



Green process for 5-(chloromethyl)furfural production from biomass in three-constituent deep eutectic solvent

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Abstract: 5-(Chloromethyl)furfural (CMF), a versatile bio-platform molecule, was first synthesized in a three-constituent deep eutectic solvent (3c-DES) including choline chloride, $AlCl_3 \cdot 6H_2O$, and oxalic acid. In particular, 3c-DES was conducive for the production of CMF from glucose and provided a CMF yield of 70% at 120 $^{\circ}$ C within 30 min. In addition, CMF yields reached up to 86, 80, 30, 29, and 35% from fructose, sucrose, cellulose, bamboo, and bamboo pulp, respectively. This study opens new avenues for the preparation of CMF.

Considering the depletion of fossil resources, it is urgent to develop biomass utilization for preparation of the alternative renewable chemicals^[1]. To date, 5-hydroxymethylfurfural (HMF) has been in the spotlight as an intermediate for the valorization of biomass into value-added chemicals, biofuels, and functional materials^[2]. However, the inevitable condensation reaction and humins formation under acidic conditions make the separation and purification of HMF enormously challenging ^[3]. Hence, it limits large-scale industrial applications of HMF as a bio-based platform chemical.

Recently, 5-(chloromethyl)furfural (CMF), as a key platform molecule, has attracted much attention for the preparation of monomers, biofuels, and versatile chemicals (Figure 1) such as 2,5-furandicarboxylate ^[4], alkoxymethylfurfurals ^[5], δ-aminolevulinic acid (ALA) ^[6], and gasoline-like C8-C10 hydrocarbons ^[7]. Compared with HMF, CMF is more stable and has excellent hydrophobicity, which markedly facilitate the isolation and purification processes ^[8]. Moreover, the most remarkable feature of CMF is that it could be obtained with higher yield directly from biomass^[5].

In early 1901, the synthesis of CMF was first realized via the reaction of carbohydrates and hydrochloric acid (HCl) ^[9]. In 1981, CMF was obtained from glucose with HCl/chlorobenzene system

with a yield of 45% ^[10]. However, it did not receive enough attention until CMF was efficiently prepared directly from glucose and cellulose with HCl/dichloroethane (DCE) system in 2008 ^[5], which broadens the road of CMF synthesis. Inspired by this work, various processes have been developed based on the typical HCl/DCE system, such as intermittent extraction^[11], microwave heating^[12], and using benzyltributylammonium chloride (BTBAC) as phase transfer catalyst ^[13]. Much effort has been devoted to the field of CMF production, but some inevitable shortcomings, such as highly corrosive concentrated acid, harsh conditions, and long reaction time should not be ignored. Thus, developing a green, safe, and high-efficient process to produce CMF from renewable biomass besides sugar is desirable.



Figure 1. 5-(Chloromethyl)furfural (CMF) as a bio-platform molecule.

In our previous work^[14], a novel method for the synthesis of CMF based on deep eutectic solvent (DES) consisting choline chloride (ChCl) and sugars was developed. The dependence on concentrated HCl was eliminated, and CMF could be prepared with 50 and 17% yield from fructose and glucose, respectively

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(Table 1, entry 5). In this work, we followed up on the DES-based synthesis of CMF with a three-constituent DES (3c-DES) including ChCl, AlCl₃·6H₂O, and oxalic acid (OA). A CMF yield up to 70% from glucose was obtained at 120 $^{\circ}$ C within 30 min (Table 1, entry 6), and the CMF yield could be further improved to 76% by intermittent extraction (Table 1, entry 7). Compared to previous reports, 3c-DES provided not only milder conditions, but also competitive yields within much shorter reaction time for the synthesis of CMF.

 Table 1. Comparison between reported methods for the synthesis of CMF from alucose.

Entry	Catalytic system	Reaction conditions	Yield (%)	Ref.
1	HCI	75±2 ℃, 24 h	45	[10]
2	HCI	100 ℃, 1 h, 3 times	81	[11]
3	HCI	80 °C, 0.25 h, microwave	39	[12]
4	HCI, BTBAC	90 °C,3h	64	[13]
5	ChCl, AlCl ₃ .6H ₂ O	120 °C,5h	17	[14]
6 ^[a]	ChCl, AlCl₃⋅6H₂O, oxalic acid	120 °C, 0.5 h	70	This work
7 ^[b]	ChCl, AlCl₃•6H₂O, oxalic acid	120 ℃, 0.5 h, 3 times	76	This work

Reaction conditions for this work: 0.4 mmol glucose, 12.5 mmol ChCl, 15 mmol oxalic acid, 2 mmol AlCl₃· $6H_2O$. [a] 15 mL DCE. [b] extracted with 15 mL DCE every 0.5 h, 3 times.

Various organic carboxylic acids have been screened in the 3c-DES/DCE system (Figure 2a). In a controlled reaction without carboxylic acid additives, CMF (17%) and HMF (2%) were detected as major products. When oxalic acid (OA) was introduced into the reaction, the yield of CMF increased to 46%, followed by malic acid (MA, 30%), citric acid (CA, 27%), formic acid (FA, 25%), succinic acid (SA, 20%), and acetic acid (HAc, 17%). After reaction, the color of the biphasic reaction system darkened due to the formation of humus in the process^[15], which was the reason that oxalic acid, as a part of 3c-DES, provided complete glucose conversion but only a moderate CMF yield (46%) (Figure S1). The effect of oxalic acid loading on the product was also explored, as shown in Figure 2b. The optimal loading of oxalic acid was 15 mmol, providing a 51% CMF yield. The introduction of oxalic acid obviously enhanced the catalytic performance of DES since both carboxylic groups and the possible chelation between oxalic acid and Al contribute to the strong Brønsted acidity [16], which promoted sugars dehydration and also HMF chlorination by in situ formation of hydrochloric acid.

Figure 2c showed the effect of various metal salts on CMF preparation. It was noted that $AICI_3 \cdot 6H_2O$ provided the highest CMF yield (51%), which was followed by $CrCI_3 \cdot 6H_2O$ (50%) and MgCl·6H₂O (48%). In addition, the resulting 3c-DES including $AICI_3 \cdot 6H_2O$, $CaCI_2 \cdot 2H_2O$, $MgCI_2$, or $AICI_3$ were liquid at room temperature, which all showed excellent "deep" and "eutectic" characters (Figure S2). In view of catalytic activity, safety, and accessibility, we selected $AICI_3 \cdot 6H_2O$ for further experiments.

Figure 2d showed the effect of AlCl₃·6H₂O loading on product distribution. A CMF yield of 25% and almost 0% HMF were obtained in the controlled experiment without AlCl₃·6H₂O. When 0.5 mmol of AlCl₃·6H₂O was introduced into the reaction system, the CMF yield was dramatically increased to 42%. Further increasing AlCl₃·6H₂O loading to 2 mmol led to a 52% CMF yield. However, when 3.5 mmol of AlCl₃·6H₂O was applied, the yield of CMF decreased to 42%. This was caused by the formation of by-products (e.g., humins) due to overmuch acid sites in the system^[15a, 17]. It is also noteworthy that AlCl₃·6H₂O loading up to 3.5 mmol led to nearly complete glucose conversion.



Figure 2. (a) Glucose conversion, CMF and HMF yields obtained in the presence of various organic acids. (b) Effects of oxalic acid loading. (c) Effects of various metal salts. (d) Effects of different loading of AlCl₃.6H₂O. (e) CMF production from glucose in 3c-DES/DCE media. Reaction conditions: 2 mmol glucose, 12.5 mmol ChCl, 15 mL DCE, 120 $^{\circ}$ C, 2 h. (a) 12.5 mmol organic acids and 2.5 mmol AlCl₃.6H₂O; (b) 2.5 mmol AlCl₃.6H₂O; (c) 15 mmol OA and 2.5 mmol metal salts; (d) 15 mmol OA.

Figure 2e showed the biphasic system for CMF production from glucose including 3c-DES phase (bottom) and organic extraction phase (DCE, top). In 3c-DES phase, glucose was dehydrated to HMF and then halogenated to CMF. CMF was further extracted into the organic phase, which effectively inhibited proton-induced degradation to HMF, LA and further condensation to humins ^[18].

It was also noticed that the synthesis of CMF in 3c-DES was greatly affected by extraction agents. As shown in Table S1,

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several industrial available aprotic solvents have been screened. Chlorinated solvents such as DCE, dichloromethane, and trichloroethane exhibited the stronger extraction ability, and the maximum CMF yield was 52, 51, and 50% at 120 $^{\circ}$ C in 2 h, respectively. Given the good performance, low reaction pressure, accessibility and fair price (about \$400 per ton), DCE was elected as the optimal extracting agent for 3c-DES based CMF production.

The effects of DCE volume were also studied (Table S1, entry 16-23). When the experiment was carried out without any extracting agent, the system was severely coked and almost no target products were detected. When the DCE volume was increased to 15 mL, the CMF yield increased significantly to 52%. Further increasing DCE volume did not greatly affect the yield of CMF. In order to improve the sustainability of extractant, the recyclability of DCE was studied (Figure S3). After evaporation, DCE (> 95% purity) was obtained and reused for five more runs, and the yield of CMF was almost unchanged.



Figure 3. Effects of reaction time and temperature on (a) CMF yield and (b) HMF yield. Reaction conditions: 2 mmol glucose, 12.5 mmol ChCl, 15 mmol OA, 2 mmol AlCl₃· $6H_2O$, 15 mL DCE.

Figure 3 shows the effects of reaction time and temperature on the yields of CMF and HMF. The reaction reached equilibrium state faster at higher reaction temperature, and the maximum CMF yield (55%) was obtained after 30 min at 120 °C. However, the DES system was likely to be destroyed at 130 °C and the yield of CMF was lower ^[19]. On the contrary, HMF yield decreased as the reaction proceeded (Figure 3b), which proved that glucose was first dehydrated to form HMF in 3c-DES, and HMF was further halogenated to CMF in the presence of protons and abundant CI⁻. Note that hydrogen bond could also be formed between HMF and ChCI (Scheme 1), which increased the stability of HMF and reduced the occurrence of side reactions (e.g., the formation of humins) ^[20]. Meanwhile, the maximum of HMF was only 6% at 130 °C in 10 min, indicating that halogenation of HMF to CMF is the fast step in this system.

Based on the discussion above, a plausible mechanism for CMF production from glucose in 3c-DES was proposed, as shown in Scheme 1. First, glucose was converted into enediolate intermediate in 3c-DES ^[2a, 21]. Under the action of Lewis acid (Al³⁺), fructose formed by isomerization and then dehydrated to HMF (path A) ^[22]. On the other hand, enediolate intermediate could be directly dehydrated into HMF catalyzed by Brønsted acid (path B) ^[21]. The sources of Cl in CMF were also further verified. During the halogenation process, the halogenation of HMF was relied on the *in-situ* generated "hydrochloric acid", which was composed of the proton ionized from oxalic acid and abundant Cl⁻ provided by ChCl and AlCl₃·6H₂O, the Cl⁻ in CMF

should be mostly provided by ChCl. To prove this hypothesis, different aluminum salts and choline bromide (ChBr) were used instead of AlCl₃·6H₂O and ChCl. When AlCl₃·6H₂O was replaced with Al₂(SO₄)₃·18H₂O, the yield of CMF decreased slightly (Table S2, entry 2), indicating that the Cl⁻ provided by AlCl₃·6H₂O was not the major source of the Cl in CMF. Replacing AlCl₃·6H₂O with AlBr₃ gave a CMF yield of 62% along with 6% of 5-(bromomethyl)furfural (BMF) (Table S2, entry 3), which also suggested that the halogen in aluminum salt contributed to only a small part of halogenation of HMF. Furthermore, using ChBr/Al₂(SO₄)₃·18H₂O/oxalic acid together led to a BMF yield of 67% (Table S2, entry 4). These results clearly proved that the halogen atoms in CMF or BMF were mainly supplied by ChCl or ChBr.



Scheme 1. Plausible mechanism for the production of CMF from glucose in 3c-DES.



Figure 4. Catalytic behavior of 3c-DES system for the transformation of glucose to CMF over 10 consecutive cycles. Reaction conditions: 0.4 mmol glucose, 12.5 mmol ChCl, 15 mmol OA, 2 mmol AlCl₃·6H₂O, 120 $^{\circ}$ C, 0.5 h, 15 mL DCE.

The reusability of 3c-DES is a key factor for the scale-up production of CMF. It was verified that after the reaction was completed, the aftertreatments of the remaining 3c-DES mixture was not required prior to the next run with new starting materials and (recycled) DCE. As shown in Figure 4, a CMF yield of 64% could still be achieved after 7 cycles with a glucose loading of 0.4 mmol. However, only 24% CMF yield and 19% HMF were obtained in the 10th cycle, probably because that the proton, Cl⁻ in the system was depleted and the system was contaminated by various byproducts, thus it could not keep the reaction going normally. Fortunarely, CMF yield could be improved back to 70% if equimolar of ChCl and oxalic acid were added to the reaction

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system (after 10 cycles). Meanwhile, it also indicated that the CI in CMF preparation was mainly provided by ChCI.

Table 2. Effects of substrate, substrate loading and water on CMF production.

Entry	Substrate	0.4 mmol substrate loading		2 mmol substrate loading	
		CMF(%)	HMF(%)	CMF(%)	HMF(%)
1	Glucose	70	<1	55	<1
2	Fructose	86	<1	78	<2
3	Sucrose ^[a]	80	<1	68	<2
4	Cellulose ^[a]	30	<1	17	<1
5	Bamboo ^[a]	29	<1	15	<1
6	Bamboo pulp ^[a]	35	<1	22	<1
7	Glucose ^[b]	70	<1	55	<1
8	Glucose ^[c]	69	<1	55	<1
9	Glucose ^[d]	63	<1	51	<1
10	Glucose ^[e]	76	<1	60	<1

Reaction conditions: 12.5 mmol ChCl, 15 mmol OA, 2 mmol AlCl₃·6H₂O, 120 $^{\circ}$ C, 0.5 h, 15 mL DCE. [a] Based on the hexose content of analyzed biomass substrates. [b] 5 wt%, [c] 10 wt%, and [d] 20 wt% water was added into reaction (based on DES weight). [e] extracted with 15 mL DCE every 30 min, 3 times.

Encouraged by the promising results obtained using 3c-DES, we then broadened the scope of substrate for CMF production using the same reaction conditions. Various biomass substrates with different loadings were tested for CMF production in 3c-DES/DCE system (Table 2), and the yields of CMF were 86, 80, 70, 30, and 29% from 0.4 mmol of fructose, sucrose, glucose, cellulose and bamboo as substrates, respectively (entry 1-5). When the substrate loading was increased to 2 mmol, CMF yields of 78 and 68% were obtained from fructose and sucrose, respectively. While untreated raw bamboo only provided 29% CMF yield, bamboo pulp prepared by the previously reported CAOSA method ^[23] provided 35% CMF yield (entry 6), which might be ascribed to that the crystallinity of cellulose in pretreated bamboo pulp was much lower than that of natural bamboo [12, 24], therefore the hydrolysis of cellulose to glucose was easier. Moreover, the effect of water was also explored. When 5~20 wt% water was added into the reaction medium, the yields of CMF were no less than 63% (entry 7-9), suggesting that the 3c-DES reaction system had good water resistance against external or in-situ generated moisture, which provided a promising application prospect of large-scale production of CMF. Intermittent extraction further increased the yield of CMF to 76% after extracting the 3c-DES phase with fresh DCE every 30 min for 3 times (entry 10).

In conclusion, a novel and specially designed 3c-DES was employed for CMF production, which exhibited several promising features including 1) eliminating the reliance on concentrated hydrochloric acid; 2) moderate reaction conditions; 3) high catalytic reactivity for glucose; 4) excellent reusability and water resistance. For commercial perspectives, ChCl as animal feed additive and plant photosynthesis promoter, oxalic acid as a natural product of plants, and AlCl₃·6H₂O as common salts are all commercially available and inexpensive. Moreover, this work also sheds some light on the study of multicomponent DES for the valorization of biomass.

Experimental Section

Materials

CMF (95%) was produced according to the literature ^[5]. HMF (99%) was purchased from Sigma-Aldrich Co. Ltd. (USA), and other analytical reagents and chemicals were purchased from Sinopharm Chemical reagent Co. Ltd. (Shanghai, China).

Preparation and recycle of DES

Each DES component was weighed and added to a round-bottom flask. The mixture was heated at 100 °C with stirring until a complete liquid phase was formed. After the reaction was completed, the organic phase was separated, and the residual DES was reused without any treatment. The new glucose and DCE were added into the reactor for the next cycle.

Typical process for the CMF production

In a typical procedure, the CMF production reacted in a 120 mL glass bottle equipped with a Teflon screw top (Beijing Synthware Glass). 2 (or 0.4) mmol substrate (based on the hexose content of analyzed biomass substrates) was introduced into DES, and 15 mL organic solvent was added in the reactor. The solution was then stirred at 120 °C. After reaction, the reactor was cooled to room temperature. The DCE phase was separated and the DES phase was extracted with 15 mL additional extraction solvent for two more times. The organic phase containing CMF and HMF was analyzed by GC-MS, while the solid phase was dissolved with deionized water and analyzed by HPLC to determine the amount of unreacted bio-based sugar.

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Keywords: 5-(chloromethyl)furfural (CMF) • carbohydrates • biomass • deep eutectic solvent

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Synthesis of CMF with 3c-DES : A novel method for the synthesis of CMF based on 3c-DES consisting ChCl, $AlCl_3 \cdot 6H_2O$, and oxalic acid was developed. The dependence on concentrated acid was eliminated, providing a green and efficient synthetic route for CMF production.