Research article

Optimizing sorbitol double dehydration: A Box-Behnken design approach with commercial sulfonic acid resin

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A R T I C L E   I N F O

A B S T R A C T

In this study, double dehydration of sorbitol into isosorbide using commercial sulfonic acid resin as a catalyst was carried out under vacuum conditions generated by water ejection. To improve the efficiency and selectivity of the process, optimum reaction conditions prescribed by temperature, catalyst loading, and reaction time were investigated using the Box-Behnken design (BBD) together with Response Surface Methodology (RSM). The results showed that using the water ejection system could increase reaction activity. Statistically, all the reaction parameters were found to significantly affect the double dehydration reaction response, including sorbitol conversion, 1,4-sorbitant yield, and isosorbide yield. Furthermore, accurate predictive equations for all the reaction responses displayed $R^2 > 95$ %, with no significant errors observed. The optimized conditions resulted in the complete conversion of sorbitol with 6.42 % 1,4-sorbitant yield and 67.55 % isosorbide yield. The equations yielded predicted values of the responses with minor variances being lower than 1 % when compared with the experimental values. However, the efficiency of the catalyst decreased steadily over recycling cycle due to reduced active sites and textural properties, likely caused by structural collapse and by-product accumulation. This work contributes to biomass valorization by optimizing the effective process for the production of isosorbide via commercial catalysts under vacuum conditions.

1. Introduction

Use of biomass resources as a substitute for petroleum, which is a finite or non-sustainable raw material, has become a trend and been largely promoted in the synthesis of chemicals [1,2]. Particularly, sorbitol, a bio-based polyol obtained from glucose as a sugar alcohol and regarded as a crucial molecular platform for the synthesis of numerous compounds or components with added value, is one of the most interesting components [3–6]. Furthermore, through a dehydration reaction, sorbitol can be used as a precursor to produce value-added chemicals such as isosorbide and sorbitant [7,8]. Isosorbide, an essential building block for bio-based polymer synthesis in the food additive, pharmaceutical, cosmetic, and surfactant industries, replaced petroleum as the main source of the chemical platform [9–11]. The process of producing isosorbides involved the double dehydration of sorbitol. The first product obtained from this dehydration reaction included several compounds from the sorbitant group, including 1,5-sorbitan, 2,6-sorbitan, 2,5-menitan, and 2,

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5-iditan. Only 3,6- and 1,4-sorbitants, on the other hand, were shown to be the intermediates of isosorbide in the second dehydration [12–14].

Traditionally, strong acids like hydrochloric acid (HCl), sulfuric acid (H_2SO_4), or triflic acid (CF_3SO_3H) are used as catalysts for this reaction [10,15]. However, using these acids has several disadvantages, including corrosion of equipment and difficulty in separating the isosorbide from the reaction mixture considering safety and the environment [16]. Consequently, several heterogeneous catalysts have been considered. In recent years, there have been several catalysts such as carbon-based acids [17], polymer-supported [18–20], metal phosphates [21,22], supported metal oxides [23], sulfated and phosphated metal oxides [4,24,25], and acid resins [26–29]. All these studies aim to develop a heterogeneous catalyst that can be used for high catalytic performance in the sorbitol dehydration reaction.

Among these catalysts, use of acid resin was discovered to give high catalytic performance due to acidic high active site with hydrophobic properties, hence facilitating the liquid elimination of the catalyst surface and enhance the dehydration reaction [27, 30–32]. The comparison of different acid catalysts in isosorbide production was studied by Boupan et al. Under the autoclave reactor, the result showed that Purolite CT269 resulted in 100 % sorbitol conversion with 42 % isosorbide selectivity after 6 h at 180 °C. However, this work has highlighted limitations under high-pressure autoclave conditions, such as equilibrium constraints due to water accumulation, affecting isosorbide yield [33]. For this reason, the dehydration reaction of sorbitol under solvent-free with steam removal was investigated to enhance the catalytic performance of sorbitol dehydration. Additionally, a highly efficient water removal system was also considered and incorporated in the study for simplicity and cost saving.

The optimization of reaction conditions—such as temperature, catalyst loading, and reaction time—is crucial for improving isosorbide yield [12,34]. A study of efficient reaction conditions is an important challenge, as the production of isosorbides should rise significantly due to industrial applications and processes. Through the design of experiment (DOE) which aims to develop an efficient design with minimal experimentation needed. The Box-Behnken Design (BBD) has been demonstrated to be a highly effective method for conducting experiments, as compared to other approaches, such as Full Factorial Design, Central Composite Design (CCD), or the Taguchi Method [35,36]. BBD is beneficial because it requires fewer experiments and avoids extreme conditions, while allowing for the examination of interactions between different factors [37–39]. To achieve the highest reaction performance, the reaction conditions can be determined by response surface methodology (RSM) and applied to processes to develop a modeling approach designed to optimize the response activity [40–42].

In the present work, we focused on optimizing the dehydration reaction of sorbitol into isosorbide using a commercial sulfonic resin catalyst under vacuum conditions generated by a water ejection system. The primary objective was to employ a commercial catalyst suitable for industrial-scale applications due to its scalability and cost-effectiveness. By using BBD and RSM, we aimed to develop predictive models to determine the optimal reaction conditions for maximizing isosorbide production. Moreover, the deactivation of the catalyst was investigated over multiple reaction cycles, aiming to detail the deactivation behavior for the further development of catalyst regeneration for use in industry.

2. Materials and methods

2.1. Materials

D-sorbitol (99 %) was the reactant for the dehydration reaction, purchased from Lab Valley Limited Partnership. A catalyst was employed, Purolite CT269, a commercial sulfonic acid resin supplied by Purolite Corporation. The standard sample is isosorbide (98 %) (Aldrich Sigma), and 1,4-sorbitan (97 %) (USP referenced) was used for high-performance liquid chromatography (HPLC) analysis. Deionized water (18.2 MOhm) was the solvent for the reaction.

2.2. Experimental design and statistical analysis

To determine the optimized condition for the dehydration reaction of sorbitol, BBD (3 factors and 3 levels) and RSM were applied to study with selected reaction parameters, listed in Table 1, consisting of reaction temperature (A) from 120 to 160 °C, catalyst loading (B) from 1 to 5%wt with respect to sorbitol, and reaction time (C) from 2 to 8 h. Moreover, the experiment was conducted in Minitab 19 giving 15 runs with 13 different experimental conditions (Three runs were identical.) including their respective catalytic conversion of sorbitol (Y_1), yield of 1,4-sorbitant (Y_2), and yield of isosorbide (Y_3). Each experiment was conducted in a random order to reduce the impact of unexplained variability. In addition, a full quadratic equation was used to interpret the main, square, and interaction effects of each parameter, as shown in Eq. (1).

Table 1
Box-Behnken design variable.

Independent variables	Levels		
	−1	0	1
Temperature (°C), A	120	140	160
Catalyst loading (%wt.), B	1	3	5
Reaction time (h.), C	2	5	8

$$Y_i = \alpha_0 + \sum_{i=1}^{3} \alpha_i X_i + \sum_{i=1}^{3} \alpha_i^2 X_i^2 + \sum_{i=1}^{2} \sum_{i \neq j}^{3} \alpha_{ij} X_i X_j \tag{1}$$

The regression coefficients for the intercept, linear, quadratic, and interaction terms are respectively represented by α_0, α_i, α_i^2, and α_{ij}, where Y_i represents the reaction responses.

2.3. Dehydration reaction

The dehydration of sorbitol was carried out in a 250-mL three-neck flask on a heating plate with a thermocouple being inserted at the center position. The reaction was operated under continuous suction using a water ejection system (consisting of a pump (SONIC AP4500, max head: 2.6 m and max output: 2600 L/h and a water aspirator pump) connected to one neck of the reactor and another neck was sealed to ensure vacuum condition, as shown in Fig. 1. In brief, sorbitol was melted and stirred at 500 rpm for 1 h. The catalyst was then added to initiate the reaction under continuous steam suction while being continuously stirred at the same speed. The reaction was studied by using Box-Behnken design (BBD) at 3 levels as displayed in Table 1, for the optimized condition.

After the reaction, the sample was taken from the reactor and diluted with deionized water for product analysis by using Waters e2695 HPLC system with a refractive index detector (Waters 2414) with a Phenomenex RezexTM RCM-Monosaccharide Ca^+ column (300 × 7.8 mm). The conversion ($C_{sorbitol}$), yield ($Y_{product}$), and selectivity ($S_{product}$) values were calculated as follows Eqs. (2)–(5):

$$C_{sorbitol} \ (\%) = \frac{N_{i,sorbitol} - N_{f,sorbitol}}{N_{i,sorbitol}} \times 100 \tag{2}$$

$$Y_{product} \ (\%) = \frac{N_{product}}{N_{i,sorbitol}} \times 100 \tag{3}$$

$$S_{product} \ (\%) = \frac{N_{product}}{N_{i,sorbitol} - N_{f,sorbitol}} \times 100 \tag{4}$$

$$Other \ (\%) = 100\% - S_{1,4\text{-sorbitan}} - S_{isosorbide} \tag{5}$$

where Other was defined as the unidentifiable products and polymerization/degradation products of humin, $N_{i,sorbitol}$ and $N_{f,sorbitol}$ represent the initial molar concentration and the final molar concentration of sorbitol, respectively, and $N_{product}$ refers to the molar concentration of product or by-product.

2.4. Optimization and validation test

Optimum condition for the double dehydration of sorbitol into isosorbide was intended to obtain maximum reaction performance by defining each response target: maximum in sorbitol conversion, minimum in 1,4-sorbitant, and maximum in isosorbide yield. To validate the relationship between the prediction models and observed results at the optimum condition, three replicates of validation tests were carried out under the same condition.

2.5. Reusability test and characterization

After the reaction, the catalyst was removed from the product by using suction filtration and Whatman Qualitative Filter Paper No.
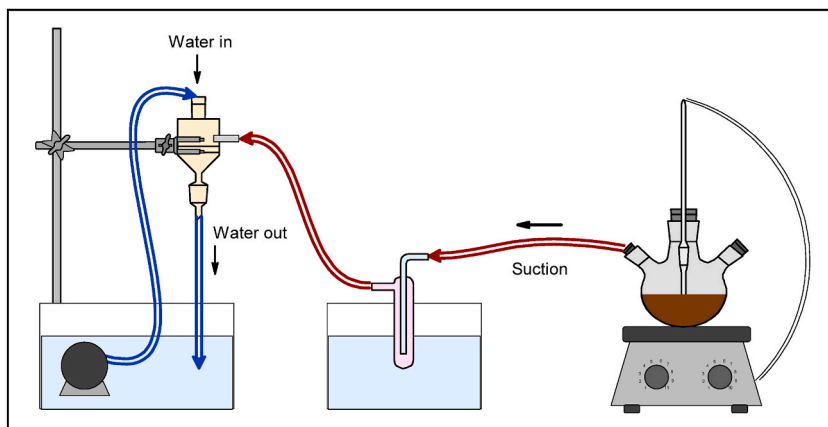

Fig. 1. Experimental setup for sorbitol dehydration with water ejector (vacuum condition).

1. The filtered catalyst was then washed with deionized water and constantly stirred for an hour. Thereafter, the spent catalyst was dried at 70 °C for 1 h before being utilized in the next reaction cycle. The process for determining the acid sites of catalysts involved the following steps. Initially, the catalyst was dried at 70 °C for 24 h, and then a sample was accurately weighed. The catalyst was then mixed with 50 mL of 0.5 M NaCl solution and stirred for 24 h. After filtering the mixture to separate the catalyst, the filtrate was titrated with a standard NaOH solution using phenolphthalein as indicator. To analyze the textural properties of the catalyst, Nitrogen Adsorption–Desorption was performed at a temperature of −196.15 °C using a NOVA200e device from Quantachrome (USA). The sample was outgassed at 80 °C under vacuum for 8 h, and the surface area was determined using the Brunauer–Emmett–Teller (BET) equation. The pore volume was calculated using the Barrett-Joyner-Halenda (BJH) equation. Finally, the functional groups of the catalyst were analyzed using a Fourier transform infrared spectrometer (FT-IR, BRUKER ALPHA II) with a transmission sample compartment. All samples were dried at a temperature of 70 °C overnight and then combined with KBr to improve their optical properties and create a uniform and mechanically stable sample for analysis.

3. Result and discussion

All reactions were operated under continuous suction conditions generated by a water ejection system, and water was pumped from the storage tank into a water aspirator pump that created suction of steam from the reactor, showing a constant pressure of 30 kPa throughout the experiment. Under this condition, the steam was continuously removed from the reaction and stored in a glass steam trap submerged in an ice bath.

3.1. Effect of reaction parameters and screening for Box-Behnken design

3.1.1. Reaction temperature
The study examined the influence of temperature on dehydration of sorbitol to isosorbide in a range of 120–180 °C, as depicted in Fig. 2(a). The temperature range was determined based on the lowest temperature at which the reaction could occur (120 °C), the suggested temperature range from literature (130–150 °C) as reported by Refs. [27,43], and the thermal stability of Purolite CT269 (180 °C). The reaction was conducted with a 5 % wt catalyst dosage for 4 h at 500 rpm under continuous water removal conditions. The optimal temperature for maximum yield of isosorbide was found to be 150 °C, with a yield of 58.24 % and complete conversion of sorbitol. In contrast, the reaction at 120 °C resulted in 58.40 % sorbitol conversion, with only 24.25 % yield of 1,4-sorbitant and 14.71 % yield of isosorbide. However, at higher temperatures of 180 °C, the yield of isosorbide was only 52.12 %, indicating that excessive temperatures can lead to product degradation and lower yield, as reported by Refs. [31,44]. Thus, a temperature of 150 °C was chosen for further optimization studies, and the temperature range of 120–180 °C was selected for the Box-Behnken design experiment.

3.1.2. Catalyst loading
The dehydration of sorbitol into isosorbide requires an acid catalyst to enhance the reaction performance, which is considered an important factor for the reaction [10,45]. The catalyst dosage varied from 0 to 5%wt. During the reaction, which was carried out in a vacuum condition while being stirred at 500 rpm for 4 h at 150 °C. Without the catalyst, the results were shown in Fig. 2(b) indicating no sorbitol conversion under this condition. On the other hand, 83.33 % sorbitol conversion and 17.29 % isosorbide yield were reported with 1%wt catalyst loading with the intermediate yield of 39.9 %, leading to the conclusion that 1%wt. Catalyst loading was insufficient to perform double dehydration. When the catalyst loading was increased from 3 to 5%wt, the isosorbide yield increased to 59.87 % and 55.64 %, respectively. The results revealed that isosorbide production requires a high acid concentration to achieve a higher reaction activity. Although the conversion of sorbitol did not change significantly, the strong acid concentration in the reaction possibly caused degradation or polymerization, which could reduce the production of intermediates and isosorbides [46,47]. Despite the lower isosorbide yield, a catalyst loading of 5%wt. was selected to study the effect of reaction time due to its higher sorbitol conversion. The loading within the range of 1–5%wt. was selected for Box-Behnken design to investigate the optimized conditions.

3.1.3. Reaction time
Fig. 2(c) shows the reaction behavior of the 5%wt. Catalysts under 150 °C and vacuum conditions for 12 h. The reaction was sampled along with reaction time for every 1 h until the reaction was stopped. As evidenced from Fig. 2(c), the increase in isosorbide
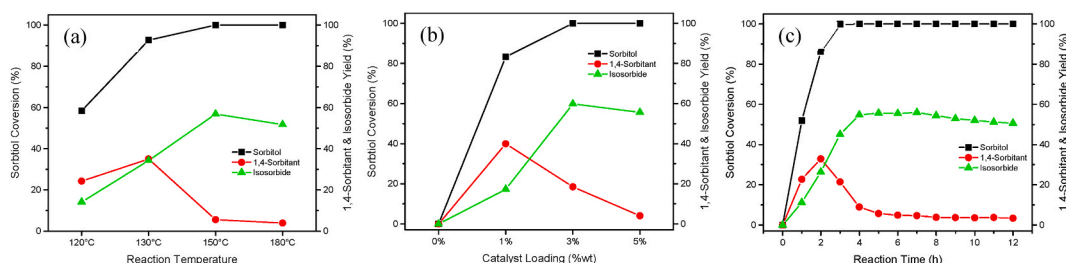

Fig. 2. (a) Effect of reaction temperature (b) Effect of catalyst loading and (c) Effect of reaction time for sorbitol dehydration reaction.

and 1,4-Sorbitant was accompanied by an increase in sorbitol conversion along with the reaction time. After 2 h, the highest amount of 1,4-sorbtiant was seen to gradually decrease. After 3 h, complete conversion of sorbitol was reached, and at 7 h, the highest isosorbide yield of 55.98 % was obtained. Following this, the yield of isosorbide decreased slightly after 7 h, which was thought to have been caused by the degradation or polymerization of the product, resulting in the creation of humin. This result agreed with the results of Ginés-Molina et al. (2017) [27] and Yamaguchi et al. (2020) [44,48]. After the reaction time of 12 h, the isosorbide yield remained at 50.66 %. Therefore, the reaction time in the range of 2–8 h was selected for Box-Behnken design experiment.

3.2. Statistical analysis and model fitting (RSM analysis)

The results of 15 experiments were shown in Table 2. The maximum reaction activity was obtained with complete conversion of sorbitol, 9.70 % of 1,4-sorbitant, and 67.80 % of isosorbide yield under 140 °C, 5%wt. Catalyst loading, and 8 h. On the other hand, the reaction under 120 °C, 1%wt catalyst dosage, and 5 h yielded the lowest activity of 16.73 % sorbitol conversion, 7.59 % 1,4-sorbitant, and 2.98 % isosorbide.

RSM as a combination of mathematical and statistical methods was employed to develop a model for optimizing the independent variables. The reaction equations in the form of quadratic equation can be respectively used as the predictive model for conversion of sorbitol (Y_1), yield of 1,4-sorbitant (Y_2), and yield of isosorbide (Y_3) with the reaction temperature (A), catalyst loading (B), and reaction time (C) being the independent variables, AB, AC, and BC being the interactions between the independent variables, and A^2, B^2, and C^2 are the quadratic terms, as shown in Eqs. (6)–(8).

$$Y_1 = -1135 + 12.69A + 68.1B + 44.5C - 0.0344A^2 - 3.91B^2 - 1.563C^2 - 0.2410AB - 0.1559AC - 0.773CB \qquad (6)$$

$$Y_2 = -786.8 + 8.992A + 65.63B + 37.68C - 0.02507A^2 - 1.197B^2 - 0.680C^2 - 0.3536AB - 0.1753AC - 2.113BC \qquad (7)$$

$$Y_3 = -257 + 2.95A - 4.1B + 1.31C - 0.00852A^2 - 2.181B^2 - 0.490C^2 + 0.1215 AB + 0.0244AC + 1.384BC \qquad (8)$$

The statistical significance of all the predictive models was studied by an analysis of variance (ANOVA) with the results shown in Table 3. The F-values of 23.86, 48.26, and 21.55 with all p-values being lower than 0.05 for the models of Y_1 to Y_3, imply that all the regression models are significant. The high F-values of 120.97 and 100.58 corresponding to Y_1 and Y_3 with small p-values (<0.001) indicated the most significance of reaction temperature in the conversion of sorbitol and isosorbide yield. Moreover, the coefficient of determination (R^2) of 0.9772, 0.9886, and 0.9749 associated with Eqs. (6)–(8), demonstrated the accuracy of the models.

The interaction between each independent variable and the response to the dehydration reaction were analyzed using contour plots. Fig. 3(a–c) displays a direct correlation between the sorbitol conversion and all the parameters. Additionally, the yield of 1,4-sorbitant increased as the reaction parameters increased, although it slightly decreased at some higher values, indicating that the second dehydration occurred under higher reaction conditions, as shown in Fig. 4(a–c). The yield of isosorbide, as depicted in Fig. 5 (a–c), followed a similar trend to sorbitol conversion. The contour plots revealed that the yield of 1,4-sorbitant increased with the reaction parameters but decreased at some higher reaction parameter levels, suggesting that there existed an optimal reaction condition at higher parameter levels to promote the conversion of the intermediate into isosorbide. Therefore, to improve the reaction performance, it is necessary to increase the reaction temperature from 140 °C and the catalyst loading from 3 %wt with a reaction time of at least 4 h.

## 3.3. Optimization of the dehydration reaction of sorbitol into isosorbide

To optimize the reaction condition, the level of reaction response was set at the maximum for sorbitol conversion and isosorbide yield and the minimum for 1,4-sorbitant yield. For the optimum condition, the calculation suggested the optimum condition for this

Table 2
Suggested experimental conditions by Box-Behnken design for double dehydration of sorbitol into isosorbide.

Runs	Temperature (°C)	Catalyst loading (% wt.)	Reaction time (h.)	Conversion of sorbitol (%), Y_1	Yield of 1,4-sorbitant (%), Y_2	Yield of isosorbide (%), Y_3
1	160	5	5	100.00	4.96	64.88
2	140	1	8	72.91	40.92	19.64
3	140	5	2	71.77	33.09	19.87
4	120	3	8	58.10	29.37	17.71
5	140	3	5	96.52	36.13	38.69
6	140	3	5	97.80	34.51	42.90
7	140	1	2	26.13	13.59	4.94
8	120	3	2	20.47	10.44	4.22
9	160	3	8	100.00	6.69	65.47
10	160	3	2	99.79	29.84	46.12
11	120	1	5	16.73	7.59	2.98
12	140	5	8	100.00	9.70	67.80
13	140	3	5	97.92	35.07	42.00
14	160	1	5	99.69	40.31	32.96
15	120	5	5	55.60	28.81	15.46

Table 3

Analysis of variance (ANOVA).

Variable		Conversion of Sorbitol, Y_1			Yield of 1,4-Sorbitant, Y_2			Yield of Isosorbide, Y_3		
Source	DF	F-Value	P-Value	Result	F-Value	P-Value	Result	F-Value	P-Value	Result
Model	9	23.86	<0.001	Significant	48.26	<0.001	Significant	21.55	0.002	Significant
A	1	120.97	<0.001	Significant	0.68	0.450	Insignificant	100.58	<0.001	Significant
B	1	24.51	<0.001	Significant	14.51	0.010	Significant	40.65	0.001	Significant
C	1	24.93	<0.001	Significant	<0.001	0.970	Insignificant	32.06	0.002	Significant
A^2	1	10.95	0.020	Significant	64.51	<0.001	Significant	1.21	0.322	Insignificant
B^2	1	14.16	0.010	Significant	14.71	0.010	Significant	7.91	0.037	Significant
C^2	1	11.44	0.020	Significant	24.05	<0.001	Significant	2.02	0.214	Insignificant
AB	1	5.82	0.060	Insignificant	138.98	<0.001	Significant	2.66	0.164	Insignificant
AC	1	5.48	0.070	Insignificant	76.92	<0.001	Significant	0.24	0.644	Insignificant
BC	1	1.35	0.300	Insignificant	111.67	<0.001	Significant	7.77	0.039	Significant
Lack-of-Fit	3	175.59	0.010	Significant	13.65	0.07	Insignificant	11.34	0.082	Insignificant
		$R^2 = 97.72$			$R^2 = 98.86$			$R^2 = 97.49$		
		$R^2_{adj} = 93.63$			$R^2_{adj} = 96.81$			$R^2_{adj} = 92.96$		
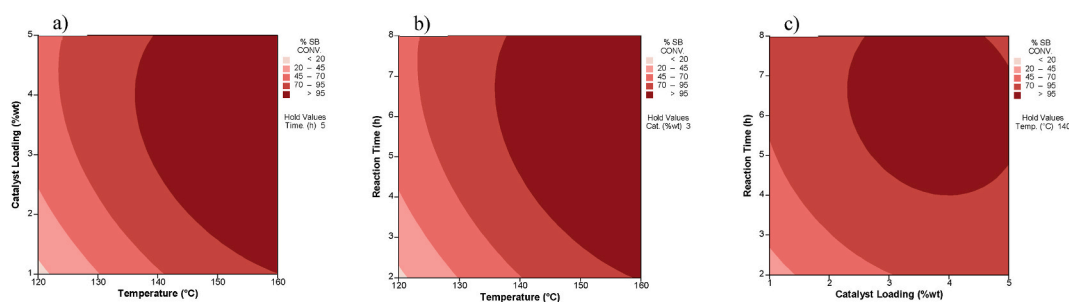
Fig. 3. Contour plots of sorbitol conversion (Y_1).
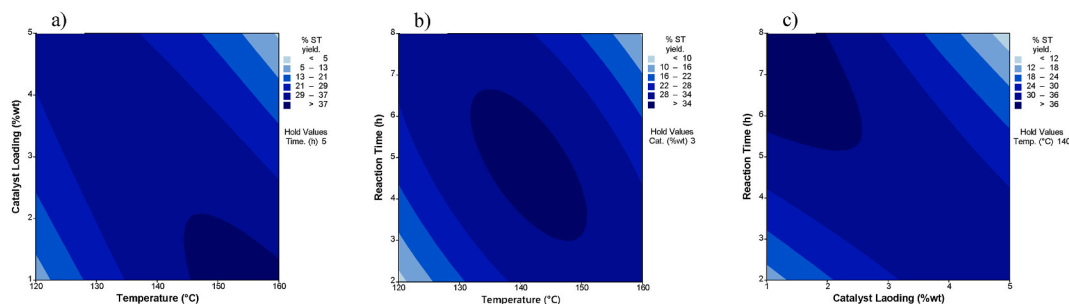
Fig. 4. Contour plots of 1,4-sorbitant yield (Y_2).
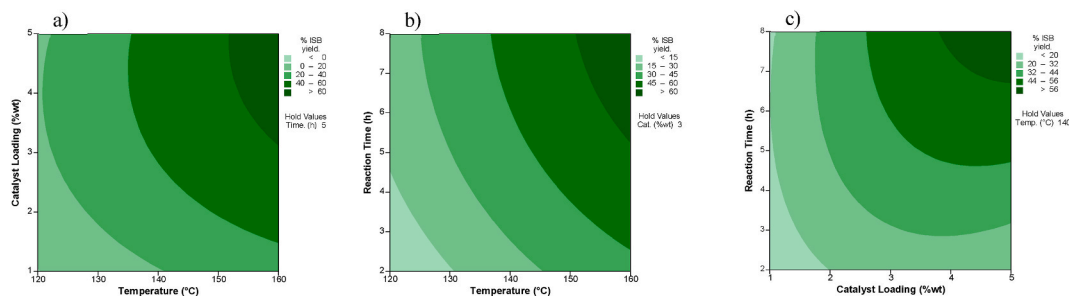
Fig. 5. Contour plots of isosorbide yield (Y_3).

reaction to be 160 °C with 4.31%wt of catalyst loading for 7.81 h (469 min), as shown in Fig. 6(a). However, according to the literature review, this suggested condition was considered overrated. A high reaction temperature with extended reaction time causes the degradation of the reaction product [31,49]. Consequently, the reaction conditions were modified by reducing the reaction time to 5 h to prevent reaction degradation and increasing the catalyst loading to 5 %wt to ensure optimum catalytic performance. Hence, three replicates of experiments were carried out under the modified optimal condition of reaction temperature at 160 °C, catalyst loading of 5%wt, and reaction time for 5 h, as shown in Fig. 6 (b).

Under the optimized conditions, Table 4 illustrates the experimental results and calculated predictive values of double dehydration reaction of sorbitol. There was a small variation in the reaction performance when compared to the predicted value. However, the predicted value of sorbitol conversion was 103.43 %, which is impossible because the complete conversion was limited to 100 % and it could be assumed that the predicted value of a completed conversion is 100 %. Moreover, the experimental and predicted values of the intermediate were respectively found to be 6.42 % and 3.74 % whereas the experimental and predicted isosorbide were respectively 67.55 % and 68.48 %. In terms of overall performance, the results were found to have a low percentage error, demonstrating a strong correlation between the observed and the projected values. Therefore, the condition could be effectively used to optimize the dehydration of sorbitol to obtain a high yield of isosorbide.

Furthermore, the research results of some dehydration reaction of sorbitol are presented to compare between this work and other studies as listed in Table 5. The results indicated that the reaction performed under the optimized conditions exhibited better performance in isosorbide production. Although the highest isosorbide yield of 82 % was observed by Yuan, Zhao et al., 2019, see entry 4, this process still required an extended reaction time of 12 h. In contrast, a 78 % isosorbide yield was obtained at the reaction time of 3 h, using Amberlyst 15, but a 7.5%wt catalyst loading was required. Therefore, the optimization of reaction condition using BBD and RSM can provide an effective reaction condition that can achieve more desirable catalytic performance for the dehydration reaction of sorbitol into isosorbide.

To clarify the catalytic performance under the optimization condition using BBD, a comparison of Purolite CT269 and Amberlyst 15 under these conditions was evaluated, as depicted in Fig. 7. The experimental results indicate that the performance of Purolite CT269 and Amberlyst 15 as catalysts in the conversion of sorbitol is comparable. Both catalysts achieve complete sorbitol conversion (100 %). Purolite CT269 yields 6.75 % sorbitan and 70.61 % isosorbide, while Amberlyst 15 yields a slightly higher 7.12 % sorbitan and a slightly lower 66.66 % isosorbide. Under the optimization condition, these results suggest that both catalysts are highly effective in converting sorbitol, with Purolite CT269 being slightly more efficient in converting the intermediate and producing isosorbide.

3.4. Reusability test and characterization

Catalyst recycling was conducted to assess the reusability of Purolite CT269 under the optimized conditions derived from BBD and RSM, as shown in Fig. 8. The results reveal a progressive decline in catalytic performance over multiple cycles. Initially, the fresh catalyst achieves complete sorbitol conversion (100 %), with a high isosorbide yield of 70.61 % and a low sorbitan yield of 6.75 % remaining. After the first cycle, while sorbitol conversion remains at 100 %, the isosorbide yield decreases to 52.53 %, and the sorbitan yield increases to 39.35 %. By the second cycle, sorbitol conversion drops to 89.30 %, with the isosorbide yield further decreasing to 31.42 %, and the sorbitan yield rising to 52.12 %. In the third cycle, sorbitol conversion reduces to 79.60 %, with an isosorbide yield of 19.14 % and a sorbitan yield of 39.64 %. Finally, in the fourth cycle, the catalyst's performance declines further, showing a sorbitol conversion of 73.79 %, an isosorbide yield of 11.34 %, and a sorbitan yield of 42.90 %. These results demonstrate significant catalytic deactivation and reduced efficiency upon recycling the catalyst under the optimization conditions.
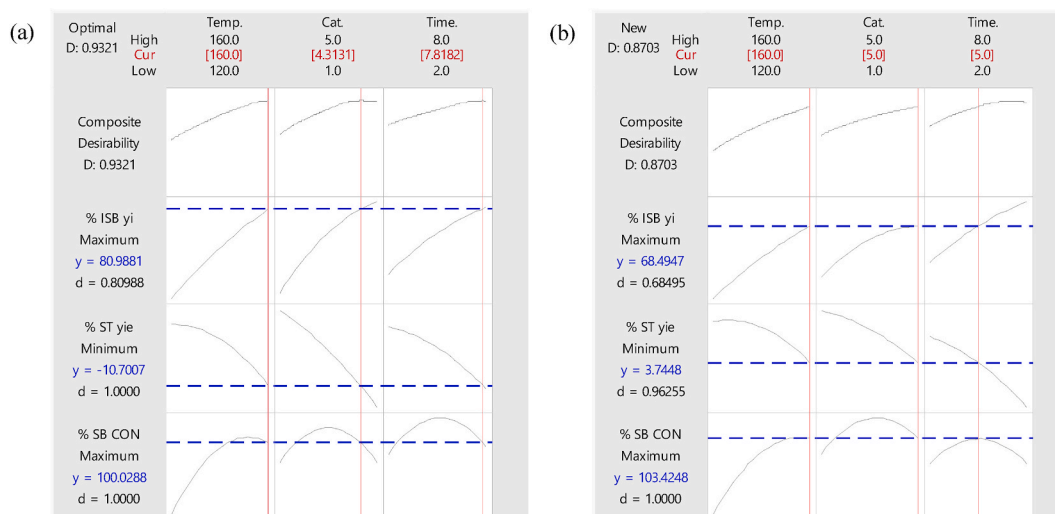

Fig. 6. The optimum conditions of double dehydration of sorbitol into isosorbide (a) Suggested condition (b) Modified condition.
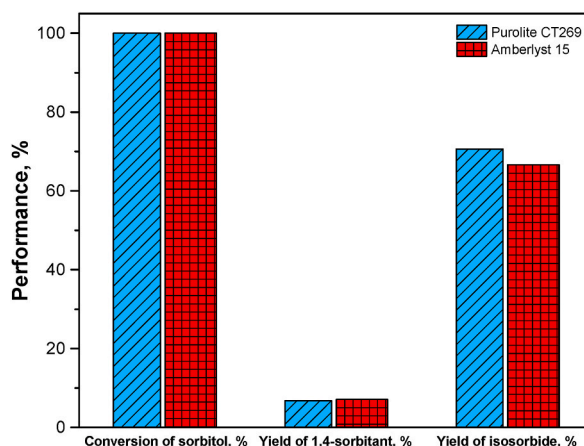
Table 4

Experimental results and predicted values of dehydration reaction of sorbitol performance.

Responses	Conversion of sorbitol (%), Y_1		Yield of 1,4-sorbitant (%), Y_2		Yield of isosorbide (%), Y_3	
	Observed	Predicted	Observed	Predicted	Observed	Predicted
1st	100.00	100.00	5.79	3.74	65.01	68.48
2nd	100.00	100.00	6.75	3.74	67.87	68.48
3rd	100.00	100.00	6.70	3.74	69.76	68.48
Average	100.00	100.00	6.42	3.74	67.55	68.48

Table 5

Comparison of the results under optimized reaction condition and other works.

Entry	Catalyst	Reaction Conditions			Reaction responses			References
		Temperature (°C)	Catalyst loading (%wt)	Time (h)	Sorbitol conversion (%)	1,4-sorbitant yield (%)	Isosorbide yield (%)	
1	None[a,c]	316.85	–	1	100	15	57	Yamaguchi et al. [48]
2	Purolite CT269[a,d]	160	5	6	100	0	42	Boupan et al. [31]
3	Purolite CT269[b,d]	140	5	12	100	0	75	Ginés-Molina et al. [27]
4	Polymer-based[b,e]	150	2	12	100	11	82	Yuan, Zhao et al. [18]
5	Amberlyst 15[b,e]	140	7.5	3	100	4	78	Inshyna et al. [50]
6	Purolite CT269[b,e]	160	5	5	100	6.42	68	This work

[a] Sorbitol solution.
[b] Solvent-free.
[c] Gas purged.
[d] Autogenous conditions.
[e] Vacuum condition.

Fig. 7. The dehydration reaction of sorbitol into isosorbide using Purolite CT269 and Amberlyst 15.

The deactivation of the Purolite CT269 catalyst was evaluated over multiple reaction cycles. Table 6 presents the properties of the catalyst after each cycle of reactions, highlighting changes in its acidic functionality. Using acid-base titration, the concentration of acid sites on the catalyst was measured, revealing a decrease from 0.0271 to 0.0108 eq H^+/g as the number of reaction cycles increased. Furthermore, the changes observed in the FTIR spectra shown in Fig. 9(a), which in the range from 500 to 4000 cm^{-1}, were evident in the functional groups post-reaction. Specifically, the band at 1173 cm^{-1}, associated with the SO_3^- group of sulfonic acid [24, 51], slightly diminished. These feature shows that the reduction in the sulfonic acid group's presence corresponds with the observed decline in catalytic performance during the sorbitol dehydration reaction, underscoring the significant loss of active sites, especially SO_3^- group, responsible for the catalyst's efficacy in the dehydration reaction of sorbitol [52–54]. Moreover, the characteristic vibration band at approximately 830, 1031, 1721, 2354 cm^{-1} in the FTIR spectrum are assigned to the stretching vibrations of C=C,
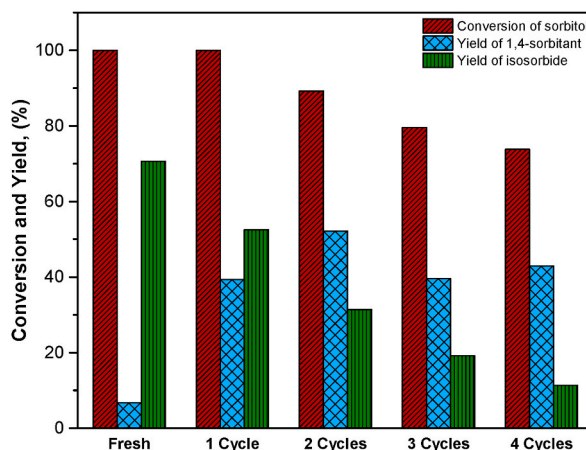
Fig. 8. The reusability of Purolite CT269 catalyst for isosorbide production of 4 cycles.

Table 6
The morphology and acid properties of Purolite CT269.

Catalyst	Acid site, (eq H^+/g)[a]	Surface area, (m^2/g)	Pore Volume, (cm^3/g)	Pore Size, (nm.)
Fresh	0.0271	35.2955	0.3385	33.2700
1 cycle	0.0163	15.8773	0.1485	32.2919
2 cycles	0.0139	18.7212	0.1598	28.6955
3 cycles	0.0123	18.0159	0.1599	30.5218
4 cycles	0.0108	17.6439	0.1472	30.0829

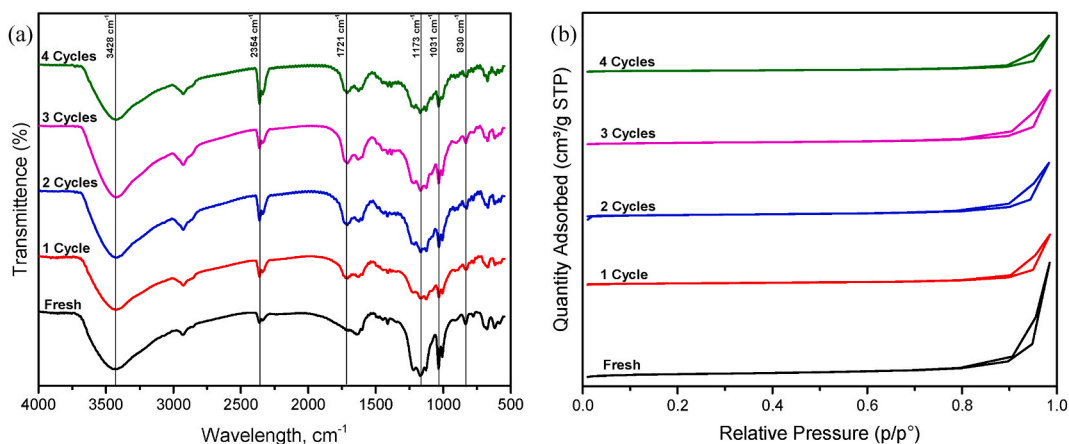[a] Measured by Acid-Base titration method.

Fig. 9. FT-IR spectra (a) Nitrogen adsorption and desorption isotherm (b) of Purolite CT269 in reusability test.

C–O, C=O and CO_2 functionalities [18,55], respectively. On one hand, the characteristics peaks of C=C and C–O gradually decrease, but on the other hand the peaks of C=O and CO_2 obviously increase. This observation implies the potential deposition of humin or a complex carbonaceous byproduct onto the catalyst surface, which could contribute to the observed increase in carbonaceous features of the catalyst [21,56].

The morphologies of PuroliteCT269 catalysts were also analyzed in multiple reaction cycles. The BET method was used to calculate the surface areas of the samples, and the results are presented in Table 6. The surface area values for all samples showed a significant decrease from 35.29 m^2/g (fresh catalyst) to an average of 16.39 m^2/g (spent catalyst). The isotherms for nitrogen adsorption and desorption for all the catalyst cycles are shown in Fig. 9(a). All samples exhibited Type IV isotherms according to the BDDT categorization and displayed Type H1 hysteresis loops according to the IUPAC classification, as illustrated in Fig. 9(b). The hysteresis loops of the samples indicated the presence of a mesoporous structure with a relative pressure (P/P0) between 0.8 and 1.0. Moreover, the observed hysteresis of all spent catalysts was about the same size but lower in terms of the quantity of adsorbed catalyst compared to

the fresh catalyst, suggesting that the pore size showed minor changes, but the pore volume of these catalysts decreased. To confirm this point, the pore size and pore volume were estimated using the BJH method. The results show that after the reaction, the pore volume and pore size declined with the number of cycles from 0.3385 to 0.1472 cm^3/g for the pore volume and 33.27 to 30.08 nm. for the pore size, for the fresh catalyst to the catalyst after four cycles. The decrease in these morphological properties might be caused by the collapse of the polymeric structure due to the reaction conditions [57] or the accumulation of reaction products and by-products on the catalyst surface and/or filling into the pore structure of the catalyst after the reaction. As previously mentioned, the characterization of the spent catalyst showed unequivocally that deactivation of the catalyst was caused by a loss of functional groups and structural decomposition due to reaction conditions, which were directly affected to the catalytic performance.

4. Conclusion

In this study, the dehydration of sorbitol to isosorbide was investigated. This study was conducted to evaluate the influence of the reaction conditions, including the reaction temperature, catalyst loading, and reaction time, under a vacuum generated by a water ejector with a commercial sulfonic resin catalyst. In addition, statistical analysis was conducted to determine the optimal conditions for the reaction. The results showed that using a water ejector system can eliminate steam from the reactor and that all reaction parameters had a significant effect on the reaction performance with the reaction temperature being the most critical factor. Prediction models for each reaction response were also generated and exhibited a high coefficient of determination (R^2) of over 95 %, with no significant errors in any of the models. Under optimal conditions, the reaction achieved complete sorbitol conversion, yielding 6.42 % 1,4-sorbitol and 67.55 % isosorbide, with a slightly deviation when comparing the reaction performance to the expected value. The efficiency of Purolite CT269 in catalyst recycling decreased steadily over time, as evidenced by a substantial reduction in the conversion of sorbitol and the yield of isosorbide across multiple cycles. The primary cause of this decline was the diminishing acidic functionality and active sites of the catalyst. Additionally, the catalyst's surface area, pore volume, and pore size also decreased, which could be attributed to structural collapse and the accumulation of by-products, leading to a decrease in catalytic efficiency. However, this work optimizes the efficient method for producing isosorbide and provides the accurate predictive models with potential application for a larger scale production in biomass valorization.

Data availability statement

The authors confirm that the data supporting the findings of this study are available within the article.

CRediT authorship contribution statement

Natthaphong Lertna: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Nitchakamol Sansawat:** Methodology, Investigation, Formal analysis, Conceptualization. **Arthit Neramittagapong:** Writing – review & editing, Validation, Supervision, Methodology, Formal analysis, Conceptualization. **Somnuk Theerakulpisut:** Writing – review & editing, Validation, Formal analysis. **Sutasinee Neramittagapong:** Writing – review & editing, Visualization, Validation, Supervision, Resources, Methodology, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

References

[1] C. Wang, X. Zhang, Q. Liu, Q. Zhang, L. Chen, L. Ma, A review of conversion of lignocellulose biomass to liquid transport fuels by integrated refining strategies, Fuel Process. Technol. 208 (2020), https://doi.org/10.1016/j.fuproc.2020.106485.

[2] P. Che, H. Ma, X. Nie, W. Yu, J. Xu, Methyl isobutyl ketone-enabled selective dehydration-esterification of sorbitol to isosorbide esters over the H-beta catalyst, Green Chem. 24 (2022) 7545–7555, https://doi.org/10.1039/d2gc02342c.

[3] H. Baniamerian, M. Høj, M.J. Beier, A.D. Jensen, Catalytic conversion of sugars and polysaccharides to glycols: a review, Appl. Catal., B 330 (2023), https://doi.org/10.1016/j.apcatb.2023.122650.

[4] M. Boupan, K. Prompang, A. Chompunuch, P. Boonma, A. Neramittagapong, S. Theerakulpisut, S. Neramittagapong, Role of calcination temperature on isosorbide production from sorbitol dehydration over the catalyst derived from Ce(IV) sulfate, J. Renew. Mater. 11 (2023) 2985–3000, https://doi.org/10.32604/jrm.2023.026397.

[5] J. Zou, D. Cao, W. Tao, S. Zhang, L. Cui, F. Zeng, W. Cai, Sorbitol dehydration into isosorbide over a cellulose-derived solid acid catalyst, RSC Adv. 6 (2016) 49528–49536, https://doi.org/10.1039/c6ra05214b.

[6] Z. Li, W. Lan, C. Liu, Biomass derived bifunctional catalyst for the conversion of cassava dreg into sorbitol, Ind. Crops Prod. 197 (2023), https://doi.org/10.1016/j.indcrop.2023.116493.

[7] C.H. Lee, H. Takagi, H. Okamoto, M. Kato, A. Usuki, Synthesis, characterization, and properties of polyurethanes containing 1,4:3,6-dianhydro-d-sorbitol, J. Polym. Sci. Polym. Chem. 47 (2009) 6025–6031, https://doi.org/10.1002/pola.23645.

[8] M. Yabushita, H. Kobayashi, A. Shrotri, K. Hara, S. Ito, A. Fukuoka, Sulfuric acid-catalyzed dehydration of sorbitol: mechanistic study on preferential formation of 1,4-sorbitan, Bull. Chem. Soc. Jpn. 88 (2015) 996–1002, https://doi.org/10.1246/bcsj.20150080.

[9] B.T. Wang, F. De Lu, F. Xu, Y.Z. Li, M.R. Kessler, Synthesis of renewable isosorbide-based monomer and preparation of the corresponding thermosets, Chin. Chem. Lett. 27 (2016) 875–878, https://doi.org/10.1016/j.cclet.2016.01.030.

[10] C. Dussenne, T. Delaunay, V. Wiatz, H. Wyart, I. Suisse, M. Sauthier, Synthesis of isosorbide: an overview of challenging reactions, Green Chem. 19 (2017) 5332–5344, https://doi.org/10.1039/c7gc01912b.

[11] F. Aricò, Isosorbide as biobased platform chemical: recent advances, Curr. Opin. Green Sustainable Chem. 21 (2020) 82–88, https://doi.org/10.1016/j.cogsc.2020.02.002.

[12] L. Wang, X. Liu, Y. Wang, W. Sun, L. Zhao, Thermodynamics and reaction kinetics of the sorbitol dehydration to isosorbide using NbOPO$_4$as the catalyst, Ind. Eng. Chem. Res. 61 (2022) 7833–7841, https://doi.org/10.1021/ACS.IECR.2C00925/ASSET/IMAGES/MEDIUM/IE2C00925_M025.GIF.

[13] J. Li, B. Wang, H. Zhang, Y. Zhang, X. Zhao, Theoretical investigation of the mechanism, performance and kinetic experimental phenomena on brønsted acidic ionic liquids catalyzed dehydration of sorbitol to isosorbide, ChemistrySelect 5 (2020) 14713–14720, https://doi.org/10.1002/slct.202004050.

[14] T. Kondo, T. Sasaki, M. Shiga, The mechanism of sorbitol dehydration in hot acidic solutions, J. Comput. Chem. 42 (2021) 1783–1791, https://doi.org/10.1002/jcc.26710.

[15] G. Flèche, M. Huchette, Isosorbide. Preparation, properties and chemistry, Starch - Stärke 38 (1986) 26–30, https://doi.org/10.1002/star.19860380107.

[16] D. Yuan, F. Xiao, N. Zhao, C. Deng, X. Huang, H. Zhang, Q. Yang, Y. Qiao, Mesoporous poly(ionic liquid) solid acid for sequential dehydration of sorbitol to isosorbide, Chem. Eng. J. 460 (2023), https://doi.org/10.1016/j.cej.2023.141780.

[17] Y. Zhang, T. Chen, G. Zhang, G. Wang, H. Zhang, Efficient production of isosorbide from sorbitol dehydration over mesoporous carbon-based acid catalyst, Appl. Catal. Gen. 575 (2019) 38–47, https://doi.org/10.1016/j.apcata.2019.01.014.

[18] D. Yuan, N. Zhao, Y. Wang, K. Xuan, F. Li, Y. Pu, F. Wang, L. Li, F. Xiao, Dehydration of sorbitol to isosorbide over hydrophobic polymer-based solid acid, Appl. Catal., B 240 (2019) 182–192, https://doi.org/10.1016/j.apcatb.2018.08.036.

[19] Y.F. Wang, B.H. Xu, Y.R. Du, S.J. Zhang, Heterogeneous cyclization of sorbitol to isosorbide catalyzed by a novel basic porous polymer-supported ionic liquid, Mol. Catal. 457 (2018) 59–66, https://doi.org/10.1016/j.mcat.2018.07.019.

[20] D. Yuan, L. Li, F. Li, Y. Wang, F. Wang, N. Zhao, F. Xiao, Solvent-free production of isosorbide from sorbitol catalyzed by a polymeric solid acid, ChemSusChem 12 (2019) 4986–4995, https://doi.org/10.1002/cssc.201901922.

[21] D. Cao, B. Yu, S. Zhang, L. Cui, J. Zhang, W. Cai, Isosorbide production from sorbitol over porous zirconium phosphate catalyst, Appl. Catal. Gen. 528 (2016) 59–66, https://doi.org/10.1016/j.apcata.2016.09.017.

[22] M. Gu, D. Yu, H. Zhang, P. Sun, H. Huang, Metal (IV) phosphates as solid catalysts for selective dehydration of sorbitol to isosorbide, Catal. Lett. 133 (2009) 214–220, https://doi.org/10.1007/S10562-009-0142-5/FIGURES/6.

[23] J. Guo, Y. Song, S. Liu, L. Huang, X. Wang, S. Liu, C. Li, Sequential dehydration of sorbitol to isosorbide over acidified niobium oxides, Catal. Sci. Technol. 11 (2021) 4226–4234, https://doi.org/10.1039/d1cy00326g.

[24] N. Lertna, P. Srisamut, N. Supapan, P. Athikaphan, S.C. Rood, A. Neramittagapong, S. Neramittagapong, Synthesis of sulfated titanium dioxide catalyst for sorbitol dehydration to isosorbide, Mater. Today Proc. 75 (2023), https://doi.org/10.1016/j.matpr.2022.11.226.

[25] J. Xia, D. Yu, Y. Hu, B. Zou, P. Sun, H. Li, H. Huang, Sulfated copper oxide: an efficient catalyst for dehydration of sorbitol to isosorbide, Catal. Commun. 12 (2011) 544–547, https://doi.org/10.1016/J.CATCOM.2010.12.002.

[26] M.J. Ginés-Molina, J.A. Cecilia, C. García-Sancho, R. Moreno-Tost, P. Maireles-Torres, Use of ion-exchange resins in dehydration reactions, in: Applications of Ion Exchange Materials in Chemical and Food Industries, Springer International Publishing, 2019, pp. 1–18, https://doi.org/10.1007/978-3-030-06085-5_1.

[27] M.J. Ginés-Molina, R. Moreno-Tost, J. Santamaría-González, P. Maireles-Torres, Dehydration of sorbitol to isosorbide over sulfonic acid resins under solvent-free conditions, Appl. Catal. Gen. 537 (2017) 66–73, https://doi.org/10.1016/j.apcata.2017.03.006.

[28] C. Dussenne, H. Wyart, V. Wiatz, I. Suisse, M. Sauthier, Catalytic dehydration of sorbitol to isosorbide in the presence of metal tosylate salts and metallized sulfonic resins, Mol. Catal. 463 (2019) 61–66, https://doi.org/10.1016/j.mcat.2018.11.004.

[29] R. Soto, D.E. Ramírez, E. Quinto Fernández, Treball Final de Grau Contribution to the kinetic study of the dehydration of sorbitol over acidic ion-exchange resins, 2022.

[30] F.M.B. Coutinho, R.R. Souza, A.S. Gomes, Synthesis, characterization and evaluation of sulfonic resins as catalysts, Eur. Polym. J. 40 (2004) 1525–1532, https://doi.org/10.1016/j.eurpolymj.2004.02.003.

[31] M. Boupan, P. Wongpakham, O. Sabangban, A. Neramittagapong, S. Theerakulpisut, S. Neramittagapong, Catalytic Performance of Acid Catalysts for Sorbitol Dehydration to Isosorbide, n.d.

[32] I. Bonnin, R. Méreau, T. Tassaing, K. De Oliveira Vigier, Selective one-pot synthesis of sorbitans (1,4-sorbitan and 3,6-sorbitan) from glucose via catalytic hydrogenation and CO2-mediated dehydration, ACS Sustain. Chem. Eng. (2023), https://doi.org/10.1021/acssuschemeng.3c08156.

[33] M.A.B.M.K. Yunus, A. Cengel, Thermodynamics: an Engineering Approach ISE, tenth ed., 2023.

[34] F. Brandi, I. Khalil, M. Antonietti, M. Al-Naji, Continuous-flow production of isosorbide from aqueous-cellulosic derivable feed over sustainable heterogeneous catalysts, ACS Sustain. Chem. Eng. 9 (2021) 927–935, https://doi.org/10.1021/acssuschemeng.0c08167.

[35] N. Botha, H.M. Inglis, R. Coetzer, W.J.L.F. Johan, Statistical Design of Experiments: an introductory case study for polymer composites manufacturing applications, in: 12th South African Conference on Computational and Applied Mechanics, SACAM 2020, EDP Sciences, 2020, https://doi.org/10.1051/matecconf/202134700028.

[36] A. Asghar, A.A.A. Raman, W.M.A.W. Daud, A comparison of central composite design and Taguchi method for optimizing fenton process, Sci. World J. 2014 (2014), https://doi.org/10.1155/2014/869120.

[37] A.K. Giri, P.C. Mishra, Optimization of different process parameters for the removal efficiency of fluoride from aqueous medium by a novel bio-composite using Box-Behnken design, J. Environ. Chem. Eng. 11 (2023) 82283877, https://doi.org/10.1016/j.jece.2022.109232.

[38] B.Q. Tran, K.Y.A. Lin, F. Boujelbane, D.N. Nguyen, Y.S. Perng, H.T. Giang Duong, H.M. Bui, Optimization of leucomalachite green degradation through electron beam and persulfate oxidation using box-behnken design and life cycle assessment, Appl. Radiat. Isot. 209 (2024), https://doi.org/10.1016/j.apradiso.2024.111335.

[39] S. Ben Moussa, Box-Behnken design for the optimization of the photocatalytic degradation of methyl orange using gold-platinum bimetallic nanoparticles doped-1D titania, J. Photochem. Photobiol. Chem. 447 (2024), https://doi.org/10.1016/j.jphotochem.2023.115284.

[40] A.N. Amenaghawon, N.I. Evbarunegbe, K. Obahiagbon, Optimum biodiesel production from waste vegetable oil using functionalized cow horn catalyst: a comparative evaluation of some expert systems, Clean Eng. Technol. 4 (2021), https://doi.org/10.1016/j.clet.2021.100184.

[41] N.M. Abd-El-Aziz, M.S. Hifnawy, A.A. El-Ashmawy, R.A. Lotfy, I.Y. Younis, Application of Box-Behnken design for optimization of phenolics extraction from Leontodon hispidulus in relation to its antioxidant, anti-inflammatory and cytotoxic activities, Sci. Rep. 12 (2022), https://doi.org/10.1038/s41598-022-12642-2.

[42] A.S. Abdulhameed, A.K.T. Mohammad, A.H. Jawad, Application of response surface methodology for enhanced synthesis of chitosan tripolyphosphate/TiO$_2$ nanocomposite and adsorption of reactive orange 16 dye, J. Clean. Prod. 232 (2019) 43–56, https://doi.org/10.1016/j.jclepro.2019.05.291.

[43] M.R. Kamaruzaman, X.X. Jiang, X. De Hu, S.Y. Chin, High yield of isosorbide production from sorbitol dehydration catalysed by Amberlyst 36 under mild condition, Chem. Eng. J. 388 (2020) 124186, https://doi.org/10.1016/j.cej.2020.124186.

[44] A. Yamaguchi, N. Mimura, M. Shirai, O. Sato, Kinetic analyses of intramolecular dehydration of hexitols in high-temperature water, Carbohydr. Res. 487 (2020) 107880, https://doi.org/10.1016/j.carres.2019.107880.

[45] F. Delbecq, M.R. Khodadadi, D. Rodriguez Padron, R. Varma, C. Len, Isosorbide: recent advances in catalytic production, Mol. Catal. 482 (2020), https://doi.org/10.1016/j.mcat.2019.110648.

[46] G. Morales, J. Iglesias, J.A. Melero, J. Moreno, R. Sánchez-Vázquez, Á. Peral, A. Cubo, Isosorbide production from sorbitol over heterogeneous acid catalysts: screening and kinetic study, Top. Catal. 60 (2017) 1027–1039, https://doi.org/10.1007/s11244-017-0794-0.

[47] H. Kobayashi, H. Yokoyama, B. Feng, A. Fukuoka, Dehydration of sorbitol to isosorbide over H-beta zeolites with high Si/Al ratios, Green Chem. 17 (2015) 2732–2735, https://doi.org/10.1039/c5gc00319a.

[48] A. Yamaguchi, N. Hiyoshi, O. Sato, M. Shirai, Sorbitol dehydration in high temperature liquid water, Green Chem. 13 (2011) 873–881, https://doi.org/10.1039/c0gc00426j.

[49] Y. Zhang, T. Chen, G. Zhang, G. Wang, H. Zhang, Mesoporous Al-promoted sulfated zirconia as an efficient heterogeneous catalyst to synthesize isosorbide from sorbitol, Appl. Catal. Gen. 562 (2018) 258–266, https://doi.org/10.1016/j.apcata.2018.06.024.

[50] O.I. Inshyna, A.M. Mylin, V.V. Brei, Solvent-free dehydration of sorbitol to isosorbide catalyzed by sulfonic acid resins, J. Chem. Technol. 29 (2021) 449–455, https://doi.org/10.15421/JCHEMTECH.V29I3.231771.

[51] Y. Yang, Z. Ding, D. Ren, C. Shang, C. Li, F. Yang, B. Zhou, S. Hao, K. Sun, S. Lee, Dense Ru single-atoms integrated with sulfoacids for cellulose valorization to isosorbide, Mater. Today Sustain. 24 (2023), https://doi.org/10.1016/j.mtsust.2023.100494.

[52] K. Ravi, A.V. Biradar, Highly active and scalable SO3H functionalized carbon catalyst synthesized from bagasse for transformation of bio-based platform chemicals into fuel precursors and its in-depth characterization studies, Fuel 321 (2022), https://doi.org/10.1016/j.fuel.2022.124008.

[53] L.J. Konwar, P. Mäki-Arvela, J.P. Mikkola, SO$_3$H-Containing functional carbon materials: synthesis, structure, and acid catalysis, Chem. Rev. 119 (2019) 11576–11630, https://doi.org/10.1021/acs.chemrev.9b00199.

[54] A.A. Dabbawala, D.K. Mishra, G.W. Huber, J.S. Hwang, Role of acid sites and selectivity correlation in solvent free liquid phase dehydration of sorbitol to isosorbide, Appl. Catal. Gen. 492 (2015) 252–261, https://doi.org/10.1016/j.apcata.2014.12.014.

[55] J. Zhang, Y. Wang, M. Hong, B. Peng, C. Bao, X. Xu, D. Li, J. Chen, B. Wang, Q. Zhang, Ferrocene-based resin as heterogeneous fenton-like catalyst for efficient treatment of high salinity wastewater at acidic, neutral, and basic pH, Chem. Eng. J. 464 (2023), https://doi.org/10.1016/j.cej.2023.142450.

[56] J.T. Hopper, R. Ma, J.B. Rawlings, P.C. Ford, M.M. Abu-Omar, Markedly improved catalytic dehydration of sorbitol to isosorbide by sol-gel sulfated zirconia: a quantitative structure-reactivity study, ACS Catal. 13 (2023) 10137–10152, https://doi.org/10.1021/acscatal.3c00755.

[57] S. Rajput, D. Nayar, Effects of polymer architecture and charged molecular crowders on hydrophobic polymer collapse, ACS Polymers Au (2024), https://doi.org/10.1021/acspolymersau.4c00011.