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TRANSFORMATION OF GLUCOSE INTO HMF AND FURFURAL IN HYDROTHERMAL REACTION CONDITIONS

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Abstract: This study focused on the conversion of glucose into high-value chemicals, specifically furfural (FFR) and 5hydroxymethylfurfural (HMF), through hydrothermal reaction processes. Glucose was decomposed under subcritical water conditions (160-220 °C) in a Teflon-lined stainless-steel reactor, and the evolution of FFR and HMF products was examined over residence times ranging from 30 to 210 minutes. The highest yields of FFR and HMF were achieved at a temperature of 220 °C and a residence time of 180 minute. Increasing the temperature from 160°C to 220°C and extending the residence time from 30 to 180 minutes enhanced the hydrolysis of glucose. The yields of FFR and HMF were determined using high performance liquid chromatography (HPLC).

Keywords: Furfural, 5-hydroxymethylfurfural, Hydrothermal reaction, HPLC

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1. Introduction

Biomass, a plentiful and renewable carbon-neutral resource, holds immense potential for producing energy and chemicals to power sustainable industries of the future (Bridgwater, 2003). Processes aimed at biomass valorization for the production of chemicals and fuels are gaining increasing attention as a pathway to sustainable manufacturing (Ragauskas et al., 2006). Such developments can be achieved through clean, selective, and efficient processes utilizing renewable raw materials, with non-edible plant biomass serving as a globally abundant carbon source for producing bio-chemicals, biofuels, and bio-energy (Cantero et al., 2015). Furan-based platform compounds, such as FFR and HMF, can be derived from biomass through hydrothermal conversion and further transformed into value-added chemicals and liquid fuels via hydrodeoxygenation, promoting efficient biomass utilization and mitigating environmental issues caused by excessive fossil fuel use (Zhao et al., 2021). The schematic representation of high-value applications of FFR and HMF is presented in Figure 1. Biomass, sourced from agricultural residues, wood, and herbaceous energy crops, consists of biopolymers like cellulose (35-50%), hemicellulose (25-30%), and lignin (25-30%) (Aida et al., 2007). Cellulose, which serves as a source of glucose, is a major constituent of biomass (Bobleter, 1994). Glucose is a versatile molecule with great potential as a starting material for various productive processes, such as serving as feedstock in biological systems for the production of bio-fuels and bio-chemicals (Corma et al., 2007). FFR is produced from pentoses such as xylose, arabinose, and lyxose, whereas HMF is obtained from hexoses, with fructose and glucose being the most prevalent sources (van Putten et al., 2013). FFR, a furan ring containing a heteroatom and an aldehyde group, serves as an organic solvent to enhance the selectivity of aromatics and unsaturated compounds in various chemical reactions (Mariscal et al., 2016). FFR, with its aldehyde group and furan ring, is a highly reactive chemical used as a feedstock for producing over 80 types of value-added chemicals and liquid fuels (Bohre et al., 2015). FFR is a significant precursor for liquid fuels, as key biofuel components such 2-methylfuran (MF), 2,5-dimethylfuran, as and methyltetrahydrofuran (MTHF) can be obtained through its hydrogenation (Ahmad et al., 2022). The reactive chemical properties of HMF unlock a wide range of opportunities for valuable applications. HMF, with an additional hydroxyl group on C5 compared to FFR, exhibits greater reactivity, enabling a wider range of highvalue applications due to its enhanced chemical properties (Kucherov et al., 2018). 2,5-Furandicarboxylic acid (FDCA), a key derivative of HMF, is among the most thoroughly researched and is obtained through the oxygenation of HMF (Sajid et al., 2018). Additionally, HMF can be transformed into liquid fuels such as 2,5dimethylfuran and 5-alkoxymethylfurfural ethers through hydrogenolysis and esterification processes (Wang et al., 2014).

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Figure 1. Pathways for high-value applications of FFR and HMF (Zhao et al., 2021).

The literature presents studies on the conversion of glucose into HMF and FFR. The study by Knezevic and colleagues provides valuable insights into the hydrothermal conversion of glucose, offering essential knowledge for sustainable chemical production processes (Knezevic et al., 2009). The yield of HMF from glucose reached 64% under conditions of 7 MPa, 200 °C, and 1.5 hours (Lee et al., 2016). Achieved simultaneous production of FFR (42%) and HMF (34%) from glucose, focusing on optimizing yields (He et al., 2020). Attained high efficiency in transforming glucose and various carbohydrates into FFR and HMF utilizing heterogeneous acid catalysts (Agirrezabal-Telleria et al., 2014). Optimized the production of HMF and FFR from glucose using dilute acid catalysts, achieving the best results at moderate temperatures and low acid concentrations (Jaswal et al., 2022; Thunyaratchatanon et al., 2021).

The primary objective of this study is to investigate the potential for producing the high-value-added compounds 5-hydroxymethylfurfural (HMF) and furfural (FFR) through the chemical conversion of glucose, a renewable and sustainable carbon source, within a hydrothermal reaction medium. Considered as alternatives to fossil fuels, such biochemicals hold strategic importance for environmentally friendly energy and material production, aligning with the principles of green chemistry. The glucose conversion process presents significant potential, both scientifically and industrially, particularly for obtaining platform chemicals in biomass-based chemical synthesis. In this study, the chemical transformations of glucose hydrothermal under conditions were systematically investigated within a temperature range of 160-220 °C and residence times varying from 30 to 210 minutes. The reactions were conducted in Teflon-lined stainless steel reactors, and the liquid products obtained from each temperature-time combination were prepared using the solid-phase extraction (SPE) method. Quantitative analysis of the resulting products was liquid performed using high-performance

chromatography (HPLC). For this analysis, a C18 column was employed, and HMF and FFR compounds were detected using a UV detector at a wavelength of 284 nm, with retention times of 7.17 and 10.05 minutes, respectively. A methanol/water mixture (18:82, v/v) was used as the mobile phase, with the flow rate set at 0.9 mL/min. This analytical method ensured the accurate and reproducible measurement of HMF and FFR yields, thereby enhancing the scientific reliability and methodological rigor of the study. The research findings indicate that the HMF yield reached 13,946.08 mg/L, particularly at 220 °C with a residence time of 180 minutes, while the FFR yield reached 864.21 mg/L at a residence time of 210 minutes. These results demonstrate that glucose can effectively decompose under appropriate hydrothermal conditions and that this decomposition can be controllably channeled into high-yield chemical synthesis. In conclusion, this study offers valuable insights into the chemical conversion processes of biomassderived feedstocks and strongly supports the potential of glucose sustainable chemistry applications. for Furthermore, the employed analytical approach (HPLC) stands out as a sensitive and reliable tool for evaluating such conversion reactions.

2. Materials and Methods

2.1. Chemical and Materials

D -Glucose (P99%) was purchased from Sigma-Aldrich. HMF (99%) was obtained from Merck, while FFR (99%) was sourced from Acros-Organics. All commercial reagents were used as supplied without additional purification. Ultrapure water (conductivity of 18.3 M Ω cm⁻¹) was generated using a Zeneer Power I instrument from Human Corporation, USA, and was utilized to the mobile phase. HPLC grade methanol (\geq 99.9%) was sourced from Sigma-Aldrich and utilized for both the mobile phase and solid phase extraction (SPE).

2.2. Experimental Studies

A total of 2.0 g of glucose was weighed into a 50 mL stainless-steel reactor, mixed with 15.0 mL of distilled water, sealed, and placed in a preheated oven at 160, 180, 200, or 220 °C for the required residence times before being cooled to room temperature. The slurries from the reactor were filtered using a Buchner funnel with filter paper to separate the solid and liquid products, after which the liquid product was subjected to solid-phase extraction to collect FFR and HMF. The resulting liquid product was subjected to solid-phase extraction (SPE) for the selective isolation of FFR and HMF, following the methodology outlined by Driffield et al., with minor modifications to suit the experimental setup (Driffield et al., 2005). The cartridge was conditioned by sequentially passing 2 mL of methanol and 2 mL of water, after which it was loaded with 1 mL of the liquid product derived from glucose. The cartridge was dried using dry air, eluted with 2 mL of methanol, and the eluate was transferred to a vial, filtered through a 0.45 µm membrane, and analyzed by HPLC-UV.

2.3. HPLC Analysis

After the reaction and extraction, the samples were analyzed using high-performance liquid chromatography (Thermo Dionex Ultimate 3000, USA), equipped with a UV detector, a pump system, and an automatic sample injector. The separation was performed using a C18 column (5 μ m, 120Å, 4.6 × 250 mm; Thermo Acclaim 120) with a constant injection volume of 10 μ L. Based on the work of Ariffin et al. a methanol/water mixture was used as the mobile phase (Ariffin et al., 2014). The mobile phase consisted of methanol and water (18:82, v/v) with a flow rate of 0.9 mL/min. The column was washed with methanol between injections to minimize sample carryover. HMF and FFR were quantified at 284 nm using a UV detector, with retention times of 7.187 minutes for HMF and 10.133 minutes for FFR. The chromatograms of FFR and HMF obtained from the experiment conducted at 220°C for 180 minutes are shown in Figure 2. The data were analyzed using the licensed Chromeleon Client software (Dionex Corporation, USA).



Figure 2. Chromatograms of FFR and HMF.

3. Results and Discussion

The results presented in Table 1 and visualized in Figures 3 and 4 clearly demonstrate the significant influence of both temperature and residence time on the yields of HMF and FFR during the hydrothermal conversion of glucose.

Table 1. HMF and FFR amounts at specific reactiontemperatures and times

Temperature	Reaction time	HMF	FFR
(°C)	(min)	(mg/L)	(mg/L)
160	60	0.13	0.01
180	60	0.64	0.02
200	60	40.53	0.74
220	60	453.28	8.32
220	30	0.19	0.00
220	60	453.28	8.32
220	90	3468.71	74.99
220	120	7590.26	205.58
220	150	11198.55	552.97
220	180	13946.08	700.55
220	210	9640.26	864.21

At a constant reaction time of 60 minutes, a temperature increase from 160 °C to 220 °C led to a substantial enhancement in HMF yield, rising from 0.13 mg/L to 453.28 mg/L, while FFR yield only modestly increased from 0.01 mg/L to 8.32 mg/L (Figure 3). The results show that the increase in temperature has supported the rise in HMF and furfural amounts (Dashtban et al., 2012). This suggests that HMF formation is more sensitive to temperature changes within this range, a trend also supported by the literature (Zhang et al., 2021). When the temperature was fixed at 220 °C, increasing the reaction time progressively boosted product yields up to a critical point. As shown in Figure 4, HMF concentration peaked at 13,946.08 mg/L at 180 minutes, but subsequently decreased at 210 minutes, indicating potential degradation or rehydration to humins or levulinic acid under prolonged thermal exposure (Girisuta et al., 2006). In contrast, FFR yield continuously increased across the entire time range, reaching its maximum (864.21 mg/L) at 210 minutes. This may reflect the higher thermal stability of FFR and a possible delay in its formation pathway, potentially via intermediate degradation of sugars such as xylose or arabinose, even if glucose was the initial feedstock (Agirrezabal-Telleria et al., 2014). These results underline that the optimization of both reaction

temperature and duration is essential to maximize specific target compounds. Moreover, the steep increase in HMF yield between 90 and 180 minutes (from 3,468.71 mg/L to 13,946.08 mg/L) emphasizes a window of high productivity that could be exploited in continuous flow or semi-batch systems for industrial applications. These findings align with kinetic profiles described in prior studies (He et al., 2020; Jin and Enomoto, 2011), affirming

the potential for glucose-based feedstocks to yield platform chemicals under finely controlled hydrothermal conditions. The results strongly support that fine-tuning operational parameters such as temperature and reaction time enables selective production of target compounds, providing a foundation for scalable and sustainable biomass valorization processes.



Figure 3. The effect of temperature on HMF and FFR amounts (60 min.).



Figure 4. The impact of reaction time on the amounts of HMF and FFR (220 °C).

4. Conclusion

The manuscript explores the hydrothermal conversion of glucose into high-value chemicals, specifically FFR and HMF. Using subcritical water conditions (160-220 °C) in a Teflon-lined stainless steel reactor, the study evaluates the effects of temperature (160°C to 220°C) and residence time (30–210 minutes) on the yields of FFR and HMF. The principal conclusions are enumerated as follows:

 The study effectively focuses on optimizing HMF and FFR yields through controlled reaction temperatures and durations. It identifies optimal conditions (220°C for FFR and 180°C for HMF), showcasing practical applications for bio-based chemical production.

- The use of HPLC analysis ensures precise quantification of product yields, reinforcing the study's credibility. The detailed experimental methodology adds reproducibility and transparency.
- Highlighting the significance of glucose as a

renewable feedstock, the research underscores its potential for sustainable chemical synthesis. The findings contribute valuable insights for industries aiming to reduce reliance on fossil fuels.

This study is well-structured and scientifically robust, offering a meaningful contribution to the field of sustainable biomass valorization. A comparative discussion with catalysts or reaction media could provide deeper insights into optimizing yields. Addressing potential environmental and economic implications of the proposed methods would broaden the research's impact. Exploring scalability for industrial applications would enhance the study's relevance to commercial processes.

Author Contributions

The percentages of the author' contributions are presented below. The author reviewed and approved the final version of the manuscript.

	K.A.
С	100
D	100
S	100
DCP	100
DAI	100
L	100
W	100
CR	100
SR	100
РМ	100
FA	100

C=Concept, D=design, S=supervision, DCP=data collection and/or processing, DAI=data analysis and/or interpretation, L=literature search, W=writing, CR=critical review, SR=submission and revision, PM=project management, FA= funding acquisition.

Conflict of Interest

The author declared that there is no conflict of interest.

Ethical Consideration

Ethics committee approval was not required for this study because of there was no study on animals or humans.

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