



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



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## ABSTRACT

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

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

Moreover, the extractive recovery of HMF from an IL has been performed using organic solvents such as ethyl acetate [13–16,23], tetrahydrofuran (THF) [24,25], methyl isobutyl ketone (MIBK) [26], and diethyl ether [27,28]. In the extraction process, water is often added to the reaction mixture prior to extraction

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.

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to improve the extraction efficiency [14–16]. Subsequently, an organic solvent is added to recover HMF. It is necessary to remove the added water from the ILs in order to reuse them, but the process of water removal involves high energy consumption.

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

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

## 2. Materials and methods

### 2.1. Materials

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

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

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

The partition of HMF between the IL (CA/CC or [Bmim]Cl) and organic phases was measured using THF, 2-butanol, ethyl acetate, MIBK, and toluene as the organic phase. The organic solvent (ca. 100 mL) was vigorously mixed with the IL (ca. 100 g) at 70 °C for ca. 10 min. After phase separation, both the phases were used (as an organic solvent-saturated IL and IL-saturated organic solvent) to study the partitioning behavior of HMF. In order to evaluate the effect of HMF concentration on the partition coefficient, HMF (5–20 mg) was dissolved in the organic solvent-saturated IL (0.5–2 g), and the solution was mixed with 2–10 g of the IL-saturated organic solvent. The final mixture was heated in an oil bath at 60–80 °C with stirring for 2 h. After separation of the IL and the organic phases, aliquots of the organic phase (ca. 10  $\mu$ L) and the IL phase (ca. 20 mg) were sampled, and their HMF contents were measured by high-performance liquid chromatography (HPLC) after dilution with an HPLC eluent.

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

### 2.3. Stability of HMF in IL

HMF (20 mg) was added to 2 g of the IL (CA/CC), and the mixture was heated at 70–120 °C with stirring. Periodically, an aliquot

(ca. 20 mg) of the mixture was sampled and diluted 250 times with water. The conditions for the HPLC analyses were the same as those described in Section 2.2.

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

### 2.4. Conversion of fructose to HMF

The IL (CA/CC, 2 g) and D-fructose were placed in a 20 mL glass vial with a final fructose concentration of 1–50% (kg/kg of IL). The mixture was heated at 60–100 °C with vigorous stirring. At appropriate intervals, an aliquot (ca. 20 mg) of the reaction mixture was sampled, and its HMF and fructose contents were measured by HPLC. The HMF yield was defined as the molar amount of HMF formed per initial molar amount of fructose.

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

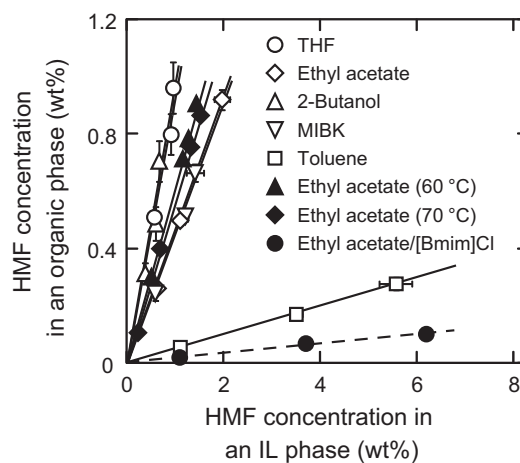
### 2.5. Formation and extractive recovery of HMF in a biphasic system

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

## 3. Results and discussion

### 3.1. Partition coefficient of HMF in a biphasic system

In these experiments, CA/CC or [Bmim]Cl was used as the IL to evaluate the partition coefficient of HMF. Fig. 1 shows the HMF concentration in the organic phase plotted against that in the IL



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

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