Catalytic conversion of sucrose to 5-hydroxymethylfurfural in green aqueous and organic medium

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Abstract

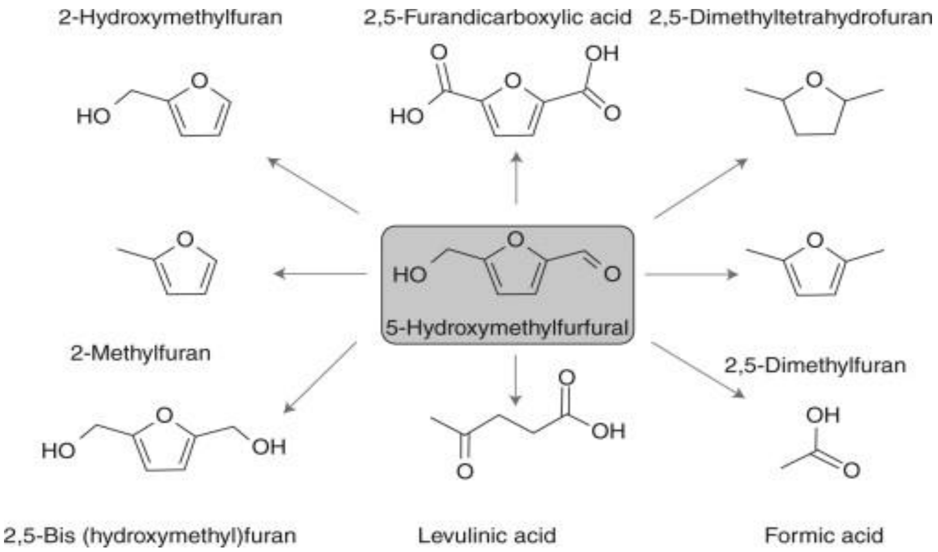
5-Hydroxymethylfurfural (HMF) is one of the promising chemicals, which can serve as a platform chemical to produce various energy chemicals. HMF can be produced from different lignocellulosic biomass derived sugars employing different catalytic processes. In this study, the synthesis of HMF was investigated from excessively available sucrose using environment friendly and cost-effective technology. Among the various solvents applied, dimethyl sulfoxide (DMSO) was found as an efficient organic solvent medium. The results elucidated the combination of *p*-

toluenesulfonic acid (*p*TSA) and chromium chloride ($CrCl_3.6H_2O$) as the best dehydrating catalyst. A relatively higher HMF yield of 55% was achieved at a lower temperature (120 °C) while at 150 °C (higher temperature) oxalic acid with higher concentration of $CrCl_3.6H_2O$ gave a maximum yield of 59.21%. The time, temperature, and concentrations affected the yields. The positive impact was found with a rise in temperature from 100 - 120 °C in *p*TSA while oxalic acid affected the yield until 150 °C. HMF yields were reported in descending order as *p*TSA>oxalic acid> maleic acid> malonic acid >succinic acid > blank at 120 °C. It was observed that the isomerization of glucose to fructose is the major barrier to achieve the high process yield. Therefore, more efforts should be made to achieve the high rate of isomerization of glucose (part of sucrose disaccharide) in order to improve the HMF selectivity by depressing the humin formation.

Keywords: 5-Hydroxymethylfurfural (HMF), sucrose, dimethyl sulfoxide (DMSO), *p*-toluenesulfonic acid (*p*TSA)

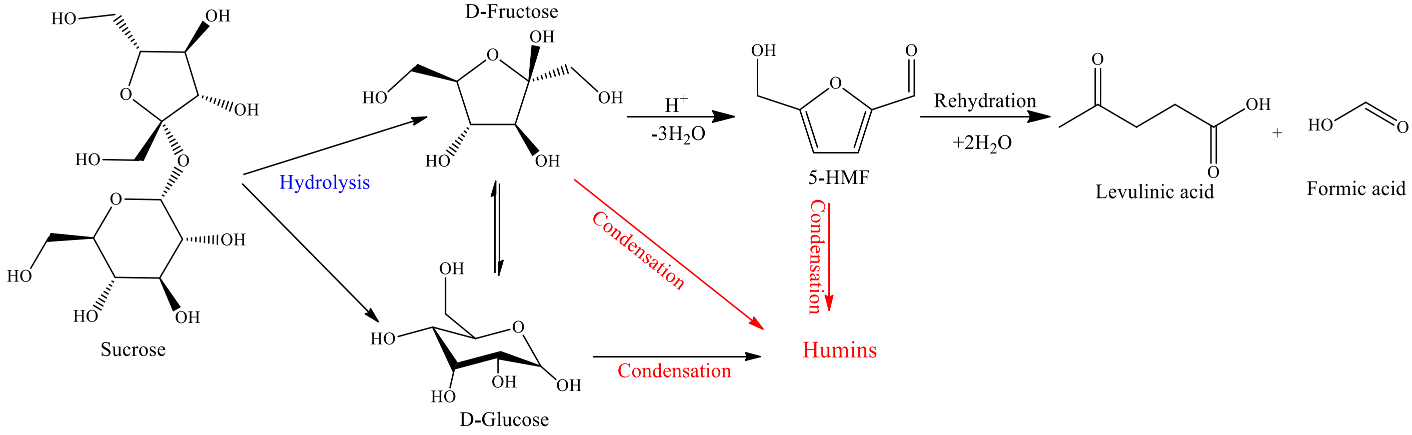
1. Introduction

The depletion of fossil fuels and their severe impacts on the environment (pollution and climate change) compelled to develop sustainable green technology for cost-effective conversion of renewable resources into high-value and energy chemicals [1–3]. One of the auspicious chemical, which can serve as a platform specie is 5-hydroxymethylfurfural (HMF), which is identified by the United States Department of Energy among the top 10 bio-based chemicals to produce from biorefinery carbohydrates [4,5]. Based on the following reasons it is also term as a "sleeping giant" in the field of intermediate chemicals (derivatives) from bio-based feedstock; (i) As a multifunctional molecule comprised of a furan ring with alcoholic and aldehyde group at the same time, (ii) it is a multipurpose intermediate, which could be further transformed into high value chemicals and biofuel products, such as 2,5- furan dicarboxylic acid, levulinic acid, dihydroxymethyl furan, dimethyl furan, and others, which are supposed to be favorable substitutes for corresponding petro-chemicals (Scheme 1) [6–8]. HMF plays a significant role among bio-derivatives due to its multi-functionality to derive high-value polymer precursors and fuel additives as well as potential chemicals feedstocks [9,10].



Scheme 1. Potential chemical feedstock derived from 5-HMF [10].

Lignocellulosic biomass (LCB) attracted considerable attention to the production of bio-derivatives being a rich source of renewable carbon [11–13]. HMF has an outstanding positions among bio-derivatives due to its multi-functionality[9]. Many efforts have been devoted to its production from LCB sugars. Fructose has been studied thoroughly for the efficient manufacturing of HMF using the different catalytic systems and high HMF yield and selectivity have been achieved [14,15]. Glucose, an integrated hexose of LCB is considered the most valuable bio-derived carbon resource [16,17]. Successful conversion of glucose is vital for the efficient conversion of biomass to biochemicals and biofuels [18]. Several studies reported the dehydration of glucose to HMF applying homogeneous [17,19] and heterogeneous [20] catalytic systems along with ionic liquids [21] and bifunctional resins [22]. However, the glucose dehydration process is still challenging and suffered from low HMF yield and selectivity [23]. It has been reported that glucose dehydration proceeded via isomerization to fructose [17,18]. Enzymatic isomerization produces equilibrium fructose yield (>50%) thermodynamically [24,25]. Whereas chemical isomerization using heterogeneous catalytic systems partially converts glucose to fructose and product solution consist of fructose with some glucose concentrations [26,27]. So enzymatic route is ideal to realize complete isomerization but is relatively inflated and time-intensive.



Scheme 2. Acid-catalyzed conversion of sucrose to HMF.

Sucrose, a natural disaccharide, yields fructose and glucose on hydrolysis, as indicated in Scheme 2. The obtained sugar mixture can be used as a feedstock to synthesize HMF using acidic catalysts similar to pure sugars [9]. Sucrose is a universally available and cheap disaccharide as compared to fructose that can serve as an alternative feedstock to provide lignocellulosic-derived glucose and fructose on hydrolysis. However, the conversion of sucrose to HMF has not been investigated extensively [28]. Mostly, mineral acids were used for the transformation of sucrose into HMF. Steinbach et al.[9] discussed the sulfuric acid (0.005 M) catalyzed conversion of sucrose using high temperature (180 – 220 °C) and obtained 25% yield of HMF from 2 wt% feed of sucrose. Bowler et al.[29] reported only an 18% yield of HMF. Although the applied H_2SO_4 concentration was 0.01 – 0.2 M and the temperature was almost similar (160–200 °C). High acid does affect the reaction time, and the maximum yield was obtained in a short time. Similarly, Tan-Soetedjo et al.,[29] observed 17% mass yield at 140 °C, applying moderate catalyst concentration (0.05 M H_2SO_4). These results indicated that the high acid concentration is not favorable for HMF yield when mineral acids were used as catalysts.

The kinetic study revealed that the proportions of unwanted side products increased enormously with an increase in process temperature. When the reported carbon balance is considered, the carbon percentage of waste products increased from 14.6% to 22.8% and 38.1% when temperature increased from 180 °C to 200 °C and 220 °C, respectively [9]. Ionic liquid improved the HMF yield and selectivity with added cost [30,31]. Improved catalytic efficiency gave the high HMF yield at low temperatures when the combination of Lewis acids and ionic liquids was used. Expending 1-ethyl-3-methylimidazolium-tetrafluoroborate ($[EMIM]BF_4$) gives 57% HMF yield from sucrose at 100 °C in 3 hours employing $SnCl_4$ catalyst [32]. This combination was even more effective when the sugar was replaced as cellobiose, and a 65% yield was obtained applying similar conditions[32].

Bronsted acids such as phosphoric acid, sulfuric acid, nitric acid, and hydrochloric acid, have been well investigated extensively so far [33,34]. However, the impact of organic acid catalysts on sucrose conversion has not been studied well. Moreover, the NH_4Cl-*p*TSA catalytic system has also the benefits of eco-friendliness and low cost, as compared to metal-based Lewis acids[17]. Lewis acids are considered suitable for the conversion of glucose into fructose, whereas organic acids were found efficient dehydration catalysts in the fructose conversion process[17,35]. Therefore, we hypothesized that as the sucrose is a disaccharide consist of two units (Glucose and Fructose), it would work efficiently for the transformation of sucrose to HMF in the presence of catalysts combination composed of Lewis acid and organic acid. The one-pot conversion would save an immense amount of time and energy. Following this approach, we have compared the effect of different Lewis acids and organic acids for sucrose conversion into HMF. Results elucidated the addition of $CrCl_3.6H_2O$ as a co-catalyst improved the HMF yield when *p*-toluenesulfonic acid (*p*TSA) and oxalic acids were used as the catalysts. The use of $CrCl_3.6H_2O$ as a co-catalyst with *p*TSA and oxalic acid has the advantages of eco-friendliness as compared to mineral acids and low cost as compared to solid acids and ionic liquids. Additionally, it is robust and could be applied for large-scale commercial production of HMF. Therefore, here in this study, few organic acids were used, particularly *p*TSA for the direct synthesis of HMF from the sucrose in water (aqueous) and DMSO (organic) medium, separately. Further, based on the above-mentioned features of pTSA, using it in its pure form as an organic acid catalyst in DMSO with $CrCl_3.6H_2O$ as a co-catalyst may enable us to synthesize the appropriate yield of HMF from sucrose, which would also provide decent literature, which has been severely lacking in this sector. Because of the solid nature of pTSA at room temperature, it can be easily recovered from the reaction system and reused, making it environmentally friendly. The system also contains Lewis acids as co-catalysts, such as $CrCl_3.6H_2O$, NH_4Cl, and $AlCl_3$, which have been shown to be suitable candidates for isomerization of glucose into fructose. According to the current study, the research question is "Can sucrose be converted to HMF effectively using organic and aqueous media with organic catalysts and Lewis acids as co-catalysts? The study's objective is to compare several organic acids catalyzed reactions to produce HMF from sucrose. The obtained results may serve as a strong tool for future sucrose to HMF conversion and will also serve as an optimized and controlled process to maximize the yield of HMF and minimize production of by-products.

2. Material and methods

2.1. Chemicals and materials

Sucrose (99%), fructose (>99.5%), glucose (99.5%), oxalic acid (99.5%), malonic acid (97%), *p*-toluenesulfonic acid (*p*TSA, 99.5%), maleic acid (99.5), and succinic acid (99.5%) were purchased from Aladdin Biotechnology Co., Ltd. (Shanghai, China). While dimethyl sulfoxide (DMSO, 99.8%), were obtained from Beijing chemical works (Beijing, China). The analytical standards of sucrose, glucose, fructose, levulinic acid, 5-hydroxymethyl furfural (HMF), and formic acid (FA) were also obtained from Aladdin Biotechnology Co., Ltd. (Shanghai, China). Ultra-pure water having 18.25 Mega ohm (MΩ) resistivity was prepared in the lab.

2.2. Experimental procedures

Conversion of sucrose into HMF was conducted using 15 mL ACE glass pressure tubes immersed in an oil bath. The required amount of sucrose was taken and a certain amount of catalyst (based on the mole ratio of sucrose) was dissolved in a 5 mL reaction solvent consisting of organic acids and H_2O at different volume ratios. Then, the pressure tube was placed in the preheated oil bath. After the specified reaction time, the tube took out of the oil bath and instantly cooled in ice-cold water to stop the reaction. The acquired sample was diluted and filtered via a 0.22-μm syringe filter and stored in the refrigerator for analysis. Later the prepared samples were subjected to HPLC for further analysis.

2.3. Analytical methods

The concentration of sucrose, glucose, fructose, HMF, formic acid (FA), and levulinic acid (LA) found out by HPLC analysis (SHIMADZU, Japan) supplied with an Aminex® HPX-87H strong acid cation exchange resin column (300 mm × 7.8 mm, Bio-Rad, USA) at 65℃ with RID-10A DRID (Differential Refractive Index Detector). Sucrose, HMF, fructose, FA, and LA analyses were conducted with the same column and 5 mM sulfuric acid solution as the eluent at a flow rate of 0.8 ml/min. Before the analysis, all the samples were filtered via a 0.22-µm syringe filter and diluted with ultra-pure water. The injection volume was 20µl per analysis and an auto-injection module was applied.

The HMF yield was calculated by the following equation:

$$X_S = \left[1 - \frac{C_{S(t)}}{C_{S(0)}}\right] \times 100\% \qquad (1)$$

$$Y_P = \left[\frac{C_P}{2 \times C_{S(0)}}\right] \times 100\% \qquad (2)$$

$$S = \left[\frac{Y_{HMF}}{X_S}\right] \times 100 \qquad (3)$$

When the sugar mixture was used for HMF production, the yield of HMF was defined as follows: The term humin is applied to glyceraldehyde, disaccharides, and other unidentified products formed during the process. These anonymous products are calculated by carbon balance (CB) according to the equation 4 [9]. Whereas, X_S = Sucrose conversion, Y_P = Product yield, C_s = concentration sucrose, (t) = time, (0) = initial time, C_p = Product concentration, S= selectivity, Y_{HMF}= Yield of HMF.

$$CB = [12 \times X_G - \{(6 \times Y_G) + (6 \times Y_F) + (6 \times Y_{HMF}) + (5 \times Y_{LA}) + (1 + Y_{FA})\}] \qquad (4)$$

3. Results and discussion

3.1. Dehydration of sucrose to HMF in an aqueous system

Water is mostly preferred as a solvent for chemical transformation due to process economics, environmental concerns, and versatile physio-chemical properties. Also, water has a higher solubility of sugars without availability and prodigious financial matters [36]. Considering these advantages, we applied water as the first-choice solvent for our sugar dehydration experiments. The dehydration method of sugar to HMF adapted by Sajid et al. [17, 35] was used as a model experiment for the screening of acid catalysts. The selected organic acids were used for sucrose conversion to HMF, and the result elucidated the catalytic superiority of *p*TSA and oxalic acid as a sugar dehydration catalyst (Table 1). Glass apparatus was used to perform the experiments, so any effect of metal ion leaching from the reaction system is eliminated. Numerous side products, such as formic acid (FA), levulinic acid (LA), glyceraldehyde, and disaccharides were detected. Quantitative analysis of the acids was performed using the HPLC system. The anonymous products (humin) are calculated by carbon balance equation 4 [9].

Table 1 Conversion of sucrose to HMF. Reaction conditions: 0.5 M sucrose and 1 M catalysts in 50 ml of ultrapure water, system heated in an oil bath at 100 °C and stirred at 200 RPM.

Catalyst	**Sucrose conversion (%)**	**Glucose yield (%)**	**Fructose yield (%)**	**LA yield (%)**	**HMF yield (%)**	**Time (h)**
*p*TSA	100	55.3	32.2	9.3	10.1	4
Oxalic acid	100	60.5	47.2	3.7	10.1	6
Malonic acid	90	62.1	37.8	10.4	0.9	8

Complete hydrolysis of sucrose was observed when oxalic acid and *p*TSA were used as catalysts, as indicated in Table 1. It can be noted from the results that the hydrolyzed sugars converted to HMF preferably with *p*TSA, but surprisingly the obtained HMF yield was the same with both acid catalysts. However, the degradation of HMF was also recorded with both catalysts, and the LA yield observed with *p*TSA was 2.5 fold higher than oxalic acid. Higher acidity of *p*TSA

(pK_{a1} = -2.8) than oxalic acid (pK_{a1} = 1.27) is the most possible reason for this preeminence activity. On the other hand, malonic acid-catalyzed sucrose hydrolyzed successfully (90%); however, the dehydration process was suffered from lower potential, and the meager yield of HMF (<1%) was noted. Hereafter, the use of malonic acid for the further experiment was terminated, and only *p*TSA and oxalic acid were applied in succeeding experiments. 96.5% fructose conversion was reported in aqueous at 200 °C and 87.2% HMF yield with a selectivity of 85.5% and 95.8% [37]. It was observed during the glucose dehydration reaction that a high conversion (98.7%) can be achieved using *p*TSA and $CrCl_3.6H_2O$ catalyst combination[17]. Ma et al., (2018) also achieved a complete conversion of sucrose at 150 °C in methyl isobutyl ketone (MIBK) with KPO_4 in 3 h while increasing the temperature to 170 °C the conversion time was reduced to 1.0 h [6]. The superiority of *p*TSA is evident from the above studies that 100 % sucrose conversion could be achieved with a lower temperature than the other catalysts. The superiority of *p*TSA is due to its more acidic nature and stability at high temperatures [38]. These results direct the poor isomerization under prevailing process parameters and necessitate the provision of some higher process environment for the successful glucose isomerization to fructose. Considering the temperature and pressure constraint, further application of water as a solvent for this process was replaced with an organic solvent to attain the higher temperature maintaining the atmospheric pressure.

3.2. Conversion of sucrose to HMF in an organic solvent medium

Since oxalic acid and *p*TSA gave the HMF yields of 23% from fructose when applied in the water medium, and 80 - 90% when applied in the DMSO phase[35]. Similarly, the *p*TSA-NH_4Cl combination yields the HMF with 47% yield when applied in a glucose dehydration experiment in the DMSO medium[17]. High boiling-point organic solvents used in fructose and glucose experiments proved the solvation superiority of DMSO for the production of HMF from sugars

[17,35]. Therefore, DMSO was selected, keeping in view of the advantages of high HMF yield from fructose and glucose, high-temperature stability, and better solvation properties toward HMF[39]. Additionally, DMSO solvates the glucose moieties by distracting their intermolecular hydrogen bonding[40]. These results in stabilized furan structure of glucose along with its good dehydration capabilities by playing the role of accepter/donor of lone pairs from its sulfur and oxygen atoms, respectively. It is also ascertained that DMSO preferably solvates the HMF carbonyl group and precludes its further degradation to humin and rehydration to LA/FA[41]. Because of these reasons, the selected solvent was used for the screening of organic acid catalysts. Organic acids, *p*TSA ($pK_{a1} = -2.8$), oxalic acid ($pK_{a1} = 1.27$), maleic acid ($pK_{a1}=1.9$), malonic acid ($pK_{a1}=2.83$) and succinic acid ($pK_{a1}=4.2$) were used, and results are shown in Figure 1 (A). Results illuminated the catalyst superiority of *p*TSA, and a 50.9 % HMF yield was obtained in 60 minutes. Maleic acid and malonic acid give the near equal yield of ~ 45%, and the obtained HMF yield was in the order of *p*TSA>oxalic acid> maleic acid> malonic acid >succinic acid > blank.

On the other hand, oxalic acid gives a yield of 46.4% at an extended reaction time of 120 minutes (Figure 1 A). Both catalysts (*p*TSA and oxalic acid) exhibited comparable reactivity, so both were applied in temperature optimization reactions.

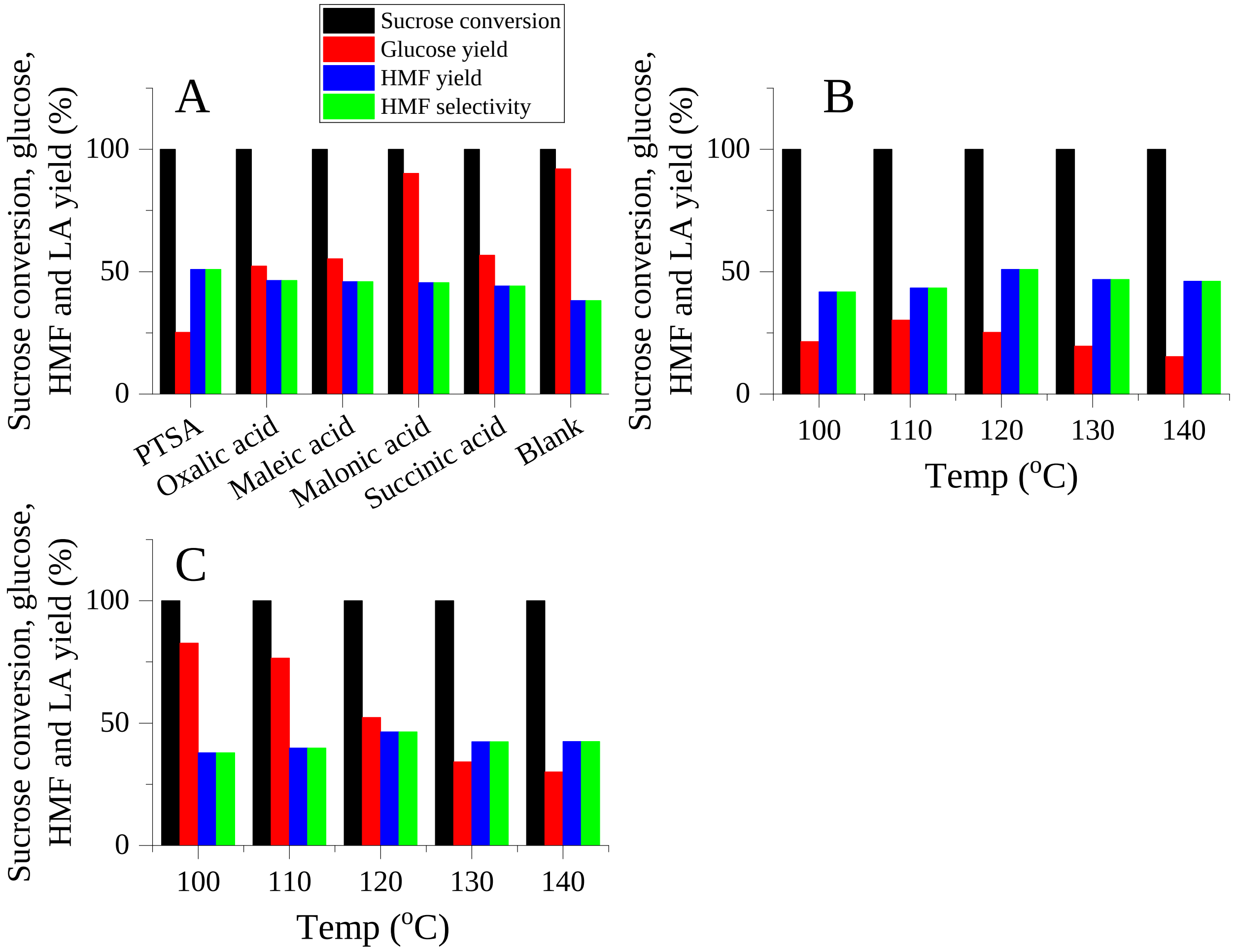


Figure 1 Conversion of 0.5 M sucrose to HMF with 1.0 M acid in 50 ml DMSO from 1 – 7 h with a string rate of 200 rpm. (A) Different acid catalysts at 120 °C; (B) *p*TSA at different temp; and (C) Oxalic acid at different temp.

3.3. Influence of temperature on the conversion of sucrose to HMF.

The rise in temperature affects positively from 100 - 120 °C, and the highest HMF yield was obtained at 120 °C (Figure 1 B and C)). When the temperature was further amplified from 120 °C to 140 °C, the inverse effect was observed for both catalysts. The overall result of an increase in temperature decrease in the processing time is also observed. On increasing temperature from 100 °C to 110 °C, yield increased from 41.7% to 43.4%, and further increase to 120 °C gives the maximum HMF yield of 50.9 % expending *p*TSA as a catalyst (Figure 1 B). On the rise beyond 120 °C, a decrease in HMF yield can be observed. The reaction time was 120, 90, 60, 30, and 15 minutes at 100, 110, 120, 130, and 140 °C, respectively. Similarly, using oxalic acid as a catalyst, HMF yield was increased from 37.8% to 39.8% when the temperature increases from 100 °C to 110 °C and a maximum of 46.4% is recorded at 120 °C (Figure 1 C). However, after this temperature displayed an inverse effect on product yield. The HMF peak was obtained after different time intervals ranging from 1-3 hours.

These results clarified that 120 °C is the optimum temperature for both catalysts, *p*TSA as well as oxalic acid. Therefore, 120 °C was applied for the screening of Lewis acids in proceeding experiments.

3.4. Comparison of different Lewis acid catalysts

Following the optimized conditions of organic acid-catalyzed sucrose conversion to the HMF, the experiment further proceeded to check the effect of different Lewis acids. Lewis acids play an active role in glucose isomerization to fructose as compared to organic acids considering the results obtained in the glucose dehydration experiments (Figure 1)[21]. NH_4Cl, $AlCl_3$, $CrCl_3.6H_2O$ were investigated as co-catalyst applying with *p*TSA and oxalic acid catalysts and obtained results are available in Table 2.

Results revealed that $CrCl_3.6H_2O$ gives the maximum HMF yield both with *p*TSA as well as with oxalic acid catalyst (Table 2). When the pure glucose was used, the maximum HMF yield was obtained with NH_4Cl however; here, NH_4Cl gives the lower yield than $CrCl_3.6H_2O$. The highest HMF yield of ~55% was obtained with *p*TSA-$CrCl_3.6H_2O$ (90 min) combination. Using oxalic acid, the HMF yield reduces to approximately 49%. NH_4Cl gives the equal HMF yield with both organic acids, however, surprisingly $AlCl_3$ gives the lower yield with *p*TSA than oxalic acid. However, the reaction time was much shorter when *p*TSA was used as compared to oxalic acid, most probably due to the higher acidity of *p*TSA than oxalic acid. Experimental results also vetted this hypothesis as the rehydration of produced HMF was recorded (LA yield = 3.35-3.73%) in *p*TSA catalyzed process. Therefore, the rehydration of produced HMF can be considered as the main cause of lower HMF yield. Furthermore, the blackish-brown color of the product solution, in the end, indicates the humin formation. Relatively lower LA yield was observed when oxalic acid was applied as an organic acid in place of *p*TSA. Lewis acids worked well as co-catalysts with *p*TSA and oxalic acid for the hydrolysis of sucrose, however, the effect on glucose dehydration was different. *p*TSA-Lewis acid efficiently converted the glucose, as indicated by the low concentration of glucose present in the reaction mixture. However, the oxalic-Lewis acid combination was less active as compared to the *p*TSA-Lewis catalyst combination, and higher glucose content was noted in the reaction mixture. The highest glucose yield (35.8%) was recorded when NH_4Cl was used; however, it dropped to one half (only 17%) when $CrCl_3.6H_2O$ was applied as a co-catalyst. This high glucose conversion contributed to the highest HMF yield. Overall the observed catalytic efficiency of Lewis acid was $CrCl_3.6H_2O$ > NH_4Cl > $AlCl_3$ for both organic acids.

Table 2 Effect of Lewis acid addition on sucrose conversion to HMF; Reaction condition; Sucrose 0.5 M with 1 M organic acid and 0.1 M Lewis acid in 50 ml DMSO heated in an oil bath at 120 °C with stirring rate of 200 RPM.

Organic acid	**Lewis acid**	**Time (min)**	**Sucrose conversion (%)**	**Glucose yield (%)**	**HMF yield (%)**	**Levulinic acid yield (%)**	**HMF Selectivity (%)**
*p*TSA	$AlCl_3$	120	100	8.52	45.3	3.35	45.3
	NH_4Cl	90	96.9	18.6	48.1	3.35	49.6
	$CrCl_3.6H_2O$	90	100	14.8	54.8	3.7	54.8
Oxalic acid	$AlCl_3$	120	100	28.9	48.32	1.5	48.3
	NH_4Cl	120	83.6	35.8	48.1	Traces	57.4
	$CrCl_3.6H_2O$	240	100	16.9	48.9	2.8	48.9

Fructose yield was meager and was challenging to detect in the product solution. In most of the cases of Lewis acid co-catalyzed reactions, only traces of fructose were observed, so quantitative results cannot be determined. Similar findings have been reported previously in the literature[42,43]. Tian et al. used DMSO and GVL solvents with Lewis acids ($AlCl_3$, $FeCl_3$, and $ZnCl_2$) alone and in combination with Brønsted acids. They found the $AlCl_3$ as the best catalyst while converted sucrose to HMF and obtained a maximum yield of 47.5% at 160 °C. Their findings are lower than the current results at high temperatures (160 °C) comparatively, which means consumption of more energy than our study (120 °C). This might be due to *p*TSA is more acidic, high acidity ensures the viability of protons for catalytic conversion [44]. Recovery and reusability of *p*TSA are its important benefits because it is solid at room temperature; hence can be recovered very easily by precipitation method which makes the process cheaper. Additionally, no human toxicity has been reported [17]. The HMF yield of 53.5% using aqueous GVL solvents catalyzed by $AlCl_3$ and the addition of salts (KCl or NaCl) at 160 °C has been reported, which is still slightly lower than our findings. Similarly, Wrigstedt et al. (2015) examined the catalytic activity of 16 metal halide catalysts in the production of HMF in a biphasic system from glucose and found out that $CrCl_3 \cdot 6H_2O$, $CrCl_2$, and $AlCl_3$ were the most capable catalysts among the selected halides while producing the yields of 35%, 25%, and 23%, respectively. Whereas, the lower HMF yield production of 1% and 2% were with catalysts $FeCl_3$ and $ZnCl_2$, respectively. Likewise, Rasrendra et al.[45] concluded slightly lower results than the present study, who examined metal halides for the synthesis of HMF using glucose as substrate in DMSO and stated that $CrCl_3$ and $CrCl_2$ presented almost the same HMF yield (54%), followed by $AlCl_3$ that resulted into a yield of about 52%. However, our findings are still considered more suitable for the commercial production of HMF because sucrose is a widely abundant and cheaper source as compared to glucose. Like molasses, a by-product of sugar processing consists of approximately 50% of sucrose, which provides a reasonable source of carbohydrates for industrial use. The reuse and recycling of leftover materials in a beneficial way is appealing to the modern era where the situation of pollution is at an alarming level and the global population is increasing rapidly enhancing the demands for food security and fossil fuels. According to Sajid et al.[17] , the dehydrated production of HMF from glucose using the same medium (DMSO and $CrCl_3 \cdot 6H_2O$ as co-catalyst) was found to lower HFM yield (36.3%) than the present study. This is mainly attributed to the conversion of glucose to HMF needs the isomerization of glucose to fructose at the first stage and then to HMF [46]. Ma et al. (2018)[6] applied verities of catalysts in a water-MIBK solvent medium. Although the addition of MIBK gave good results but MIBK has some health concerns; hence not selective. Stout et al. (2008)[47] studied the exposure of mice to MIBK and concluded it caused kidney and liver tumors in the animal. It is also evident from other studies that spectrum of kidney lesions upon short-term exposures to MIBK[48,49]. In contrast, Hallare et al., 2006 [50] and Chen et al., [51] studied DMSO's effects on zebrafish and found no toxic effect or lower effect in zebrafish embryos [50,51].

Our results explained the $CrCl_3.H_2O$ as the best Lewis acid co-catalyst; however, some unreacted glucose is also present in the reaction solution (Table 2), which indicates the partial conversion of glucose. To process this remaining glucose, reaction temperature and catalyst concentration were further optimized. Even though the quantification of various side products is challenging, color change from colorless to blackish-brown partially confirms the formation of these unwanted side products.

3.5. Effect of temperature on conversion of sucrose to HMF

The temperature impact on the *p*TSA-$CrCl_3.6H_2O$ catalyzed conversion of sucrose into HMF was investigated applying a temperature span of 120-150 ℃. As the 120 ℃ was the optimum temperature in the pure organic acid-catalyzed process and a decrease in temperature decreased the HMF selectivity (Figure 2 B and C) therefore, the lower temperature has not been investigated further in this experiment.

When a mixed acids catalyst (*p*TSA-$CrCl_3.6H_2O$) was applied, the temperature impact was different from the sole *p*TSA catalyzed process. HMF yield decreased with the increase in temperature beyond 120 ℃ (Figure 2 A). The maximum HMF yield was again at 120 ℃, similar to the sole organic acid-catalyzed process. Hence, 120 ℃ was the optimum temperature for this process. A different trend in temperature increase beyond 120 ℃ was noted by Ma et al. and Tian et al.[6,44]. It is mainly attributed to the high acidic nature of *p*TSA and with increase in temperature may enhance side reactions of rehydration of HMF occurs[52].

Surprisingly, the synergy of oxalic acid and $CrCl_3.6H_2O$ catalyzed process was entirely different from the *p*TSA-catalyzed process. As indicated in Table 2, unreacted glucose was present largely (17% - 36%) in the reaction solution. The increase in temperature converts the glucose successfully, and an incremental escalation in HMF yield was experienced. The maximum HMF yield of 52% was obtained at 150 °C (Figure 2 B). Combine catalyst (oxalic acid and $CrCl_3.6H_2O$) proficiently dehydrated the glucose at elevated temperature, which moderately increased the HMF yield. Side reactions were also stimulated with the rise of temperature. LA yield was nearly 7% at 150 °C in the oxalic acid-catalyzed process, whereas at 120 °C there was only 3%. Similarly, the increasing viscosity and color darkness also indicate the increase in humin concentrations at elevated temperatures [6,44]. It is might be due to the lower acidity of oxalic acid that needs a high temperature to hydrolyze the glycosidic linkage [53].

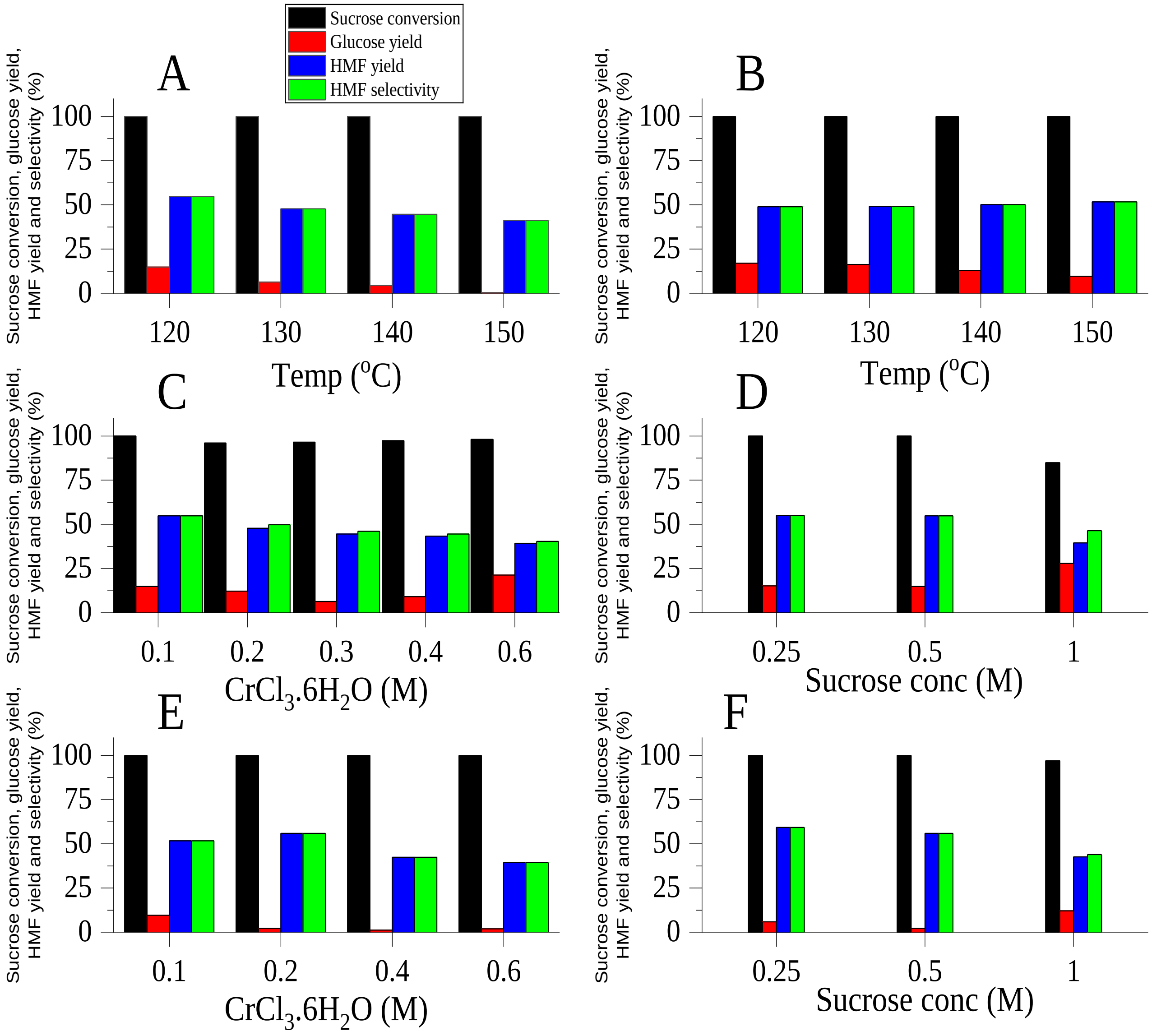


Figure 2 Conversion of sucrose to HMF; (A) 0.5 M Sucrose with 1 M *p*TSA and 0.1 M $CrCl_3.6H_2O$ at different temperatures; (B) 0.5 M Sucrose with 1 M oxalic acid and 0.1 M $CrCl_3.6H_2O$ at different temperatures; (C) 0.5 M Sucrose with 1 M *p*TSA and 0.1 – 0.6 M $CrCl_3.6H_2O$ at 120 °C; (D) 0.25 – 1.0 M Sucrose with 1 M *p*TSA and 0.1 M $CrCl_3.6H_2O$ at 120 °C; (E) 0.5 M Sucrose with 1 M pTSA and 0.1 – 0.6 M $CrCl_3.6H_2O$ at 150 °C; (F) 0.25 – 1.0 M Sucrose with 1 M oxalic acid and 0.2 M $CrCl_3.6H_2O$ at 150 °C.

3.6. Concentration effects on the conversion of sucrose to HMF

The dependency of product yield on the catalyst quantity was investigated by navigating the $CrCl_3.6H_2O$ concentration from 0.1 M to 0.6 M, and the results are displayed in Figure 2 (C and E). Inverse effects were observed on HMF yield with an increase in $CrCl_3.6H_2O$ concentration when *p*TSA was used (Figure 2 C). HMF yield reduces with an increase in catalyst concentration under optimized temperature and organic acid concentration. Therefore, the results showed that 0.1 M is the optimized concentration of $CrCl_3.6H_2O$ for the *p*TSA catalyzed process. The substrate concentration effect was explored by varying the initial sucrose contents between 0.25 – 1.0 M. Small change in HMF yield was noted with variation in initial sucrose concentration, when sucrose contents were amplified from 0.25 M to 0.5 M, HMF yield decreased to 54.8% from 55.1%. However, a further increase from 0.5 M to 1.0 M decreased the product yield to 40% (Figure 2 D). A small increase in the product yield was acquired with a lower sucrose concentration (0.5 M to 0.25 M sucrose). Still, the high level is beneficial for industrial applications and to obtain a high production rate. Therefore, 0.5 M initial sucrose concentration is recommended. The pattern is similar to the previous studies [6,53]. This is might be attributed to the side reactions between HMF and sugars molecules under a high concentration of substrate and catalysts [6].

3.7. Effect of time on the conversion of sucrose to HMF

Conversion of sucrose into HMF was studied by performing experiments using optimized parameters of *p*TSA as well as oxalic acid as catalysts for a prolonged reaction time of 5 h. Sucrose conversion increased with time, and almost a complete transformation was achieved in 1 h for 0.25 M and in 2 h for 0.50 M at 120 °C which different than concluded Ma et al. and Tian et al. [6,44] at 160 °C in 3 h, which indicates the catalytic superiority of *p*TSA, though the achieved a complete conversion in 1 h at 170 ℃, so, *p*TSA and $CrCl_3.6H_2O$ combination is more suitable in term of time and energy. However, the maximum HMF yield was achieved with different time intervals and strongly depends on initial sucrose concentration. As shown in Figure 3 (A), conversion time was increased from 60 minutes to 120 minutes when initial sucrose contents were increased from 0.25 M to 0.5 M using 1 M *p*TSA and 0.1 M $CrCl_3.6H_2O$ concentrations. Fructose, released by the hydrolysis of sucrose consumed rapidly by the reactive system, whereas initial glucose conversion was shallow. The maximum glucose yield with almost equal concentration was observed in the first 15 minutes of the reaction. Glucose expended gradually with the time and complete conversion was observed between 3-5 h. Product yield reached a peak value of 55.1% in 60 minutes and 54.83% in 90 minutes with 0.25 M and 0.50 M sucrose concentrations, respectively, and then a gradually decreasing trend was observed. An increase in concentration to two-fold increased the reaction time; however, the incremental rise in HMF yield is not so large. 0.5 M sucrose concentration is more selective because of the high production rate. However, a comprehensive economic analysis is required to evaluate the comparative financial impact.

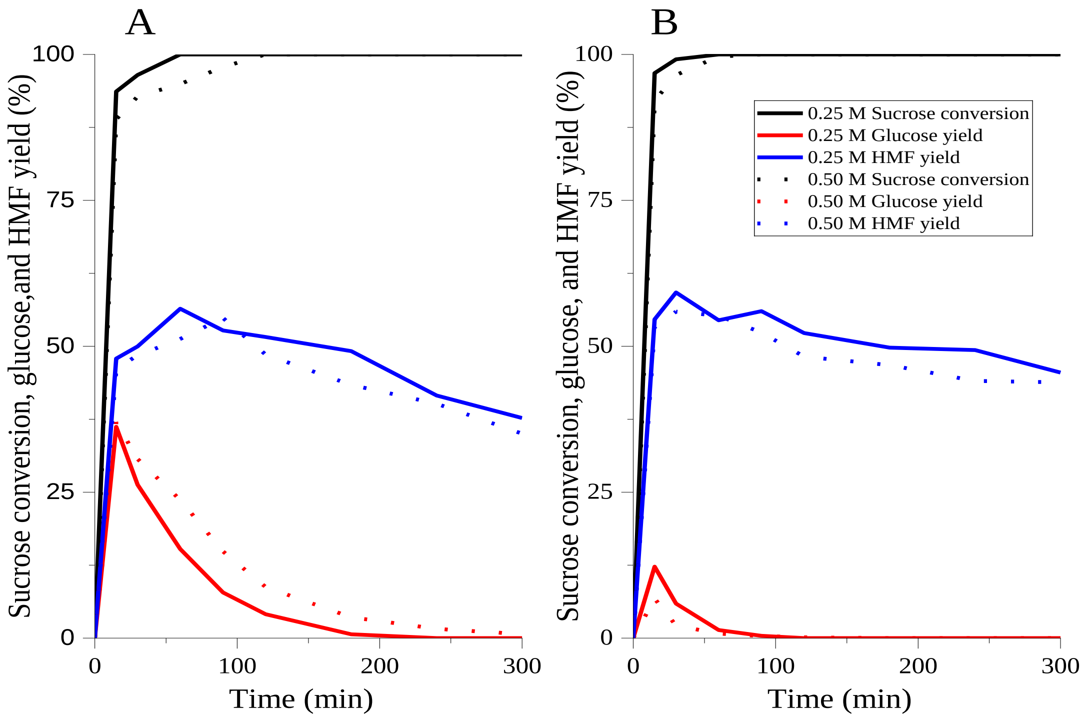


Figure 3 Effect of time on transformation of sucrose into HMF. (A) 0.25 and 0.5 M Sucrose with 1 M *p*TSA and 0.1 M $CrCl_3.6H_2O$ at 120 °C; (B) 0.25 and 0.5 M Sucrose with 1 M oxalic acid and 0.2 M $CrCl_3.6H_2O$ at 150 °C.

Similar to the *p*TSA catalyzed process, complete sucrose conversion was achieved in less time using 0.25 M sucrose as compared to 0.5 M sucrose concentration applying oxalic acid catalyst, as indicated in Figure 3 (B). Glucose yield was maximum in the first 15 min; however, the level was quite low as compared to the *p*TSA catalyzed process because the $CrCl_3.6H_2O$ contents were two-fold and the temperature applied was relatively high, i.e. 150 °C. Similar to the *p*TSA-catalyzed process, HMF yield reached a peak value of 59.21% and 55.9% in 30 min with 0.25 M and 0.50 M sucrose concentrations, respectively. An increase in catalyst strength did not affect the reaction time. Oxalic acid-catalyzed conversion of sucrose to HMF is more selective than *p*TSA catalyzed process, and high HMF yield is obtained in only 30 minutes. The reaction time is much less as compared to *p*TSA catalyzed process due to rigorous process parameters, i.e. the used $CrCl_3.6H_2O$ concentration was twice that *p*TSA-catalyzed process, and the applied temperature was high (150 °C) as compared to the *p*TSA-catalyzed process (120 °C). The oxalic acid-catalyzed process is more selective than *p*TSA catalyzed process in terms of reaction time and process yield. However, the applied temperature and catalyst concentration is relatively high. High temperature makes the process energy-intensive and energy-sensitive, so delicate control is required.

4. Conclusions

Different media (aqueous and organic) and catalysts combinations were investigated to evaluate the suitable biphasic system for the conversion of sucrose to HMF. It is concluded that the *p*TSA- $CrCl_3.6H_2O$ and oxalic acid- $CrCl_3.6H_2O$ were more suitable. 100% conversions were found using both the catalysts in organic medium with selected Lewis acids. Furthermore, the *p*TSA- $CrCl_3.6H_2O$ combination was superior as compared to the latter one. The effects of temperature and concentration were also noted. The optimum temperature was found to be 120 °C while in the case of oxalic acid, the highest yield was obtained at 150 ℃. Inverse effects were observed on HMF yield with an increase in $CrCl_3.6H_2O$ concentration when *p*TSA was used and 0.1 M was reported as the ideal concentration of $CrCl_3.6H_2O$ with a 0.5 M of the substrate. However, the maximum HMF yield was achieved with different time intervals depending on initial sucrose concentration. The kinetic analysis of the designed conversion scheme and investigation of *p*TSA catalytic potential is recommended in order to explore the potential of organic acids as future acidic catalysts with reduced environmental concerns.

Declaration of Competing Interest

The authors declare no conflict of interest.

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