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Catalytic Dehydration of Biomass-Derived Feedstocks to Obtain 5-Hydroxymethylfurfural and Furfural

Biomass-produced furanics, furfural and 5-hydroxymethylfurfural (5-HMF), are considered as vital platform chemicals used in the production of active pharmaceutical ingredients (APIs), commodity goods, and fuels. The primary challenge associated with their production pertains to the high cost involved in scaling up to industrial levels. Consequently, it is essential to explore more cost-effective options that yield efficient end products. In this study, the use of Lewis and Brønsted acids such as HCl and $AlCl_3$ enhances the isomerization of glucose through catalytic dehydration into 5-HMF. It was observed that employing moderate reaction conditions increased the yield of 5-HMF to 44.94 % and 50.60 % respectively, with changes in HCl concentration and $AlCl_3$ mass loading. The suitable conditions to achieve the highest yield of 5-HMF were 100 μL of HCl, 0.75 g of $AlCl_3$, reaction temperature 150 °C, and reaction time 4 h. In the second experiment, corncob was converted into furfural in the presence of 20 % H_2SO_4, in combination with NaCl as a promoter. The optimal conditions under which a yield of 44.77 % was achieved were as follows: 50 mL of 20 % H_2SO_4, reaction temperature 140 °C, 0.5 g of NaCl, 5 g of corncob, and reaction time 160 min. Furthermore, a proposed reaction mechanism was outlined to elucidate the pathway for the production of the aforementioned platform chemicals.

Keywords: Furfural, Hydroxymethylfurfural, 5-HMF, catalysts, dehydration, biomass, glucose, corncob, extraction.

Introduction

The ongoing decline of fossil fuel reserves resulting from the persistent utilization of petroleum and coal feedstocks, coupled with the pressing climate emergency, has spurred the scientific community to prioritize the exploration of bio-based alternatives [1]. In response, biorefinery concept has emerged to investigate and yield economically viable products for fossil fuel compounds, thereby contributing to a reduction in greenhouse gas emissions [2]. In recent research, significant interest has resulted in the development of bio active platform chemicals. Various platform chemicals, such as succinic acid, levulinic acid, 5-hydroxymethylfurfural (5-HMF), and furfural could be synthesized from biomass resources as reported by [3, 4]. Furfural and 5-HMF holds unique position among bio-active chemicals due to their physical and chemical properties, comprising aldehyde, furan ring components, and alcohol. According to the U.S. Department of Energy (US DOE), furfural and 5-HMF are designated as two of the "top 10" platform chemicals for specialty and bulk chemicals [5]. These platform compounds are typically synthesized by acid-catalyzed dehydration of C6 and C5 sugars, which are obtained from the hydrolysis of cellulose and hemicellulose. For the past few years, researchers main focus is to study the optimization conditions for furfural and 5-HMF production from biomass [6–8], investigating the separation and extraction methods to increase the selectivity and yield [9, 10].

5-HMF production from biomass shows promising properties among the platform chemicals as reported by the US DOE and can be easily transformed into active pharmaceutical ingredients (APIs) as well as other valuable chemicals [11]. Biomass-produced agrobased resources such as lignocellulose, are vital resource for the synthesis of 5-HMF and are highly abundant in the environment. It usually follows a three-step reaction under acidic conditions involving hydrolysis of cellulose to glucose to form fructose through isomerization followed by dehydration to 5-HMF [12]. Different approaches are employed by researchers for the conversion of starch-rich agricultural waste into 5-HMF [13]. 5-HMF conversion from biomass-derived residues is mostly investigated via optimization of reaction parameters such as catalyst loading, temperature, pressure, and reaction time. Yosuke M. et al. applied liquid-liquid extraction for the synthesis of 5-HMF from monosaccharides using methyl isobutyl ketone (MIBK) solvent. An 85 % yield of 5-HMF was achieved by addition of Lewis acid which promotes isomerization of glucose into five membered ring structure [14]. A combination of Lewis and Bronsted acid catalysts was employed by Huixiang and his team in the synthesis of 5-HMF from carbohydrates using a low boiling point (BP) solvent [15]. From their work, about 70 % of 5-HMF was achieved when isopropyl alcohol (IPA) solvent was used.

Furfural, on the other hand, possesses outstanding applications in the production of active pharmaceutical ingredients, polymeric materials, food additives, cosmetics, pesticides, insecticides, disinfectants, etc. [16, 17]. Their synthesis involves acid-catalyzed dehydration of hemicellulose or furan-containing compounds as crucial C5 sugar components. A wide range of agro-based biomass sources can be used for the synthesis of furfural. For instance, Adebayo and his colleagues synthesized furfural and furfuryl alcohol from corncob, elephant grass, sunflower, and baobab pulp in a Lewis acid medium [18]. Likewise, furfural synthesis was achieved from agro-based biomass resources such as rice husk, sugarcane bagasse, cotton seeds, and oat hulls via heterogeneous acid catalysts [19]. One major challenge faced by researchers focuses on improving the yield and purity of furfural by optimizing the reaction conditions such as temperature, catalyst loading, solvent used, and reaction time.

This research explores the variation of Brønsted acid (HCl) and Lewis's acid ($AlCl_3$) as catalysts in the conversion of glucose into 5-HMF under moderately optimized conditions using a high pressure batch reactor. Additionally, the synthesis of another platform chemical viz furfural was studied using corncob as the primary feedstock in the conversion process. In the furfural synthesis, NaCl was employed as a promoter to augment the hydrolysis and dehydration of corncob into furfural. To elucidate the reaction pathway to produce these platform chemicals, a plausible reaction mechanism is proposed in this work.

Experimental

Materials

Corncob was purchased from the local market (delivered from farmland Jetysu region of Kazakhstan); all other chemical reagents used in this experiment were obtained from Sigma-Aldrich: D-(+)-Glucose monohydrate, ≥ 99 %; 5-hydromehtylfurfural (5-HMF), ≥ 99 %; Furfural, 99 %; Ethylene Glycol, 99.8 %; Isopropyl alcohol (IPA), 99.5 %; Methanol (HPLC grade), ≥ 99.8 %, Dichloromethane (DCM), ≥ 99.9 %; Aluminium chloride anhydrous ($AlCl_3$), Sodium chloride (NaCl), 99.8 %; Hydrochloric acid (HCl), ≥37 %; and Sulfuric acid (H_2SO_4).

5-HMF Synthesis

To a 150 mL high pressure batch reactor (Buchi-1297840), 2 g of glucose, $AlCl_3$ (0.25–1.5 g), HCl (50–200 μL), 45 mL of IPA, and 5 mL of deionized (DI) water were added and gently stirred to obtain a homogenous solution mixture. The homogeneous mixture was heated in a high pressure reactor at 10 bar at a temperature of 150 °C for 4h at a stirring rate of 350 rpm. After the reaction was stopped, the mixture was quickly collected and filtered under vacuum and the analyte was extracted with ethyl acetate and solvent removed under reduced pressure. An approximate mass of light brown solution was obtained, which was separated into organic and aqueous phases. Samples taken from two phases were filtered through a 0.22 μm syringe filter and diluted with methanol for HPLC analysis. The concentrate was preserved in clean Pyrex glass vials for further analysis. The 5-HMF yield was calculated as follows:

$$\text{5-HMF yield (\%)} = \frac{N_{\text{5-HMF}}}{N_{\text{glucose}}} \times 100\ \%,$$

where $N_{\text{5-HMF}}$ denotes the moles of 5-HMF produced and N_{glucose} represents the moles of glucose used. To confirm the effectiveness of the chosen method, all experiments were carried out in triplicate.

Furfural Synthesis

5 g of corncob, 0.5 g of NaCl, and 50 mL of 20 % H_2SO_4 was prepared under the fume hood. The mixture was transferred into a high pressure batch reactor (Buchi-129784, Germany) at 10 bar, where the reaction was carried out separately at different temperatures of 100, 120, 140, 160, and 180 °C for 160 min. The distillate was filtered and extraction carried out by liquid-liquid approach using dichloromethane (DCM) sol-

vent after which the furfural was separated under reduced pressure using rotavap (Buchi R-210). Furfural yield was calculated as follows:

$$\text{Furfural yield (\%)} = \frac{N_{\text{Furfural}}}{N_{\text{hemicellulose}}} \times 100\ \%\ ,$$

where N_{Furfural} is the mole of furfural product after reaction and extraction and $N_{\text{hemicellulose}}$ is the mole of hemicellulose (pentose) content in corncob.

The hemicellulose content used was based on literature values obtained by several researchers from the National Institute of Technology, India. According to their findings, the hemicellulose content obtained from lignocellulosic dry corncob is between 26–36 % [20]. The average of the reported amount (31 %) was used in calculating the theoretical mass of the hemicellulose content in our corncob. Furfural content was calculated based on the concentrations obtained by UHPLC where samples were measured according to the calibration (with R^2 0.9962) prepared for furfural analysis. All experiments were carried out in triplicates to confirm the effectiveness of the chosen methods.

Scheme of the 5-HMF and furfural production from glucose and corncob respectively is presented in Figure 1.

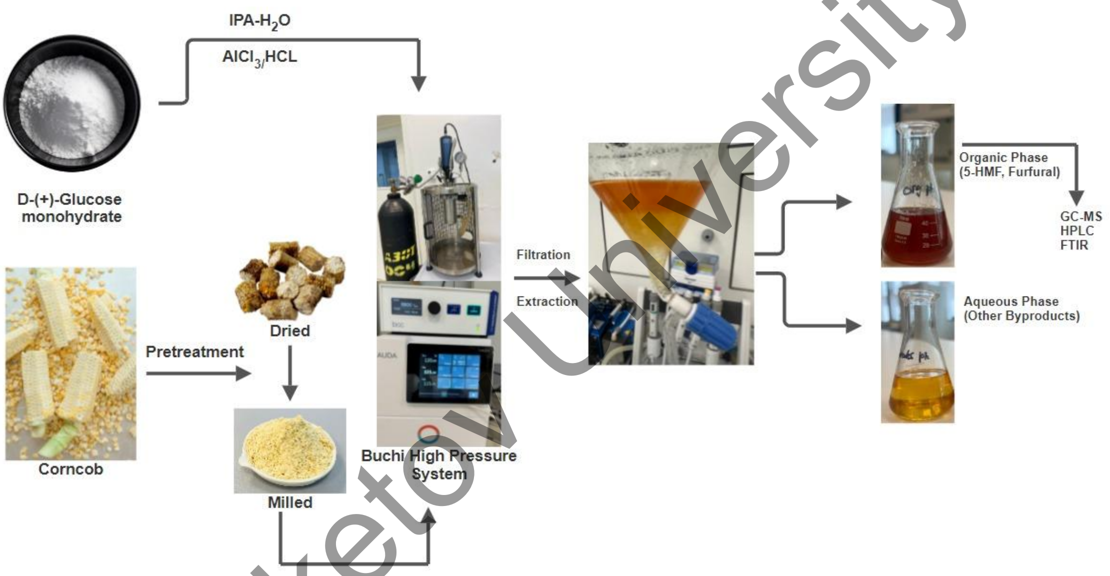


Figure 1. Process flowsheet of 5-HMF and furfural production from glucose and corncob respectively

Characterization

Characterization analyses were performed qualitatively and quantitatively for pure standards and synthesized products. Prior characterization of the pure furfural standard, purification was carried out by a simple distillation process as the furfural changed color to dark brown due to improper preservation. Furfural and 5-HMF were characterized by FTIR, UHPLC, and GCMS to understand the physical and chemical features. The functional groups were detected using FTIR spectrometer (Thermo Scientific Nicolet iS10, USA) to study the chemical composition of furfural and 5-HMF. All spectra were recorded in the range 4000–500 cm^{-1} with a scanning speed of 1 cm^{-1}s^{-1} and a 4 cm^{-1} resolution. 5-HMF concentration obtained from glucose conversion was analyzed by UHPLC (Ultimate 3000, Thermo Fisher Scientific, USA) and equipped with a UV detector (C18 column, 150 mm length, particle size 1.9-micron, diameter 2.1 mm). The eluent used was a mixture of water: methanol (80:20, v/v) at a flow rate of 0.2 mL/min. The column temperature was 30 °C and the sample injection volume was 1 μL. The analysis was repeated two times and the 5-HMF was measured at 284 nm wavelength and quantified using an external standard calibration curve with series of dilutions ranging from 0.5 mg/L to 30 mg/L. The quantitative analysis of furfural used the same parameters as for the analysis of 5-HMF. The only difference is the change in wavelength from 284 nm to 275 nm for furfural analysis. A TSQ 8000 Evo Triple Quadrupole GC-MS/MS (Thermo Fisher Scientific) instrument with ion source temperature of 200 °C, the operating system at 70 eV, capillary temperature of 200 °C, with injection split (20:1 ratio, 1 μL) at 270 °C injector temperature was used to perform qualitative analysis of the synthesized products. 5 % phenyl residues: 95 % methyl polysiloxane capillary column (Trace GOLD TG-5MS-GC Column 30 m × 0.25 μm × 0.25 mm, Thermo) was used. The oven temperature was programmed as follows: initially at 60 °C for 5 min, increased to 260 °C at a flow rate of 15 °C/min and maintained at 260 °C for 20 min, and finally increased to 270 °C rate 2 °C/min, maintained at 270 °C for 5 min. Helium (He) was used as the carrier gas at a flow rate of 1 mL/min. The full scan of the EI ionization mode was carried out in the range of m/z 45–600. Data collection, compound identification, and peak processing were performed with Xcalibur (Thermo Scientific).

Results and Discussion

The purchased furfural standard was purified and characterized by FTIR, GCMS, and HPLC to study their physicochemical properties. FTIR was as well measured for the as-prepared sample products and compared with pure standards and feedstocks. The results obtained by FTIR showed prominent peaks in which different functional groups were identified by comparison with literature data. In Figure 2, the chemical composition of glucose, corncob, synthesized 5-HMF and furfural as well as pure 5-HMF and furfural standards are presented.

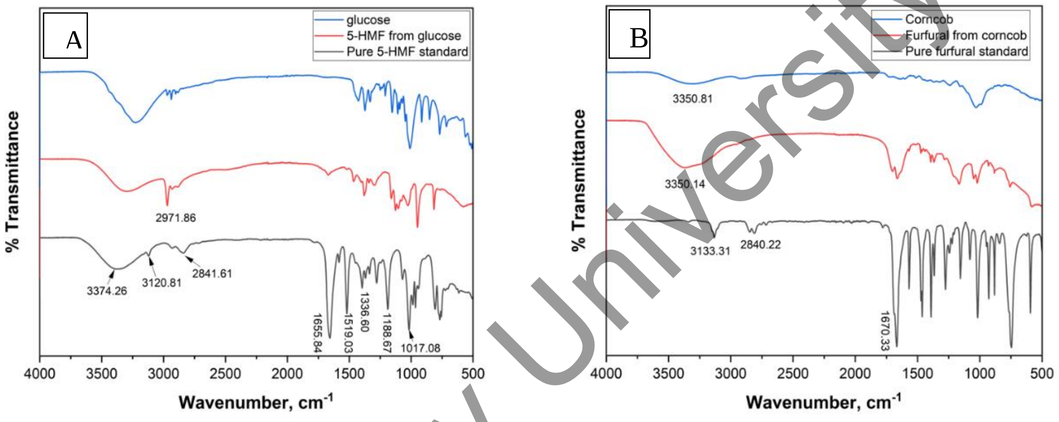


Figure 2. FTIR spectra of 5-HMF (A) and furfural (B)

The IR spectra of glucose, 5-HMF, and pure 5-HMF standard in Figure 2(A) show the chemical composition consistent with molecular structures and expected functional groups, confirming the identity of these compounds. Though peaks were observed in the same spectral region from all samples, in overall, the pure 5-HMF standard shows peaks with higher intensities compared with that of raw glucose and 5-HMF obtained from glucose. A broad absorption band at 3374.26 cm^{-1} was observed in all three materials at the same position which could be attributed to the stretching vibrations of 5-HMF hydroxyl groups [21]. The absorption bands in the region 3120.81–2841.61 cm^{-1} from pure 5-HMF standard through synthesized 5-HMF were attributed to the presence of methylene group (-CH_2-). Further, the pure 5-HMF standard possesses a sharp band at 1655.84 cm^{-1}, which was assigned to the stretching vibration of C=O (carbonyl group). However, this prominent was not so recognizable in the raw glucose and 5-HMF samples produced from glucose. The presence of C-O stretching vibration was justified by absorption peaks at 1017 cm^{-1} and 1188 cm^{-1} in all samples as already reported [22].

Figure 2(B) shows the IR spectra of pure furfural standard, furfural produced from corncob and raw corncob. In the pure furfural spectrum, moderate intensity bands at 2810 and 2840.22 cm^{-1} represent C-H stretch for the aldehyde group while at 3133.31 cm^{-1}, the presence of aliphatic C-H stretch was recorded, at the same time these peaks were not observed in corncob and furfural synthesized from corncob. At a wavelength of 1670.33 cm^{-1}, the presence of the conjugated carbonyl group showed an intense peak confirming the presence of the carbonyl functional group in the furfural compound. This is also observed in the same region from furfural-derived corncob. This occurs in the conjugated unsaturated aldehyde region but not the ketone group. The spectral range between 881 to 745.69 cm^{-1} could be attributed to the C-H bending vibration while at 1460.98 cm^{-1}, the –C=C functional group was recorded [23]. The spectral region between 881–876 cm^{-1} and 773–770 cm^{-1} is indicative of the –CH out-of-plane bending vibrations associated with aromatic rings and their derivatives where these peaks are recorded in pure furfural and that of furfural derived from corncob [24]. In summary, more intense peaks are observed in pure furfural standard and synthesized furfural compared with raw corncob spectra.

GC-MS/MS qualitative analysis was performed to confirm glucose and corncob transformation into 5-HMF and furfural respectively. From the result, the purity and molecular composition of 5-HMF and furfural was confirmed by qualitative analysis using a TSQ 8000 triple quadruple GC-MS/MS analytical instrument. The chromatogram exhibited distinctive retention time at 3.62 min and 4.16 min for 5-HMF and furfural respectively showing the mass-to-charge ratio (m/z) and relative abundance of all fragments generated during the bombardment by electron impact ionization process as shown in Figure 3.

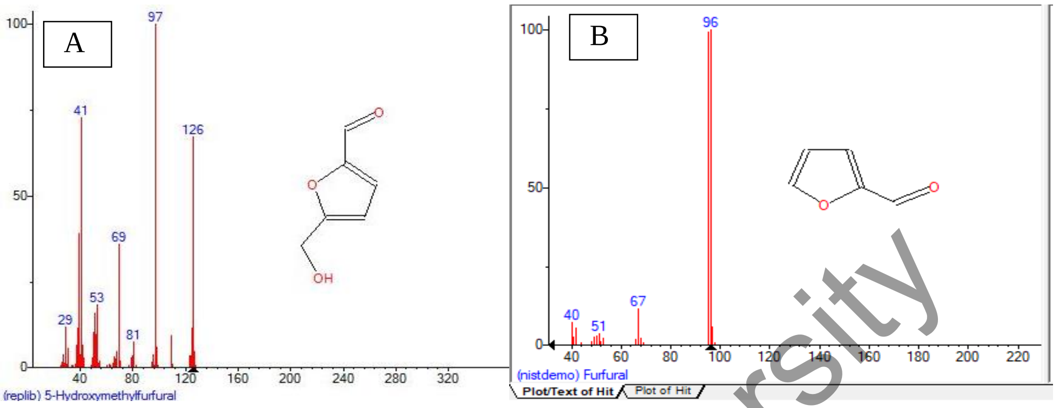
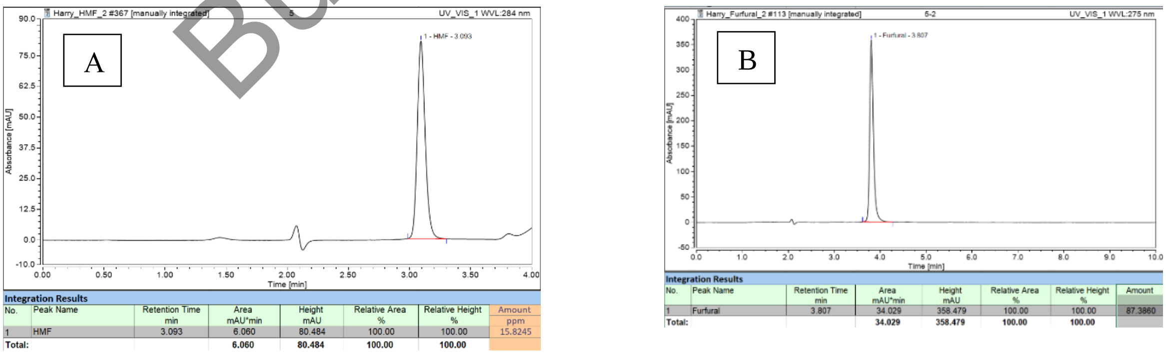


Figure 3. GC-MS/MS qualitative test for 5-HMF (A) and furfural (B) from glucose and corncob respectively

The spectrum of the 5-HMF derivative with m/z 126 corresponds to the molecular mass of the parent ion (M). A methyl group loss fragment (–CH_3) at m/z 97 denotes the base peak, while oxidative products (e.g., HCOOH) and fragments resulting from furan ring opening forming dehydrated products are also observed after bombardment (Fig. 3(A)). In addition, fragments resulting from substituents or side chains may also be evident. For furfural fragments, as shown in Figure 3(B), the m/z value at 96 corresponds to the molecular mass of furfural as well as the base peak since it shows the highest intensity amongst all other fragments. Importantly, a fragment with m/z 67 corresponds to a furanic cation which plays a vital role in furfural synthesis. The fragments obtained from as prepared 5-HMF, and furfural are in agreement with those already reported in the literature.

A quantitative and qualitative analysis was carried out with UHPLC ultimate 3000 (Thermo Scientific) with UV-vis detector at 284 and 275 nm wavelength for 5-HMF and furfural respectively (Fig. 4). Prior to analysis, a calibration curve was prepared using pure 5-HMF and furfural standard. The correlation coefficients 0.9999 and 0.9998 for 5-HMF and furfural respectively proved the efficiency of the curve.



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount ppm
1	HMF	3.093	6.060	80.484	100.00	100.00	15.8245
Total:			**6.060**	**80.484**	**100.00**	**100.00**	

Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1	Furfural	3.807	34.029	358.479	100.00	100.00	87.3860
Total:			**34.029**	**358.479**	**100.00**	**100.00**	

Figure 4. UHPLC analysis for 5-HMF (*A*) and furfural (*B*) synthesized from glucose and corncob respectively

An intense peak in Figure 4(A) was determined at a retention time of 3.093 min for 5-HMF with the highest concentration of 257.87 mg/L amongst all synthesized samples. Furfural confirmation test was also conducted on UHPLC where a furfural peak was observed at 3.807 min as shown in Figure 4(B).

Effect of HCl Volume and $AlCl_3$ Loading Towards 5-HMF Production from Glucose

The synthesis of 5-HMF from glucose conversion exhibits potential pathways, inclusive of both direct dehydration and intermediated routes, possibly involving compounds like fructose as reported by [25]. Lewis acids, such as $AlCl_3$, VCl_3, and $SnCl_4$ are found to be useful in the glucose isomerization to fructose compared with Brønsted acids. Furthermore, fructose then undergoes dehydration in the presence of Brønsted acid (HCl) leading to the formation of 5-HMF. Figure 5(A) shows the effect of HCl volume for 5-HMF conversion from glucose. The study aimed to investigate the impact of variations in HCl volume and $AlCl_3$ catalyst loading on 5-HMF yield. Different HCl volumes, ranging from 50 to 250 μL, were tested in a 50 mL IPA:H_2O ratio to facilitate the conversion of glucose into 5-HMF. The experimental procedure involved heating the reaction mixture in a high pressure batch reactor to 150 °C and maintaining a steady temperature for a residence time of 4 h.

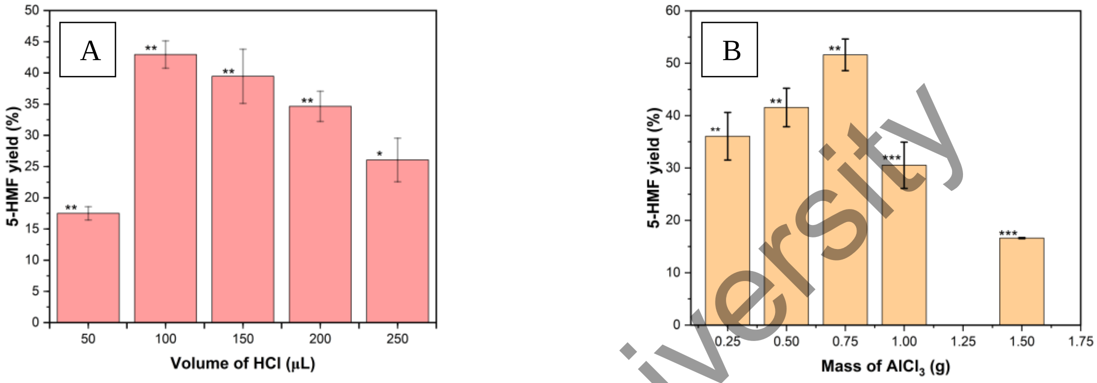


Figure 5. HCl concentration (A) and $AlCl_3$ mass loading (B) variation for 5-HMF production from glucose (Asterisks denotes level of significance based on one sample t-test assuming statistical significance at * = :$P < 0.05$ ** = :$P<0.005$ *** = :$P <0.0005$)

The 5-HMF yield exhibited an increase from 17.51 % to 42.94 % when HCl volumes of 50 and 100 μL were respectively used (Fig. 5(A)). However, as the HCl volume was further increased to 150–250 μL, the 5-HMF yield gradually decreased within the range of 39.46 % to 26.06 %. Based on the findings, the optimal conditions were determined to be a 100 μL HCl volume and 1 g of $AlCl_3$. Between 100–200 μL HCl volume shows a good trend in transforming glucose to 5-HMF. However, the yield is relatively low when too low or too high concentration of HCl was tested as shown in Figure 5(A). This trend is similar to the work that was already reported by [26-27]. As widely accepted, the formation of 5-HMF requires relatively moderate conditions. Increasing the acidity of the medium might facilitate the dehydration reaction but highly acidic medium may not be favorable as seen in the trend of product yield. In addition, choosing a higher temperature for highly acidic medium might convert the 5-HMF to levulilic acid as an intermediate [28]. The results obtained from statistical data prove that the difference the triplicates of each experiment conducted towards 5-HMF synthesis was highly significant ($p < 0.05$). To summarize, a moderate HCl concentration is required for a good yield of 5-HMF while low or higher concentration may suppress the glucose conversion to 5-HMF.

Empirical research was conducted by varying the mass of $AlCl_3$ to monitor the yield of 5-HMF, aiming to determine the optimal quantity of $AlCl_3$ conducive to the conversion of glucose into 5-HMF, as depicted in Figure 5(B). To study the effect of $AlCl_3$ mass loading, different masses varied from 0.25–1.5 g of $AlCl_3$ dosage were used. The maximum yield of 51.60 % was reached when 0.75 g of $AlCl_3$ was used in the presence of 100 μL HCl for a reaction time of 4 h at 10 bar pressure. Increasing the mass of $AlCl_3$ from 0.25 to 0.75 g shows a good correlation by increasing the yield of 5-HMF yield while further increment of $AlCl_3$ mass results in low yield. Increasing trends were found in the work of [29], however, they did not include further increment of $AlCl_3$ dosage in their research. One possible reason for the yield decline after increasing the mass of $AlCl_3$ could be related to the agglomeration of the catalyst due the higher amount in solution or possibility of converting the glucose into other byproducts such as humins.

Effect of Temperature on Corncob Dehydration into Furfural Using H_2SO_4/NaCl Medium

In the furfural synthesis from corncob via a Brønsted acid catalysed dehydration reaction method in the presence of NaCl, effect of temperature variation on corncob conversion into furfural was the main parameter studied. To achieve furfural, Cl^- ions in the presence of 20 % H_2SO_4 enhance the transformation of corncob hemicellulose layers during dehydration process to produce furfural. H_2SO_4 serves as a catalyst while addition of NaCl as a promoter. From the results, furfural synthesis from corncob using a high pressure batch system significantly impacts the yield when temperature was varied (Fig. 6).

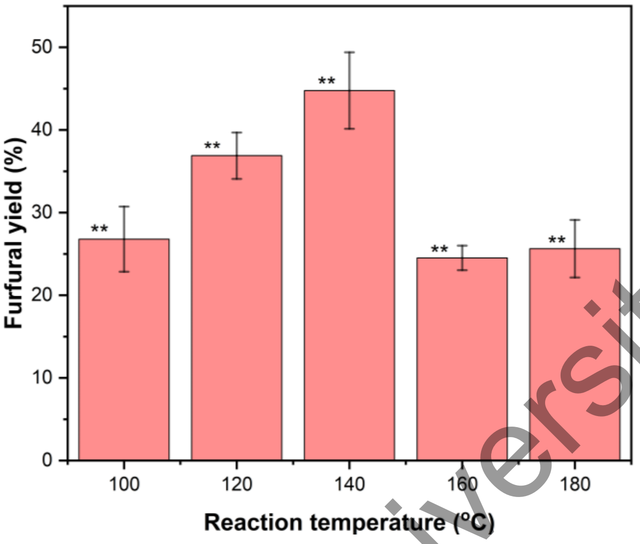


Figure 6. Effect of temperature on corncob dehydration into furfural using H_2SO_4/NaCl medium (Asterisks denotes level of significance based on one sample t-test assuming statistical significance at at * = :P < 0.05 ** = :P<0.005 *** = :P <0.0005)

As can be seen in Figure 6, NaCl dramatically promoted the conversion of corncob into furfural in the presence of H_2SO_4 catalyst at a reaction temperatures ranging from 100 °C to 180 °C at 10 bar pressure in 160 min reaction time. The highest furfural yield of 44.77 % was obtained for 140 °C reaction temperature while the lowest yield (24.52 %) at 160 °C reaction temperature. From the outcome and the chemistry involved in the synthesis, it could be attributed to the fact that corncob dehydration of hemicellulose (pentose) according to this reaction is highly favoured at moderate temperatures. The reaction likely proceeds efficiently at a reaction temperature of 140 °C leading to higher furfural yield. In contrast, the choice of higher reaction temperature may be too aggressive for this reaction resulting in the low yield. This could also occur due to undesired side reactions or the rehydration of furfural into other by-products such as humins and levulinic acid. The results obtained from statistical data proves that the difference the triplicates of each experiment conducted towards furfural synthesis was highly significant ($p < 0.005$). The results obtained highlight the importance of temperature optimisation in achieving a higher yield.

Reaction Mechanism

The reaction routes for glucose conversion into 5-HMF are shown in Figure 7(A). Glucose conversion in the presence of Brønsted and Lewis acids proceeded through a coupled route, involving the use of $AlCl_3$ for isomerization of glucose to fructose and the fructose dehydration in the presence of halogen to produce 5-HMF. 5-HMF degradation may occur, leading to the formation of byproducts such as formic acid, levulic acid, or humins [30]. In Figure 7(B), the furfural reaction pathway is divided into two major steps: in the first step, hydrolysis of corncob into a pentosan derivative, xylose may occur, which is further converted into furfural in the second step via a dehydration process [31].

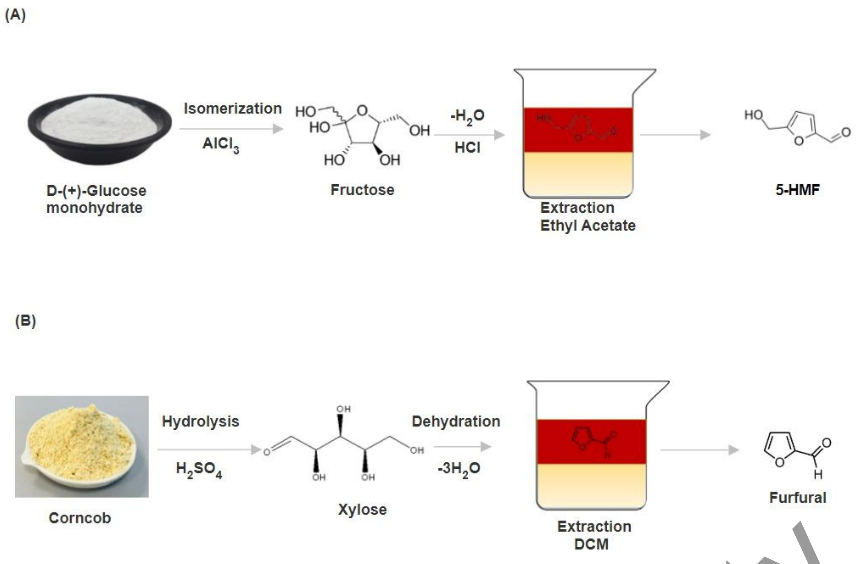


Figure 7. Possible reaction mechanism for 5-HMF and furfural production from glucose and corncob respectively

The use of H_2SO_4 acts as a catalyst in both steps, resulting in the production of furfural from corncob. The use of NaCl helps to increase furfural yield, serves as a promoter, as well as aids in the stabilization of oxonium or carbocation intermediates for the H_2SO_4 catalyst.

Conclusions

This study highlights the impact of Brønsted and Lewis acids in the catalytic conversion of biomass-derived glucose and corncob into 5-Hydroxymethylfurfural (5-HMF) and furfural, respectively. The results obtained clearly demonstrate that selecting optimal conditions, including concentration, reaction temperature, reaction time, catalyst, and solvent system, is crucial for achieving high yield when transforming various biomass feedstocks into their respective products. HCl and $AlCl_3$ have been demonstrated to exhibit effective conversion mechanisms when used in conjunction with IPA, H_2O, and 20 % H_2SO_4 to produce 5-HMF and furfural. The addition of NaCl as a promoter significantly enhances the conversion of corncob into furfural when H_2SO_4 is employed as a catalyst. Impressive yields of 42.94 % for 5-HMF (HCl concentration variation), 51.6 % for 5-HMF ($AlCl_3$ mass loading variation) and 44.77 % for furfural were achieved. This research work also proposed a plausible mechanism for glucose and corncob conversion into the aforementioned platform chemicals.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. CRediT: **Harry Kwaku Megbenu** conceptualization, data curation, investigation, methodology, validation, visualization, writing original draft & editing; **Zhanat Azhikhanova** data curation, methodology, & formal analysis; **Gulnaz Ingkar** data curation, methodology & formal analysis; **Nurzhan Rakhimgaliyev** data curation, methodology & formal analysis; **Mels Aizada** data curation, methodology & formal analysis; **Almaz Kenzheshov** data curation, methodology & formal analysis; **Almas Askarov** data curation, methodology & formal analysis; **Minavar Shaimardan** conceptualization, data curation, formal analysis, resources, supervision, & validation; **Nurxat Nuraje** conceptualization, data curation, formal analysis, funding acquisition, resources, supervision, validation, & editing.

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Conflict of interest

The authors declare no conflict of interest.

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