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Research Article

Response surface methodology for glucose conversion by applying deep eutectic solvent (DES) as green solvent

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ABSTRACT: Glucose is a monosaccharide-type carbohydrate that serves as a fundamental building block of biomass which processed into several valuable compound. In this research, glucose was hydrolyzed using a Deep Eutectic Solvent (DES) as the solvent and $AlCl_3$ as the catalyst to produced furan based products. DES was utilized as green solvent with ionic liquid properties. DES was synthized by mixed the chloroform and oxalic acid by equal molar ratio. Meanwhile, varied temperature and catalyst concentration were investigated as key variables during the glucose hydrolysis based on design of experiment by central composite design (CCD). The glucose conversion results were tested using the UV-Vis spectrophotometer. The percentage of glucose conversion were analyzed using the Response Surface Methodology (RSM) with Design Expert Version 13 software. The results of RSM analysis show that glucose conversion increases linearly with rising reaction temperature. Interestingly, the high conversion was reached with 120°C and 105°C. The high catalyst concentration decreased the conversion percentage at hydrolysis process while the lower catalyst showed the reciprocal ways. The reaction temperature and $AlCl_3$ catalyst concentration that can be recommended for optimum conditions from the Design Expert data processing results are 112.869% and 1.913% with a predicted conversion value of 93.844%.

Keywords: *Deep eutectic solvent; hydrolysis; glucose conversion, response surface methodology*

1. INTRODUCTION

The cellulose component originating from biomass, when hydrolyzed under acidic reaction conditions, produces glucose as a precursor for levulinic acid. The conversion of lignocellulosic biomass to levulinic acid involves the hydrolysis of cellulose to glucose, followed by the isomerization of glucose to fructose. Fructose undergoes dehydration under acidic conditions to form 5-hydroxymethylfurfural (5-HMF), which is subsequently converted to levulinic acid [8].

Deep eutectic solvents (DES) are a new class of ionic liquids (ILs) derived from biodegradable natural compounds, such as choline, amino acids, and carboxylic acids [1]. DES has the chemical and physical properties of biodegradability, high thermal stability, low volatility, and cheapness, which are classified as the newest green solvent [15]. DES is defined as a solvent consisting of two components, namely quaternary ammonium salts as hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD), which are capable of forming a new eutectic phase that is characterized by a lower melting point than each of its constituent components [2]. The most effective DES was found to be DES formed by choline chloride and oxalic acid because it shows the formation of strong hydrogen bonds between HBA and HBD [5].

To accelerate the reaction rate in the hydrolysis process, a catalyst is required. A catalyst is a substance that can accelerate the rate of a chemical reaction at a certain temperature by lowering its activation energy without being changed or consumed by the reaction itself [14]. The types of catalysts often used in the glucose hydrolysis process by previous researchers are homogeneous and heterogeneous catalysts.

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Compared to homogeneous catalysts, heterogeneous catalysts have the advantage of being able to be separated from the reaction mixture so that they are easily regenerated [10], have high catalyst activity and selectivity, catalyst do not corrode the reaction column, can be used repeatedly after being regenerated, are easily separated because they are different phases, and disposal of used catalysts does not cause pollution [8].

Heterogeneous catalysts are starting to be developed because they have several advantages, such as being easier to synchronize the catalyst and product and having a smaller waste impact on the environment. Several metal chlorides are strong Lewis acids, and upon exposure to air, they can hydrolyze to form basic salts, thereby lowering the pH of the solution. However, research conducted by Peng et al. (2010) explained that several transition metal chlorides (such as $CrCl_3$, $FeCl_3$, and $CuCl_2$) and group IIIA metal chlorides ($AlCl_3$) showed higher catalytic activity for reactions. Based on these results, it was concluded that $AlCl_3$ is more profitable in the isomerization process of glucose and has better selectivity for glucose conversion than $CrCl_3$ [11].

The conversion of glucose to levulinic acid is a critical step in transforming biomass into valuable platform chemicals. Levulinic acid is an important precursor for producing various biofuel compounds, fuel additives, polymers, antifreeze agents, pharmaceutical industries, herbicide additives, plasticizers, gasoline additives, and diesel [4]. This reaction involves a series of complex catalytic mechanisms, including isomerization, dehydration, and rehydration. Transition metal chloride $AlCl_3$ acts as a strong Lewis acid. This catalyst interacts with the carbonyl group of glucose, facilitating isomerization to fructose. This isomerization is an important step in the reaction pathway because fructose is more easily dehydrated to hydroxymethylfurfural (HMF) [7]. The final stage involves the rehydration reaction of HMF, which produces levulinic acid and formic acid. Metal ions from $AlCl_3$ can help break the carbon bonds of HMF through protonation mechanisms and stabilize reaction intermediates [3].

Based on previous studies, the hydrolysis process was carried out using environmentally friendly catalysts with low temperatures, so that the process is more profitable. In this study, glucose hydrolysis was carried out using DES solvent and $AlCl_3$ catalyst. This economical DES catalytic system demonstrates great potential for biorefinery applications and offers new insights into biomass utilization using commercially available catalysts. This study focuses on mild temperature (hydrolysis at 120°C for 90 minutes) without the formation of by-products such as humin. Response Surface Methodology (RSM) method was applied using Design Expert Version 13 software for analyzed the influence of hydrolysis process variables. The results of glucose conversion were tested using a UV-Vis spectrophotometer.

2. EXPERIMENTAL

2.1. Material. The Glucose, aluminum (III) chloride ($AlCl_3.6H_2O$) which is preheated at a temperature of 105°C, oxalic acid ($C_2H_2O_4$), sulfuric acid (H_2SO_4), and phenol were supplied from Merck. Choline chloride (ChCl) was supplied from Sigma Aldrich. A standard analytical grade of levulinic acid 98% (Sigma Aldrich) was used for analysis of the desired products.

2.2. Analysis. ***2.2.1. UV-Vis spectroscopy analysis.*** The glucose conversion of samples was determined by the phenol-sulphate method using UV-Vis absorption Thermo Scientific™ GENESYS™ 150. The wavelength used for glucose detection is 485 nm.

2.2.2. Statistic analysis. The experiment was designed using Design Expert V.13 with variations in temperature and catalyst concentration. Central Composite Design (CCD) method was used to show the influence of independent variables on the response of the experimental area. The effect of reaction temperature (X_1) and catalyst concentration (X_2) is designed at three different levels, namely low, medium, and high with codes for each level (-1, 0, and +1) and tabulated in Table 1.

Table 1. Variables level of independent parameter for central composite design.

Independent Parameter	Symbol		Range and Level		
	Uncoded	Coded	-1	0	+1
Temperature (°C)	X_1	X_1	90	105	120
Catalyst Concemtration (%)	X_2	X_2	1	3	5

2.3. Deep eutectic solvent (DES) synthesis. The synthesis of deep eutectic solvent (DES) was carried out by combining a hydrogen bond acceptor (ChCl) and a hydrogen bond donor ($C_2H_2O_4$) in a 1:1 molar ratio [5]. The mixture was heated at 60 °C until a clear homogeneous liquid is formed. The mixture was stored in the desiccator.

2.4. Glucose hydrolysis. Glucose solution, 4% was mixed with 2.5 mL DES and varied catalyst concentrations according to the experimental design in Design Expert. The mixture was heated in a Scott bottle and connected to a Liebig condenser. The hydrolysis process was conducted for 90 minutes at 300 rpm, with the temperature varied according to the Design Expert V.13.

Table 2. DES characteristics.

Measurement	Result	Theoretical Range	Reference
pH	0.47	0.057-1.278	[12]
Viscosity	3.37 (mPa.s)	126.1 (mPa.S)	[13]
Density	1.0872 (g/cm³)	1280 (g/cm³)	[13]

3. RESULT AND DISCUSSION

3.1. Deep eutectic solvent (DES) characteristics. Deep eutectic solvent (DES) is used as a substitute for ionic liquids (ILs). The DES used has a dual role as a solvent and catalyst as can be seen in Table 2. The pH test result is 0.47, indicating highly acidic conditions. This is in accordance with the research of Skulcova et al. (2018), which states that DES ChCl: Oxa has a pH range of 0.057-1.278 at a temperature range of 23-60°C [12]. The results of research conducted by Hermanto et al. (2023) state that the more acidic a solution is, the faster the chemical reaction is, so that the addition of DES can increase the yield of 5-HMF, which is the reaction pathway in converting into levulinic acid compounds. The addition of DES in the glucose dehydration process accelerates the conversion of glucose into HMF. Dehydration of 5-HMF with

DES solvent has a higher yield than without DES [6].

Based on Skulcova et al. (2017), DES formed from ChCl-Oxa with a molar ratio of 1:1 has a high density and viscosity [13]. However, Hermanto et al. (2023) explained that higher DES viscosity and density result in lower 5-HMF yields. Mass transfer is hampered by the extensive hydrogen bonds in DES, which can cause lower yields [6]. This statement is also in line with the results of Li et al. (2009), who found that the addition of water from 0% to 40% of the fructose dehydration process with DES increased the yield of 5-HMF from 72.1% to 87.9%. Therefore, the addition of water to the DES synthesis process is very important to reduce the viscosity and density of DES. This also shows that DES has a promising tolerance to high water concentrations.

3.2. Influence of temperature and catalyst concentration on glucose conversion. The reaction mechanism showed that the isomerization of glucose to fructose. In DES medium condition, glucose is isomerized to fructose through ionic interaction with DES and catalyzed by $AlCl_3$. Fructose then undergoes a dehydration reaction, producing hydroxymethylfurfural (HMF). HMF is then converted into levulinic acid formate and acid through a rehydration reaction. To determine the products formed in the reaction, the samples were analyzed using Fourier-transform infrared spectroscopy (FTIR). The IR spectrum of the first run sample with operating conditions of 120°C and 1% $AlCl_3$ catalyst as displayed in Figure 1, showed a broad absorption band at 3350 cm^{-1} and 3346 cm^{-1} indicating the presence of O-H hydrogen bonds. The peak below 3000 indicates the presence of C-H bonds. The presence of a broad and sharp peak at 1717 cm^{-1} in the sample shows similarity to the 5000 ppm levulinic acid standard which has a broad and sharp peak at 1634 cm^{-1}. This responds to the presence of the C=O functional group in the molecule. The double bond region in the range of 1750-1700 cm^{-1} describes simple carbonyl compounds such as ketones, aldehydes, esters, or carboxyls [9]. From this spectrogram, we found that levulinic acid might generated from the DES rehydration glucose process.

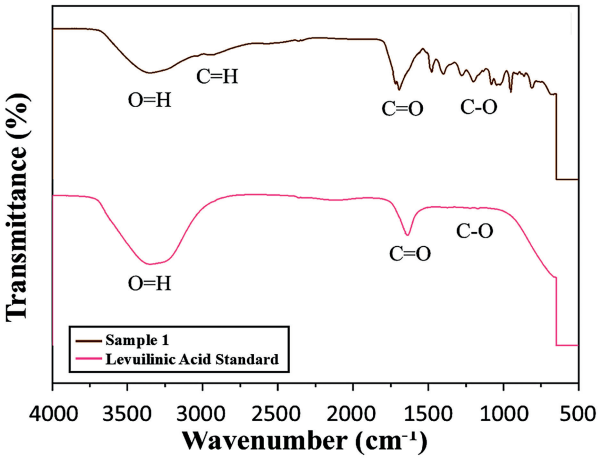

Figure 1. Fourier-transform infrared spectra (FT-IR) of run 1 test results compare to Levulinic acid standard.

The selection of the temperature range and catalyst concentration was based on our previous study where it had been carried out with hydrolyzate of *Acacia crassicarpa* wood with an HCl catalyst. The glucose conversion of *Acacia crassicarpa* hydrolyzate with DES shows in Figure 2. It shows that high conversion occurred at 105°C which later chosen as the middle temperature for the experimental design.

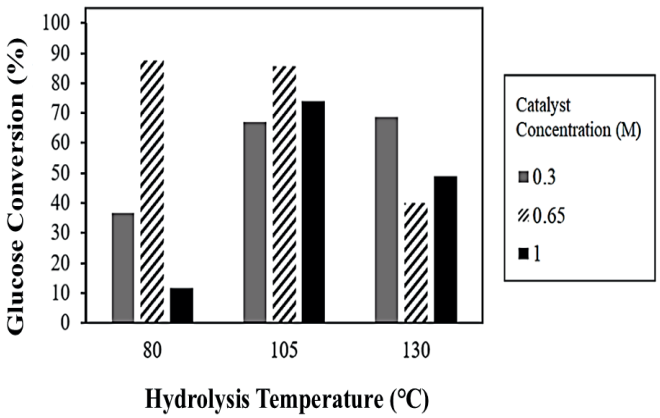

Figure 2. Results for converted glucose content from the hydrolysis process of *Acacia crassicarpa* hydrolysate.

Based on Figure 2, it can be observed that temperature significantly affects glucose conversion. Raising the temperature from 80°C to 105°C, results in higher glucose conversion. However, when the temperature reached 130°C, the rate of glucose conversion gradually dropped. Based on Hak (2022), the degradation of DES's activities, causing the DES properties less than ideal. As a result, operating conditions for hydrolysis that were below 130°C were selected.

The response surface analysis of glucose conversion is presented in Table 3, with a total of 13 experimental runs analyzed using the design tool.

Table 3. Run experimental by Design Expert V.13.

Std	Run	Factor 1 X_1:Temp °C	Factor 2 X_2:Catalyst Con. %	Respone Glucose Conversrsion %
2	1	120	1	97.53
4	2	120	3	96.80
10	3	105	2	97.87
6	4	126.213	2	99.82
1	5	90	1	97.52
11	6	105	2	90.55
9	7	105	2	99.05
5	8	83.787	2	47.80
8	9	105	3.41421	71.07
12	10	105	2	84.71
7	11	105	0.58578	70.26
3	12	90	3	40.64
13	13	105	2	97.07

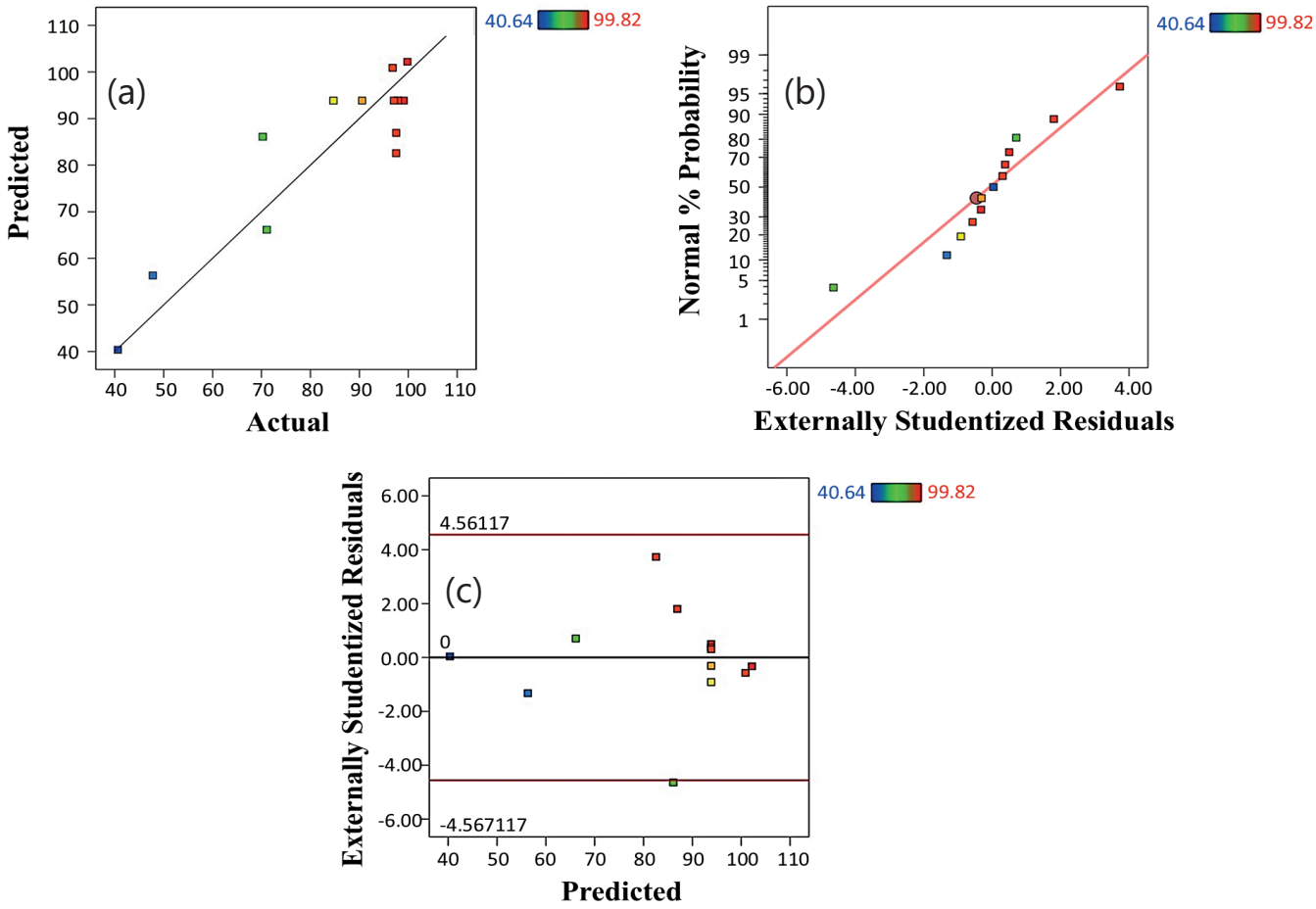

Figure 3. Model graph of: (a) predicted versus actual for glucose conversion, (b) normal probability plots of residuals glucose conversion, and (c) residuals versus predicted response glucose conversion.

The results of converted glucose measurements obtained using a UV-Vis spectrophotometer were input as Y_1 response data in the Design Expert V.13 application, utilizing a Central Composite Design (CCD) and a quadratic model. The CCD with 3-level 2-factor is used to analyze interactions or relationships between responses and variables. The glucose conversion result (Y_1) is the response to the variables tested in code units, namely reaction temperature (X_1) and catalyst concentration (X_2). The second-order polynomial model for glucose conversion results is in equation (1). Y_1 present glucose conversion response (%), X_1 present reaction temperature, and X_2 present catalyst concentration.

$$Y_1 = 93.84 + 16.22X_1 - 7.06\,X_2 + 14.04\,X_1X_2 - 7.30\,X_12 - 8.87\,X_2^2 \quad (1)$$

These models have shown adequacy between observed and predicted results where the coefficient of determination (R^2) for glucose conversion results is close to 1. The R^2 value is 0.8277 as shown in Figure 3. These results indicate that 82.77% of the response variability can be explained by the model, while the remaining 17.23% cannot be explained, possibly due to noise or other variables not observed in this study. The effect of reaction temperature and catalyst concentration on glucose conversion can be seen from the p-value of the Analysis of Variation (ANOVA) results. Table 4 displays the result of the analysis of variance (ANOVA), which indicated that quadratic models are suitable for analysing experimental data.

Based on the results of the ANOVA analysis, the p-value showed the significance of the magnitude of the variable's influence. A p-value below 0.05, indicates that the reaction temperature variable (X_1) and the interaction between reaction temperature and catalyst concentration (X_1X_2) have a significant influence on the glucose conversion process. A p-value above 0.1000 indicates that the model provisions are not significant. The F-value of the model is 6.73 and ANOVA (6.726) which higher than F table (3.97), indicating that the model is significant (see Table 4 and 5). There is only a 1.33% chance that an F value of this size could occur due to noise. The lack of fit test F-value of 6.36 can occur due to noise with a probability of 5.29%.

The significance of each coefficient is determined by using a Pareto graph from the Minitab Statistics 21 application as shown in Figure 4. It can be seen that the linear coefficient of the interaction coefficient between X_1 and X_2 also has a significant effect with a P-value <0.05 compared to other variables in glucose conversion. The coefficient results are convincing and are at the 99% significance level by rejecting the null hypothesis at the 1% significance level. The pareto graph shows that the reaction temperature is the most significant factor that can influence the glucose conversion yield (see Figure 4).

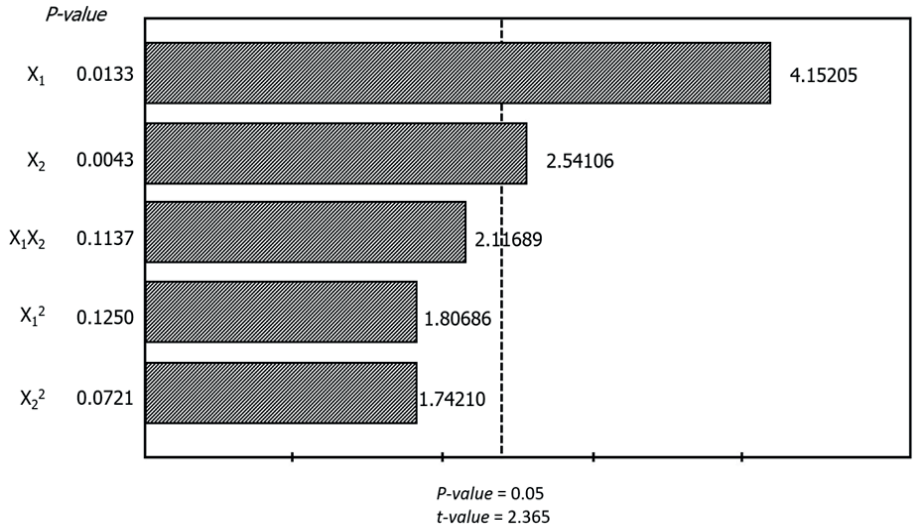

Figure 4. Pareto chart of glucose conversion.

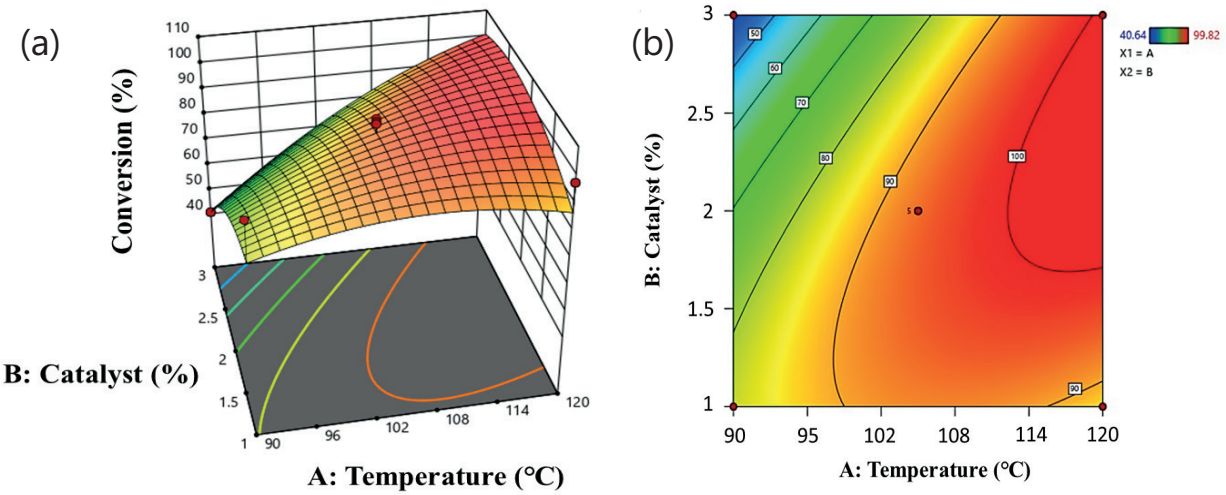

Figure 5. 3D (a) and 2D (b) surface interaction plots for glucose conversion.

Table 4. Variance analysis for glucose conversion characteristics.

Source	Sum of Squares	df	Mean Square	F-value	P-value	
Model	4105.07	5	821.01	6.73	0.0133	significant
X_1-Temperature	2104.43	1	2104.43	17.24	0.0043	
X_1-Catalyst Concentration	398.53	1	398.53	3.26	0.1137	
X_1X_2	788.21	1	788.21	6.46	0.0386	
X_1^2	370.47	1	370.47	3.03	0.1250	
X_2^2	547.02	1	547.02	4.48	0.0721	
Residual	854.49	7	122.07			
Lack of fit	706.50	3	235.50	6.36	0.0529	
Pure error	148.00	4	37.00			
Cor total	4959.57	12				
R^2	0.8277					
Adjusted R^2	0.7046					

Table 5. Regression analysis (ANOVA).

Source	Sum of Square	df	Mean Square	F-value	$F_{0.05}$
Regression (SSR)	4104.98	5	820.996	6.726	>3.97
Residual	854.49	7	122.07		
Total (SST)	4959.57	12			

Figure 5 shows the 2D and 3D response surface plots for the interaction between two factors. Interaction effects among the variables are considered occurred within a range. The quadratic effect of temperature and reaction time on glucose conversion was observed. The glucose conversion data showed that reaction temperature and reaction time had a quadratic effect on the response. The conversion of glucose rose linearly as the reaction temperature rose. Figure 5(a) shows that enhance the temperature might increase the glucose conversion. As can be seen in the Figure 5(b) where the red area shows high temperature and significant variable for glucose conversion. However, higher catalyst concentrations result in decreased glucose conversion, as observed in the data. The excess is no longer required once the level of catalyst meets the needs of the reaction. Excess catalyst has little effect on the reaction taking place [5]. The main product of this reaction is levulinic acid. The reaction runs optimally from the Design Expert data processing at a temperature of 112.869°C with a catalyst concentration of 1.913%. The conversion of glucose reaches up to 93.844% under these conditions.

4. CONCLUSION

Highly Deep eutectic solvent (DES) was successfully synthesized using ChCl and oxalic acid with a pH of 0.47, a density of 1.0872 g/m^2, and a viscosity of 3.37 mPa.s. The results from RSM using the CCD method indicate that the temperature variable significantly affects glucose conversion and levulinic acid yield. However, the concentration of the catalyst $AlCl_3$ does not have a significant effect on the formation of levulinic acid yield.

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CREDIT AUTHOR STATEMENT

Syelvia Putri Utami: Supervision, Conceptualization, Methodology, Writing-Reviewing and Editing. **Rizki Falah Romaito:** Investigation, Data curation, Formal analysis, Writing-Original draft preparation. **Dini Wulandari:** Investigation, Visualization, Data curation, Formal analysis. **Yelmida Aziz:** Data curation, Writing-Reviewing and Editing.

DECLARATIONS

Conflict of 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.

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