

Optimization of Process Variables in the Synthesis of Isoamyl Isovalerate Using Sulfonated Organic Heteropolyacid Salts as Catalysts

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Based on single factor experiments, a three level, four variable central composite designs were carried out to establish a quadratic regression model for the catalytic synthesis of isoamyl isovalerate over sulfonated organic heteropolyacid salts as a function of molar ratio of alcohol to acid, reaction time, the amount of water-carrying agent and the amount of catalyst. The optimum conditions were obtained as follows: n (isoamyl alcohol) : n (isovaleric acid) = 1.1:1, amount of catalyst was 6.4% of acid, reaction time 2 h and water-carrying agent 10 mL. Under these conditions, the yield of isoamyl isovalerate reached 97.5%. The ionic liquid could be reused six times without noticeable drop in activity. Under optimum conditions, catalysts showed a superior catalytic efficiency and reusability due to better superacidity, lower molecular transport resistance and self-separation characteristics.

Keywords: heteropolyacids, ionic liquid, esterification, isoamyl isovalerate, response surface methodology

Introduction

Esters from esterification are widely used in chemical industries as important intermediates, and also as important components of many spices.¹ Various mineral acids, such as H₂SO₄, HCl and H₃PO₄, have been used as catalysts for esterification. Heterogeneous acidic catalysts, heteropoly acids,²⁻⁵ super solid acid (SO₄²⁻/ZrO₂, SO₄²⁻/SnO₂, etc.),⁶⁻⁹ acid ion exchange resin^{10,11} and metal phosphate,¹² have also been carried out on the esterification of carboxylic acids. However, these acidic catalytic processes have been proposed and major drawbacks associated with product selectivity, recycling of spent catalysts and environmental safety and disposal remain to be solved.^{13,14}

Heteropolyacid catalysts (HPA) have been used in a wide range of acid-catalyzed reactions due to their bis-function characteristics of strong Brønsted acidity and oxidizing catalytic properties.¹⁵⁻¹⁸ The increasing interest for their investigations is mainly due to their desirable properties, such as high activity, good selectivity and mild

reaction conditions. However, despite of their strong acidic characteristics, HPAs have one or more problems related to inferior solubility in polar solvents, small surface area and catalyst recyclability, which limit the further applications. Consequently, studies regarding the improvement of their drawbacks have been developed by modified catalysts such as Brønsted acid functionalized ionic liquid (IL) catalysts.¹⁹⁻²⁴ In many studies, improvements in catalytic performance of these catalysts were achieved by enhancing acid properties to increase surface area and modify the structure of catalysts.²⁵

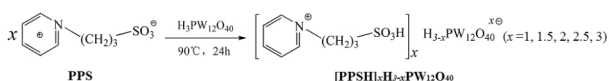
In this study, a series of single factor experiments were performed to examine the supported heteropolyacid ionic liquids for the esterification of isoamyl alcohol with isovaleric acid. And the effects of alcohol/acid molar ratio, reaction time, the amount of water-carrying agent and the amount of catalyst were studied. Furthermore, response surface methodology (RSM), an efficiently statistical technique, was applied to determine the optimum operating conditions with minimum number of experiments.²⁶⁻²⁹

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Experimental

Catalyst preparation and characterization

The organic tungstophosphoric acid (TPA) catalysts were prepared and characterized by infrared (IR), nuclear magnetic resonance (NMR), thermogravimetry (TG) and acidity determination in the laboratory following the procedure outlined in the literature.^{30,31} All the chemicals were research grade and were used without further purification unless otherwise stated. The catalysts were abbreviated as $[\text{PPSH}]_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$; $x = 1.0\text{-}3.0$, PPS = pyridinium propyl sulfobetaine. The formation of $[\text{PPSH}]_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ reaction undergoes based on the following reaction:



Activity testing

Isovaleric acid, isoamyl alcohol and catalysts were placed in a 100 mL three-necked flask equipped with a reflux condenser, a funnel and a magnetic stirrer. The mixture was stirred at a desired temperature and time in an oil bath. Upon completion, the reaction mixture was cooled to room temperature. Owing to the self-separation characteristic of the reaction system, the IL catalysts would easily be separated and remain in the lower layer as colloidal phase. After filtration, the lower layer consisting of IL catalysts was dried under vacuum overnight for reuse after being washed with diethyl ether three times and the upper layer was distilled to get isoamyl isovalerate. Chemical analysis of the products was performed by gas chromatography Agilent 6890N GC, equipped with a flame ionization detector (FID) and HP-5 capillary column. Reactants and products were identified by comparison with authentic samples. Methyl laurate was used as internal standard. The yield was determined by the weight of isoamyl isovalerate distilled at a specific temperature range of ca. 190-193 °C from the products.

Experimental design and mathematical model

RSM was a collection of mathematical and statistical techniques that was utilized to design experiments, build models and analyze the effects of the several independent variables. RSM was an effective tool to study the individual and interactive effects of these factors in order to find the target value.^{26,27} The Box-Behnken experimental design was chosen to study the combined effects of reaction

time, alcohol/acid mole ratio, amount of water-carrying agent and amount of catalyst on the yield of isoamyl isovalerate by RSM. The experimental design was carried out by four chosen independent process variables at four levels including reaction time (x_1), alcohol/acid mole ratio (x_2), amount of water-carrying agent (x_3) and amount of catalyst (x_4) shown in Table 1. A 3⁴ full-factorial Box-Behnken experimental design with coded levels was used, leading to a total of 29 experimental sets, which included 24 factorial points and 5 centering points. Four variables were designed at levels by associated plus signs (+1) with high levels, zero (0) indicating center value and minus signs (-1) with low levels. The coded values of these factors were obtained according to equation 1 as follows:

$$x_i = \frac{X_i - X_0}{\Delta X_i} \quad (1)$$

where x_i was the independent variable coded value, X_i was the independent variable real value, X_0 was the independent variable real value at the center point, and ΔX_i was (variable at high level-variable at low level)/2. The independent variables and their levels, real values are presented in Table 1.

The second-order model was performed to predict the optimum value and correlate the response variable to the independent variable. The quadratic equation model was described according to equation 2:

$$Y = \beta_0 + \sum_{i=1}^4 \beta_{ii} X_i^2 + \sum_{i=1}^4 \beta_{ii} X_i^2 + \sum_{i < j=1}^4 \beta_{ij} X_i X_j \quad (2)$$

where Y was the predicted response, x_i and x_j were the coded levels of the independent variables, β_0 was the center point of the system, β_i , β_{ii} , β_{ij} were the linear terms, the squared terms for the variable i , and the interaction terms between variables i and j , respectively.

Results and Discussion

Comparison of activity of organic TPA salts catalysts

It is known that esterification rates are influenced by many factors in catalytic esterification reactions. Catalytic properties of TPA with different composition ratios of propane sulfonated IL have been examined, and the results are listed in Table 2 (entry 1-6). From Table 2, we could find that $[\text{PPSH}]_{1.5}\text{H}_{1.5}\text{PW}_{12}\text{O}_{40}$ catalyst showed the best catalytic activity with 95.6% of isoamyl isovalerate. In our previous research,³¹ we found that $[\text{PPSH}]_{2.0}\text{HPW}_{12}\text{O}_{40}$ catalyst showed best catalytic activity

Table 1. Parameter levels and coded values in the experimental design

Factor	Symbol	Range and level		
		-1	0	1
Reaction time / h	x_1	1	1.5	2
Alcohol/acid mole ratio	x_2	1.05	1.1	1.15
Amount of water-carrying agent / mL	x_3	7.5	10	12.5
Amount of catalyst / wt. %	x_4	5	6	7

Table 2. The yield of isoamyl isovalerate by esterification of isoamyl alcohol with isovaleric acid over $[\text{PPSH}]_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ under different conditions

entry	Catalyst	Amount of catalyst / wt. %	Alcohol/acid molar ratio	Reaction time / h	Amonut of water-carrying agent / mL	Yield of isoamyl isovalerate / %
1	$\text{H}_{3,0}\text{PW}_{12}\text{O}_{40}$	6	1.1:1	1.5	10	91.9
2	$[\text{PPSH}]_{2,0}\text{H}_{2,0}\text{PW}_{12}\text{O}_{40}$	6	1.1:1	1.5	10	90.2
3	$[\text{PPSH}]_{1,5}\text{H}_{1,5}\text{PW}_{12}\text{O}_{40}$	6	1.1:1	1.5	10	95.6
4	$[\text{PPSH}]_{2,0}\text{HPW}_{12}\text{O}_{40}$	6	1.1:1	1.5	10	88.7
5	$[\text{PPSH}]_{2,5}\text{H}_{0,5}\text{PW}_{12}\text{O}_{40}$	6	1.1:1	1.5	10	70.9
6	$[\text{PPSH}]_{3,0}\text{PW}_{12}\text{O}_{40}$	6	1.1:1	1.5	10	66.1
7	$[\text{PPSH}]_{1,5}\text{H}_{1,5}\text{PW}_{12}\text{O}_{40}$	4	1.1:1	1.5	10	70.7
8	$[\text{PPSH}]_{1,5}\text{H}_{1,5}\text{PW}_{12}\text{O}_{40}$	5	1.1:1	1.5	10	81.3
9	$[\text{PPSH}]_{1,5}\text{H}_{1,5}\text{PW}_{12}\text{O}_{40}$	7	1.1:1	1.5	10	91.5
10	$[\text{PPSH}]_{1,5}\text{H}_{1,5}\text{PW}_{12}\text{O}_{40}$	8	1.1:1	1.5	10	91.1
11	$[\text{PPSH}]_{1,5}\text{H}_{1,5}\text{PW}_{12}\text{O}_{40}$	6	1.0:1	1.5	10	86.6
12	$[\text{PPSH}]_{1,5}\text{H}_{1,5}\text{PW}_{12}\text{O}_{40}$	6	1.05:1	1.5	10	89.8
13	$[\text{PPSH}]_{1,5}\text{H}_{1,5}\text{PW}_{12}\text{O}_{40}$	6	1.15:1	1.5	10	94.8
14	$[\text{PPSH}]_{1,5}\text{H}_{1,5}\text{PW}_{12}\text{O}_{40}$	6	1.2:1	1.5	10	95.0
15	$[\text{PPSH}]_{1,5}\text{H}_{1,5}\text{PW}_{12}\text{O}_{40}$	6	1.25:1	1.5	10	91.0
16	$[\text{PPSH}]_{1,5}\text{H}_{1,5}\text{PW}_{12}\text{O}_{40}$	6	1.1:1	0.5	10	67.5
17	$[\text{PPSH}]_{1,5}\text{H}_{1,5}\text{PW}_{12}\text{O}_{40}$	6	1.1:1	1.0	10	92.4
18	$[\text{PPSH}]_{1,5}\text{H}_{1,5}\text{PW}_{12}\text{O}_{40}$	6	1.1:1	2.0	10	93.7
19	$[\text{PPSH}]_{1,5}\text{H}_{1,5}\text{PW}_{12}\text{O}_{40}$	6	1.1:1	1.5	5	91.3
20	$[\text{PPSH}]_{1,5}\text{H}_{1,5}\text{PW}_{12}\text{O}_{40}$	6	1.1:1	1.5	7.5	92.1
21	$[\text{PPSH}]_{1,5}\text{H}_{1,5}\text{PW}_{12}\text{O}_{40}$	6	1.1:1	1.5	12.5	89.1
22	$[\text{PPSH}]_{1,5}\text{H}_{1,5}\text{PW}_{12}\text{O}_{40}$	6	1.1:1	1.5	15	78.3

on the preparation of benzaldehyde glycol acetal. In this study, $[\text{PPSH}]_{1,5}\text{H}_{1,5}\text{PW}_{12}\text{O}_{40}$ catalysts showed a superior catalytic efficiency. The reason is that the size of isoamyl alcohol is larger than glycol's in the system. Therefore, isoamyl alcohol molecule could hardly transfer and form active carbenium intermediates, which inhibited catalytic activity of the sample on the esterification. Meanwhile, more PPS of catalyst also inhibited the molecular transport. Therefore, $[\text{PPSH}]_{1,5}\text{H}_{1,5}\text{PW}_{12}\text{O}_{40}$ catalysts showed good catalytic activity due to better superacidity and lower molecular transport resistance. It is noteworthy that

$[\text{PPSH}]_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ catalysts tend to dissolve completely in reaction medium and form a homogeneous system during the initial stage of the reaction. However, the system gradually became turbid milky at prolonged reaction time and the $[\text{PPSH}]_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ catalysts eventually precipitated upon completion of esterification reaction. "Self-separation" characteristics of the catalytic system induces high catalytic activity and readily facilitates separation of products as well as recovery and recycling of catalysts.^{21,32} Esterification is a typical acid-catalyzed reaction. Detailed investigations to optimize various reaction parameters were conducted using

[PPSH]_{1.5}H_{1.5}PW₁₂O₄₀ as catalyst since it was also less toxic and cost effective besides showing high product selectivity.

Optimization of reaction conditions

Catalyst dosage plays a very important role during the esterification reaction. Finding the optimum catalyst dosage has the priority among all reaction parameters due to its high effectiveness to the whole process. Optimum catalyst dosage also can provide enough active moieties for the esterification reaction. Since esterification is a reversible reaction, it is prerequisite to operate under excessive amount of one of the reactants in order to shift the reaction towards production of ester. In this work, an excessive amount of isoamyl alcohol was always introduced over isovaleric acid to favor catalyst solubility during the reaction. Furthermore, since water is inevitably formed during esterification, continuous removal of water during reaction process would be helpful for high ester yield. In this regard, cyclohexane was used as water-carrying agent to remove water. Again, the [PPSH]_{1.5}H_{1.5}PW₁₂O₄₀ catalyst was chosen for optimization of various reaction parameters. In particular, the effects of reaction time (x_1), isoamyl alcohol/isovaleric acid molar ratio (x_2), amount of water-carrying agent (x_3) and amount of catalyst (x_4 ; i.e., amount of [PPSH]_{1.5}H_{1.5}PW₁₂O₄₀) were investigated over various ranges. The corresponding symbols for experimental variables and respective coded levels representing various parameter ranges are summarized in Table 1. Accordingly, an optimal catalytic activity corresponding to an ester was observed for the [PPSH]_{1.5}H_{1.5}PW₁₂O₄₀ catalyst with level 0. Under the conditions: $x_1 = 1.5$ h, $x_2 = 1.1$ mol/mol, $x_3 = 10$ mL and $x_4 = 6$ wt.%, as depicted in Table 2 (entry 3, 8-22), the yield of isoamyl isovalerate was 95.6%.

RSM experiments and studying

RSM differs from classical experimental procedures, considered the effect of factors and their interactions involved to reduce the number of cumbersome experiments and get the optimal conditions.³³ Independent variables and their levels for the Box-Behnken design used in this study are shown in Table 1. To verify the models, 29 runs of experiment were conducted and the obtained response values are shown in Table 3. It could be seen that the experimental values and calculated values had no observable difference.

The predicted quadratic model related the yield of isoamyl isovalerate with four independent factors (reaction time, alcohol/acid molar ratio, amount of water-carrying agent and amount of catalyst) was expressed as follows,

$$Y = +95.59 + 5.38x_1 + 0.45x_2 - 1.34x_3 + 2.78x_4 - 6.32x_1^2 - 2.40x_2^2 - 6.67x_3^2 - 4.17x_4^2 + 1.87x_1x_3 + 0.95x_1x_4 + 5.31x_2x_3 - 0.14x_1x_2 - 1.96x_2x_3 - 3.59x_3x_4 \quad (3)$$

where x_1 , x_2 , x_3 and x_4 were the coded values of the best variables reaction time, alcohol/acid molar ratio, amount of water-carrying agent and amount of catalyst, respectively; Y was the response of yield of isoamyl isovalerate.

Analysis of variance (ANOVA) of the regression model was employed to seek out the significance of the effects of parameters on esterification process (Table 4). The significance of regression model was examined by F -test and p -value. As shown in Table 4, the computed F -value (19.32) was much larger than the tabular F -value (3.70), which was desirable as it indicated that the model obtained from equation 3 gave a good prediction at 1% level of significance. In addition, the p -value for the model less than 0.0001 also meant that the model term was significant. In the study, x_1 , x_2 , x_4 , x_1x_3 , x_1x_4 and x_2x_3 were significant factors. Furthermore, the coefficient of determination (R^2) of the model was 0.9016, which implied that 90.16% of the variation could be explained by the fitted model. In general, the quadratic regression model with the R^2 value higher than 0.90 was considered as possessing a considerable high correlation.^{34,35} On investigating R^2 value, the predicted R^2 of 0.7399 was in reasonable agreement with the adjusted R^2 of 0.9016. The adequacy precision of 15.864 was much greater than 4, which indicated that the model could be used to navigate the design space. The desirable results represented that the chosen quadratic model was appropriate in predicting the response variables for the experimental data.

Response surface plots facilitated the interaction study of the process variables with isoamyl isovalerate yield for esterification of isovaleric acid. The three dimensional (3-D) response plots and contour plots of reaction time, alcohol/acid molar ratio, amount of water-carrying agent and amount of catalyst are shown in Figures 1 and 2, respectively.

The variation of yield of isoamyl isovalerate with reaction time and alcohol/acid molar ratio was presented in Figures 1a and 2a. The interaction between reaction time and amount of catalyst is given in Figures 1c and 2c. It could be seen that the yield of isoamyl isovalerate changed little compared to the effect of time. With increasing amount of catalyst, the yield increased, passing through a maximum and then decreased slightly. Certainly, the esterification could not be conducted at a very high molar ratio. As it could be seen, the yield reached a maximum value around 1.1 and then declined.

Table 3. Experimental design and response value

Experimental No.	Variable and level				Yield of isoamyl isovalerate / %	
	Reaction time / h	Alcohol/acid ratio	Amount of water-carrying agent / mL	Amount of catalyst / wt. %	Expt.	Calc.
1	-1	-1	0	0	80.03	80.91
2	1	-1	0	0	90.60	91.93
3	-1	1	0	0	83.76	82.08
4	1	1	0	0	93.78	92.56
5	0	0	-1	-1	78.49	79.72
6	0	0	1	-1	83.49	84.23
7	0	0	-1	1	93.56	92.48
8	0	0	1	1	84.18	82.60
9	-1	0	0	-1	79.58	77.90
10	1	0	0	-1	88.42	86.75
11	-1	0	0	1	79.58	81.56
12	1	0	0	1	92.23	94.22
13	0	-1	-1	0	83.90	85.45
14	0	1	-1	0	88.78	90.28
15	0	-1	1	0	87.89	86.70
16	0	1	1	0	84.91	83.67
17	-1	0	-1	0	81.81	80.44
18	1	0	-1	0	89.28	87.45
19	-1	0	1	0	72.15	74.02
20	1	0	1	0	87.11	88.51
21	0	-1	0	-1	91.71	91.10
22	0	1	0	-1	79.39	81.38
23	0	-1	0	1	87.99	86.04
24	0	1	0	1	96.92	97.57
25	0	0	0	0	93.45	95.59
26	0	0	0	0	95.63	95.59
27	0	0	0	0	96.06	95.59
28	0	0	0	0	96.97	95.59
29	0	0	0	0	95.84	95.59

Figures 1b and 2b presented the three dimensional and contour plots related to yield of isoamyl isovalerate as a function of reaction time and amount of water-carrying agent under constant alcohol/acid molar ratio and amount of catalyst. As it could be seen on the three-dimensional response surface, the yield of isoamyl isovalerate changing slightly to the maximum meant that the reaction time on the response showed a more significant influence in comparison to the amount of water-carrying agent. With a further increase in time, a significant decrease in yield occurred. Hence, an optimum reaction time was needed due to the fact that conversion of isovaleric acid was strongly dependent on it. In addition, the two-dimensional contour lines demonstrated

that the combined effects of the above parameters on the yield of isoamyl isovalerate were significant.

The plots of the yield of isoamyl isovalerate as a function of alcohol/acid molar ratio and amount of water-carrying agent are presented in Figures 1d and 2d. The yield increased significantly before amount of water-carrying agent reached 10mL, but insignificant change was observed for molar ratio over 10 mL. Meanwhile, the yield improved gradually as alcohol/acid molar ratio increased but changed slightly when molar ratio exceeded 1.1. The saddle shape of the plots showed that the relationships between alcohol/acid molar ratio and amount of water-carrying agent are likely to affect the esterification.

Table 4. Estimated regression coefficients and corresponding statistical *t*- and *P*-values for yield of isoamyl isovalerate

Source	Sum of squares	Degrees of freedom (DF)	Mean square	<i>F</i> value	Prob > <i>F</i>	Significance
model	1152.13	14	82.29	19.32	< 0.0001	a
x_1	346.80	1	346.80	81.40	< 0.0001	a
x_2	2.45	1	2.45	0.57	0.4610	—
x_3	21.57	1	21.57	5.06	0.0410	b
x_4	92.85	1	92.85	21.79	0.0004	a
x_1x_2	0.076	1	0.076	0.018	0.8959	—
x_1x_3	14.03	1	14.03	3.29	0.0911	b
x_1x_4	3.63	1	3.63	0.85	0.3717	—
x_2x_3	15.44	1	15.44	3.63	0.0777	b
x_2x_4	112.89	1	112.89	26.50	0.0001	a
x_3x_4	51.70	1	51.70	12.13	0.0037	a
x_1^2	258.92	1	258.92	60.77	< 0.0001	a
x_2^2	37.41	1	37.41	8.78	0.0103	b
x_3^2	288.18	1	288.18	67.64	< 0.0001	a
x_4^2	112.61	1	112.61	26.43	0.0001	a
Residual	59.65	14	4.26	—	—	—
Lack of fit	52.88	10	5.29	3.12	0.1417	—
Pure error	6.77	4	1.69	—	—	—
Cor total	1211.78	28	—	—	—	—

^aHighly significant; ^bsignificant.

The interaction effect of alcohol/acid molar ratio and amount of IL on the reaction is shown in Figures 1e and 2e. The plot indicated that the maximum value (96.92%) was associated with high alcohol/acid molar ratio and amount of IL. The yield reached relatively high value (91.71%) at low alcohol/acid molar ratio of 1.05 and amount of IL of 5 wt.%, further demonstrated that the interaction between alcohol/acid molar ratio and amount of IL was significant on the yield of isoamyl isovalerate.

Figures 1f and 2f represent the relationship between amount of water-carrying agent and amount of IL. The effect of interaction of the two variables was significant with an ellipse mound shape. With increasing amount of water-carrying agent and amount of IL, the yield of isoamyl isovalerate initially increased, passing through a maximum (93.56%) and thereafter decreased. The yield was good at low amount of water-carrying agent and high amount of IL. From the analysis of the response surface plots, amount of IL showed a more significant influence on the response surface in comparison to amount of water-carrying agent.

Attaining optimum conditions and model verification

Based on the 29 experimental data, the model predicted the optimum yield for esterification of isovaleric

acid over $[\text{PPSH}]_{1.5}\text{H}_{1.5}\text{PW}_{12}\text{O}_{40}$ could reach 97.82%, with the optimal process conditions of reaction time 1.77 h, alcohol/acid molar ratio 1.12, amount of water-carrying agent 9.97 mL and amount of IL 6.37 wt.%. For convenience, the optimum parameters could be replaced by reaction time 2 h, alcohol/acid molar ratio 1.1, amount of water-carrying agent 10 mL and amount of IL 6.4 wt.%. In order to verify the adequacy of the model, three parallel experiments were conducted, under the conditions above and the average yield reached 97.53%, which meant that the predicted and experimental data had a good agreement.

Recycling of the catalyst

To assess the reusability of $[\text{PPSH}]_{1.5}\text{H}_{1.5}\text{PW}_{12}\text{O}_{40}$ for esterification of isoamyl alcohol, the reused catalyst was filtered from the system and washed by diethyl ether and dried under vacuum for 5 h at 70 °C for further reaction. As illustrated in Figure 3, the results showed that the catalyst was repeatedly used 6 times without major loss of catalytic activity, which demonstrated that the $[\text{PPSH}]_{1.5}\text{H}_{1.5}\text{PW}_{12}\text{O}_{40}$ was rather durable and had the potential for practical applications.

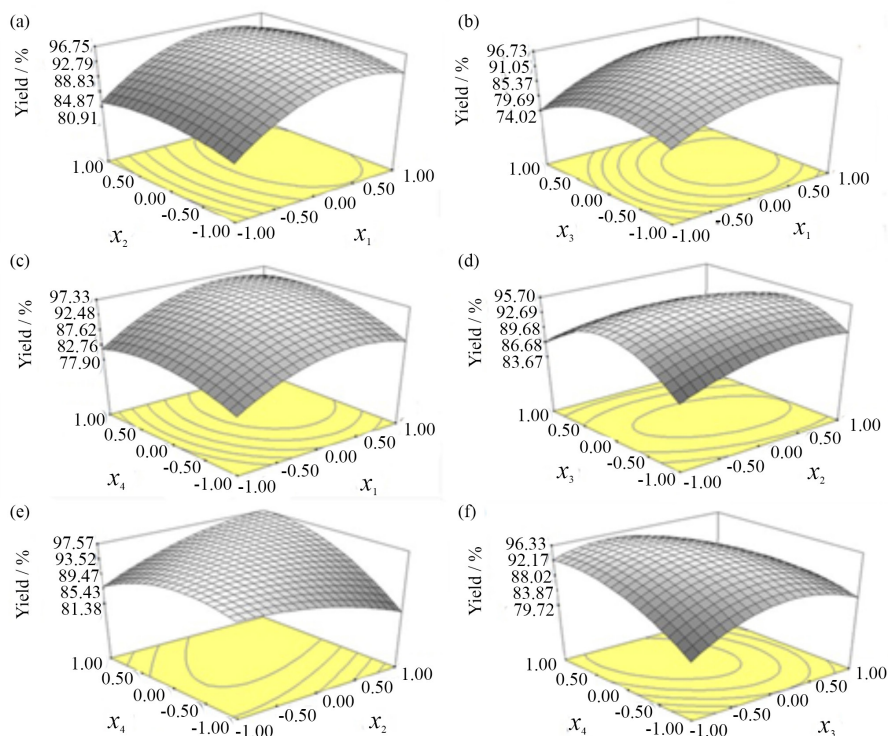


Figure 1. Response surface plots showing the predicted values of yield of isoamyl isovalerate, (a) effect of reaction time and alcohol/acid molar ratio, (b) reaction time and amount of water-carrying agent, (c) reaction time and amount of catalyst, (d) alcohol/acid molar ratio and amount of water-carrying agent, (e) alcohol/acid molar ratio and amount of catalyst, and (f) amount of water-carrying agent and amount of catalyst. Other variables are held at constant level.

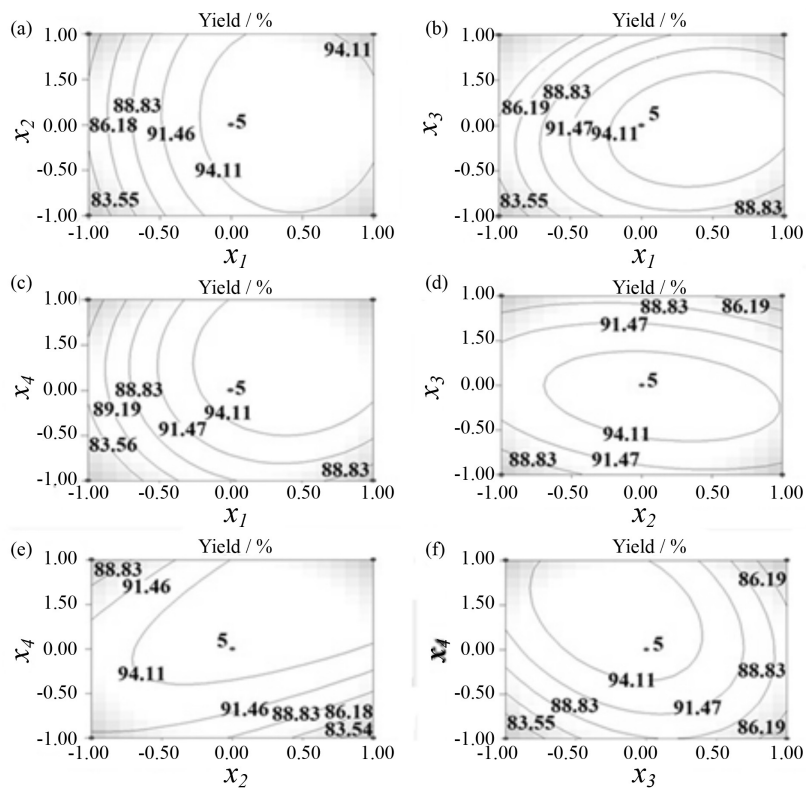


Figure 2. Contour plots showing the predicted values of yield isoamyl isovalerate, (a) effect of reaction time and alcohol/acid molar ratio, (b) reaction time and amount of water-carrying agent, (c) reaction time and amount of catalyst, (d) alcohol/acid molar ratio and amount of water-carrying agent, (e) alcohol/acid molar ratio and amount of catalyst, and (f) amount of water-carrying agent and amount of catalyst. Other variables are held at constant level.

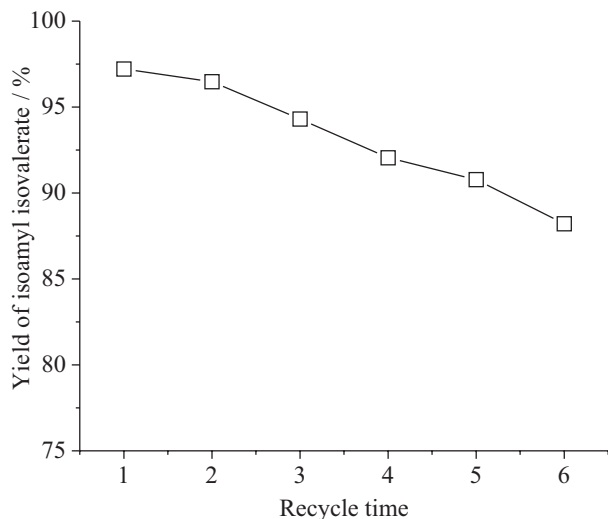


Figure 3. Catalyst recycling in the esterification of isovaleric acid with isoamyl alcohol. Reaction conditions: alcohol/acid molar ratio 1.1, catalyst $[PPSH]_{1.5}H_{1.5}PW_{12}O_{40}$ 6.4 wt.%, reaction time 2 h, water-carrying agent 10 mL.

Conclusions

The response surface methodology based on Box-Behnken experimental design was employed for optimization and analysis of esterification of isoamyl alcohol using $[PPSH]_{1.5}H_{1.5}PW_{12}O_{40}$. The optimum conditions were as follows: n (isoamyl alcohol) : n (isovaleric acid) = 1.1:1, the amount of catalyst of 6.4% to acid, the amount of water carrying agent 10 mL and reaction time 2 h. Under the optimized conditions, the yield of isoamyl isovalerate reached 97.53%, in close agreement with values predicted by the mathematical model (97.82%). Further stability study revealed that these catalysts not only possess desirable self-separation characteristics but also recyclability during esterification. Thus, these heteropolyacid-based ILs are effective catalysts for the synthesis of ester, and have potential applications for industrial production of ester.

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