

One Step Microwave Synthesis of 5-Hydroxymethylfurfural from Bamboo in Presence of Low Transition Temperature Mixture

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Microwave assisted synthesis of 5-hydroxymethylfurfural (HMF) using hydrolysate produced from dilute acid hydrolysis of bamboo with low transition temperature mixture (LTTM) as a green solvent was performed. Bamboo was a fast-growing plant with high cellulose content in the biomass, which made it suitable as the raw material for HMF production. LTTM was produced from hydrogen bond acceptor and donor, which in this study were choline chloride and malic acid, respectively. Microwave irradiation was used as it is faster and energy saving than conventional heating methods. A two-factors three-levels full factorial design with temperature and reaction time as the manipulating variables was employed and a linear model was constructed with R^2 of 0.9640 and p-value of 0.0115, indicating good reliability and significant. ANOVA analysis informed that only the temperature was significant, where the optimum point was 120 °C and 10 min with HMF yield of 10.7951 %. A follow up study was conducted at 140 °C and 5 min and had found that the system established an equilibrium of temperature at 120 °C between the heat loss by evaporation of water and heat gained by microwave irradiation. The shorter reaction time also resulted in higher HMF yield of 10.9410 %, possibly due to lower degree of unwanted side reaction (i.e., rehydration of HMF into levulinic acid). This study shows that it is possible to directly utilise the hydrolysate of bamboo without further separation of glucose in conversion into HMF, a valuable green and sustainable platform chemical.

1. Introduction

The energy consumption had been steadily increasing over the decades, which inevitably resulted in increased emissions of greenhouse gas and other harmful substances. Related to this issue, biomass-derived biofuels were widely regarded as carbon neutral and held an advantage over the other renewables like solar and wind by its capabilities to produce green and sustainable biochemicals and bioproducts (Seo et al., 2022). In one example, 5-hydroxymethylfurfural (HMF) stood out as a great green chemical produced from biomass.

HMF is a platform chemical and intermediate for further synthesis into various other value-added products such as levulinic acid and furan compounds like 2,5-bis(hydroxymethyl)furan and 2,5-dimethylfuran (DMF) (Lim and Rashidi, 2023). DMF has higher research octane number and energy density, denoted as a significant candidate as biofuel (Román-Leshkov et al., 2007), and potentially better than other biofuel such as bioethanol due to lower water solubility (Hoang et al., 2021).

In current state, HMF is converted from monosaccharides such as glucose and fructose via acid-catalysed dehydration reaction (Endot et al., 2021). Between the two sugars, fructose can achieve higher selectivity and yield but was limited by the higher material cost and lower availability than glucose (Agarwal et al., 2018). Glucose is widely available in the form of cellulose from biomass, particularly lignocellulosic biomass, however the high recalcitrance of the lignocellulose matrix had prevented the direct utilisation of cellulose (Son Le et al., 2022). Pre-treatments such as acid hydrolysis are available to reduce the recalcitrance and unlock the cellulose

for further conversions, however the recovery and refinery of glucose from the acidic hydrolysate incurred some 30 % of the capital cost (Morales et al., 2017). As the conversion of glucose into HMF is an acid-catalysed reaction, it may be possible to directly utilise the acidic hydrolysate without further separation.

Solvent played a major role in the HMF production, acting as a medium for dissolution of materials and occasionally also doubled as catalyst (Son Le et al., 2022). Organic solvents like dimethyl sulfoxide and tetrahydrofuran were commonly used due to the high abundance, low cost, and high sugar solubility (Zuo et al., 2023), but they suffer from drawbacks like high energy and costs for separation (Wang et al., 2013) and unfavourable toxicity and flammability (Soh and Eckelman, 2016). Ionic liquids (IL) like [EMIM]Cl-based IL was also used, and study had shown that the material costs for the IL contributed significantly on the overall process costs (Zhao et al., 2022). Green solvent such as low transition temperature mixture (LTTM) had been suggested and studied in the HMF production. LTTM can be produced from cheap and non-toxic materials with relatively simpler synthesis process (Plotka-Wasyłka et al., 2020). (Chen et al., 2020) used LTTM consisted of choline chloride (ChCl) as the hydrogen bond acceptor (HBA) and citric acid as the hydrogen bond donor (HBD) to produce HMF from wood dust hydrolysate and obtained a yield of 23.51 %. The study had suggested that the hydrogen bond network in the LTTM played a significant role in HMF yield, and H₂SO₄ was determined to be an effective catalyst in dehydration of glucose to HMF in LTTM system. However, the glucose-rich hydrolysate was produced from consecutive steam explosion and enzymatic hydrolysis, which was relatively complicated than, for example, acid hydrolysis using H₂SO₄ to produce acidic hydrolysate ready to be converted into HMF.

In this exploratory study, the hydrolysate from acid hydrolysis using H₂SO₄ of bamboo was directly used as the raw material to be converted into HMF in LTTM consisted of ChCl/malic acid. The LTTM had been studied and proven to be effective in HMF production in a previous study (Abdul Manaf et al., 2023) Bamboo was used as the biomass due to its high cellulose content and abundance. Furthermore, microwave irradiation was used as the heating method instead of conventional methods like oil bath or electrical heater as it was faster and cleaner (Gomes and Pastre, 2020). The high-water content in the bamboo hydrolysate also acted as a great microwave absorbent (Amer et al., 2019). Full factorial design was also employed to optimise and understand the interaction between the parameters (i.e., reaction temperature and time) and the HMF yield. Ultimately, this study aims to explore the viability of using H₂SO₄ in subsequent acid hydrolysis of biomass and conversion to HMF, potentially providing a simpler and effective method to synthesize the HMF from lignocellulosic biomass.

2. Materials and Methods

2.1 Materials

The bamboo was sourced locally within the vicinity of Perak, Malaysia. Malic acid (>99.5 %) was purchased from R&M Chemicals, and ChCl (>99%) was from Sigma Aldrich. The H₂SO₄ solutions were diluted from 95-97 % H₂SO₄ (analytical grade) from Fisher Chemical, and NaOH solution was prepared from NaOH pellets (analytical grade) from R&M Chemicals. Acetonitrile (gradient grade) was purchased from Merck.

2.2 Synthesis of LTTM

ChCl and malic acid was used as the constituents of the LTTM, and the method used was by Abdul Manaf et al. (2023). The ratio used was 1:1 by mass. In a typical preparation experiment, 100 g of ChCl was measured in a clean beaker, and then 100 g of malic acid was gradually added and mixed into the ChCl to form a homogenous solid powder mixture. The mixture was then subjected to heating via oil bath at 90 °C with stirring. In the first few minutes, the mixture was stirred manually with a glass mixing rod until it melted into a viscous liquid, and then continued to stir with magnetic stirring bar for at least 6 h until the LTTM appeared clear. The LTTM was also subjected to sonication to remove air bubbles trapped. Lastly, the LTTM was stored in an airtight bottle at chilled temperature of 5 °C for further uses.

2.3 Dilute acid hydrolysis of bamboo

The bamboo collected was firstly reduced into fine particles of <250 µm, and dried in an oven (UF110, Memmert) at 105 °C for at least 12 h. 0.5 M H₂SO₄ was used for the hydrolysis of bamboo and prepared via dilution from 98 % concentrated sulfuric acid. A 500 mL PTFE-lined steel autoclave reactor was used for the process. Prior to the run, the bamboo sample was dried again at 105 °C for at least 12 h. Then, 40 g of bamboo sample and 400 mL of 0.5 M sulfuric acid was added into the PTFE-liner and mixed vigorously using magnetic stirring bar for 1 h to completely wet the bamboo with the acid solution. After that, the PTFE liner was closed and locked into the steel autoclave. The hydrolysis process was conducted at 140 °C for 2 h in the oven (UF110, Memmert). Following that, the product was allowed to cool down until room temperature before it was filtered, and the liquid hydrolysate was stored in a glass bottle at -5 °C to avoid any unwanted side reactions and degradation.

2.4 Microwave assisted HMF synthesis

The experiment was conducted using a 103 L modified microwave synthesis reactor (Dixon, Malaysia) that can provide 3,000 W power, as shown in Figure 1. The ratio between the LTTM and hydrolysate was 2:1 by mass. Prior to the experiment, both of the materials were mixed together with magnetic stirring at 300 rpm until a homogenous phase was obtained. 30 g of the mixed sample was added into a two-neck round bottom flask, and the sample-containing flask was installed into the microwave reactor as shown in Figure 1. The top head of the flask was connected to a condenser with a constant supply of 15 °C chilled water. The side head was used to insert the thermostat connected to the control panel to monitor and control the temperature. A magnetic stirring bar was also added into the flask to provide 300 rpm stirring during the reaction. After the installation, the experiment was then started according to the designed temperatures and times. The product was left in the oven with condenser flowing to avoid excessive loss of water vapour until the temperature dropped back to room temperature. The product was then collected into vials and stored in -5 °C for further characterisations.

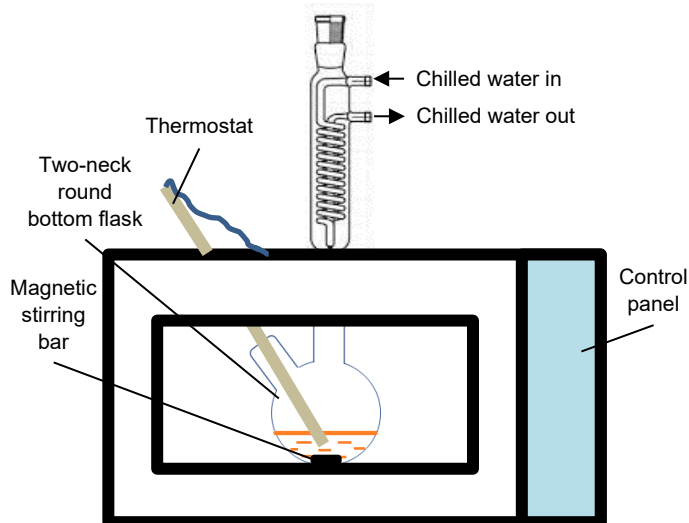


Figure 1: Schematic diagram of microwave synthesis reactor used in this study.

A two-factors three-levels full factorial design was employed to study the effect of reaction temperature and time toward the HMF yield. Design Expert v13 software was used to assist in the design of experiment. The studied range were 80-120 °C and 10-30 min for temperature and time, respectively, and the design of experiment was presented in Section 3 Result and Discussions with the corresponding HMF yield as the response.

2.5 Characterization and quantification of samples and products

High-performance liquid chromatography (HPLC) coupled with reflective index detector (RID) and ultraviolet-visible light detector (UV-Vis) (Shimadzu, Japan) was used to analyse and quantify the samples and products. Prior to the analysis, the samples were neutralized with 1.0 M NaOH solution until a pH of 5-7, and the amount of NaOH solution added was recorded as the dilution factor. The neutralized samples were filtered through a 0.45 µm PTFE syringe filter and then they were ready for analysis. The HMF yield and glucose conversion were calculated as in Eq(1) and Eq(2).

$$\text{HMF yield}\% = \frac{\text{moles of HMF in product}}{\text{moles of glucose in sample}} \times 100\% \quad (1)$$

$$\text{Glucose conversion}\% = \frac{\text{moles of glucose in sample} - \text{moles of glucose in product}}{\text{moles of glucose in sample}} \times 100\% \quad (2)$$

2.6.1 Glucose content

The glucose content analysis in the hydrolysate and the products were conducted using HPLC. Column used was Agilent Infinity Lab Poroshell EC-C18 column (4.6 x 250 mm, 4µm). A mixture of 80 % acetonitrile and 20 % deionized water, filtered and degassed prior to the analysis, was used as the mobile phase. The mobile phase flow rate was 1.2 mL/min, oven temperature was 30 °C, and the injection sample volume was 5 µL. The glucose content was quantified using an external calibration curve correlating the peak area with actual concentration.

2.6.2 HMF content

The HMF content analysis in the products were performed using Agilent Hi-Plex-H column (7.7 x 300 mm, 8 μ m) with UV-Vis detector. The mobile phase used was 0.0085 M H₂SO₄, filtered and degassed prior to the analysis. The mobile phase flow rate was 0.6 mL/min, oven temperature of 60 °C, and the injection sample volume was 20 μ L. The HMF content was quantified based on the peak area using an external calibration curve.

3. Results and Discussion

3.1 Optimization of microwave HMF synthesis

Table 1 shows the results from the full factorial design for HMF yield. When the reaction temperature was ≥ 100 °C, the HMF yields reached above 9 %, a huge difference with those at 80 °C (i.e., Run 7 and Run 8). This indicates that reaction temperature played a significant role in affecting the HMF. By comparing Run 1 and 5, the reaction time seems to not have significant trend toward the HMF yield, suggesting minor effect of reaction time toward HMF yield due to low amount of glucose in the hydrolysate (13.60 g/L) and the glucose was quickly used up to produce HMF and side products. This data was further analysed by ANOVA to provide deeper insights into the effects of each parameter. The glucose conversion was assumed to be >99 % as the glucose content in the product was located well below the limit of the external calibration curve, indicating an extremely low concentration of glucose remaining in the products, resulting in low HMF selectivity of below 10.90 % . (Shen et al., 2014) had observed similar low selectivity of HMF (2.74 %) in single phase system with water, and side products like levulinic and lactic acids having 47.88 % selectivity due to rehydration of HMF.

Table 1: Full factorial design of microwave HMF synthesis

Run no.	Temp. (°C)	Reaction Time (min)	HMF yield (mol%)
1	120	30	9.7919
2	100	20	10.7951
3	100	20	9.0806
4	100	20	9.3307
5	120	10	10.6146
6	100	20	9.1099
7	80	10	2.0361
8	80	30	4.0118

3.2 ANOVA analysis

Table 2 presents the results from ANOVA analysis of the optimization of microwave HMF synthesis. The model F-value of 26.80 and p-value of 0.0115 indicate that the model obtained is significant, and the regression coefficient R² of 0.9640 points out that the data fits the model well. Among the terms, only the temperature is significant with p-value of 0.0031. The other terms, time and the combined AB, were not significant. Generally, this result is in agreement with the observation in Section 3.1

Table 2: ANOVA analysis results for HMF yield based on 2FI model.

Source	Sum of Squares	df	Mean Square	F-value	p-value	Remark
Model	53.83	3	17.94	26.80	0.0115	Significant
A- Temperature	51.54	1	51.54	76.97	0.0031	Significant
B- Time	0.3324	1	0.3324	0.4963	0.5319	Not significant
AB	1.96	1	1.96	2.92	0.1858	Not significant
Std. Dev.	0.8183		R ²	0.9640		
Mean	8.10		Adjusted R ²	0.9280		
C.V. %	10.11		Predicted R ²	NA		
			Adeq Precision	13.2599		

Figure 2a and 2b show the contour plot of the design and the prediction vs actual value of the model, respectively. The contour plot illustrates that the high HMF yield is located at far right of the plot, where the temperature was high. The vertical axis that indicates reaction time has minor effect toward HMF yield as discussed in ANOVA analysis, however the contour has shown that at high temperature, lower reaction time

favours the HMF yield (as coloured in bright red). The optimum point is also located at the far bottom right corner (i.e., 120 °C and 10 mins). This may be due to the unwanted side reaction, the HMF produced from dehydration of glucose was rehydrated to form levulinic acid (Choudhary et al., 2013). At high temperatures, the glucose reacted quickly to form HMF, and if the reaction prolonged (>10 min in this case) the HMF starts to rehydrate and forms levulinic acid, reducing the resultant HMF yield. Hence, a higher temperature and shorter time may result in higher HMF yield. The simplified coded equation for this model is presented in Eq(3).

$$\text{HMF yield\%} = 6.61 + 3.59A \quad (3)$$

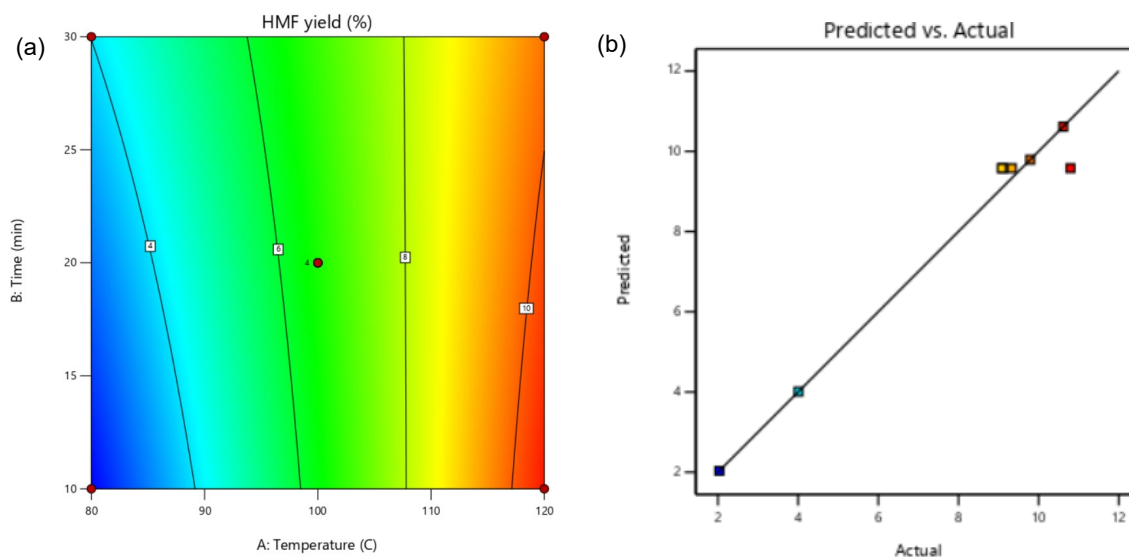


Figure 2: (a) Contour plot and (b) Prediction vs actual plot of the full factorial design for HMF yield.

3.3 Follow up study

As discussed in Figure 2a, the optimum point is located at far bottom right of the plot, and the HMF yield may be further increased with higher temperature and reaction time. A follow up study at 140 °C and 5 min was conducted and obtained a HMF yield of 10.9410 %, which is slightly higher than max yield of 10.7951 %. It was noted that during the microwave synthesis, the temperature recorded never went higher than 120 °C due to the equilibrium achieved by evaporation of water presents in the sample mixture. The shorter reaction time supports the effect of prolonged reaction time on the promotion of unwanted side reaction (i.e., rehydration of HMF into levulinic acid), however the HMF yield is still lower than literature values, for example 23.51 % (Chen et al., 2020), indicates the possibility of effect of other factors (e.g., presence of inhibitory compounds, effect of pressure, etc.) toward HMF yield.

4. Conclusions

Full factorial design employed in this study is reliable and significant with R^2 of 0.9640 and p-value of 0.0115. From ANOVA analysis, only the temperature is the significant term affecting toward the HMF yield, where the optimum point obtained is 120 °C and 10 mins, with a maximum HMF yield of 10.7951 %. The contour plot reveals that lower reaction time may favours higher HMF yield by reducing the rehydration of HMF into levulinic and lactic acids. A follow up study at 140 °C and 5 min has a HMF yield of 10.9410 %, which supports the speculation. However, the setup is not able to go higher than 120 °C during the reaction due to the equilibrium of heat loss by evaporation of water. This study did not evaluate the effect of side products from acid hydrolysis of bamboo toward the HMF yield, which can be included in future works.

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