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# Short Communication

# Influence of alkali and alkaline earth metal salts on glucose conversion to 5-hydroxymethylfurfural in an aqueous system

Elliot Combs <sup>a</sup>, Basak Cinlar <sup>a</sup>, Yomaira Pagan-Torres <sup>b</sup>, James A. Dumesic <sup>b</sup>, Brent H. Shanks <sup>a,\*</sup>

<sup>a</sup> Department of Chemical and Biological Engineering, Iowa State University, 1140L BRL, Ames, IA 50011, USA

<sup>b</sup> Department of Chemical and Biological Engineering, University of Wisconsin-Madison, 3014 Engineering Hall, 1415 Engineering Drive, Madison, WI, 53706, USA

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# 1. Introduction

The efficient production of versatile intermediate compounds from biomass constitutes a challenge for establishing a sustainable chemical industry. One such potential intermediate in the production of polymers and fine chemicals is 5-hydroxymethylfurfural (HMF) [1]. The ideal production of HMF is via dehydration of a hexose such as glucose or its polysaccharide due to high abundance and low cost. Although considerable research has been performed on HMF production from fructose, its efficient production from glucose presents a greater challenge due to the higher stability of the glucopyranose ring [2].

Most efforts directed towards HMF production have utilized one of the following two strategies: combining isomerization of glucose to fructose with subsequent dehydration of fructose, or employing metal complexes to activate the glucose ring selectively for the formation of HMF. In the former approach, both a Bronsted acid and a base or Lewis acid are needed in concert as isomerization is a baseor Lewis acid-catalyzed reaction and dehydration is catalyzed primarily by protons [3]. In the latter approach, glucose complexation with metals (such as copper or chromium in the presence of ionic liquids) has been shown to activate the glucose ring for selective HMF production [2].

The highest reported HMF yields to date have been reported using ionic liquids [2]. However, the processing of ionic liquids is significantly challenged due to high costs associated with product purification and the sensitivity of ionic liquids to water [4]. It is believed the high activity observed using ionic liquids can be attributed to their ability to form

## ABSTRACT

The aqueous phase acid-catalyzed reaction of glucose to 5-hydroxymethylfurfural (HMF) was performed with the addition of alkali and alkaline earth metal salts. Previous studies investigated this reaction in a biphasic system using salts to enhance the partitioning of HMF and suppress undesired products thereby increasing the overall selectivity. The results of this study suggest the presence of alkaline earth salt/glucose interactions that affect glucose conversion and HMF yield. While sulfate salts tended to lead to higher activity than chloride salts, the further addition of HCl led to decreased conversion through a competitive anion effect.

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complexes with glucose, thereby activating the glucosyl ring and holding it in a particular orientation that enables selective dehydration. If the same effect could be achieved with complexation agents in water, the disadvantages of ionic liquids could be avoided [5].

Several groups have recently explored the biphasic conversion of glucose to HMF using a reactive aqueous phase and an immiscible organic phase which selectively extracts HMF as it is produced. This strategy enhances the selectivity towards HMF by minimizing the formation of side products due to the tendency of HMF to degrade in acidic aqueous environments [1]. In one approach, a homogeneous Lewis acid is used in concert with a strong Brønsted acid (HCl) to facilitate the isomerization of glucose into fructose and the subsequent dehvdration to HMF [6]. Other work has demonstrated the possibility of producing HMF from glucose through the use of water-compatible Lewis acids in a nearly neutral pH environment, alleviating processing concerns in terms of the materials of construction and environmental impact [7]. Both studies feature the use of concentrated salts to increase the in situ partitioning of HMF to the organic phase. Previous work has investigated the catalytic effects of a range of inorganic salts on the conversion of glucose and other sugars to HMF [8]. However, the results do not provide sufficient consideration for the salts' effects in conjunction with an HCl catalyst, as may be present in a biphasic reaction system.

An in-depth effect of alkali and alkaline earth metal salts in saturated aqueous solutions has been examined for the dehydration of glucose and fructose [9,10]. While the addition of NaCl, CaCl<sub>2</sub> and MgCl<sub>2</sub> did not improve the HMF yields from fructose significantly, their saturated solutions did result in improved yields from glucose. This was attributed to complexation of the salts with glucose, in which the cations bound to the oxygens of glucose, creating a

<sup>\*</sup> Corresponding author. Tel.: +1 515 294 1895; fax: +1 515 294 1269. *E-mail address:* bshanks@iastate.edu (B.H. Shanks).

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positively charged molecule that could subsequently interact with water molecules in the proper orientation to facilitate dehydration [9]. The anions' role in the mechanism was also explored. <sup>13</sup>C NMR spectra of glucose in saturated salt solutions at room temperature revealed that chloride ions (notably in MgCl<sub>2</sub> and LiCl) donated electron density to the C-1, C-3, and C-5 carbons of glucose [11]. Sulfate ions, although more bulky than halides, were found in a separate study to donate electron density indiscriminately to the carbons of glucose [9]. The sulfate ions were found to enhance the HMF selectivity through the suppression of condensation reactions forming insoluble humins, which was noticed in the reaction with chloride ions. Sulfate ions were also posited to participate in hydrogen bonding with water and with hydroxyl protons of glucose, thereby contributing further to the complexation matrix [9].

Although this alkali/alkaline earth metal salt complexation has been demonstrated in saturated solutions at room temperature, comprehensive studies have not been performed at lower concentrations and elevated temperatures in the presence of HCl. This communication reports the direct effects of salt interaction under typical conditions that have been utilized in past reaction studies [1,12].

# 2. Experimental

# 2.1. Materials

Hydrochloric acid (12 N, Fisher), glucose (99%, Fisher), sodium chloride (99%, Fisher), potassium chloride (99%, Fisher), magnesium chloride hexahydrate (99%, Fisher), calcium chloride dihydrate (99%, Fisher), magnesium sulfate heptahydrate (98%, EMD), calcium sulfate (98%, EMD), and calcium phosphate dibasic (30.0%–31.7% as Ca, Fisher) were used as purchased.

#### 2.2. Reaction experiments

To prepare the reaction mixture, hydrochloric acid was added to nanopure water until a pH value of 1.5 was achieved using a glass electrode (6.0233.100, Metrohm) connected to a Metrohm 798 MPT Titrino automatic titrator. Glucose and salt were added to achieve 5 wt.% glucose and the desired concentration of salt. For the biphasic reactions, the organic phase was prepared by mixing methyl-isobutyl ketone (MIBK) with 2-butanol in the ratio of 7:3 (w/w) with an aqueous/organic phase ratio of 1:2 (w/w) as described in the literature [1,12].

The reaction experiments were performed at 160 °C in 10 ml thick-walled glass vial batch reactors under stir bar agitation of 400 rpm. The vials were heated by submersion in a preheated bath of Dow Corning 550 Fluid on a Fisher Scientific Isotemp hot plate with an attached thermocouple. Samples were taken post-reaction after cooling the vials rapidly in an ice bath.

# 2.3. UPLC analysis

Samples were filtered through a 0.2  $\mu$ m nylon filter (Cobert Assoc.) prior to dilution. Analysis of the samples was performed using a Waters ACQUITY UPLC H-Class system. HMF analysis was performed using an ACQUITY UPLC BEH C18 column (Waters 186002350) at 35 °C and an ACQUITY UPLC photodiode array (PDA) e $\lambda$  detector at 254 nm. Glucose analysis was performed using an Acquity UPLC BEH Amide column (Waters 186004801) at 65 °C and a Waters 2414 Refractive Index (RI) detector at 50 °C.

## 3. Results and discussions

Initially, the effect of salts on glucose conversion was examined by adding 0.8 M Group I–II chlorides (NaCl, KCl, CaCl<sub>2</sub>, and MgCl<sub>2</sub>) into a 5 wt.% glucose solution of pH 1.5 at 160 °C in a sealed thick-walled glass vial reactor under ambient pressure. The glucose time-conversion results for these experiments are shown in Fig. 1-a. The final results after 60 min are also detailed in Table 1 (Entries 1–4 and 6). Rapid heat transfer in the vials was assumed and no time delay in the kinetic profile was taken into account. All of the chloride salts improved glucose conversion relative to the base case of HCl without salt addition. CaCl<sub>2</sub> and MgCl<sub>2</sub> addition led to the greatest improvement in conversion. As shown in Fig. 1-b, the increased rate of glucose conversion corresponded to higher HMF yields. The alkali metal salts (NaCl and KCl) increased the yield only slightly. Of the salts, the MgCl<sub>2</sub> produced the highest HMF yields. However, the conversion leveled off after ca. 40 min while the HMF yield began to decrease, indicating a successive HMF degradation as the reaction continued. This confirms findings from literature on the interaction of chloride ions with the HMF molecule leading to its degradation [9,10].

It has been shown in the literature that the presence of alkaline earth metal salts accelerates glucose decomposition rates [9,10]. When saturated solutions of MgCl<sub>2</sub> and CaCl<sub>2</sub> were examined for their ability to decompose glucose,  $Ca^{2+}$  was found to be more selective towards HMF, while Mg<sup>2+</sup> showed higher selectivity towards levulinic acid, one of the HMF degradation products [10]. It is reasonable to presume in this study that the higher activity of MgCl<sub>2</sub> led to more HMF degradation, producing levulinic acid after the 40 minute mark. The higher rates of HMF formation and degradation from Mg<sup>2+</sup> may be due to a stronger interaction relative to  $Ca^{2+}$ , leading to the further degradation of HMF and the formation of side products. Alkaline earth metal cations have been shown to form bidentate complexes involving the C-1 and C-3 hydroxyl groups of glucose [13]. It is possible therefore that the formation of these complexes can assist in the conversion of glucose to HMF and its subsequent degradation.

Due to the enhanced HMF yields with MgCl<sub>2</sub> addition, the effects of varying its concentration were explored. Entries 5, 6, 7, and 8 of Table 1 illustrate the effects of MgCl<sub>2</sub> at concentrations of 0.4 M, 0.8 M, 1.6 M, and 3.2 M, respectively. The 5 wt.% glucose feed solution corresponded to a glucose concentration of approximately 0.3 M. As predicted, an increase in salt concentration led directly to an increase in the overall conversion. However, the decrease in



**Fig. 1.** Glucose conversion (a) and HMF yield (b) in the presence of 0.8 M salt solutions, 5 wt% glucose, T = 160 °C; (HCl only ( $\Box$ ), HCl with: NaCl ( $\bigcirc$ ), KCl ( $\triangle$ ), MgCl<sub>2</sub> (+), CaCl<sub>2</sub> ( $\diamond$ )).

#### Table 1

Effect of salts in the aqueous phase on glucose conversion and molar HMF selectivity and vield after 60 min at 160 °C.

Entry	Catalyst	Salt	Salt concentration (M)	Conversion (mol%)± S.D.	Selectivity (mol%)± S.D.	Yield (mol%)± S.D.
1	HCl	-	-	$10.0 \pm 1.3$	$23.1 \pm 1.9$	$2.3\pm0.1$
2	HCl	NaCl	0.8	$13.4 \pm 1.2$	$24.9\pm0.8$	$3.3\pm0.2$
3	HCl	KCl	0.8	14.4	23.6	3.4
4	HCl	$CaCl_2$	0.8	$18.0\pm4.4$	$22.0\pm5.1$	$3.8 \pm 0.1$
5	HCl	$MgCl_2$	0.4	$11.1\pm2.3$	$25.0\pm6.7$	$2.7\pm0.2$
6	HCl	$MgCl_2$	0.8	$15.3\pm2.4$	$28.8 \pm 4.7$	$4.3\pm0.4$
7	HCl	$MgCl_2$	1.6	$21.1 \pm 1.4$	$20.4 \pm 1.7$	$4.3\pm0.2$
8	HCl	$MgCl_2$	3.2	$31.4 \pm 2.4$	$22.5 \pm 1.6$	$7.0\pm0.03$
9	HCl	$MgSO_4$	0.8	$24.0\pm1.7$	$26.3\pm2.4$	$6.3\pm0.2$
10	HCl	$MgSO_4$	1.6	$27.7\pm0.8$	$40.2\pm3.8$	$11.2\pm1.1$
11 <sup>a</sup>	HCl	CaSO <sub>4</sub>	0.8	$11.9 \pm 1.2$	$14.8 \pm 1.5$	$1.7\pm0.04$
12 <sup>a</sup>	HCl	$CaHPO_4$	0.8	$5.16 \pm 1.25$	$20.2\pm6.0$	$0.99 \pm 0.067$
13	-	$MgCl_2$	0.4	$11.3 \pm 1.2$	$23.6\pm2.2$	$2.6\pm0.06$
14	-	$MgCl_2$	0.8	$15.6 \pm 1.2$	$25.0\pm2.8$	$3.9\pm0.19$
15	-	$MgCl_2$	1.6	$20.7 \pm 1.0$	$34.1\pm2.7$	$7.1\pm0.89$
16	-	$MgCl_2$	3.2	$23.6\pm0.9$	$47.2 \pm 1.2$	$11.1\pm0.2$
17	-	MgSO <sub>4</sub>	0.8	$45.1\pm0.7$	$17.2\pm2.0$	$7.7 \pm 1.0$
18	-	$MgSO_4$	1.6	$40.7\pm4.2$	$29.5\pm3.0$	$11.9\pm0.1$

<sup>a</sup> Salt not completely soluble, reaction solution was an opaque salt/glucose suspension.

selectivity with 1.6 M MgCl<sub>2</sub> demonstrated the aforementioned effect of MgCl<sub>2</sub> in the degradation of HMF in acidic media.

Further experiments were performed to probe the role of the anion in activating glucose in the selective conversion to HMF. The salts MgSO<sub>4</sub>, CaSO<sub>4</sub>, and CaHPO<sub>4</sub> were selected to screen different anions with alkaline earth cations. Reactions were performed under the same conditions as the chloride salts at concentrations of 0.8 M in the presence of HCl. The solubility of CaSO<sub>4</sub> and CaHPO<sub>4</sub> in water was limited, even at elevated temperatures, and they formed viscous suspensions when prepared in solution. The reaction results with these salts are given in Entries 9-12 in Table 1. The low activities of CaSO<sub>4</sub> and CaHPO<sub>4</sub> were likely due to internal transport limitations within the solution due to the increased viscosity and density of insoluble particles. The activity of MgSO<sub>4</sub>, however, was found to be higher than that of MgCl<sub>2</sub>, and a higher concentration of MgSO<sub>4</sub> led to greater HMF selectivity over MgCl<sub>2</sub> (Entries 9 and 10 vs. 6 and 7). This indicated a stronger effect of the sulfate ion on activating the glucose ring leading to higher conversion. The literature has discussed the complexation of magnesium ions with the glucose ring via ring activation [11]. Because the selectivity was found to be higher with MgSO<sub>4</sub> than with MgCl<sub>2</sub> in the presence of HCl, this suggested that sulfate ions do not complex with the HMF molecule to facilitate its degradation as is the case with chloride ions.

In order to gain a better perspective of these anion effects, reactions were performed under the same conditions using only water (without adding HCl) as the solvent. The salts MgCl<sub>2</sub> and MgSO<sub>4</sub> were both tested, the former varying in concentrations of 0.4 M, 0.8 M, 1.6 M, and 3.2 M, and the latter at 0.8 M and 1.6 M. The results from these reactions are shown in Entries 13–18 of Table 1. Interestingly, the lack of HCl did not decrease the overall glucose conversion. This contradicts results from literature reporting the dependence of glucose dehydration to HMF on the number of available protons [14]. This implied that the acid-catalyzed dehydration of glucose can occur without the addition of a strong acid to supply excess protons. Instead, the addition of salts contributed ionic strength to and alters the activity coefficient of the solution, lowering the effective pH and facilitating the dehydration. In these reactions without a strong acid catalyst, the values for conversion with MgCl<sub>2</sub> did not change significantly (except at 3.2 M), whereas an increase in selectivity was observed at higher concentrations of MgCl<sub>2</sub>. The reaction with MgSO<sub>4</sub>, on the other hand, experienced a great increase in glucose conversion versus the reaction with HCl and the same concentration of MgSO<sub>4</sub>, although the selectivity dropped. This indicated a competitive effect between the chloride and sulfate anions, leading to a tradeoff of glucose conversion (with sulfate ions) and selective HMF production (with the incorporation of both sulfate and chloride ions). It is possible that the chloride donation of electron density to glucose C-1, C-3, and C-5 occurred more readily than the donation from the bulkier sulfate group. As a result, the sulfate ions interacted predominantly with the surrounding water molecules instead of the glucose itself, leading to lower overall conversion while at the same time providing conditions for HMF to be more selectively formed.

An organic phase was added to the system as discussed in the literature [1,12]. As shown in Fig. 2, both MgCl<sub>2</sub> and MgSO<sub>4</sub> experienced gains in conversion and selectivity with MgSO<sub>4</sub> performing better than MgCl<sub>2</sub>, much like the aqueous system. This result was due to a stabilizing effect of the organic phase on HMF, hindering its serial conversion following glucose dehydration. The partition coefficient was also calculated for all three systems, defined as the ratio of HMF concentration in the organic phase to that in the aqueous phase. This coefficient followed the increasing order of HCl only <MgCl<sub>2</sub><MgSO<sub>4</sub>, with values of 1.41, 1.98, and 2.24 respectively, indicating greater extracting potential of the organic phase through the increased ionic strength of the aqueous phase. This demonstrated a two-fold benefit of using metal salts in such a biphasic system, taking into account both the enhancement in reactivity and the improved in situ partitioning to the organic phase.

#### 4. Conclusions

The introduction of alkali and alkaline earth salts, especially magnesium salts, into the acidic media was found to enhance both the glucose conversion and the yield of HMF. This enhancement was likely via glucose complexation with the salts. The activity of MgSO<sub>4</sub> was greater than MgCl<sub>2</sub>, and the HMF selectivity increased with higher sulfate ion concentrations. Selectivity in this system increased further with the addition of HCl, although the conversion decreased. Improved yields in the biphasic system with these added salts could be explained by a combination of increased activity and enhanced in situ partitioning of HMF into the organic phase to stabilize HMF and prevent side product formation.

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**Fig. 2.** Effect of biphasic extraction on glucose conversion and HMF selectivity and yield in the presence of HCl only, HCl with 0.8 M MgCl<sub>2</sub>, and HCl with 0.8 M MgSO<sub>4</sub> after 60 min at 160 °C.

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