. These issues were not observed when ethyl
6 acetate or MIBK were used. Furthermore, ethyl acetate can be more easily removed
7 than MIBK, because the evaporation enthalpy of ethyl acetate is lower than that of
8 MIBK. Based on these reasons, ethyl acetate was used for the rest of the study.

9 The dependence of the partition coefficient on temperature was evaluated next in the
10 60–80 °C range. Although the partition coefficient increased at lower temperatures, the
11 IL had a higher viscosity at temperatures below 60 °C that made stirring difficult.
12 Therefore, the optimum temperature for the extractive recovery of HMF was 70 °C.

13 On the other hand, when [Bmim]Cl and ethyl acetate were used, the partition
14 coefficient was very small (ca. 0.01). This result implies that [Bmim]Cl is unsuitable for
15 the extractive recovery of HMF.

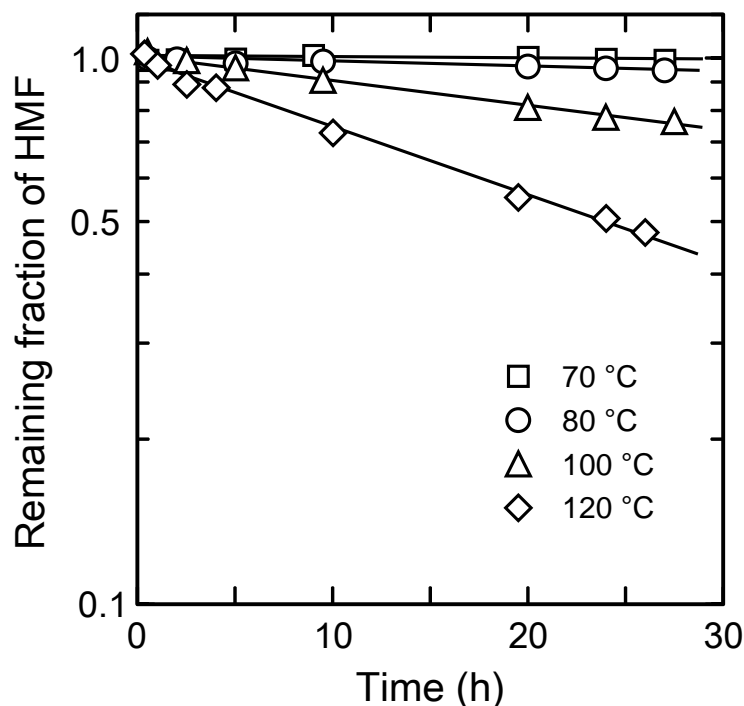
16

17 3.2. Stability of HMF in IL

18 The stability of HMF in the IL (CA/CC) was evaluated and the results are shown in
19 Fig. 2. Most of the HMF did not decompose over time and HMF was stable at
20 temperatures below 80 °C. When the temperature was higher than 100 °C, the
21 decomposition followed the first-order kinetics. At a temperature of 120 °C, only 51% of
22 the HMF remained after 24 h. The reaction mixture gradually turned into dark brown
23 over time at higher temperatures, suggesting the formation of humin from HMF.

1 Therefore, it is preferable to perform the reactions at temperatures below 100 °C.

2



3

4 Fig. 2. Stability of HMF in CA/CC at different temperatures at 70–120 °C.

5

6 There are some reports that suggest that formic and levulinic acids are formed as
7 byproducts of the rehydration of HMF in subcritical water [9,10]. However, in ILs, some
8 contradictory results have been observed. Some reports suggest that both formic and
9 levulinic acids are formed [15,30], whereas a report by Stahlberg et al. [31] and the
10 results of the present study suggest that while humin is formed, neither formic acid nor
11 levulinic acid is formed. The contradictory results indicate that the experiments were
12 performed in different ILs under various conditions, suggesting that small differences
13 in the conditions greatly influence the reaction behavior.

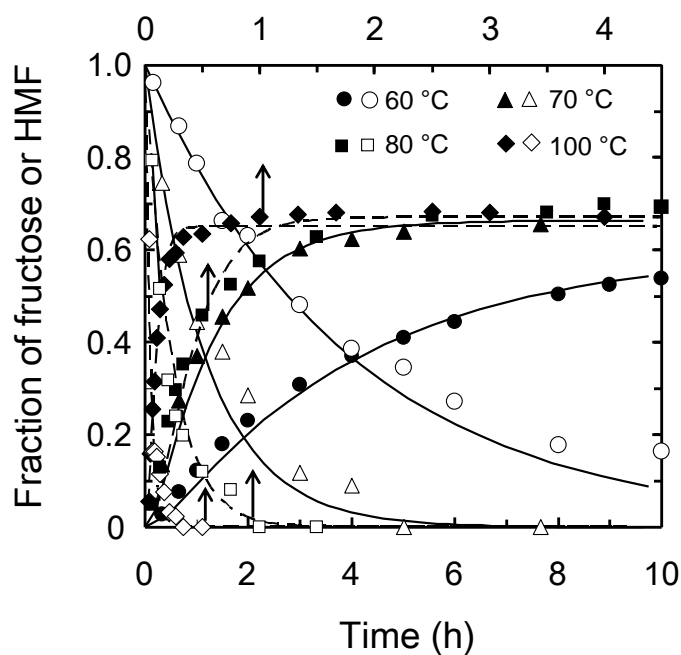
14

1

2 3.3. Kinetic analysis of the formation of HMF in ILs

3 Fig. 3 shows the time trend for the formation of HMF and the decrease in the amount
4 of fructose. In the 70–100 °C range, fructose was completely consumed. However, the
5 final yield was ca. 66%, implying that 34% of the fructose was converted into byproducts.
6 In addition, the formation of HMF began during the initial period of the reaction at each
7 temperature, and its decrease was not observed. These results suggest that the
8 byproducts would be directly formed from fructose.

9



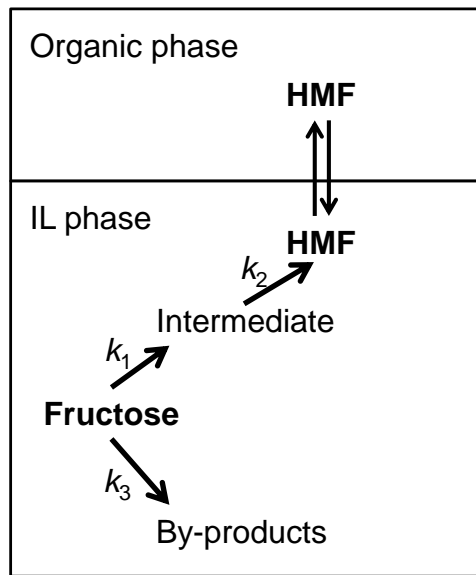
10

11 Fig. 3. Time trend of the fraction of HMF formed and the fructose consumed in the IL at
12 60–100 °C. The open and closed symbols represent fructose and HMF, respectively.
13 The curves are the calculated results.

14

15

1



2

3 Fig. 4. Schematic illustration of the formation mechanism of HMF and its partition into the
4 organic phase.

5

6 It was reported that the formation of some intermediates occurred during the
7 consecutive conversion of fructose to HMF in various reaction media [5,6,8,13,14,32]. In
8 order to simplify the reaction model, it was assumed that only one intermediate was
9 formed (Fig. 4). Further, a kinetic analysis was performed based on equations (1)–(4).

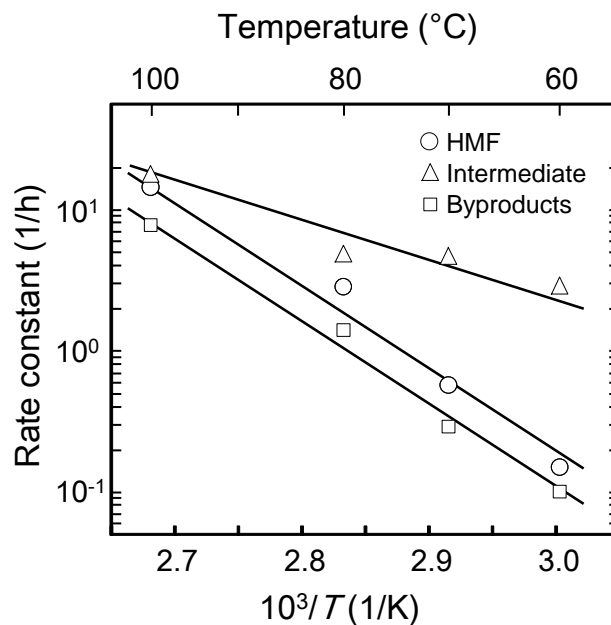
10
$$\frac{dC_F}{dt} = -(k_1 + k_3)C_F \quad (1)$$

11
$$\frac{dC_I}{dt} = k_1C_F - k_2C_I \quad (2)$$

12
$$\frac{dC_{HMF}}{dt} = k_2C_I \quad (3)$$

$$\frac{dC_{BP}}{dt} = k_3 C_F \quad (4)$$

2 where C_i is the concentration of the component i , k_j is the rate constant ($j=1, 2, 3$), and F,
 3 HMF, I, and BP refer to fructose, HMF, the intermediate, and the byproducts,
 4 respectively. Fig. 5 shows the rate constants that were determined by fitting the
 5 calculated results to the experimental data and determining the best fit using the
 6 Solver add-in in Microsoft® Excel 2010. A good fit was obtained between the calculated
 7 and the experimental results (Fig. 3), indicating that the proposed reaction model was
 8 reasonable. The activation energy corresponding to each reaction step was also
 9 calculated (Fig. 5) and the values were determined to be ca. 110 kJ/mol for fructose to an
 10 intermediate and for fructose to byproducts and ca. 54 kJ/mol for an intermediate to
 11 HMF. These values are reasonable for chemical reactions; they agree well with the
 12 previously reported results [4,6,13–15,18,19,28] and are somewhat higher than the
 13 results by Xiao et al. [17].



14

1 Fig. 5. Arrhenius plots of the formation of HMF, the intermediate, and the byproducts.

2

3 3.4. Influence of the fructose concentration

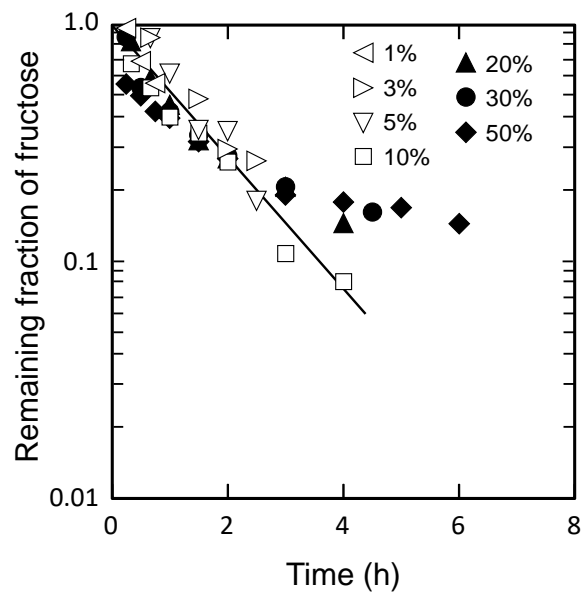
4 Because HMF is a raw material for fuels, high productivity is required to lower the
5 cost. One of the means for achieving this is to increase the initial fructose concentration.

6 Fig. 6 shows the time trend of the decrease in the fraction of fructose at 70 °C, when the
7 initial fructose concentration is in the range of 1–50% (kg/kg of IL). On a

8 semi-logarithmic plot, a straight line was observed at low fructose concentrations ($\leq 10\%$
9 (kg/kg of IL)) and the rate of decrease in the fructose concentration could be expressed

10 by the first-order kinetics. However, when the fructose concentration was greater than
11 20% (kg/kg of IL), the decrease in the fraction of fructose did not vary linearly with time

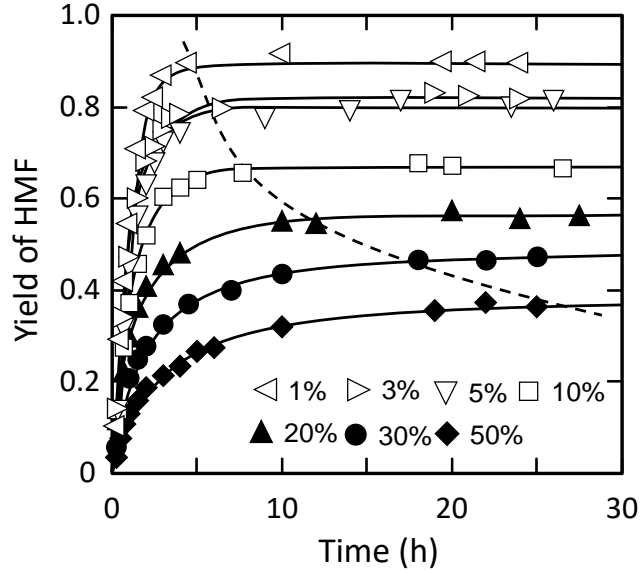
12 and became slower during the later stages of the reaction, suggesting that the reaction
13 did not follow first-order kinetics.



14

15 Fig. 6. Effect of the initial fructose concentration on the time trend of the decrease in the

1 fraction of fructose at 70 °C. The open and closed symbols respectively represent the data
2 obtained using initial fructose concentrations of 1–10% (kg/kg of IL) and 20–50%.

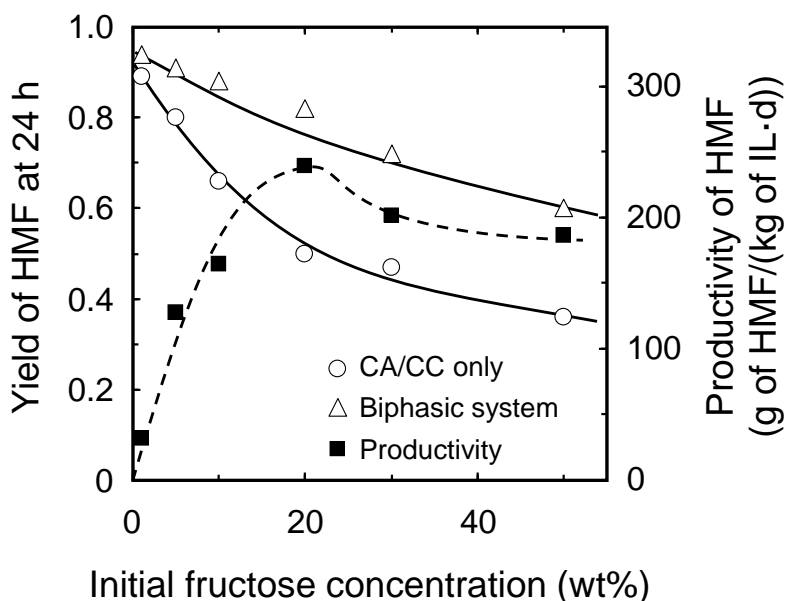


3
4 Fig. 7. Time trend of the fraction of HMF formed at various initial fructose concentrations at
5 70 °C. The symbols mean the same as in Fig. 6. The intersection of the dashed-curve
6 and the time trends represents the time at which the formation of HMF almost
7 reached the equilibrium at each fructose concentration.

8
9 Under all the conditions studied, the formation of HMF reached equilibrium within
10 30 h (Fig. 7). However, the time, at which the reaction reached equilibrium, became
11 shorter upon decreasing the initial fructose concentration, as shown by the
12 dashed-curve in Fig. 7. The HMF yield nearly reached equilibrium within 5 h, when the
13 fructose concentration was 1% (kg/kg of IL), whereas it took ca. 27 h to reach
14 equilibrium when the fructose concentration was 50% (kg/kg of IL). In addition, the
15 equilibrium yield appeared to depend on the fructose concentration, and decreased with
16 increasing fructose concentration. The reaction mechanism could also change with a

1 change in the fructose concentration. The above phenomena could be elucidated as
 2 follows. When the fructose concentration was lower than 5% (kg/kg of IL), the solution
 3 contained more than 95% of the IL. Under such conditions, the reaction would be
 4 strongly affected by the properties of the IL. As the fructose concentration became
 5 higher, the influence of the IL on the reaction behavior would decrease. In these states,
 6 fructose by itself or its derivatives including HMF would play the role of the reaction
 7 medium. Owing to the change in the reaction medium, the reaction mechanism and the
 8 equilibrium yield could be expected to change.

9
 10



11

12 Fig. 8. Effect of the initial fructose concentration on the equilibrium yield and productivity of
 13 HMF at 70 °C in CA/CC only and in a CA/CC-ethyl acetate biphasic system. The closed
 14 squares with the dashed-curve represent the productivity of HMF (g of HMF/(kg of
 15 IL·d)) when the optimum reaction time calculated from Fig. 7 was adopted. The weight

1 ratio of ethyl acetate and CA/CC was 10:1 in the biphasic system.

3 3.5. Biphasic reactions

4 The HMF yield decreased with an increasing fructose concentration, as described
5 above. In order to efficiently recover HMF, a biphasic reaction was performed using
6 ethyl acetate at 70 °C for 24 h, where the fructose concentration ranged from 1% to 50%
7 (kg/kg of IL). The addition of ethyl acetate did not improve the yield of HMF
8 significantly, for fructose concentrations less than 10% (kg/kg of IL) (Fig. 8). On the
9 other hand, when the fructose concentration was 20–50% (kg/kg of IL), the yield was
10 greatly improved. Since the yield generally improves by increasing the ratio of the
11 organic phase to the IL phase, the yield could be improved further by continuously
12 replacing the organic solvent.

13 The productivity of HMF was evaluated next. Higher fructose concentrations were
14 accompanied by a higher HMF equilibrium concentration. However, a longer time was
15 required for the reaction to reach equilibrium for higher fructose concentrations.
16 Therefore, an optimum fructose concentration exists for achieving the best productivity.
17 The productivity was calculated by considering the time taken to reach equilibrium for
18 a given fructose concentration. As shown in the dashed-curve in Fig. 8, while the
19 productivity increased with increasing fructose concentration for fructose
20 concentrations lower than 20% (kg/kg of IL), it decreased at higher fructose
21 concentrations owing to the longer time required to reach equilibrium. Therefore, 20%
22 (kg/kg of IL) was the optimum fructose concentration, in the present study.

1 **4. Conclusions**

2 The kinetic model considered in this study for the formation of HMF predicted the
3 experimental results in the CA/CC system well. It was assumed that parallel and
4 consecutive reactions occurred at low initial fructose concentrations and that HMF was
5 stable. Meanwhile, the reaction behavior greatly changed when the initial fructose
6 concentration increased, especially when it was greater than 20% (kg/kg of IL). The
7 addition of ethyl acetate to the CA/CC phase was effective in improving the equilibrium
8 yield of HMF at high initial fructose concentrations.

9

10

11 **References**

12 [1] P. Carniti, A. Gervasini, M. Marzo, Absence of expected side-reaction in the
13 dehydration reaction of fructose to HMF in water over niobic acid catalyst, *Catal.*
14 *Commun.* 12 (2011) 1122–1126.

15 [2] R. Huang, W. Qi, R. Su, Z. He, Integrating enzymatic and acid catalysis to convert
16 glucose into 5-hydroxymethylfurfural, *Chem. Commun.* 46 (2010) 1115–1117.

17 [3] C. Moreau, R. Durand, S. Razigade, J. Duhamet, P. Faugeras, P. Rvalier, P. Ros, G.
18 Avignon, Dehydration of fructose to 5-hydroxymethylfurfural over H-mordenite,
19 *Appl. Catal. A145* (1996) 211–224.

20 [4] X. Qi, M. Watanabe, T.M. Aida, R.L. Smith, Jr., Catalytic dehydration of fructose into
21 5-hydroxymethylfurfural by ion-exchange resin in mixed-aqueous system by
22 microwave heating, *Green Chem.* 10 (2008) 799–805.

23 [5] J.N. Chheda, Y. Roman-Leshkov, J.A. Dumesic, Production of

- 1 5-hydroxymethylfurfural and furfural by dehydration of biomass-derived mono- and
2 poly-saccharides, *Green Chem.* 9 (2007) 342–350.
- 3 [6] Y. Roman-Leshkov, J.A. Dumesic, Solvent effects on fructose dehydration to
4 5-hydroxymethylfurfural in biphasic system saturated with inorganic salts, *Top*
5 *Catal.* 52 (2009) 297–303.
- 6 [7] Y. Yang, C. Hu, M.M. Abu-Omar, Conversion of carbohydrates and lignocellulosic
7 biomass into 5-hydroxymethylfurfural using $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ catalyst in a biphasic
8 solvent system, *Green Chem.* 14 (2012) 509–513.
- 9 [8] Y. Roman-Leshkov, J.N. Chheda, J.A. Dumesic, Phase modifiers promote efficient
10 production of hydroxymethylfurfural from fructose, *Science* 312 (2006) 1933–1937.
- 11 [9] M. Bicker, J. Hirth, H. Vogel, Dehydration of fructose to 5-hydroxymethylfurfural in
12 sub- and supercritical acetone, *Green Chem.* 5 (2003) 280–284.
- 13 [10] F.S. Asghari and H. Yoshida, Kinetics of decomposition of fructose catalyzed by
14 hydrochloric acid in subcritical water: Formation of 5-hydroxymethylfurfural,
15 levulinic, and formic acids, *Ind. Eng. Chem. Res.* 46 (2007) 7703–7710.
- 16 [11] A.P. Abbott, D. Boothby, G. Capper, D.L. Davies, R.K. Rasheed, Deep eutectic
17 solvents formed between choline chloride and carboxylic acids: Versatile
18 alternatives to ionic liquids, *J. Am. Chem. Soc.* 126 (2004) 9142–9147.
- 19 [12] S. Hu, Z. Zhang, Y. Zhou, B. Han, H. Fan, W. Li, J. Song, Y. Xie, Conversion of
20 fructose to 5-hydroxymethylfurfural using ionic liquids prepared from renewable
21 materials, *Green Chem.* 10 (2008) 1280–1283.
- 22 [13] X. Qi, M. Watanabe, T.M. Aida, R.L. Smith, Jr., Fast transformation of glucose and
23 di-/polysaccharides into 5-hydroxymethylfurfural by microwave heating in an ionic

- 1 liquid/catalyst system, *ChemSusChem* 3 (2010) 1071–1077.
- 2 [14] Z. Wei, Y. Li, D. Thushara, Y. Liu, Q. Ren, Novel dehydration of carbohydrates to
3 5-hydroxymethylfurfural catalyzed by Ir and Au chlorides in ionic liquids, *J. Taiwan*
4 *Inst. Chem. Eng.* 42 (2011) 363–370.
- 5 [15] X. Qi, M. Watanabe, T.M. Aida, R.L. Smith, Jr., Efficient process for conversion of
6 fructose to 5-hydroxymethylfurfural with ionic liquids, *Green Chem.* 11 (2009)
7 1327–1331.
- 8 [16] P. Wang, H. Yu, S. Zhan, S. Wang, Catalytic hydrolysis of lignocellulosic biomass into
9 5-hydroxymethylfurfural in ionic liquid, *Biores. Technol.* 102 (2011) 4179–4183.
- 10 [17] Y. Xiao and Y.-F. Song, Efficient catalytic conversion of the fructose into
11 5-hydroxymethylfurfural by heteropolyacids in the ionic liquid of 1-butyl-3-methyl
12 imidazolium chloride, *Appl. Catal. A Gen.* 484 (2014) 74–78.
- 13 [18] J. Zhang, Y. Cao, H. Li, X. Ma, Kinetic studies on chromium-catalyzed conversion of
14 glucose into 5-hydroxymethylfurfural in alkyimidazolium chloride ionic liquid,
15 *Chem. Eng. J.* 237 (2014) 55–61.
- 16 [19] L. Hu, Z. Wu, J. Xu, Y. Sun, L. Lin, S. Liu, Zeolite-promoted transformation of
17 glucose into 5-hydroxymethylfurfural in ionic liquid, *Chem. Eng. J.* 244 (2014)
18 137–144.
- 19 [20] B. Liu, Z. Zhang, Z.K. Zhao, Microwave-assisted catalytic conversion of cellulose into
20 5-hydroxymethylfurfural in ionic liquids, *Chem. Eng. J.* 215–216 (2013) 517–521.
- 21 [21] S. Xiao, B. Liu, Y. Wang, Z. Fang, Z. Zhang, Efficient conversion of cellulose into
22 biofuel precursor 5-hydroxymethylfurfural in dimethyl sulfoxide–ionic liquid
23 mixtures, *Biores. Technol.* 151 (2014) 361–366.

- 1 [22] Y. Li, H. Liu, C. Song, X. Gu, H. Li, W. Zhu, S. Yin, C. Han, The dehydration of
2 fructose to 5-hydroxymethylfurfural efficiently catalyzed by acidic ion-exchange
3 resin in ionic liquid, *Biores. Technol.* 133 (2013) 347–353.
- 4 [23] S. Hu, Z. Zhang, Y. Zhou, J. Song, H. Fan, B. Han, Direct conversion of inulin to
5 5-hydroxymethylfurfural in biorenewable ionic liquids, *Green Chem.* 11 (2009)
6 873–877.
- 7 [24] L. Lai, Y. Zhang, The effect of imidazolium ionic liquid on the dehydration of fructose
8 to 5-hydroxymethylfurfural, and a room temperature catalytic system,
9 *ChemSusChem* 3 (2010) 1257–1259.
- 10 [25] J. Young, G. Chan, Y. Zhang, Selective conversion of fructose to
11 5-hydroxymethylfurfural catalyzed by tungsten salts at low temperatures,
12 *ChemSusChem* 2 (2009) 731–734.
- 13 [26] F. Tao, H. Song, L. Chou, Hydrolysis of cellulose by using catalytic amounts of FeCl₂
14 in ionic liquids, *ChemSusChem* 3 (2010) 1298–1303.
- 15 [27] G. Yong, Y. Zhang, J.Y. Ying, Efficient catalytic system for the selective production of
16 5-hydroxymethylfurfural from glucose and fructose, *Angew. Chem. Intl. Ed.* 47
17 (2008) 9345–9348.
- 18 [28] C. Moreau, A. Finiels, L. Vanoye, Dehydration of fructose and sucrose into
19 5-hydroxymethylfurfural in the presence of 1-H-3-methyl imidazolium chloride
20 acting both as solvent and catalyst, *J. Mol. Catal. A Chem.* 253 (2006) 165–169.
- 21 [29] M. Avalos, R. Babiano, P. Cintas, J.L. Jimenez, J.C. Palacios, Greener media in
22 chemical synthesis and processing, *Angew. Chem. Intl. Ed.* 45 (2006) 3904–3908.
- 23 [30] X. Qi, M. Watanabe, T.M. Aida, R.L. Smith, Jr., Efficient catalytic conversion of

1 fructose into 5-hydroxymethylfurfural in ionic liquids at room temperature,
2 ChemSusChem 2 (2009) 944–946.

3 [31] T. Stahlberg, M.G. Sorensen, A. Riisager, Direct conversion of glucose to
4 5-(hydroxymethyl)furfural in ionic liquids with lanthanide catalysts, Green Chem.
5 12 (2010) 321–325.

6 [32] M.J. Antal, Jr., W.S.L. Mok, G.N. Richards, Mechanism of formation of
7 5-(hydroxymethyl)-2-furaldehyde from D-fructose and sucrose. Carbohydr. Res. 199
8 (1990) 91–109.

9