# Highly efficient and *N*-bromosuccinimide-mediated conversion of carbohydrates to 5-hydroxymethylfurfural under mild conditions

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**Abstract** Highly efficient and selective conversion of different carbohydrates to 5-hydroxymethylfurfural (HMF) has been successfully performed with *N*-bromosuccinimide (NBS) as a promoter. In the presence of single NBS, a 64.2 % yield of HMF from fructose was obtained in *N*-methylpyrrolidone for 2 h. The effects of time, temperature and reaction media are discussed. It was concluded that the preliminary bromination of substrate could improve the generation of HMF compared to the direct dehydration process. Moreover, the HMF yield could be elevated to 79.6 and 82.3 % when FeCl<sub>3</sub> and SnCl<sub>4</sub> were used as the additives, respectively. Furthermore, the addition of CrCl<sub>3</sub> facilitated the conversion pathway from glucose, sucrose, inulin, or cellulose to HMF. A 57.3, 68.2, 62.4, or 6.1 % yield of HMF was, respectively, obtained in the presence of CrCl<sub>3</sub> and NBS under mild conditions, which will therefore generate a promising application strategy for biomass transformation.

**Keywords** Dehydration · Carbohydrates · *N*-Bromosuccinimide · 5-Hydroxymethylfurfural · Biomass conversion

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### Introduction

Nowadays, producing fuels and chemicals from renewable sources instead of fossil resources has become a most attractive research area in the chemistry field. Biomass feedstocks are considered as promising alternatives because of their abundance, renewability and worldwide distribution [1–3]. Particular attention has been paid to the conversion of different carbohydrates to value-added chemicals, in which 5-hydroxymethylfurfural (HMF), a valuable intermediate used in the production of fine chemicals, pharmaceuticals, and thermoresistant polymers, and produced from the dehydration of carbohydrate, is very interesting and significant [4].

In the last decade, fructose, sucrose and inulin have been employed as the reactants for the preparation of HMF using sustainable methods [5]. For the fructose dehydration, general protonic acids or Lewis acids can be employed as the catalysts [6, 7]. Antal et al. [8, 9] reported the dehydration of D-fructose with  $H_2SO_4$  as a catalyst in subcritical water at 250 °C, and gained a yield of HMF as high as 53 %. Moreover, Bicker et al. [10] found that the yield of HMF reached 78 % at 180 °C in the presence of H<sub>2</sub>SO<sub>4</sub> when supercritical acetone-water mixture was employed as a reaction medium. Furthermore, Roman-Leshkov et al. [11] reported a two-phase reactor system with HCl as the catalyst. In this work, the D-fructose was dehydrated in the aqueous phase with HCl as a catalyst. Otherwise, DMSO and poly(1-vinyl-2pyrrolidinone) were added to suppress the undesired side reactions. The product 5-HMF was continuously extracted into an organic methylisobutylketone (MIBK) phase modified with 2-butanol to enhance the partitioning from the reactive aqueous solution. As a result, it was found that 80 % HMF selectivity at a 90 % conversion was achieved for 10 wt% D-fructose solution. In addition, a continuous microreaction process has been set up based on the HCl-catalyzed dehydration of fructose in pure aqueous solution in order to improve the "green" synthesis of HMF [12]. As a result, the process conditions were deliberately shifted to high temperatures and pressures (185 °C, 17 bar) in only 1 min, and the product HMF was obtained with 54 % yield at 71 % fructose conversion. On the other hand, Chheda et al. [13] found that a good selectivity for HMF at high conversion from polysaccharides, such as sucrose, starch, cellobiose, and xylan, can be obtained using mineral acid (HCl, H<sub>2</sub>SO<sub>4</sub> or H<sub>3</sub>PO<sub>4</sub>) as the catalyst in a biphasic reactor system, which was composed of the reactive aqueous phase modified with DMSO and the organic extracting phase consisting of a 7:3 (w/w) MIBK–2-butanol mixture. Also, Ilgen et al. [14] reported that 25 and 57 % yields of HMF were obtained, respectively, from inulin and sucrose using p-toluenesulfonic acid as catalyst in melt systems consisting of choline chloride (ChCl) and up to 50 wt% of carbohydrates.

Recently, the development of novel and efficient catalytic systems has become a hot topic for the synthesis of HMF from the dehydration of carbohydrates [15]. For example, strong acid cation exchange resins [16–18], H-form zeolites [19, 20], metal chlorides [21–24], and supported heteropolyacids [25] have been employed for the dehydration of fructose to HMF. In addition, acidic ionic liquids have also been used as catalysts or solvents in the dehydration of carbohydrates [26–30]. Neutral ionic liquids can promote the dehydration reaction due to the enhanced dissolution of catalysts and substrates; for example, Moreau et al. [26] reported that

the ILs  $[bmim]PF_6$  and  $[bmim]BF_4$  are suitable reaction media for the dehydration of D-fructose with Amberlyst-15 as a catalyst. Moreover, Zhao et al. [27] found that, in the IL [emim]Cl, chromium(II) chloride (CrCl<sub>2</sub>) could efficiently catalyze the dehydration of D-fructose, leading to a yield of HMF close to 70 %. In addition, several special ILs, such as 1-[H]-3-methylimidazolium chloride and choline chloride/citric acid, are also employed as both solvent and catalyst for the generation of HMF from fructose [28]. Recently, we have studied the dehydration of sugar with acidic ionic liquid. It was found that N-methyl-2-pyrrolidonium-based and N-methyl-morpholinium-based ionic liquids showed high catalytic activity for the dehydration of fructose or sucrose in the organic solvents [29, 30]. Most of these systems suffer from the need for relatively high reaction temperatures and poor yields or low product selectivities. For instance, the poor yield arose from the decomposition and polymerization of HMF after it was produced, and the main byproducts included levulinic acid, formic acid and humin among other components [5, 31, 32]. The production of HMF in a high yield and by a cost-effective technique is still a challenge.

It is well known that *N*-bromosuccinimide (NBS) can mediate the oxidation and dehydrogenation of alcohols in most organic solvents [33–35], while the promotion of NBS on the selective dehydration of carbohydrates is still vacant. Previous investigations have indicated that the existence of bromide is helpful for the selective conversion of sugar owing to its nucleophilic ability [23, 36]. In this work, we have focused on using a cheap, easy-to-use and nucleophilic NBS instead of corrosive inorganic acid as the catalyst for direct dehydration of fructose to HMF. Moreover, the mediation of NBS on conversion of polysaccharides in the presence of metal chlorides is also investigated and discussed.

### **Results and discussion**

The dehydration of carbohydrates to 5-hydroxymethylfurfural

To start with, the catalytic performance of different *N*-substituted succinimides was investigated in the dehydration of fructose (Scheme 1), where a 10.0 mol% catalyst was employed for a catalytic reaction for 1 h at 90 °C, and the corresponding dehydration results are summarized in Table 1.



Scheme 1 The dehydration of D-fructose with different N-substituted succinimides

Entry	Reactant	Catalyst <sup>a</sup>	Time (h)	Yield (%) <sup>b</sup>
1	Fructose	no	1	0.8
2	Fructose	N-Bromosuccinimide	1	56.1
3	Fructose	N-Chlorosuccinimide	1	36.2
4	Fructose	N-Iodosuccinimide	1	31.6
5	Fructose	N-Hydroxysuccinimide	2	1.0
6	Fructose	N-Chlorophthalimide	1	31.0
7	Fructose	N-Hydroxyphthalimide	2	0.6
8	Fructose	Phthalimide	2	0.9
9	Glucose	N-Bromosuccinimide	1	3.2
10	Sucrose	N-Bromosuccinimide	1	32.4
11 <sup>c</sup>	Fruc. + Gl.	N-Bromosuccinimide	1	27.9
12	Inulin	N-Bromosuccinimide	1	24.1

Table 1 Synthesis of HMF from carbohydrate with different catalysts

Reaction conditions: 1.0 g substrate, 10.0 mol% catalyst, in 12 mL NMP, reaction temperature 90 °C <sup>a</sup> The molecular structure of catalysts is shown in the following:



<sup>b</sup> The results are obtained by HPLC analysis

<sup>c</sup> The mass ratio of fructose and glucose is 1:1

It can be seen that the dehydration of fructose occurs only slightly with Nmethylpyrrolidone (NMP) as the solvent in absence of any catalyst, in which only 0.8 % yield of HMF is obtained (entry 1), while, in the presence of 10.0 mol% NBS, the yield of HMF can be elevated to 56.1 % (entry 2). Moreover, the catalytic performances of other N-substituted succinimides were also investigated. It was found that N-chlorosuccinimide (NCS) and N-iodosuccinimide (NIS) exhibit comparative activities, and 36.2 or 31.6 % yield of HMF is obtained with NCS or NIS, respectively (entries 3 and 4). In order to reveal further the promotion effect of these organic molecules, N-hydroxysuccinimide (NHC) and N-chlorophthalimide were also chosen as the catalysts for the fructose dehydration. It was found that only 1.0 % yield of HMF is obtained with NHC for 5 h, and 31.0 % yield of HMF is obtained with N-chlorophthalimide for 2 h (entries 5 and 6), which showed that halide-substituted imides are more favorable in the dehydration. Furthermore, the experimental data with N-hydroxyphthalimide and phthalimide as the promoters also validate this point, in which only 0.6 and 0.9 % yield of HMF were obtained (entries 7 and 8). In addition, it was also seen that NBS is more efficient than NCS and NIS under similar conditions, which indicated that the bromo group probably

has an important role in the catalytic reaction. Also, it was concluded that the preliminary bromination of substrate could improve the generation of HMF compared to the direct dehydration process.

Moreover, several representative carbohydrates were further studied as the reactants for HMF production. It was found that only 3.2 % of HMF is obtained for the conversion of glucose in the presence of NBS, which indicates that the catalytic efficiency of NBS is closely related to the reaction substrate (entry 9). On the other hand, the HMF yields of 32.4, 27.9 and 24.1 % were obtained when sucrose, fructose + glucose (1:1), and inulin, respectively, are employed as reactants (entries 10–12). Thus, it can be concluded that NBS can promote the conversion of numerous carbohydrates to HMF, and that the ketose is more easily dehydrated than aldose in this reaction system.

Effect of reaction time in the fructose dehydration

The effect of reaction time in the dehydration of fructose with NBS is outlined in Fig. 1. In the dehydration of fructose, the yield of HMF increases gradually before 60 min, and the yield of HMF remains almost unchanged during the period of 60–120 min, in which 62.2 % yield of HMF was obtained for 120 min at 90 °C. However, the HMF yield began to decline when the reaction time was further prolonged, which shows that the conversion of HMF to by-product is probably more rapid than the generation of HMF after 120 min.

Effect of temperature in the fructose dehydration

The effect of temperature in the dehydration of fructose with NBS as a catalyst is presented in Fig. 2. It is seen that the yield of HMF increases from 40 to 100  $^{\circ}$ C, and the yield decreases after 100  $^{\circ}$ C, which is probably attributed to the occurrence



Fig. 1 Effect of reaction time in the dehydration of fructose with NBS as the catalyst (reaction conditions: 1.0 g reactant, 10.0 mol% catalyst, in 12 mL solvent, reaction temperature 90  $^{\circ}$ C)



Fig. 2 Effect of reaction temperature in the dehydration of fructose with NBS as the catalyst. (reaction conditions: 1.0 g reactant, 10.0 mol% catalyst, in 12 mL solvent, 2.0 h)

<b>Table 2</b> The conversion ofcarbohydrate to HMF with NBS	Entry	Substrate	Solvent	Yield of HMF (%) <sup>a</sup>	
in different solvents	1	Fructose	EtOH	8.9	
	2	Fructose	DMF	29.3	
	3	Fructose	CH <sub>3</sub> CN	7.6	
Reaction conditions: 1.0 g	4	Fructose	DMSO	47.5	
NBS catalyst, in 12 mL solvent.	5	Fructose	$CCl_4$	1.9	
reaction time 2 h, temperature	6	Sucrose	DMSO	31.0	
100 °C	7	Inulin	DMSO	22.5	
<sup>a</sup> The results are obtained by HPLC analysis	8	Sucrose	DMF	14.8	

of side reactions. Here, the highest yield of HMF is  $64.2 \ \%$  at  $100 \ ^{\circ}C$  for 2 h with NBS as the catalyst in the dehydration reaction (Fig. 2).

Effect of solvents in the fructose dehydration

Different solvents, including polar [ethanol, *N*,*N*-dimethyl formamide (DMF), acetonitrile, DMSO] and non-polar one (CCl<sub>4</sub>), were employed in the dehydration of fructose (Table 2). As a result, a 47.5 % yield or a 29.3 % yield of HMF with DMSO or DMF, respectively, as a solvent is superior to the 7.6 % yield or 8.9 % yield with acetonitrile or ethanol, respectively, as a solvent. Otherwise, due to the limited solubility of fructose, the dehydration reaction is scarcely performed when carbon tetrachloride is used as a solvent. So, it is concluded that polar and aprotic solvent is more suitable for this reaction system, which can be attributed to its better solubility and differentiating effect. In addition, DMSO is also a favorable

Entry	Substrate	Catalyst	Solvent	Yield (%) <sup>a</sup>
1	Fructose	$FeCl_3 + NBS$	NMP	79.6
2	Fructose	$SnCl_4 + NBS$	NMP	82.3
3	Glucose	NBS	DMSO	2.7
4	Glucose	$SnCl_4 + NBS$	DMSO	29.9
5	Glucose	$SnCl_2 + NBS$	DMSO	10.5
6	Glucose	$CrCl_3 + NBS$	DMSO	57.3
7	Sucrose	$SnCl_4 + NBS$	NMP	40.7
8	Inulin	$SnCl_4 + NBS$	NMP	47.2
9 <sup>b</sup>	Cellulose	$SnCl_4 + NBS$	NMP	4.9
10	Sucrose	$CrCl_3 + NBS$	DMSO	68.2
11	Inulin	$CrCl_3 + NBS$	DMSO	62.4
12 <sup>b</sup>	Cellulose	$CrCl_3 + NBS$	DMSO	6.1

Table 3 Dehydration of various carbohydrate to HMF with NBS and metal chlorides

Reaction conditions: 1.0 g reaction substrate, 10.0 mol% NBS catalyst, in 12 mL solvent, reaction time 2 h, temperature 100  $^{\circ}\mathrm{C}$ 

<sup>a</sup> The results are obtained by HPLC analysis

<sup>b</sup> The reaction is performed at 140 °C for 3 h

solvent for the dehydration of fructose to HMF due to its ability to prevent the formation of by-products such as levulinic acid and humin. Furthermore, a 31.0 or 14.8 % yield of HMF was obtained in the presence of 10.0 mol% NBS from sucrose when DMSO or DMF, respectively, is used as solvent. For the conversion of inulin to HMF, a yield of 22.5 % is obtained, which is very near to that obtained in NMP solvent.

Dehydration of carbohydrates with NBS and metal chlorides

In the following, the combination of NBS and metal chlorides were employed as catalyst system for the conversion of different carbohydrates to HMF. As indicated in Table 3, the yield of HMF is increased to 79.6 and 82.3 % when FeCl<sub>3</sub> and SnCl<sub>3</sub> are employed as the additives, respectively (entries 1 and 2). For the conversion of glucose, only 2.7 % of HMF is obtained with NBS as the catalyst in DMSO solvent. However, 29.9, 10.5 or 57.3 % yields of HMF are respectively obtained in the presence of SnCl<sub>4</sub>–NBS, SnCl<sub>2</sub>–NBS or CrCl<sub>3</sub>–NBS catalytic system (entries 3–5). On the other hand, the yields of HMF are 40.7, 47.2 and 4.9 % for the conversion of sucrose, inulin and cellulose, respectively, in the presence of NBS and SnCl<sub>4</sub> (entries 6–8). Yields of 68.2, 62.4 or 6.1 % HMF are respectively obtained for conversion of sucrose, inulin, or cellulose in the presence of NBS and CrCl<sub>3</sub> in DMSO solvent (entries 9–12). These results showed that the addition of metal Cr facilitates the conversion pathway from glucose, sucrose, inulin, respectively, or cellulose to HMF in this catalyst system.

# Experimental

Reagents and equipment

Fructose, glucose, sucrose, inulin, cellulose, lactose, NBS, NCS, NIS, NHC, anhydrous ethanol, acetonitrile, *N*-chlorophthalimide, *N*-hydroxyphthalimide, phthalimide, FeCl<sub>3</sub>, SnCl<sub>4</sub>, SnCl<sub>2</sub>, CrCl<sub>3</sub>, NaHCO<sub>3</sub>, acetic acetate, and Na<sub>2</sub>SO<sub>4</sub> were analytical grade and used without further purification. The solvent including NMP, ethanol, acetonitrile, DMF, DMSO and CCl<sub>4</sub> was rectified before being used.

The NMR spectra were recorded on an INOVA 500MHZ spectrometer. The qualitative analysis was performed using an Agilent 6890/5973 GC–MS, and the quantitative analysis was performed by the Agilent 2100 HPLC with UV and Refractive Index detectors.

Reaction conditions for the dehydration of different carbohydrates

Typical procedure for the dehydration of carbohydrate is as follows: 1.0 g substrate, NBS (10.0 mol%) and 12 mL NMP solution are charged in order into a 100-mL flask equipped with magnetic stirring and a condenser, The atmosphere inside is replaced with nitrogen before the flask is airproofed. Under stirring, the flask is preheated to the certain temperature with an oil bath and then kept there for the necessary time. After the reaction, the obtained mixture is decanted into a volumetric flask with anhydrous ethanol as diluter, and then analyzed by HPLC with UV and Refractive Index detectors.

Typical separation procedure for HMF

After the reaction, the mixture is transferred into a flask, and then a saturated aqueous solution of NaHCO<sub>3</sub> is added. The obtained liquid mixture is stirred with a magnetic stirrer overnight and extracted three times with acetic acetate, and then the organic phase is collected. After being dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, the organic layer is distilled under reduced pressure to obtain the pure HMF as a main product. The purity is more than 98 % from HPLC analysis.

## Conclusion

In summary, the efficient and catalytic synthesis of HMF from different carbohydrates has been successfully performed with NBS as the promoter under mild conditions. A 64.2 % yield of HMF is obtained from fructose in the presence of only NBS for 2 h at 100 °C. The effects of the reaction temperature and reaction time in the fructose dehydration are examined. Moreover, the addition of  $CrCl_3$  facilitated the conversion pathway from glucose, sucrose, inulin, or cellulose to HMF. This efficient catalyst system containing NBS will therefore generate a promising application strategy for biomass transformation.

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