

Friedel-Crafts sulfonylation catalyzed by chloroaluminate ionic liquid immobilized on magnetic nanoparticles: Optimization by response surface methodology

Lan N. T. Nguyen¹, Ngan T. T. Luu¹, Huy H. Le¹, Ha T. T. Phan², Viet B. Nguyen¹,

& Thi X. T. Luu²

¹Faculty of Chemical Engineering and Food Technology, Nong Lam University, Ho Chi Minh City, Vietnam

²Faculty of Chemistry, University of Science, Vietnam National University of Ho Chi Minh City, Ho Chi Minh City, Vietnam

ARTICLE INFO

Research Paper

Received: May 16, 2022

Revised: June 16, 2022

Accepted: July 11, 2022

Keywords

Ionic liquid

Magnetic nanoparticles

Response surface methodology

Sulfone

Sulfonylation

*Corresponding author

Nguyen Thi Ngoc Lan

Email:

ntngoclan@hcmuaf.edu.vn

ABSTRACT

This study focused on optimizing the Friedel-Crafts sulfonylation reaction between 1,3-dimethoxybenzene and p-toluenesulfonic anhydride using chloroaluminate ionic liquid immobilized on magnetic nanoparticles as the catalyst. Various reaction conditions including the ratio between reagents (0.9:1.0 - 1.1:1.0), the catalyst amount (0.1 - 0.3 g), reaction temperature (100 - 120°C), and time (1 - 3 h) were optimized using response surface methodology based on a central composite design model. The results showed that the optimal reaction conditions were achieved at 115°C for 2.3 h, using 0.24 g of catalyst with a reagent ratio of 1.0:1.0, resulting in the highest sulfones yield of 82%.

Cited as: Nguyen, L. N. T., Luu, N. T., Le, H. H., Phan, H. T. T., Nguyen, V. B., & Luu, T. X. T. (2023). Friedel-Crafts sulfonylation catalyzed by chloroaluminate ionic liquid immobilized on magnetic nanoparticles: Optimization by response surface methodology. *The Journal of Agriculture and Development* 22(6), 78-91.

1. Introduction

Sulfones are organosulfur compounds with structural formula $R-S(O)_2-R'$, where R and R' are organic groups. Under different reaction conditions, the carbon bearing sulfonyl group can be converted to a cation, an anion or a radical (Trost & Kalnmals, 2019). Therefore, sulfones were used as intermediates in many organic synthesis processes (Leusen et al., 1977; Swenson et al., 2002; Li & Corey, 2005). Among them, aryl sulfones have wide applications such as agrochemicals (Michaely et al., 1988), polymers (Robello et al., 1993; MacKinnon & Wang, 1998). For aryl sulfones preparation, Friedel-Crafts sulfonylation is one of the most common methods (Figure 1). The electrophilic substitution reaction of arenes and sulfonylating reagents is catalysed by various Lewis acid such as metal salts (Marquié et al., 2001; Fleck et al., 2006), metals with or without solvent (Bandgar & Kasture, 2001; Jang et al., 2006), solid acids (Choudary et al., 2000), ionic liquids (Nara et al., 2001; Bahrami et al., 2008). Although aryl sulfones can be obtained with moderate to high yield (50 - 90%), the catalysts are difficult to recover and reuse.

With the development of green chemistry, various alternative methods were introduced for chemical processes. Recent studies mainly focused on applying eco-friendly catalysts for organic syntheses. For example, our group successfully synthesized chloroaluminate ionic liquid immobilized on magnetic nanoparticles and then applying this catalyst for Friedel-Crafts sulfonylation (Nguyen et al., 2022). The material overcomes the disadvantages of homogeneous and heterogeneous catalysts in terms of dispersion, reuse and can be recovered easily after the reaction by external magnets.

As most organic synthesis reactions, the yield of Friedel-Crafts sulfonylation also strongly depends on the reaction conditions such as the molar ratio, the time, temperature of reaction and of course, the amount of catalyst. These factors are often correlated with each other, so it is necessary to investigate their interaction effects. Response surface methodology (RSM) is a useful statistical tool which is widely applied for optimization in many fields such as extraction (Zhang et al., 2018; Yu et al., 2019; Andres et al., 2020), organic synthesis (Hamsaveni et al., 2001; García-Cabeza et al., 2015; He et al.,

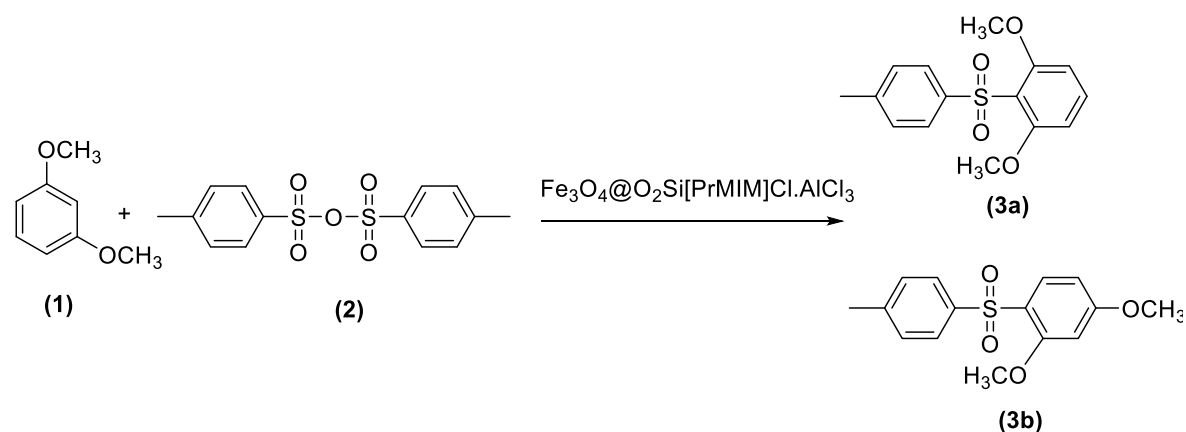


Figure 1. The Friedel-Crafts sulfonylation between 1,3-dimethoxybenzene and p-toluenesulfonyl chloride catalyzed by $\text{Fe}_3\text{O}_4@O_2\text{Si}[\text{PrMIM}]\text{Cl}\cdot\text{AlCl}_3$.

2017), nanomaterial synthesis (Perez et al., 2017; Abdulhameed et al., 2019; Sarsfield et al., 2021). This study, therefore, aimed to apply RSM to optimize a Friedel-Crafts sulfonylation between 1,3-dimethoxybenzene and p-toluenesulfonic anhydride using chloroaluminate ionic liquid immobilized on magnetic nanoparticles as the catalyst.

2. Materials and Methods

2.1. Materials

1,3-dimethoxybenzene, 1-methylimidazole, (3-chloropropyl) trimethoxysilane, anhydrous aluminum chloride were purchased from Sigma-Aldrich (Germany) while n-hexane, ethyl acetate, diethyl ether, ammonia solution, sodium sulphate, sodium hydroxide, iron (II) sulphate heptahydrate, iron (III) nitrate nonahydrate were provided by Xilong (China). Other chemical compounds including p-toluenesulfonic anhydride and ethanol absolute were from Acros (Belgium) and Prolabo (France), respectively.

2.2. Methods

2.2.1. Preparation of catalyst

Magnetic Fe_3O_4 nanoparticles (MNPs) were prepared by the modified chemical coprecipitation method (Safari & Zarnegar, 2013). Typically, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (6.0 mmol) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (12.0 mmol) were dissolved in 100 mL distilled water. Under mechanical stirring at 500 rpm, the mixture were dropped slowly into a 500 mL beaker containing 200 mL NaOH 0.25 M solution within 1 h at 80°C. The black precipitated particles were washed with distilled water (2 x 100 mL) until pH 7 and dried at 150°C for 4 h.

For $\text{Fe}_3\text{O}_4@O_2\text{Si}[\text{PrMIM}]\text{Cl} \cdot \text{AlCl}_3$, a mixture of (3-chloropropyl) trimethoxysilane (20

mmol) and 1-methylimidazole (20 mmol) in a round-bottom 25 mL flask were stirred at 80°C for 3 days. After reaction completion, the mixture of products was washed with diethyl ether (3 x 5 mL) and the solvent was removed under vacuum pressure (Safari & Zarnegar, 2013). Then, MNPs (1.0 mmol), 3-methyl-1-(3-trimethoxysilylpropyl)-1H-imidazole-3-ium chloride (2.0 mmol), absolute ethanol (5.0 mL), and 28% ammonia solution (0.2 mL) were added into a round-bottom 25 mL flask and stirred at room temperature for 24 h. After reaction completion, $\text{Fe}_3\text{O}_4@O_2\text{Si}[\text{PrMIM}]\text{Cl}$ was separated by an external magnet, washed with ethanol (2 x 5 mL) and left to dry in a desiccator. In the next step, anhydrous aluminum chloride AlCl_3 (4.0 mmol), was added slowly into a 25 mL round-bottom flask containing $\text{Fe}_3\text{O}_4@O_2\text{Si}[\text{PrMIM}]\text{Cl}$ dispersed in 5 mL of absolute ethanol. The mixture was stirred at room temperature for 12 h. Finally, the catalyst $\text{Fe}_3\text{O}_4@O_2\text{Si}[\text{PrMIM}]\text{Cl} \cdot \text{AlCl}_3$ was washed with ethanol (2 x 5 mL) and put into a desiccator overnight.

2.2.2. Typical procedure for the Friedel-Crafts sulfonylation

1,3-dimethoxybenzene, p-toluenesulfonic anhydride and catalyst were added into a 5 mL round-bottom flask assembled with the condenser. The reaction mixture was heated for a specific period of time. After completion of the reaction, the mixture of products was cooled and extracted with ethyl acetate (4 x 5 mL) and the solid catalyst was separated by using a magnetic bar. The organics were washed with water (2 x 10 mL), dried with anhydrous Na_2SO_4 and the solvent was removed using a rotary evaporator (Heidolph, Germany). Sulfones were purified by column chromatography using eluent as a mixture of n-hexane and ethyl acetate (8:2 v/v) and identified by ¹H and ¹³C NMR spectroscopy.

2.2.3. Experimental design

Four important parameters of the reaction were studied, including temperature (X_1), reaction time (X_2), amount of catalyst (X_3), and molar ratio of 1,3-dimethoxybenzene to p-toluenesulfonic anhydride (X_4). Screening experiments were conducted to evaluate the effects of each factor. The temperature was investigated in a range of 80 - 110°C while reaction time was kept from 0.5 -

2.0 h. The mixture of 1,3-dimethoxybenzene and p-toluenesulfonic anhydride were investigated at different ratios of 0.9:1.0 - 1.2:1.0 and the amount of catalyst was in a range of 0.1 - 0.2 g. Then the reaction conditions of sulfone synthesis were optimized by RSM combined with a central composite design (CCD). The range and levels of the factors used in the experiment design were list in Table 1.

Table 1. Experimental range and levels of the factors

Factors	Level		
	-1	0	+1
X_1 (Temperature/°C)	100	110	120
X_2 (Reaction time/h)	1	2	3
X_3 (Amount of catalyst/g)	0.1	0.2	0.3
X_4 (Molar ratio)	0.9:1.0	1.0:1.0	1.1:1.0

2.2.4. Analytical method

Gas chromatography system (Agilent, USA) with a capillary column (30 m x 0.25 mm x 0.25 μ M) was used for analyzing sulfone yields. The carrier gas flow rate is 21.6 mL of hydrogen/min. The GC oven temperature program was 60°C (1 min hold), 20°C/min to 300°C (10 min hold) for a total runtime of 23 min. Aryl sulfones yield and conversion were determined by the following formula:

$$\text{Yield} = \frac{m_1 \cdot b}{m_2} \times 100\%$$

$$\text{Conversion} = \frac{m_3}{m_4} \times 100\%$$

Where

m_1 : mass of the crude product after the reaction (g)

b: percent composition of the product based on the *gas chromatography/flame ionization detector analyses*

m_2 : mass of the product in theory (g)

m_3 : mass of 1,3-dimethoxybenzene after the reaction (g)

m_4 : mass of 1,3-dimethoxybenzene before the reaction (g)

2.2.5. Statistical analysis

All experiments were carried out 2 times. Optimal data were designed and analysed using a software JMP (v.14, SAS Institute, USA). The effects of reaction time, reaction temperature, the reagent ratio and the amount of catalyst were evaluated by ANOVA at 95% confident interval using a software Statgraphics Centurion (v.XVI, Statgraphics Technologies, USA).

3. Results and Discussion

3.1. Screening experiments

The effect of reaction time on the sulfone yield was depicted on the Figure 2. The conditions were fixed at the ratio of 1,3-dimethoxybenzene and *p*-toluenesulfonic anhydride as 1.0:1.0, temperature of 110°C with 0.2 g $\text{Fe}_3\text{O}_4@\text{O}_2\text{Si}$. [PrMIM]Cl. AlCl_3 as catalyst. For a chemical reaction, it takes a certain time for the substrate and reagent to react with each other, so as the

reaction time is increased from 0.5 to 2 h, the yield also increases gradually. When the reaction time increases to 2 h, the conversion reaches 100% and the yield reaches its maximum value of 83%. Therefore, 2 h was chosen as the appropriate time for the sulfonylation and fixed for further experiments.

Figure 3 shows the change of reaction yield when increasing the temperature from 80 to 110°C. The sulfonylation was carried out at ratio of 1,3-dimethoxybenzene and *p*-toluenesulfonic anhydride as 1.0:1.0 with 0.2 g of catalyst for 2 h. At 80°C, the yield of sulfone reached 41% and gradually increased, the highest reaction yield was 83% at 110°C. The possible reason was that the Friedel-Crafts sulfonylation is an endothermic reaction, so a higher temperature can make the substrate convert completely and obtain a higher yield. Then, the suitable temperature for the reaction was chosen as 110°C and fixed for next experiments.

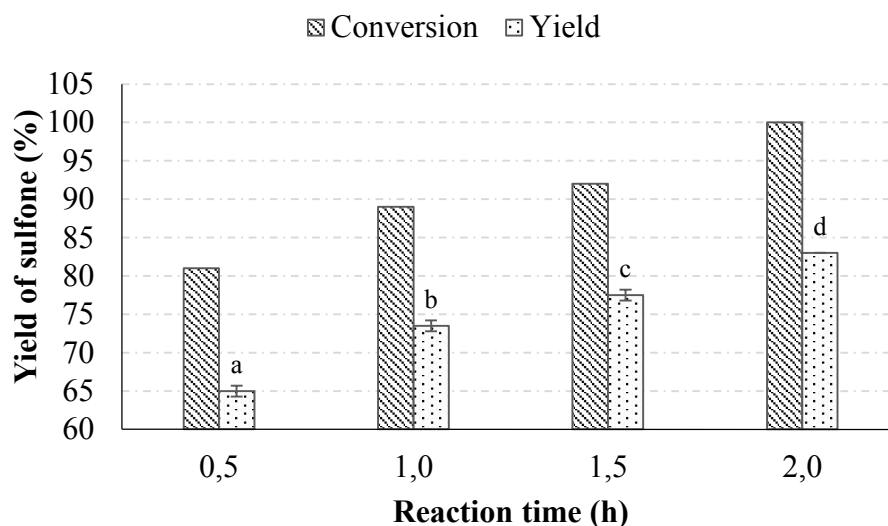


Figure 2. Effect of reaction time on the yield of sulfone. * The letters a,b,c,d represent the difference of the treatments; **Yields were calculated based on the gas chromatography/flame ionization detector analyses.

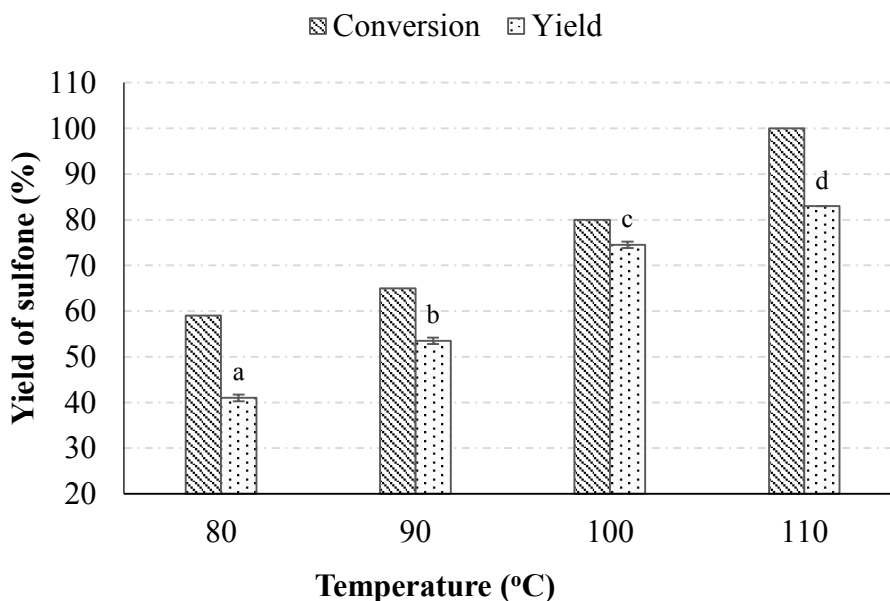


Figure 3. Effect of temperature on the yield of sulfone. *The letters a,b,c,d represent the difference of the treatments; **Yields were calculated based on the gas chromatography/flame ionization detector analyses.

To investigate the effect of catalyst amount, sulfone was synthesized at fixed ratio of 1,3-dimethoxybenzene and *p*-toluenesulfonic acid anhydride as 1.0:1.0, temperature of 110°C and reaction time of 2 h. The amount of $\text{Fe}_3\text{O}_4@ \text{O}_2\text{Si}[\text{PrMIM}]\text{Cl}.\text{AlCl}_3$ used for the reaction was investigated from 0.1 to 0.2 g. Friedel-Crafts sulfonylation is an electrophilic substitution, it requires the presence of Lewis acid as a

catalyst. That means the yield and conversion of the reaction will be higher when the catalytic amount is increased. As seen in Figure 4, when the amount of catalyst was increased to 0.2 g, sulfone was obtained with the highest yield. Therefore, the catalyst used for the following experiments is 0.2 g.

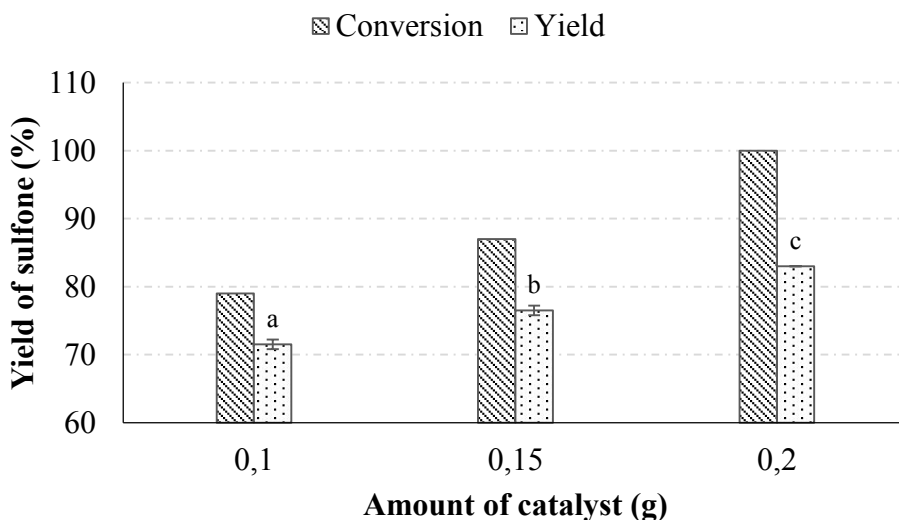


Figure 4. Effect of catalyst amount on the yield of sulfone. *The letters a,b,c represent the difference of the treatments; **Yields were calculated based on the gas chromatography/flame ionization detector analyses.

After the reaction, *p*-toluenesulfonic anhydride was converted to acid and removed in the aqueous phase. So, in order to evaluate the appropriate molar ratio of reagents, the reaction was carried out at 110°C for 2 h with 0.2 g of catalyst and the moles of 1,3-dimethoxybenzene was varied from 0.9 to 1.2 mmol. When the substrate:reagent ratio increases to 1.0:1.0, the

yield of sulfone reaches the maximum value and the reaction is converted completely. While the molarity of 1,3-dimethoxybenzene exceeds 1.0 mmol, the reduced product content leads to a decrease in sulfone yield. This shows that the suitable ratio between 1,3-dimethoxybenzene and *p*-toluenesulfonic anhydride for the reaction should be 1.0:1.0 (Figure 5).

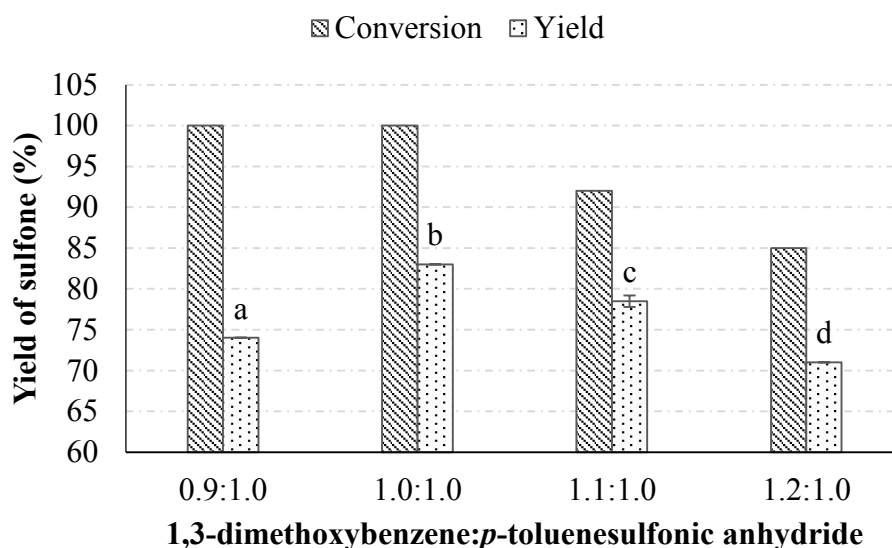


Figure 5. Effect of substrate:reagent ratio on the yield of sulfone. *The letters a,b,c,d represent the difference of the treatments; **Yields were calculated based on the gas chromatography/flame ionization detector analyses.

3.2. Optimization of reaction conditions by RSM

Based on the results of the single-factor experiments, reaction conditions including temperature (X_1), reaction time (X_2), amount of catalyst (X_3) and molar ratio (X_4) were selected as independent variables for the optimization process. The CCD design and reaction yield results are presented in Table 2.

It can be seen that the reaction yield is varied from 65 to 83%. Besides, the RSM model describing the relationship between the reaction yield and the reaction conditions was determined as follows:

$$Y = 80.5 + 1.2778X_1 + 1.1667X_2 + 2.9444X_3 + 1.3333X_4 - 1.3125X_2X_3 + 1.3125X_3X_4 - 3.6667X_3^2 - 3.1667X_4^2$$

Table 2. Design model and results of response surface experiments

Entry ^a	Temperature (°C)	Time (h)	Amount of catalyst (g)	Molar ratio ^b	Yield ^c (%)
	X ₁	X ₂	X ₃	X ₄	(3a:3b)
1	120	3	0.1	1.1:1.0	70 (10:90)
2	110	2	0.1	1.0:1.0	72 (9:91)
3	100	3	0.3	0.9:1.0	68 (17:83)
4	100	2	0.2	1.0:1.0	75 (9:91)
5	100	1	0.1	0.9:1.0	65 (11:89)
6	120	1	0.1	1.1:1.0	66 (14:86)
7	100	3	0.1	1.1:1.0	68 (11:89)
8	100	3	0.3	1.1:1.0	73 (15:85)
9	120	3	0.3	0.9:1.0	72 (14:86)
10	110	2	0.3	1.0:1.0	80 (16:84)
11	110	1	0.2	1.0:1.0	74 (9:91)
12	120	1	0.3	1.1:1.0	76 (2:98)
13	110	2	0.2	1.0:1.0	83 (17:83)
14	110	3	0.2	1.0:1.0	82 (16:84)
15	110	2	0.2	1.0:1.0	83 (15:85)
16	120	3	0.1	0.9:1.0	73 (12:88)
17	120	2	0.2	1.0:1.0	81 (13:87)
18	100	3	0.1	0.9:1.0	68 (10:90)
19	120	1	0.3	0.9:1.0	72 (8:92)
20	100	1	0.1	1.1:1.0	66 (14:86)
21	110	2	0.2	1.1:1.0	79 (13:87)
22	100	1	0.3	1.1:1.0	76 (9:91)
23	120	3	0.3	1.1:1.0	78 (9:91)
24	120	1	0.1	0.9:1.0	65 (9:91)
25	100	1	0.3	0.9:1.0	71 (2:98)
26	110	2	0.2	0.9:1.0	74 (15:85)

^a Experiments are conducted at random. ^b 1,3-dimethoxybenzene : *p*-toluenesulfonic anhydride.

^c Yields were calculated based on the GC/FID analyses.

The analysis results show that the regression model has R² value of 0.93 with *P-value* is less than 5%. Therefore, this RSM model is appropriate to predict the reaction yield for the Friedel-Crafts sulfonylation reaction between 1,3-dimethoxybenzene and p-toluenesulfonic anhydride using chloroaluminate ionic liquid immobilized on magnetic nanoparticles as the catalyst.

According to the effect summary results (Table 3), it can be seen that the reaction yield is influenced by the linear effects of all 4 factors: temperature (X_1), reaction time (X_2), amount of catalyst (X_3), molar ratio (X_4); the quadratic effects of X_3 , X_4 and the interaction effects

between X_2 and X_3 , X_3 and X_4 . The influence of these factors on the reaction yield is depicted by three-dimensional surface response and 2D contour plots in Figure 6 with the red area representing the highest yield, while the blue area representing the lower results. The reaction yield began to increase to the central value, and then tend to decrease or approach the horizontal line with increasing reaction time, temperature, catalyst amount and molarity of 1,3-dimethoxybenzene. In which, the amount of catalyst (X_3) is the most influential factor. Besides, the isomer selectivity between para and ortho does not change significantly when investigating the influence of four factors.

Table 3. Coefficients in the regression equation

Sources	Variables	Coefficient value	<i>P-value</i>	
	Constant	80.5	<0.0001	Significant
Linear effects	X_1	1.2778	0.0322	Significant
	X_2	1.1667	0.0469	Significant
	X_3	2.9444	0.0001	Significant
	X_4	1.3333	0.0267	Significant
Quadratic effects	X_1^2	-1.6667	0.2533	
	X_2^2	-1.6667	0.2533	
	X_3^2	-3.6667	0.0225	Significant
	X_4^2	-3.1667	0.0427	Significant
Interaction effects	X_1X_2	0.9375	0.1182	
	X_1X_3	0.1875	0.7410	
	X_2X_3	-1.3125	0.0370	Significant
	X_1X_4	-0.1875	0.7410	
	X_2X_4	-0.1875	0.7410	
	X_3X_4	1.3125	0.0370	Significant

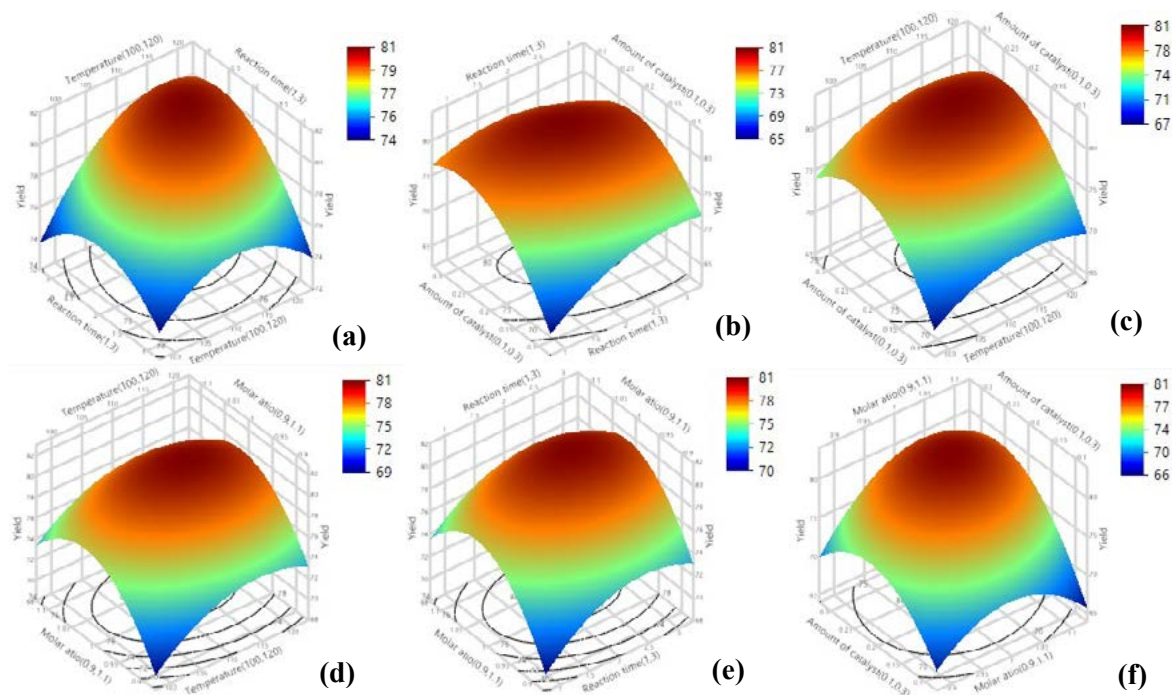


Figure 6. Response surface (3D) show the effect of the temperature and reaction time (a), reaction time and amount of catalyst (b), temperature and amount of catalyst (c), temperature and molar ratio (d), reaction time and molar ratio (e), amount of catalyst and molar ratio (f) on the reaction yield.

Numerical optimization was performed to predict the reaction yield and the profile was summarized in Figure 7. The optimal conditions for Friedel-Crafts sulfonylation are the temperature 115°C, the reaction time 2.3 h, the catalyst amount 0.24 g and the molar ratio 1.0:1.0. The predicted yield under the optimal conditions is 82%. To evaluate the compatibility of the results obtained from the regression equation by RSM with the experiment, the sulfonylation was carried out at the selected optimal conditions. Compared with the model results, the actual yield obtained from verification experiment is $81 \pm 0.7\%$. With an error of less than 5%, that means the measured yield is suitable for the predicted value of the quadratic regression equation.

4. Conclusions

This study applied response surface methodology combined with CCD to investigate the effect of reaction temperature, reaction time, amount of catalyst, molar ratio on the yield of Friedel-Crafts sulfonylation between 1,3-dimethoxybenzene and p-toluenesulfonic anhydride using chloroaluminate ionic liquid immobilized on magnetic nanoparticles as the catalyst. The results showed that all investigated factors have significant effects on the sulfone yield and the predicted optimal values for this reaction are determined as follows: temperature 115°C, reaction time 2.3 h, amount of catalyst 0.24 g and ratio of 1,3-dimethoxybenzene and p-toluenesulfonic anhydride 1.0:1.0. At the

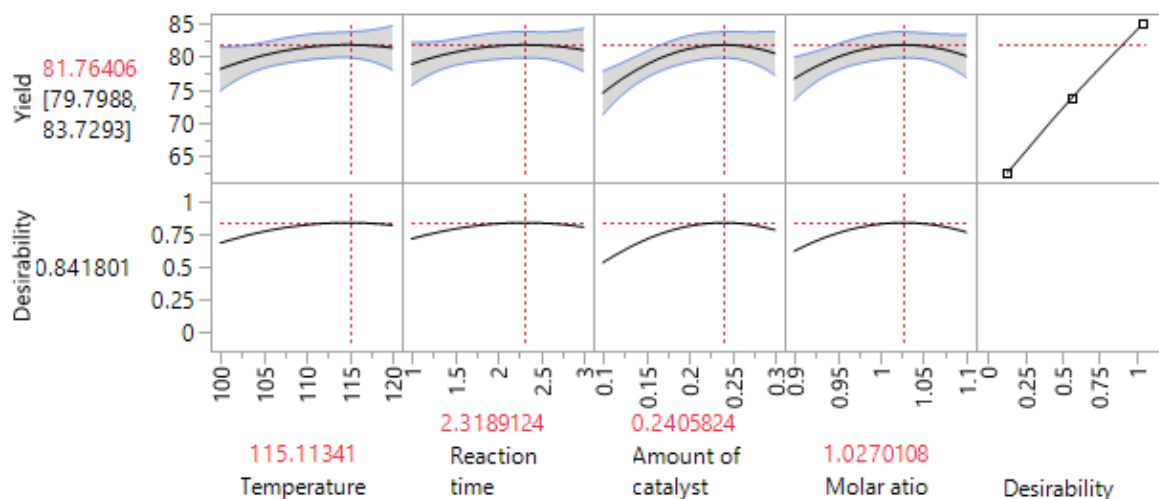


Figure 7. Optimal condition prediction model.

optimal reaction conditions, the reaction yield of the Friedel-Crafts sulfonylation could achieve 82%.

Conflict of interest

The authors declare no conflict of interest.

Acknowledgements

The authors would like to thank Nong Lam University, Ho Chi Minh City for sponsoring our research (project number: CS-CB21-CNHH-02).

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