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RESEARCH ARTICLE

Optimisation of Reaction Parameters of Fructose Dehydration into 5-Hydroxymethylfurfural Using Lewis Acid Hydrogel Catalysts: A Response Surface Methodology Approach

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Abstract

Recent discoveries shed light on 2,5-dimethylfuran (DMF) as a promising biofuel substitute for internal combustion engines. Hydrogenolysis can transform 5-hydroxymethylfurfural (5-HMF) into DMF, and 5-HMF is regarded as a platform chemical in biofuels and petrochemicals. Fructose, being more reactive, is the preferred precursor for 5-HMF synthesis using acid catalysts. While the PEGDA-3SMP-H Lewis acid hydrogel catalyst has been utilized for this conversion, statistical optimisation of reaction parameters remained. The present study aims to rectify this by employing response surface methodology and optimising key reaction parameters. A deep eutectic solvent (DES) medium was used for conducting the reaction, while high-performance liquid chromatography (HPLC) was used to analyse samples. The critical variables influencing 5-HMF yield from fructose dehydration by PEGDA-3SMP-H include reaction time, temperature, and fructose:catalyst ratio. Statistical techniques confirmed through a normal probability plot indicating a linear distribution of data points. Design-Expert software generates 3D surface and contour plots, illustrating the impact of reaction parameters on fructose conversion. Elevated temperature aids the reaction, but excessive time results in 5-HMF rehydration and the formation of side products. A low fructose:catalyst ratio favours 5-HMF production, while high ratios yield lower 5-HMF due to insufficient catalysts. Numerical optimisation pinpoints ideal parameters - temperature (125 °C), time (4.3 h), and fructose:catalyst ratio (2.7) — predicting a 56.91% 5-HMF yield. Experimental verification closely aligns with the model's predictions, yielding 59.01%, affirming its robustness. This study enhances understanding of how key reaction parameters influence the yield of 5-HMF from fructose with the PEGDA-3SMP-H catalyst, providing valuable insights for biofuel synthesis.

Keywords: 5-HMF formation, Fructose dehydration, Hydrogel catalysts, optimising parameters, Response surface methodology

Introduction

5-Hydroxymethylfurfural (5-HMF) is an important chemical used in biofuels and petrochemicals. The US Department of Energy recognizes it as one of the top ten valuable biochemicals (Guo et al., 2017; Dharmapriya et al., 2023a). While glucose is the most common natural sugar, fructose is more reactive and is the preferred choice for making 5-HMF using acid catalysts, and hence, this method is becoming popular (Lansalot-Matras and Moreau, 2003). The chemical 5-HMF can be used to synthesise important C-6 furan derivatives and non-furanic compounds (Newth, 1951; Rosatella et al., 2011; Zou et al., 2019; Wu et al., 2021; Dharmapriya et al., 2023b). In recent years, there has been a significant surge in the number of research papers dedicated to the field of 5-HMF chemistry (Hou et al., 2021). In recent findings, it has come to light that 2,5-dimethylfuran (DMF) could serve as a promising substitute for biofuel in internal combustion engines. An approach for synthesising DMF involves treating biomass and breaking it down into glucose or fructose. Subsequently, selectively removing three oxygen atoms from glucose or fructose through dehydration leads to the formation of 5-HMF. Finally, 5-HMF can be transformed into DMF through hydrogenolysis. Consequently, in recent years, numerous researchers have concentrated on utilizing biomass sources, such as glucose, fructose and starch, to convert to 5-HMF. This investigation aims to enhance the conversion efficiency of glucose or fructose into 5-HMF using diverse catalysts and solutions (Hu et al., 2011; Qian et al., 2015; Alipour et al., 2017). A diverse array of both homogeneous and heterogeneous acid catalysts have been harnessed for the dehydration of fructose. Homogeneous acid catalysts include mineral acids such as HCl, H_2SO_4, H_3PO_4, organic acids like formic acid, ionic liquids like 1-butyl-3-methylimidazolium chloride, H-formed zeolites, Amberlite-15, strong acid cation exchange resins, and metal ions including Cr, Al, Cu, Pt, Rh, Li, Fe) while heterogeneous types include composite like nanofibres (Seri et al., 2001; Asghari and Yoshida, 2006; Zhao et al., 2007; Qi et al., 2008, 2009, 2010; Zhang et al., 2015; Dibenedetto et al., 2015; Zhang et al., 2019; Li et al., 2021; Karimi et al., 2021; Dharmapriya et al., 2023b). Although homogeneous catalysts exhibit efficacy, achieving significant fructose conversion (70-90%) and substantial 5-HMF yield (40-90%), industrial applications lean towards heterogeneous catalysts. The appeal lies in their recyclability, long-term stability, straightforward separation methods, minimal equipment corrosion, heightened product selectivity (60-90%), and the reduction of final product contamination with acid catalysts (Qi et al., 2011; Karimi et al., 2015, 2021).

Ion exchange resins, such as Amberlyst-36, display remarkable versatility in various solvent media. Amberlyst-36, niobium phosphate (NbP), and niobium silicate (NbS) have been utilised to achieve 54-60% yield of 5-HMF under low temperatures and pressures, and, more importantly, Amberlyst-36 demonstrated a noteworthy 70% selectivity at 140 °C (Souzanchi et al., 2021). This highlights the diverse approaches in optimising the fructose dehydration processes. Additionally, the use of deep eutectic solvents (DES) is considered environmentally friendly and cost-effective for carbohydrate conversion compared to traditional methods in water or non-polar solvents (Hansen et al., 2021; Matsumiya and Hara, 2015; Zuo et al., 2021, 2018).

Response surface modelling (RSM), an empirical statistical method, regulates the regression model and utilizes conditions employing quantitative data acquired from relevant designed experiments. The primary goal of RSM is to identify the optimal set of process operational variables. Statistical experimental sketch of an adsorption process can minimize the variability of the process, time of experimentation and cost, while enhancing the process output. The RSM method has been extensively used in chemical engineering and optimisation of sorption processes (Singh et al., 2011; Gadekar and Ahammed, 2019).

Hydrogels, essential in complex device fabrication and biomedical applications such as tissue engineering, are hydrophilic, insoluble polymers. Poly (ethyleneglycol) (PEG), a biocompatible and non-immunogenic hydrogel, finds diverse applications, including drug delivery, tissue engineering, bioprinting, sensor tech, and wastewater treatment (Dharmapriya et al., 2021a,b, 2022). Poly (ethyleneglycol)diacrylate (PEGDA), a PEG derivative, has lower density compared to traditional resins and swells in an aqueous medium, leading to increased pore size. One of our previous studies aimed to synthesise novel, reusable, hydrogel-based heterogeneous acid catalysts modified with 3-sulfopropyl methacrylate potassium salt (3-SMP) to assess their efficacy in dehydrating fructose in invert sugar syrup into 5-HMF (Dharmapriya et al., 2023b). While few reports discuss sulfonic acid group-modified catalysts for fructose dehydration, the present study focused solely on PEGDA hydrogel-based catalysts modified with the sulfonic acid group for this reaction. Notably, this marked the first instance of PEGDA serving directly as a catalyst host in carbohydrate conversion. Intriguingly, catalytic ability increased with reuse cycles. This study explores the application of response surface methodology to optimise reaction parameters for enhancing 5-HMF yield. The DES medium and a pressure bottle were employed in the reaction process.

Materials and Methods

Materials

D-fructose ($C_6H_{12}O_6$, 99.5%), polyethylene glycoldiacrylate ($C_5H_{10}O_4$, 99%, MW: 700), cholinechloride ($C_5H_{14}NO \cdot Cl$, 99%), 5-hydroxymethylfurfural ($C_6H_6O_3$, 99%), 1-ethyl-2-pyrrolidone ($C_6H_{11}NO$, 99%), and 3-sulfopropylmethacrylate potassium salt ($C_7H_{11}KO_5S$, 98%) were purchased from Sigma-Aldrich. 2,2-dimtehoxy-2 phenylacetonphenone ($C_{16}H_{16}O_3$, 99%) was purchased from ACROS. Each solution was prepared using ultrapure water. All chemicals utilized were either of analytical grade or the highest purity obtainable.

Synthesis of Lewis acid PEGDA-modifier hydrogel catalysts and application

The synthesis of the novel PEGDA-3SMP-H, outlined in a previous study (Dharmapriya et al., 2023b), involves the following steps. First, Tinkercad design software (*https://www.tinkercad.com*) was used to create a distinctive mould design. Subsequently, the hydrogel is synthesised through photoradical polymerization by mixing PEGDA and 3SMP in a 1:7 ratio in 1 ml of deionized (DI) water. Then, 200 μL of a 3% solution of 2,2-dimethoxy-2-phenylacetophenone (photoinitiator) was added to the solution and shaken well. Next, the uniform mixture was poured into a 3D printed mould and solidified under a UV irradiation lamp (365 nm, 100 W) for 5 min. After solidification, the PEGDA-3SMP-K hydrogel catalysts were removed from the mould and cleaned them with DI water. Subsequently, 0.2 g of PEGDA-3SMP-K hydrogel catalysts was soaked in 25 mL of 3 M HCl solution for 24 h on a rotary shaker with a 110-rpm rotation speed. After soaking, the hydrogel catalysts were cleaned with DI water until the pH of

the immersed water stabilized. Finally, the washed hydrogel catalysts were oven-dry overnight at 65°C (Dharmapriya et al., 2023b). The experiments in this study focused on synthesising DESs by physically mixing specific raw materials known as hydrogen bond donor (HBA) and hydrogen bond acceptor (HBD). Choline chloride (ChCl) served as the HBA, while fructose acted as the HBD (Hayyan et al., 2013). The characterization of the synthesised novel PEGDA-3SMP-H has also been described previously (Dharmapriya et al., 2023b).

In a standard procedure of fructose dehydration using the catalysts, 0.2 g of pure fructose, PEGDA-3SMP-H hydrogel catalyst (with 25% SMP weight-content relative to fructose weight), 1.0 g of ChCl, and 4.0 g of DI water were combined in a 20 mL high-pressure glass bottle and positioned in a temperature-controlled oil bath. The experiment was carried out at 120 °C for 6 h. Subsequently, the samples were rapidly cooled in an ice bath to terminate the reaction. The resulting solutions were diluted and subjected to analysis using HPLC (Dharmapriya et al., 2023b).

Response surface methodology approach

In this approach, the 3-level 3-factor Box–Behnken experimental design was applied to determine and validate parameters for fructose dehydration into 5-HMF. Those parameters are called factors, and they were fructose: catalyst ratio, temperature (°C), and time (hours) while initial fructose concentration was kept as a constant input parameter. The levels of three factors were coded as -1 (low), 0 (central point) and 1 (high). Table 1 illustrates the Box–Behnken design model's variables and levels. A total of 18 experiments were employed in this research work to optimise the effects of the three main independent parameters on the 5-HMF yield. Coefficient of determination (R^2), Pareto analysis of variance (ANOVA), and statistical and response plots were used to analyse the results obtained (Table **??**)(Tripathi et al., 2009; Ali et al., 2021; Rosly et al., 2021).

Results and Discussion

Response surface methodology approach

To optimise significant variables, the BBD approach was used. The major input variables that mainly influence the yield of 5-HMF from fructose dehydration by PEGDA-3SMP-H are reaction time, reaction temperature and fructose:catalyst ratio. Statistically designed experiments were applied to determine the individual and combined effects of these three variables on the fructose yield by the catalyst (Equation 1).

$$\begin{aligned} Y = {} & +54.71 - 0.8000A + 4.91B - 8.80C \\ & - 8.82AB + 4.49AC - 2.39BC \\ & - 21.35A^2 - B^2 - 13.18C^2 \end{aligned} \quad (1)$$

The positive and negative signs in front of the expressions in the above equation indicate that these expressions affect the response synergistically and antagonistically, respectively (Asfaram et al., 2017; Ali et al., 2021). Reaction temperature (B), and interaction parameters (AC) with positive coefficients have a synergistic effect on 5-HMF yield, whereas reaction time (A), catalyst amount (C), interaction parameters (AB and AC), and quadratic parameters (A^2, B^2 and C^2) with negative coefficients have an inhibitory effect on 5-HMF yield (Dharmapriya et al., 2023c).

Multiple regression analysis was used to evaluate the response coefficient for the model, and the ANOVA technique was used to assess the adequacy of the model, and to understand the correlation between input variables and responses. Table 3 summarises the ANOVA results for 5-HMF yield by PEGDA-3SMP-H. The model F-value of 14.96 implies that the model is significant, which is further

Table 1. Coded levels for the independent variables in the Box-Behnken design for converting fructose into 5-HMF through dehydration.

Variables	Code	Units	Coded variables levels		
			-1	0	+1
Time	A	hrs	1	5.5	10
Temperature	B	°C	80	110	140
Fructose:catalyst ratio (mass)	C	g	1	5.5	10

Table 2. Experimental design matrix for 5-HMF yield by PEGDA-3SMP-H and comparison of actual and predicted values using Box–Behnken design.

Run	Variables			Response	
	Time (A)	Temperature (°C) (B)	Ratio (C)	5-HMF yield (%)	
				Actual value	Predicted value
1	5.5	110	5.5	55.22	54.71
2	5.5	110	5.5	52.19	54.71
3	5.5	140	10.0	22.33	27.06
4	5.5	110	5.5	53.48	54.71
5	5.5	140	1.0	56.21	49.43
6	5.5	110	5.5	54.79	54.71
7	1.0	110	1.0	28.33	34.27
8	5.5	110	5.5	55.79	54.71
9	10.0	110	1.0	18.11	23.68
10	1.0	80	5.5	13.45	12.24
11	10.0	80	5.5	29.12	28.28
12	1.0	140	5.5	38.85	39.70
13	5.5	110	5.5	56.78	54.71
14	5.5	80	10.0	15.23	22.01
15	5.5	80	10.0	39.56	34.84
16	10.0	110	10.0	21.00	15.06
17	1.0	110	10.0	13.25	7.68
18	10.0	140	5.5	19.25	20.46

Table 3. ANOVA and model summary statistics of response surface quadratic model for 5-HMF yield from fructose by PEGDA-3SMP-H.

Source	Sum of squares	df	Mean square	*F*-value	*p*-value	
Model	4830.22	9	536.69	14.96	0.0004	significant
A-time	5.12	1	5.12	0.14	0.7154	
B-Temperature	192.86	1	192.86	5.38	0.0490	
C-Ratio	619.52	1	619.52	17.27	0.0032	
AB	310.99	1	310.99	8.67	0.0186	
AC	80.73	1	80.73	2.25	0.1720	
BC	22.80	1	22.80	0.64	0.4483	
A^2	1989.01	1	1989.01	55.44	<0.0001	
B^2	292.68	1	292.68	8.16	0.0213	
C^2	758.57	1	758.57	21.14	0.0018	
Residual	287.00	8	35.88			
Lack of fit	273.44	3	91.15	33.61	0.0010	significant
Pure error	13.56	5	2.71			
Cor total	5117.23	17				
Response (Y)	**SD**	**CV**	R^2	**Adj.** R^2	**Pred.** R^2	**AP**
5-HMF yield	5.99	16.77	0.9439	0.8808	0.1412	10.53

supported by having majority of p-values of less than 0.05. There is only a 0.04% chance that such large F-value could occur due to noise.

In this case, B, C, AB, A^2 and B^2, and C^2 are significant model terms. Values greater than 0.1000 suggest that the model terms are not significant. The R^2 value for Equation 1 was determined to be 0.9439, indicating that the model can explain 94.39% of the total deviation in response and only 5.61% cannot. Usually, the best-fitted model should have at least R^2 value of 0.8000. The closeness of the R^2 value to 1 and the lower standard deviation (SD) (Table 3) show that the quadratic model developed can predict the response within the range of input variables. Diagnostic plots such as predicted vs. actual, residual vs. run, normal plot vs. residuals that are shown in Figure 1 (a) to (c) respectively, were also used to assess the fitness goodness of fit of the model (Ali et al., 2021).

The comparison of model-predicted values based on Equation 1 to experimental values [Figure 1(a)] demonstrated that the quadratic model chosen can investigate the relationship between the input variables (A-time, B-temperature, and C-ratio), and the response (5-HMF yield). According to the normal probability plot as shown in Figure 1(b), all data points are linearly distributed and lie next to a straight regression line, indicating that the selected model fits well. The acceptance of this model is also shown in Figure 1(c), where the residuals are arbitrarily distributed around the zero line of the graph.

The three-dimensional (3D) surface and contour plots for the model were created with Design-Expert software, in which two parameters/variables were varied at a time while the other persisted constant at the centre level (zero level). Figures 2(a) to (c) show 3D surface and contour plots, demonstrating the interaction effects of process parameters/variables on the 5-HMF yield. The interaction effect of reaction temperature (B) and reaction time (A) while keeping ratio (C) at a fixed level is depicted in Figure 2(a). The 3D plot shows that higher temperature and longer time favour fructose up to a point; however, beyond that time, 5-HMF yield decreases due to side reactions and 5-HMF rehydration to form levulinc acid and formic acid. Temperature is a key factor affecting fructose to 5-HMF conversion. An elevated temperature provides extra energy, making it easier for molecules to overcome the activation energy barrier and facilitating the reaction. Higher temperatures also lead to increased molecular movement and collision frequency, enhancing the chances of successful reactions. The interaction effect of ratio (C) and time (A) while keeping the reaction temperature (B) at a fixed level, is depicted in Figure 2(b). It demonstrates that when the fructose:catalyst ratio is low (indicating a comparable/ higher percentage of catalyst amount respect to the fructose is present in the medium such as 50%w/w, 40%w/w, as the ratio is low), increasing reaction time facilitates fructose dehydration into 5-HMF. However, exceeding the reaction time decreases 5-HMF yield due to other side reactions and 5-HMF rehydration and degrade fructose and 5-HMF into humin with extended time. Catalytic site availability and surface area explain the consistency in results. A catalyst provides an alternative path with a low activation energy. High concentration of the catalyst provides more active centres for the reaction. More catalyst leads to higher product output within the same timeframe, maximising substrate utilisation. The interaction effect of ratio (C) and temperature (B) while keeping the time (A) at a fixed level is depicted in Figure 2(c). It is demonstrated that when the fructose-to-catalyst ratio is low (indicating a higher amount of catalyst present in the medium compared to fructose), increasing the reaction temperature facilitates fructose dehydration into 5-HMF. However, a

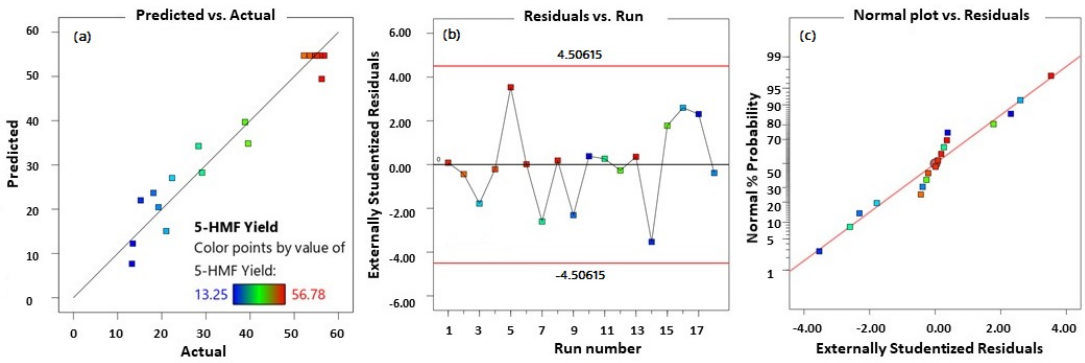

Figure 1. Model validation diagnostic plots for 5-HMF yield by PEGDA-3SMP-H. (a) the plot of predicted values vs. actual values, (b) the normal probability plot of studentized residuals, (c) studentized residual vs. the run number.

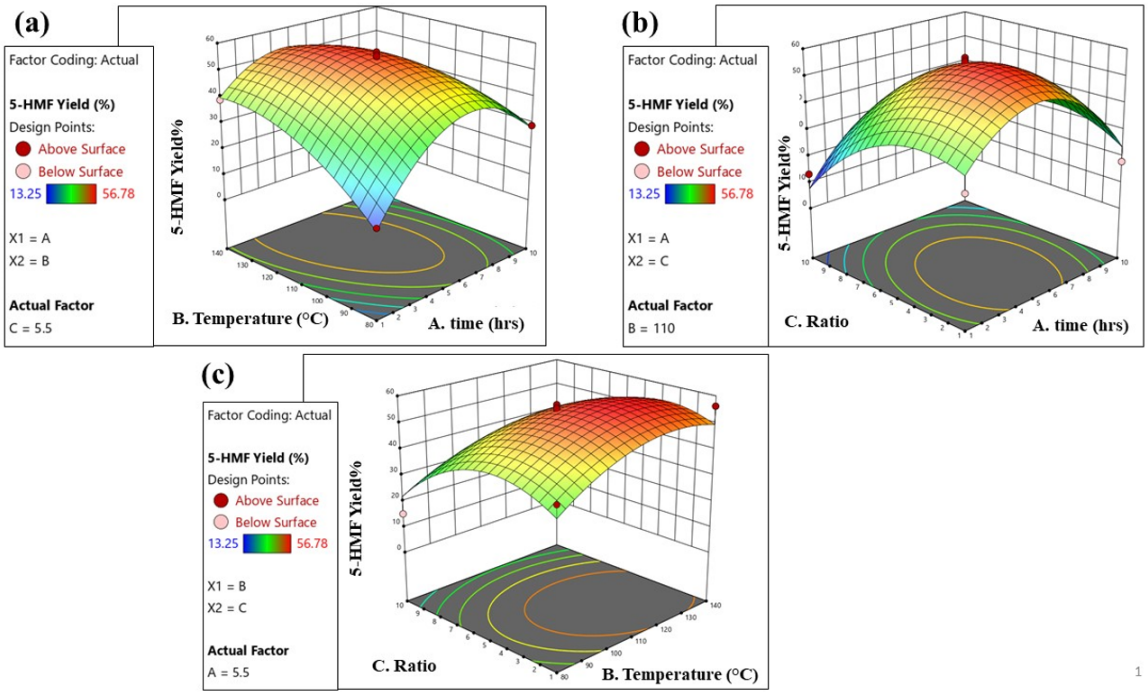

Figure 2. Three-dimensional response surface and contour plots showing combined effects of (a) temperature and time; (b) ratio and time, (c) ratio and temperature.

high fructose:catalyst ratio indicates that an insufficient amount of catalyst is available for fructose dehydration, resulting in decreased 5-HMF yield.

To optimise process parameters/variables and achieve maximum 5-HMF yield, the function of desirability, which can range from 0.00 (undesirable) to 1.00 (highly desirable), was used (Ali et al., 2021). Numerical optimisation was applied to discover the best set of input variables at which the highest 5-HMF yield could be achieved. Reaction

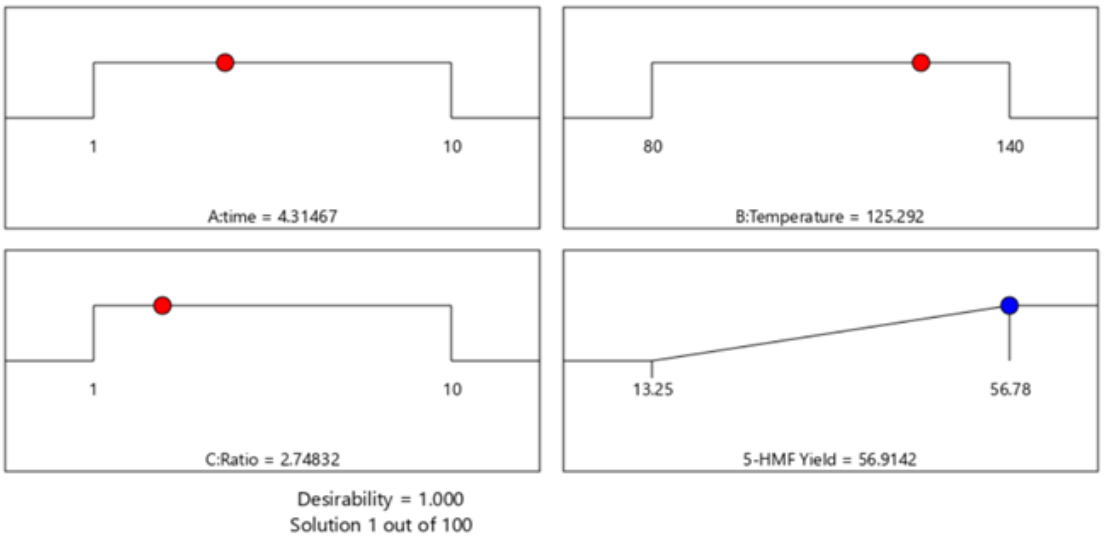

Figure 3. Desirability ramp for numerical optimisation of 5-HMF yield.

time, fructose to catalyst ratio, and reaction temperature were set as "in range", and the target 5-HMF yield was set as "maximum" to achieve the best possible response for 5-HMF yield as illustrated in Figure 3. The experimental parameters were verified using the conditions predicted by the BBD model. The prime parameters predicted by the BBD model were, temperature (A) of 125 °C, time (B) of 4.3 h, and a fructose:catalyst ratio (C) of 2.7. The optimised 5-HMF yield predicted by the BBD model was 56.91%. However, the experimentally obtained value was 59.01%. The experimentally obtained 5-HMF yield is close to the model-suggested value (Dharmapriya et al., 2023c).

Conclusion

In recent revelations, DMF emerges as a promising biofuel substitute for internal combustion engines. The synthesis route involves biomass treatment, converting it to glucose or fructose. Dehydration of glucose or fructose yields 5-HMF, transformable into DMF through hydrogenolysis. Researchers focus on utilizing biomass sources, such as glucose, fructose, and starch, for 5-HMF conversion, crucial in biofuels and petrochemicals. This study introduces PEGDA hydrogel-based catalysts with a sulfonic acid group, marking PEGDA's inaugural role as a direct catalyst host in carbohydrate conversion. Response surface methodology optimises parameters, utilizing DES medium and a pressure bottle. RSM guides regression models, employing quantitative data from designed experiments. Key variables influencing 5-HMF yield from fructose dehydration are reaction time, temperature, and fructose: catalyst ratio. ANOVA and model summary statistics affirm the fitness of the response surface quadratic model. The normal probability plot confirms model validity, showing linear distribution and proximity to the regression line. Design-Expert software generates 3D surface and contour plots, illustrating the impact of reaction parameter on fructose conversion. Elevated temperature aids the reaction; however, excessive time leads to side reactions and 5-HMF rehydration. A low fructose:catalyst ratio favours 5-HMF production, while high ratios yield lower production of 5-HMF due to insufficient

catalyst. Numerical optimisation identifies optimal conditions (temperature: 125 °C, time: 4.3 h, fructose:catalyst ratio: 2.7), predicting a 56.91% 5-HMF yield. Experimental verification yields a close value of 59.01%, affirming the reliability of the model.

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