

The Synthesis of Benzyl Acetate as a Fragrance and Flavoring Agent with Green Solvents

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Synopsis

Benzyl acetate, which has a crucial role in the industry as a flavor and fragrance component, is important for human health to be obtained with a green and clean process. For this purpose, the esterification reaction of acetic acid (AA) and benzyl alcohol (BA) was investigated using five different ionic liquids (ILs) as catalysts. 1-Ethyl-3-methylimidazolium hydrogen sulfate, [EMIM] [HSO₄], 1-Ethyl-3-methylimidazolium tetrafluoroborate [EMIM] [BF₄], 1-methyl-3-octylimidazolium tetrafluoroborate [OMIM] [BF₄], 1-ethyl-3-methylimidazolium bis [(trifluoromethyl)sulfonyl] imide [EMIM] [NTf₂], and 1,3-diethylimidazolium bis [(trifluoromethyl)sulfonyl] imide [DEIM] [NTf₂] were used as catalysts. The best catalytic performance was obtained with 1-Ethyl-3-methylimidazolium hydrogen sulfate, [EMIM] [HSO₄]. The influence of different anions and cations in the ILs structure, the reaction conditions such as initial acid/alcohol ratio, the catalyst amount, the reaction temperature, and the time on conversion were observed. The Box–Behnken experimental design of response surface methodology was applied to estimate the relationship between acid conversion (%) and reaction parameters. According to the model, in all esterification experiments carried out at 110°C, the optimum conditions for maximum conversion were AA:BA molar ratio of 1:1, IL molar ratio of 0.66, and reaction time 4 hours. Under these conditions, 90.34% acid conversion was achieved. [EMIM] [HSO₄] can be used for up to three cycles with minimal loss in activity.

INTRODUCTION

Organic esters are valuable products in the chemical industry. One of the short-chain carboxylic acid esters, benzyl acetate, is used as a flavor and fragrance component in the food and cosmetics industry. The Council of Europe approved the use of benzyl acetate in foodstuffs in 2000 and included in the list of substances granted-A. In addition, it is considered safe as a flavor ingredient by the Flavor and Extract Manufacturers Association (FEMA). Although benzyl acetate is found naturally in cloves, chamomile, jasmine, and hyacinth, extracts obtained from these plants are not sufficient to meet the worldwide usage volume (about 10,000 tons per year). Therefore, it is obtained by many different chemical methods. Most commonly used method is the esterification reaction of acetic acid (AA) and benzyl alcohol (BA) (1–2).

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The esterification reaction is an equilibrium reaction. It is carried out without or with catalyst. Because of the low rate of the carboxylic acid's autoprotolysis, the reaction proceeds very slowly without catalyst in the medium and takes a long time to equilibrate. Therefore, by adding an acid catalyst to be used as a proton donor, the reaction occurs faster (3). Esterification reactions are generally carried out in the presence of homogeneous or heterogeneous catalysts. Various mineral acids such as H_2SO_4 , HCl , H_3PO_4 , HF , *p*-toluene sulfonic acid are used as homogeneous catalysts in different studies (4–8). Although these acids have high catalytic activity and selectivity, they have significant disadvantages. It causes corrosion of the equipment, excessive side reaction, and severe environmental pollution, and it must be neutralized at the end of the reaction. Besides, it is very difficult to remove the mineral acid from the reaction medium and reuse them as a catalyst (9). In order to eliminate these problems, heterogeneous catalyst systems have been developed. Zeolites, ion-exchange resins such as Amberlyst 15 and heteropolyacids are used as catalysts in the esterification reactions of carboxylic acids. However, over time, heterogeneous catalysts also have problems that will affect the esterification reaction, such as a low number of active groups, high mass transfer resistance, long reaction times, low thermal stability, and catalyst residue control (10–21).

Since the esterification reactions are reversible reactions, according to the Le Chatelier principle, the yield can be increased by shifting the excess of one of the reactants into the medium or removing the water formed at the end of the reaction by shifting the balance to the direction of the product. One of the techniques used to remove water is to add azeotrope with water by adding a water-trapping solvent such as hexane, benzene, toluene (22). However, in these processes, considerable energy is needed to recover the solvent or remove excess reactant. Besides, the loss of volatile organic solvents to the atmosphere increases the cost of production and causes environmental pollution (23).

Esterification reaction systems need to be developed to reduce environmental pollution and production costs, easy separation of the product from the reaction medium, and reuse of catalysts with high selectivity and reactivity. For this purpose, the importance of ionic liquids (ILs) has been increasing in recent years due to their polarity and hydrophobic structure, and it has been used in many fields such as polymerization (24,25), alkylation (26,27), dehydration (28,29), oxidation (30,31), and acetalization (32,33). Since 2002, ILs have been proposed to be used as catalysts to improve esterification reactions (34). These substances stand out as an environmentally acceptable reaction medium due to their low vapor pressure, high thermal stability, adjustable acidity, recoverability, and low toxic effects (35–42). ILs, depending on their solubility, ensure that the reaction medium is homogeneous in the first steps of esterification reactions and heterogeneous toward the end of the reaction. Thus, they are easily separated from the product and reused many times (43).

ILs act as catalysts in the esterification reaction of carboxylic acids and alcohols. At the end of the reaction, the water in the medium must be removed to obtain high ester conversion. Water passes into the IL phase and does not react. The ester is separated by decantation at the end of the reaction (44–47).

Response surface methodology was developed in 1951 by Box and Wilson as an experimental design method (48). This method is a combination of statistical and mathematical techniques used for modeling and analysis of engineering problems. The experimental design establishes a relationship between the parameters that affect the system and the process outputs in processes. With this technique, savings (reduction) can be mentioned in

the number of experiments, reactants, time, financial inputs, and energy. Also, experimental errors are minimized. Statistical methods measure the change of controllable variables affecting the process and their interactions through experimental design (49).

This study aims to consider environmentally friendly and reusable ILs as an alternative to conventional solvents used as catalysts in the esterification reaction of AA with BA and to optimize the reaction conditions. There are no published studies on the estimation of reaction parameters for benzyl acetate esterification reaction catalyzed by the ILs ([EMIM] [HSO₄], [EMIM] [BF₄], [OMIM] [BF₄], [EMIM] [NTf₂], and [DEIM] [NTf₂]) in this study. For this purpose, the effects of variables such as the structure of ILs, initial acid/alcohol molar ratio, catalyst amount, reaction temperature, and reaction time on acid conversion were investigated. Optimum conditions were studied using the Box–Behnken experimental design of the response surface methodology.

EXPERIMENTAL

MATERIALS

The chemicals acetic acid (100%) and benzyl alcohol (>99.5%) used in this work were purchased from Merck (Darmstadt, Germany) and used without any purification. For this study, the ILs (>99%), 1-Ethyl-3-methylimidazolium hydrogen sulphate [EMIM] [HSO₄], 1-Ethyl-3-methylimidazolium tetrafluoroborate [EMIM] [BF₄], 1-methyl-3-octylimidazolium tetrafluoroborate [OMIM] [BF₄], 1-ethyl-3-methylimidazolium bis [(trifluoromethyl)sulfonyl] imide [EMIM] [NTf₂], and 1,3-diethylimidazolium bis [(trifluoromethyl)sulfonyl] imide [DEIM] [NTf₂] were supplied by IoLiTec (Heilbronn, Germany) and used without any pretreatment. Aqueous NaOH solution was prepared by 0.1 N NaOH Titrisol (Merck), which was used for the acid analysis.

REACTION MECHANISM

The reaction mechanism of the esterification between AA and BA catalyzed by ILs can be explained by the following equations:

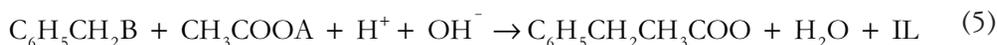
Firstly, the IL was divided into anion and cation (Eq. 1).



Then, the BA and AA, intermediate complexes with the anion and cation of the IL, respectively, were formed (Eq. 2–4). The alcohol formed by the strong interaction between the anion of the IL and the hydroxyl group of the alcohol can be activated by a Lewis-type complex formed with the Lewis acidic cation.



At the end of the reaction, ester and water are formed as products. With the formation of the ester, the catalyst becomes free. All steps are basic and irreversible, and the stage of final product formation is the rate-determination stage (Eq. 5) (50,51).



PROCEDURE OF ESTERIFICATION REACTION

Esterification experiments were conducted in a 100 mL three-necked round-bottom flask glass reactor. Esterification of AA and BA catalyzed by IL experiments were conducted in a 100 mL three-necked round-bottom flask glass reactor. The reaction was carried out by effective mixing by adding simultaneously certain amounts of AA (20 mmol), BA (20 mmol), and IL (10 mmol) (for AA:BA:IL molar ratio of 1:1:05) to the preheated reactor. The reactor was placed in a temperature-controlled oil bath with a mixer heater with a contact thermometer (IKA C-MAG HS7, IKA, Staufen, Germany.), and the reaction temperature was controlled. A reflux condenser was connected to the reactor to prevent evaporation losses during the reaction. The reaction mixture was effectively stirred with the magnetic stirrer.

At the end of the reaction, a certain amount of sample was titrated with phenolphthalein indicator with 0.1 N NaOH, and acid conversion (%) was calculated by determining the amount of acid remaining in the phase without reacting (52–54). Trials were repeated at least twice for each case. The experiment was performed until reproducible results were obtained. The acid value (AV) was determined by Eq. 6.

$$\text{Acid Value} \left(\frac{\text{mol}}{\text{L}} \right) = \frac{N \times f \times S}{T} \quad (6)$$

where N is the normality of NaOH, f is the factor of 0.1 N NaOH, S is the volume of the titrant (mL), and T is the volume of the sample (mL). The conversion (X) was calculated by comparing the AV of the initial acid (AV_0) to the AV of acid at time t (AV_t), using Eq. 7.

$$X (\%) = \frac{AV_0 - AV_t}{AV_0} \times 100 \quad (7)$$

[EMIM] [HSO_4] was used as a catalyst in the esterification reaction; biphasic layers are formed at the end of the reaction after cooling the solution to room temperature. The upper layer contains the desired ester product, while the bottom layer contains the IL, unreacted reactants, and water. The product (ester) can be easily removed from the reaction medium by decanting without any additional cost. Since the unreacted acid may be present in both phases, the acid analysis was carried out in both phases.

[EMIM] [BF_4] was used as a catalyst in the reaction, the IL was precipitated as a solid, and the liquid phase consists of ester and unreacted reactants (55). The organic phase was analyzed to calculate the acid, which remained unreacted.

[DEIM] [NTf_2], [EMIM] [NTf_2], and [OMIM] [BF_4] were used as the catalyst in the reaction, and the reaction medium was not biphasic because the ester was dissolved in the IL after cooling the solution to room temperature (56). In this case, the acid analysis was carried out in the reaction mixture.

EXPERIMENTAL DESIGN AND BOX-BEHNKEN MODELING

The response surface methodology is used to determine the mathematical relationship between the dependent variable (response) and the independent variables and to optimize the response variable affected by the various process parameters. This method also describes the effect of single or multiple combinations of independent variables on the process response (57).

The Box-Behnken experimental design of response surface methodology was applied to estimate the conversion of AA (%) and reaction parameters. For this purpose, the Design-Expert® Software Version 7 Trial (Stat-Ease, Inc., USA) was used in which the experimental studies will be performed for the esterification reaction of AA with BA. In the study, the effect of three process parameters on acid conversion (%) was investigated to determine the catalyst activity of ILs.

Box-Behnken experimental design was made with three levels and three factors. A total of 17 experiments were designed, including five center points. Three parameters affecting the esterification reaction, acid/alcohol mole ratio (x_1), IL mole ratio (x_2), and time (x_3), were determined as the process parameters in the system, and these parameters were chosen as independent variables. Variable levels and coded values were shown in Table I. The conversion of AA (%) was selected as the dependent variable (58).

The response surface function of the parameters that affect the process is expressed as follows (59) (Eq. 8):

$$Y = f(x_1, x_2, \dots, x_k) + \varepsilon \quad (8)$$

where Y is the dependent variable or response, x_i is the independent variable, f is the function of response, and ε is the experimental error.

The second-order polynomial equation (Eq. 9) represents the response surface method as shown in the following (60):

$$Y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^k \beta_{ij} x_i x_j + \varepsilon \quad (9)$$

where β_0 is the constant regression coefficient, β_i , β_{ii} , β_{ij} are the interaction coefficients, and k is the factor number.

The statistical analysis of the experimental data was carried out with the Design-Expert program. Analysis of variance (ANOVA) was used to explain the effect of variables on the mathematical model obtained in the selected study range.

Table I
Variable Levels and Coded Values in the Experimental Design

Independent variable	Symbol	Range and level		
		-1	0	1
Acid/alcohol molar ratio	x_1	1.0	1.5	2
IL molar ratio	x_2	0.25	0.50	0.75
Reaction time (h)	x_3	4	6	8

RESULTS AND DISCUSSION

Time, temperature, catalyst ratio, and acid/alcohol mole ratio parameters were investigated in detail for the esterification experiments. Besides, the experimental design of the studies was conducted to determine the effects of the interactions of the variables in the system used separately and on each other.

The effect of the presence and type of ILs used as catalysts in esterification reactions on acid conversion was investigated. For this purpose, firstly, esterification of AA and BA without catalyst was carried out according to the experimental procedure described. The obtained results of the conversion of AA (%) were presented in Figure 1.

The rate of catalyst-free esterification reaction is prolonged under atmospheric conditions. The reaction rate depends on the rate of catalysis of the carboxylic acid itself. For a faster reaction, a catalyst is added to the reaction medium to serve as a proton donor to the carboxylic acid (61). For this purpose, ILs consisting of [EMIM]⁺, [OMIM]⁺, and [DEIM]⁺ cationic groups and [HSO₄]⁻, [BF₄]⁻, and [NTf₂]⁻ anionic groups were used as catalysts.

EFFECT OF EXPERIMENTAL VARIABLES

For industrial esterification reactions, the kinetic study of the conversion is of great importance for process design and economy. In order to investigate the esterification reaction, kinetics of AA with BA catalyzed by [EMIM] [HSO₄], experiments were done with AA:BA:[EMIM] [HSO₄] molar ratio of 1:1:0.5 at 110°C. While only 39.59% of AA was converted to benzyl acetate at the end of 1 h, this conversion increased to 85.3% at the end of 8 h, and the system came to equilibrium at the end of this period. The effect of time on acid conversion (%) was shown in Figure 2. It can be seen that the conversion of AA will not change after this time. For this reason, 4, 6, and 8 h, which are the critical stages of the conversion, were chosen as the reaction time in the optimization experiments performed in the later stages of the study.

Generally, in esterification reactions, high temperature increases the reaction rate and acid conversion (62). Therefore, three different temperatures were selected to find the

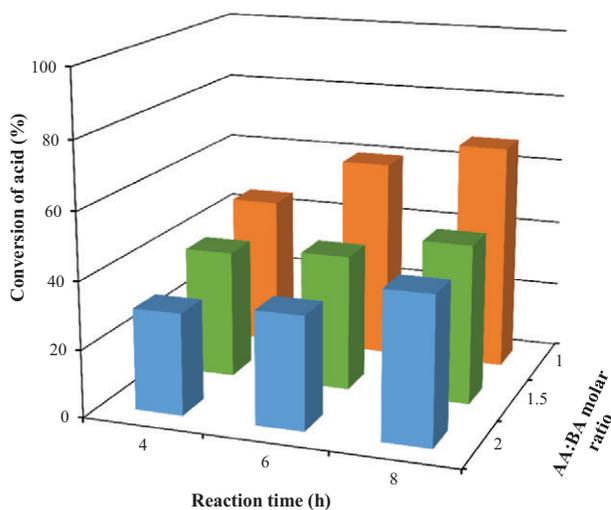


Figure 1. Conversion of acid (%) for acetic acid and benzyl alcohol esterification without catalyst at 110°C.

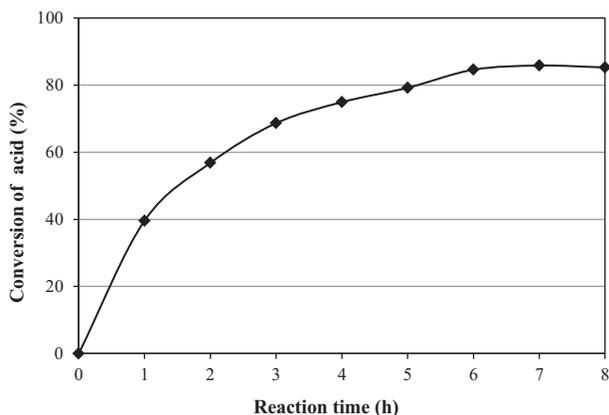


Figure 2. Effect of time on the conversion of acid (%) using [EMIM] [HSO₄] as catalyst. (AA: BA: [EMIM] [HSO₄] molar ratio 1:1:0.5, T=110°C)

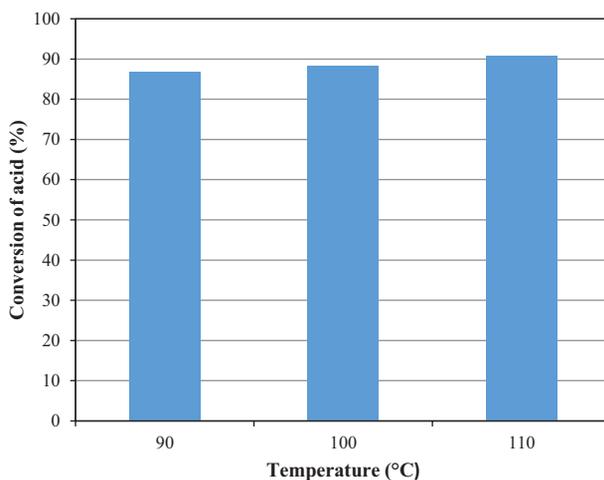


Figure 3. Effect of temperature on the conversion of acetic acid (AA) (%) using [EMIM] [HSO₄] as catalyst. (Reaction conditions: AA: BA: [EMIM] [HSO₄] molar ratio 1:1:0.75, τ = 8 h)

highest acid conversion for the esterification reaction system. The boiling temperatures of the reactants and the product (benzyl acetate) were taken into consideration when making the selection. In order to investigate the effect of temperature on the esterification reaction of AA with BA catalyzed by [EMIM] [HSO₄], experiments were performed for 8 h with AA:BA:[EMIM] [HSO₄] molar ratio of 1:1:0.75 at 90–100°C and 110°C. The results were shown in Figure 3. It has been determined that 110°C is the reaction temperature at which the conversion of acid close to 90% is achieved.

The effect of AA to BA molar ratio on the esterification reaction was investigated experimentally. Similar to previous studies in the literature, AA:BA molar ratio of 1, 1.5, 2 was selected. The experiments at 4, 6, and, 8 h in which [EMIM] [HSO₄] mole ratio was 0.75 were carried out at 110°C. The results were given in Figure 4. It was seen that as the number of acid increases, the conversion in the reaction decreases. It shows that when the

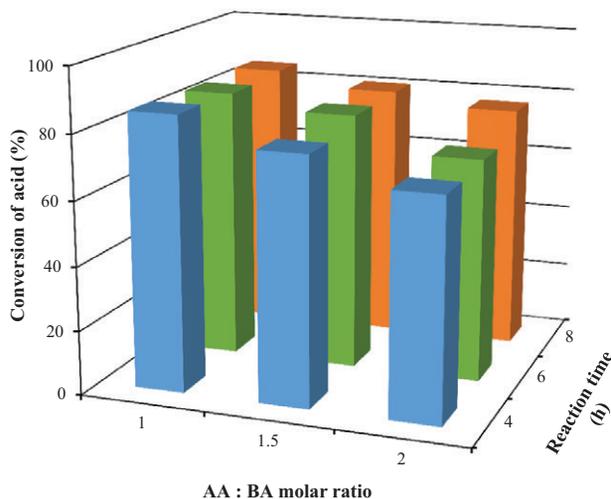


Figure 4. Effect of acid/alcohol molar ratio on the conversion of acid (%) using [EMIM] [HSO₄] as catalyst at T = 110°C.

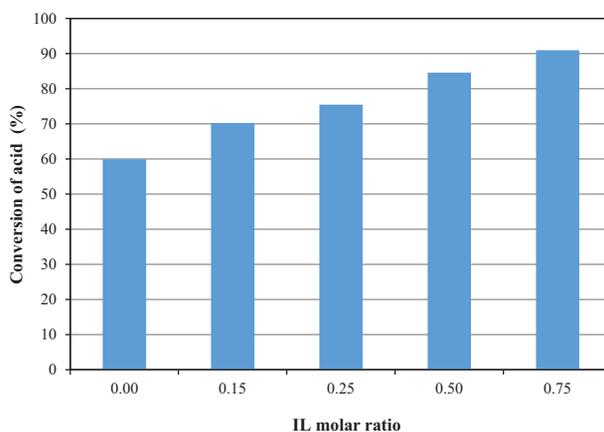


Figure 5. Effect of amount of catalyst on the conversion of acid (%) using [EMIM] [HSO₄] as catalyst. (Reaction Conditions: AA:BA = 1:1 T = 110°C, τ = 6 h)

initial acid concentration is excess in the reaction medium, the reversible esterification reaction is more effective in the reverse direction. Therefore, the conversion is low due to a large amount of product formed.

Conventional acidic catalysts used in esterification reactions cause corrosion of process equipment and pose a threat to environment. Experiments were carried out to get an idea about the amount of ILs used as catalysts to eliminate these disadvantages. In this study in which high conversion was aimed using an optimum catalyst, the relationship between the change of IL amount and conversion AA:BA:[EMIM] [HSO₄] molar ratio was investigated by experiments between 1:1:0.15 and 1:1:0.75. Figure 5 showed that AA conversion increases with an increasing amount of IL in the reaction. For this reason, in optimization experiments, IL molar ratios were studied as 0.25, 0.50, and 0.75.

BOX-BEHNKEN EXPERIMENTAL DESIGN

At this stage of the work, the studying range was determined by considering the preliminary experiment and critical limit values of the process variables (time, acid/alcohol molar ratio, and IL molar ratio). These values were entered into the "Design Expert" program, and the experimental set was designed (Table II).

Box–Behnken design, which is one of the most widely used methods for RSM in the literature (63–66), was chosen as the experimental design method to be studied. The main objective of this method is to evaluate the many variables and to minimize the number of experiments required. In addition, process variables are examined and used to model the system's response to these variables. Experiments were carried out according to the test procedure mentioned earlier, provided that the experimental conditions were the same for each catalyst.

The conversion of acid (%) obtained with AA:BA:[EMIM] [HSO₄] molar ratio of 1:1:0.75 at 110° C for 6 h was presented in Figure 6. It was seen that 91% of acid was converted to benzyl acetate if [EMIM] [HSO₄] was used, 82% of acid was converted if [DEIM] [NTf₂] was used, 77% of acid was converted if [EMIM] [NTf₂] was used, 75% of acid was converted to benzyl acetate if [OMIM] [BF₄] was used, and 72% of acid was converted to benzyl acetate when [EMIM] [BF₄] was used. The comparative list of catalytic activity for the ILs was as follows:

Table II
The Experimental Design and Response Values for [EMIM] [HSO₄]

Experiment number	x_1	x_2	x_3	Conversion of acid (%) Y
1	1.0	0.25	6	77.96
2	1.0	0.50	4	85.59
3	1.0	0.50	8	85.30
4	1.0	0.75	6	91.00
5	1.5	0.25	4	63.50
6	1.5	0.25	8	71.44
7	1.5	0.50	6	80.40
8	1.5	0.50	6	79.96
9	1.5	0.50	6	79.13
10	1.5	0.50	6	79.27
11	1.5	0.50	6	79.44
12	1.5	0.75	4	83.96
13	1.5	0.75	8	87.54
14	2.0	0.25	6	42.82
15	2.0	0.50	4	68.58
16	2.0	0.50	8	76.94
17	2.0	0.75	6	77.92

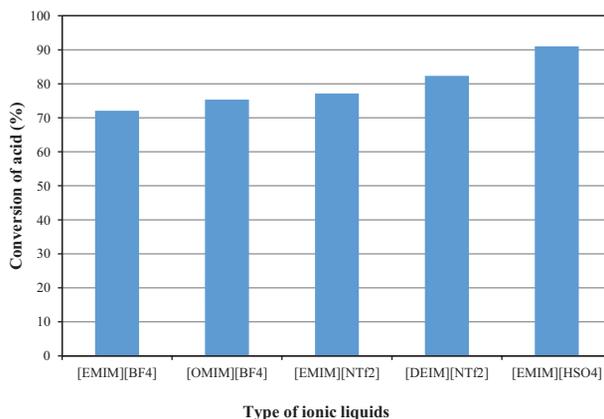
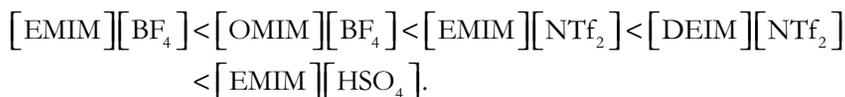


Figure 6. Comparison of ionic liquids by acid conversion (%).



The catalytic performance in esterification reactions depends on acidity. ILs with strong acidity have high catalytic activity. The formation of the anion in the structure of the IL from an acidic proton-containing component plays an important role in the activation of the reaction. According to the obtained data, $[\text{BF}_4]^- < [\text{NTf}_2]^- < [\text{HSO}_4]^-$ was found to compare anion activities. We can explain this situation according to the degree of acidity of ions. The acidity levels of the anions used were $[\text{BF}_4]^- < [\text{NTf}_2]^- < [\text{HSO}_4]^-$. Hydrogen sulfate ($[\text{HSO}_4]^-$) ion shows stronger acidity than $[\text{NTf}_2]^-$ and $[\text{BF}_4]^-$ anions (67). Accordingly, the highest conversion was obtained when $[\text{EMIM}][\text{HSO}_4]$ was used.

Comparing the cation activities of ILs, the catalytic activity of $[\text{OMIM}][\text{BF}_4]$ is higher than that of $[\text{EMIM}][\text{BF}_4]$. This is because the octyl group in the imidazole ring is more lipophilic (apolar) than the ethyl group. Similarly, the catalytic activity of $[\text{DEIM}][\text{NTf}_2]$ was higher than that of $[\text{EMIM}][\text{NTf}_2]$. Here again, the 1,3 diethyl group is more apolar than the ethyl group, so the dispersibility of ILs is also higher and therefore, may increase catalytic activity (68).

In general, it is known that higher conversion efficiencies of acidic catalysts are obtained in esterification reactions (69–71). Chrobok et al. stated that the increase in the mole fraction of H_2SO_4 in the structure of the catalyst they used increased the yield of the ester (72). Similar results were obtained in our study, and the highest acid conversion value with $[\text{EMIM}][\text{HSO}_4]$ among ILs was obtained. Therefore, the optimization and modeling results were presented with data from the benzyl acetate esterification reaction performed using this IL as the catalyst.

STATISTICAL ANALYSIS

The data obtained as a result of the experimental studies using the Box–Behnken method revealed the quadratic model equation in the actual factors shown in the following (Eq. 10):

Table III
ANOVA for the Response Surface Quadratic Model

Source	Sum of squares	Degrees of freedom	Mean square	F-value	p-value
Model	1926.26	9	214.03	19.51	0.0004
x_1	588.07	1	588.07	53.60	0.0002
x_2	1005.76	1	1005.76	91.68	< 0.0001
x_3	47.97	1	47.97	4.37	0.0748
x_1x_2	72.76	1	72.76	6.63	0.0367
x_1x_3	18.71	1	18.71	1.71	0.2329
x_2x_3	4.75	1	4.75	0.43	0.5315
x_1^2	37.55	1	37.55	3.42	0.1068
x_2^2	126.39	1	126.39	11.52	0.0115
x_3^2	25.25	1	25.25	2.30	0.1730
Residual	76.79	7	10.97		
Lack of fit	75.68	3	25.23	90.33	0.0004
Pure error	1.12	4	0.28		
Cor. total	2003.06	16			
Std Dev.				3.31	
R^2				0.9617	
R^2_{adj}				0.9124	
Adeq R^2				16.556	

$$Y = 87.35 - 11.35x_1 + 94.41x_2 - 8.27x_3 + 34.12x_1x_2 + 2.16x_1x_3 - 2.18x_2x_3 - 11.94x_1^2 - 87.66x_2^2 + 0.61x_3^2 \quad (10)$$

where x_1 , x_2 , x_3 representing three experimental variables, namely acid/alcohol molar ratio, IL molar ratio, and reaction time, respectively; and Y (response) is the conversion of acid (%).

Equation 10 indicates that the conversion of AA (%) increases with increasing IL molar ratio x_2 and decreases with acid/alcohol molar ratio x_1 . The most effective parameter was the IL molar ratio.

ANOVA was performed to test the accuracy of the polynomial equation consisting of parameters affecting the conversion of acid (%) (Table III).

With this method, the significant degree of linear, quadratic and binary interaction of each variable forming the model was determined by F-test and $p > F$.

From Table III, model terms with the p -value were important terms that affect the response. Values of "Prob > F" less than 0.05 indicate model terms are significant. The Model F-value of 19.51, and The "Lack of Fit F-value" of 90.33 implied the model and the Lack of Fit was significant. In this case x_1 , x_2 , x_1x_2 , x_2^2 are significant model terms.

The fact that the regression coefficient is close to 1 indicates that the relationship between independent and dependent variables is well expressed by the model. The R-squared value

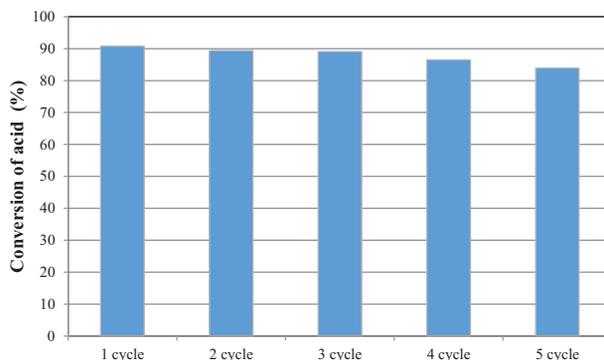


Figure 7. Performance of recycled [EMIM] [HSO₄] catalyst
(Reaction Conditions: AA: BA: [EMIM] [HSO₄] = 1:1: 0.75, T = 110°C, t = 8 h).

of 0.9617 and R^2_{adj} value was found 0.9124. These two values were close to each other shows that the conversion of acid (%) estimated by the obtained model equation was quite adjacent to the conversion of acid (%) obtained by experimental data. “Adeq Precision” measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The ratio of the model found as 16.556 indicated an adequate signal. This model can be used to navigate the design space. These statistical data showed that the quadratic model obtained can be used to predict acid conversion (%) within the range of the variables studied.

The three dimensional and contour plots of the variables on the conversion of acid (%) are shown in Figure 8A, B, and C. These graphs show the mutual effect of the other two parameters by keeping one of the parameters constant (61).

Figure 8A represents the interaction between acid/alcohol molar ratio and IL molar ratio. Conversion of acid (%) decreased with acid/alcohol mole ratio and increased with IL mole ratio. More than one of the reactants causes the balance to shift toward the products. However the increase in the acid/alcohol mole ratio, the excess acid (%) in the medium did not increase the acid conversion (%). It can be explained by the dilution of alcohol and IL with excess acid in the reaction medium, as in previous studies (63,67,73).

The interaction between acid/alcohol mole ratio and time is shown in Figure 8B. It is clear that the conversion of acid (%) increased with increasing the reaction time and decreased with the acid/alcohol mole ratio.

Figure 8C shows the interaction between time and IL molar ratio. The plot revealed that the conversion of acid (%) decreased slightly with time, and at the point where the IL mole ratio is maximum, the conversion of acid (%) is the highest. This might be due to active sites in the reaction medium increase with the amount of IL (74). As a result, the IL molar ratio is a more important parameter than the reaction time for the esterification reaction; also it can be seen from the ANOVA table.

RECYCLE AND REUSE OF IL

One of the most important factors in the ability of ILs to reduce the cost of the esterification process is the possibility to be reused. The recycling and reuse of the used IL will both reduce the production cost and its impact on the environment because it is not thrown into the environment (62). The reusability of [EMIM] [HSO₄], which had the

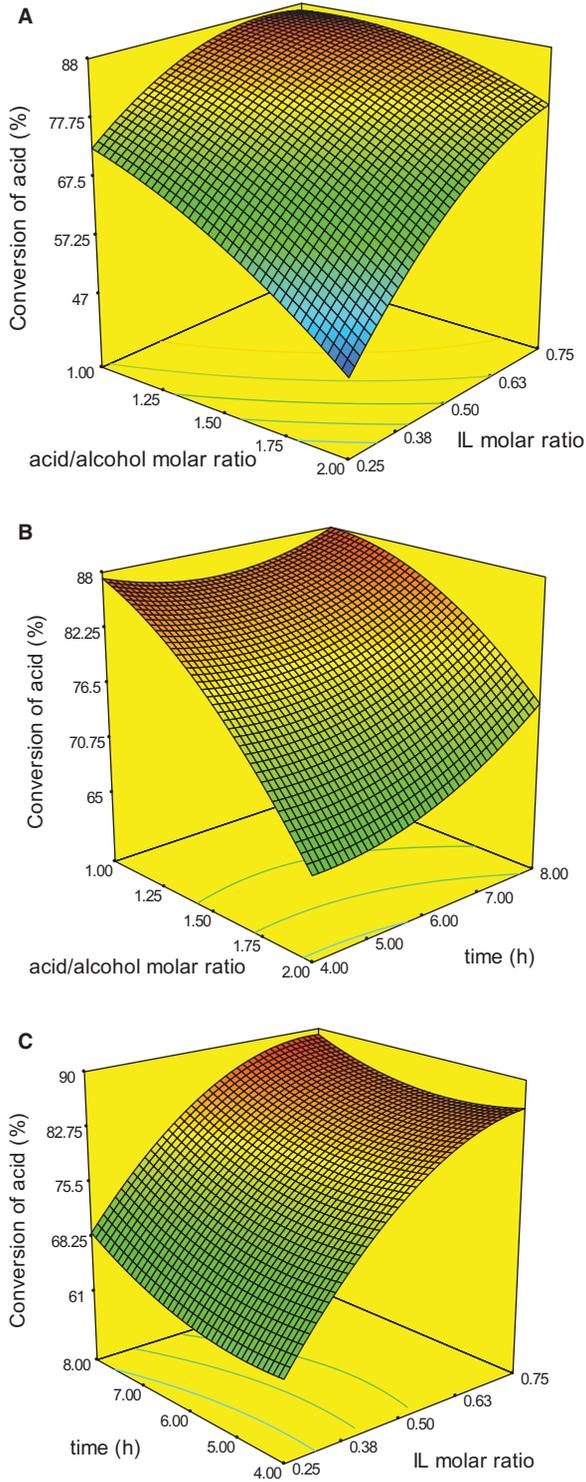


Figure 8. Response surface plots and contours of the conversion of acid. (A) Effect of the molar ratio of AA:BA and molar ratio of IL, (B) Effect of molar ratio of AA:BA and time, (C) Effect of time and molar ratio of IL.

highest conversion, was investigated in benzyl acetate esterification reaction. The experiments were carried out with AA:BA:[EMIM] [HSO₄] molar ratio of 1:1:075 at 110° C for 8 hours. At the end of the reaction, the upper phase and the lower phase (IL and water) were separated by simply decantation. The IL was dried under vacuum (0.01 Torr) at 100° C (overnight). The reusability of the IL was investigated by repeating the same experimental procedure five times for the recycled IL. Figure 7 represents that the catalytic activity of [EMIM] [HSO₄] did not change until the third run, but began to decrease slightly with the next use.

CONCLUSIONS

In this study, the obtaining of benzyl acetate, which gives artificial jasmine scent and apple, banana flavors to various cosmetics and personal care products like perfumes, lotions, hair creams, and perfumes, by esterification method was investigated. For this purpose, five different ILs were used as a catalyst for the esterification reaction of AA with BA. The results showed that the highest acid conversion was obtained in the esterification reaction, in which [EMIM] [HSO₄] was used as a catalyst. The response surface methodology based on the Box–Behnken design for optimizing the reaction parameters was applied using this IL. The optimum conditions were AA:BA molar ratio of 1:1, IL molar ratio of 0.66, and reaction time of 4 h. Under these conditions, 90.34% acid conversion was achieved. ANOVA was performed to test the suitability of the proposed second-degree model in order to determine the effect levels of the independent variables affecting the acid conversion. According to the statistical results obtained, it was seen that the most crucial factor affecting the reaction was the amount of IL. As a result, the IL used in this study proved to be an excellent catalyst for the esterification of AA and BA. This study has been a green approach obtaining the ester with high efficiency, and easy separation and recovery of the IL used as a catalyst from the product. In future research, it is important to study that different esters, which are frequently used in personal care products, can also be obtained using this method.

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REFERENCES

- (1) D. McGinty, D. Vitale, C. S. Letizia, and A. M. Api, Fragrance material review on benzyl acetate, *Food Chem Toxicol.*, 50, 363–384 (2012).
- (2) R. Lamba, S. Kumar, and S. Sarkar, Esterification of decanoic acid with methanol using Amberlyst 15: reaction kinetics, *Chem Eng Commun.*, 205, 281–294 (2018).
- (3) J. Lilja, J. Aumo, T. Salmi, D. Y. Murzin, P. M. Arvela, M. Sundell, K. Ekman, R. Peltonen, and H. Vainio, Kinetics of esterification of propanoic acid with methanol over a fibrous polymer-supported sulphonic acid catalyst, *Appl Catal A-Gen.*, 228, 253–267 (2002).
- (4) H. J. Bart, J. ReIdetschlager, K. Schatkaj, and A. Lehmann, Kinetics of esterification of levulinic acid with n-butanol by homogeneous catalysis, *Ind Eng Chem Res.*, 33, 21–25 (1994)
- (5) J. Lilja, D. Y. Murzin, T. Salmi, J. Aumo, P. Maki-Arvela, and M. Sundell, Esterification of different acids over heterogeneous and homogeneous catalysts and correlation with the Taft equation, *J Mol Catal-A Chem.*, 182, 555–563 (2002).

- (6) R. A. Troupe and K. A. Kobe, Kinetics of methanol-lactic acid reaction, *Ind Eng Chem Res.*, 42, 1403–1409 (1950).
- (7) R. A. Troupe, K. A. Kobe, Kinetics of ethyl alcohol lactic acid reaction, *Ind Eng Chem Res.*, 49, 847–855 (1957).
- (8) Y. Liu, E. Lotero, and J. G. Goodwin, Effect of carbon chain length on esterification of carboxylic acids with methanol using acid catalysis, *J Catal.*, 243, 221–228 (2006).
- (9) F. Xu, H. Chen, H. Zhang, X. Zhou, and G. Cheng, Protophilic amide ionic liquid assisted esterification and catalysis mechanism, *J Mol Catal-A Chem.*, 307, 9–12 (2009).
- (10) Y. Tsai, H. Lin, and M. Lee, Kinetics behavior of esterification of acetic acid with methanol over amberlyst 36, *Chem Eng J.*, 171, 1367–1372 (2011).
- (11) P. Delgado, M. T. Sanz, and S. Beltran, Kinetic study for esterification of lactic acid with ethanol and hydrolysis of ethyl lactate using an ion-exchange resin catalyst, *Chem Eng J.*, 126, 111–118 (2007).
- (12) Y. Seo and W. H. Hong, Kinetics of esterification of lactic acid with methanol in the presence of cation exchange resin using a pseudo-homogeneous model, *J Chem Eng Jpn.*, 33, 128–133 (2000).
- (13) G. D. Yadav and H. B. Kulkarni, Ion-exchange resin catalysis in the synthesis of isopropyl lactate, *React Funct Polym.*, 44, 153–155 (2000).
- (14) A. Engin, H. Haluk, and K. Gurkan, Production of lactic acid esters catalyzed by heteropoly acid supported over ion-exchange resins, *Green Chem.*, 5, 460–466 (2003).
- (15) Y. Zhang, L. Ma, and J. Yang, Kinetics of esterification of lactic acid with ethanol catalyzed by cation-exchange resins, *React Funct Polym.*, 61, 101–114 (2004).
- (16) J. Gangadwala, S. Mankar, S. Mahajani, A. Kienle, and E. Stein, Esterification of acetic acid with butanol in the presence of ion-exchange resins as catalysts, *Ind Eng Chem Res.*, 42, 2146–2155 (2003).
- (17) S. H. Ali and S. Q. Merchant, Kinetic study of Dowex 50 Wx8-catalyzed esterification and hydrolysis of benzyl acetate, *Ind Eng Chem Res.*, 48, 2519–2532 (2009).
- (18) P. E. Jagadeeshbabu, K. Sandesh, and M. B. Saidutta, Kinetics of esterification of acetic acid with methanol in the presence of ion exchange resin catalyst, *Ind Eng Chem Res.*, 50, 7155–7160 (2011).
- (19) M. Lee, J. Y. Chiu, and H. Lin, Kinetics of Catalytic Esterification of propionic acid and n-Butanol over Amberlyst 35, *Ind Eng Chem Res.*, 41, 2882–2887 (2002).
- (20) V. V. Mali and M. P. Deosarkar, Esterification of acetic acid with butanol in the presence of solid acid catalyst, *Intl J Adv Sci Eng Technol.*, 4, 245–248 (2016).
- (21) A. Mittal, S. Nair, and K. Deshmukh, The kinetic comparison study of catalytic esterification of butyric acid and ethanol over Amberlyst 15 and Indion-190 resins, *Intl J Innovat Res Sci Eng Technol.*, 4, 5860–5867 (2015).
- (22) T. Suman, S. Srinivas, and S. M. Mahajani, Entrainer based reactive distillation for esterification of ethylene glycol with acetic acid, *Ind Eng Chem Res.*, 48, 9461–9470 (2009).
- (23) A. Chinnappan and H. Kim, Environmentally benign catalyst: Synthesis, characterization, and properties of pyridinium dicationic molten salts (ionic liquids) and use of application in esterification, *Chem Eng J.*, 187, 283–288 (2012).
- (24) P. Kubisa, Application of ionic liquids as solvents for polymerization processes. *Prog Polym Sci.*, 29, 3–12 (2004).
- (25) J. Lu, F. Yan, and J. Texter, Advanced applications of ionic liquids in polymer science, *Prog Polym Sci.*, 34, 431–448 (2009).
- (26) S. Singhal, S. Agarwal, M. Sing, S. Rana, S. Arora, and N. Singhal, Ionic liquids: green catalysts for alkene-isoalkane alkylation, *J Mol Liq.*, 285, 299–313 (2019).
- (27) C. P. Huang, Z. C. Liu, C. M. Xu, B. H. Chen, and Y. F. Liu, Effects of additives on the properties of chloroaluminate ionic liquids catalyst for alkylation of isobutane and butene, *App Catal A-Gen.*, 277, 41–43 (2004).
- (28) Z. Zhu, Y. Ri, M. Li, H. Jia, Y. Wang, and Y. Wang, Extractive distillation for ethanol dehydration using imidazolium-based ionic liquids as solvents, *Chem Eng Process.*, 109, 190–198 (2016).
- (29) G. Yu, C. Dai, L. Wu, and Z. Lei, Natural gas dehydration with ionic liquids, *Energy Fuels*, 31, 1429–1439 (2017).
- (30) K. R. Seddon and A. Stark, Selective catalytic oxidation of benzyl alcohol and alkylbenzenes in ionic liquids, *Green Chem.*, 4, 119–123 (2002).
- (31) I. F. Mena, E. Diaz, C. Pérez-Farías, S. Stolte, I. Moreno-Andrade, J. J. Rodriguez, and A. F. Mohedano, Catalytic wet peroxide oxidation of imidazolium-based ionic liquids: catalyst stability and biodegradability enhancement, *Chem Eng J.*, 376, Article ID: 120431 (2019).

- (32) Y. Wang, D. Jiang, and L. Dai, Novel Brønsted acidic ionic liquids based on benzimidazolium cation: synthesis and catalyzed acetalization of aromatic aldehydes with diols, *Catal Commun.*, 9, 2475–2480 (2008).
- (33) N. Gupta, G. L. Kad, and J. Singh, Acidic ionic liquid [BMIM] HSO₄: an efficient catalyst for acetalization and thioacetalization of carbonyl compounds and their subsequent deprotection, *Catal Commun.*, 8, 1323–1328 (2007).
- (34) Y. Deng, F. Shi, J. Beng, and K. Qiao, Ionic liquid as a green catalytic reaction medium for esterifications, *J Mol Catal A Chem.*, 165, 33–36 (2001).
- (35) Y. Leng, J. Wang, D. Zhu, X. Ren, H. Ge, and L. Shen, Heteropolyanion-based ionic liquids: reaction-induced self-separation catalysts for esterification, *Angew Chem.*, 121, 174–177 (2009).
- (36) Z. Wei, F. Li, H. Xing, S. Deng, and Q. Ren Reactivity of bronsted acid ionic liquids as dual solvent and catalyst for fischer esterifications, *Korean J Chem Eng.*, 26, 666–672 (2009).
- (37) K. E. Johnson, R. M. Pagni, and J. Bartmess, Brønsted acids in ionic liquids: fundamentals, organic reactions, and comparisons, *Monatsb Chem.*, 138, 1077–1101 (2007).
- (38) V. I. Parvulescu and C. Hardacre, Catalysis in ionic liquids, *Chem Rev.*, 107, 2615–2665 (2007).
- (39) F. Shi, Y. Gu, Q. Zhang, and Y. Deng, Development of ionic liquids as green reaction media and catalysts, *Catal Surv Asia.*, 8, 179–186 (2004).
- (40) B. Wu, W. Liu, Y. Zhang, and H. Wang, Do we understand the recyclability of ionic liquids, *Chem Eur J.*, 15, 1804–1810 (2009).
- (41) B. Peric, E. Martí, J. Sierra, R. Cruanas, and M. A. Garau, “Ecotoxicity and biodegradability of ionic liquids,” in *Recent Advances in Pharmaceutical Sciences II*, D. M. Torrero, D. Haro, J. Vallès. Eds. (Transworld Research Network, Kerala, India, 2012), pp. 89–113.
- (42) Z. Yaacob, N. A. M. Nordin, and M. A. Yarmo, Ionic liquid supported acid-catalysed esterification of lauric acid, *Malaysian J Anal Sci.*, 15, 46–53 (2011).
- (43) T. Welton, Room temperature ionic liquids: solvents for synthesis and catalysis, *Chem Rev.*, 99, 2071–2083 (1999).
- (44) S. Liu and J. Xiao, Toward green catalytic synthesis-transition metal-catalyzed reactions in non-conventional media, *J Mol Catal A-Chem.*, 270, 1–43 (2007).
- (45) P. A. Ganeshpure, Ionic liquids: environment-friendly solvents and catalysts for the future, *Asian J Exp Sci.*, 22, 113–115 (2008).
- (46) D. K. N. Chau, H. T. N. Le, P. T. Nguyen, and T. N. Le, A rapid way to synthesize brønsted acidic ionic liquid and its application as an efficient catalyst for esterification, *Green Chem Lett. Rev.*, 7, 167–173 (2014).
- (47) Y. Yu, L. Hua, W. Zhu, Y. Shi, T. Cao, Y. Qiao, and Z. Hou, Ionic liquid-catalyzed internal redox esterification reaction, *Synthetic Commun.*, 43, 1287–1298 (2013).
- (48) D. Baş and İ. H. Boyacı, Modeling and optimization I: usability of response surface methodology, *J Food Eng.*, 78, 836–845 (2007).
- (49) N. Aslan and Y. Cebeci, Application of Box–Behnken design and response surface methodology for modeling of some Turkish coals, *Fuel*, 86, 90–97 (2007).
- (50) S. Kuchibhotla and P. S. T. Sai, Enhancement of esterification reaction between ethanol and sulphuric acid using ionic liquids, *Indian Chem Eng.*, 55, 143–152 (2013).
- (51) A. Stark, “Ionic Liquid Structure-Induced Effects on Organic Reactions,” in: *Ionic Liquids. Topics in Current Chemistry*, B. Kirchner. Ed. (Springer, Berlin, Heidelberg, 2008), Vol. 290, pp. 41–81.
- (52) D. Naydenova, H. Hasseb, G. Maurerb, and H. J. Bart, Esterifications in ionic liquids with 1-alkyl-3-methylimidazolium cation and hydrogen sulfate anion: conversion and phase equilibrium, *Open Chem Eng J.*, 3, 17–26 (2009).
- (53) X. U. Junming, J. Jianchun, Z. Zhiyue, and L. Jing, Synthesis of tributyl citrate using acid ionic liquid as catalyst, *Process Saf Environ.*, 88, 28–30 (2010).
- (54) A. N. Masri, M. A. Mutalib, W. Z. N. Yahya, N. F. Aminuddin, and J. M. Leveque, Rapid esterification of fatty acid using dicationic acidic ionic liquid catalyst via ultrasonic-assisted method, *Ultrason Sonochem.*, 60, 104732 (2020).
- (55) C. Chiappe, S. Rajamani, and F. A. D’Andrea, Dramatic effect of the ionic liquid structure in esterification reactions in protic ionic media, *Green Chem.*, 15, 137–143 (2013).
- (56) P. A. Ganeshpure, G. George, and J. Das, Brønsted acidic ionic liquids derived from alkylamines as catalysts and mediums for Fischer esterification: Study of structure-activity relationship, *J Mol Catal A-Chem.*, 279, 182–186 (2008).

- (57) T. Evlik, Y. S. Aşçı, N. Baylan, H. Gamsızkan, and S. Çehreli, Reactive separation of malic acid from aqueous solutions and modeling by artificial neural network (ANN) and response surface methodology (RSM), *J Dispers Sci Technol.*, 1–10 (2020).
- (58) G. E. P. Box and D. W. Behnken, Some new three level designs for the study of quantitative variables, *Technometrics*, 2, 455–475 (1960).
- (59) N. Baylan and S. Çehreli, Removal of acetic acid from aqueous solutions using bulk ionic liquid membranes: a transport and experimental design study, *Sep Purif Tech.*, 224, 51–61 (2019).
- (60) F. B. Şen, Y. S. Aşçı, B. Bekdeşer, M. Bener, and R. Apak, Optimization of Microwave-Assisted Extraction (MAE) for the Isolation of Antioxidants from Basil (*Ocimum basilicum* L.) by Response Surface Methodology (RSM), *Anal Lett.*, 52, 2751–2763 (2019).
- (61) S. G. Kalghatgi and B. M. Bhanage, Green syntheses of levulinic esters using ionic liquid 1-Methylimidazolium hydrogen sulphate [MIM][HSO₄] in solvent free system. *J Mol Liq.*, 281, 70–80 (2019).
- (62) X. X. Han, H. Du, C. T. Hung, L. L. Liu, P. H. Wu, D. H. Ren, S. J. Huang, and S. B. Liu, Synthesis of novel halogen-free Brønsted–Lewis acidic ionic liquid catalysts and their applications for synthesis of methyl caprylate, *Green Chem.*, 17, 499–508 (2015).
- (63) X. Wu, X. Han, L. Zhou, and A. Li, Catalytic performance of acidic ionic liquid in esterification of benzyl alcohol with butyric acid, *Indian J Chem.*, 51, 791–799 (2012).
- (64) X. Han and L. Zhou, Optimization of process variables in the synthesis of butyl butyrate using acid ionic liquid as catalyst, *Chem Eng J.*, 172, 459–466 (2011).
- (65) C. Beula and P. S. T. Sai, Kinetics of esterification of palmitic acid with ethanol- optimization using statistical design of experiments, *Int J Chem Eng Appl.*, 4, 388–392 (2013).
- (66) K. Chen, W. Yan, X. Zhang, Y. Kuang, X. Tang, and X. Han, Optimization of process variables in the synthesis of isoamyl isovalerate using sulfonated organic heteropolyacid salts as catalysts, *J Braz Chem Soc.*, 26, 600–608 (2015).
- (67) D. J. Tao, Y. T. Wu, Z. Zhou, J. Geng, X. B. Hu, and Z. B. Zhang, Kinetics for the esterification reaction of n-butanol with acetic acid catalyzed by noncorrosive brønsted acidic ionic liquids, *Ind Eng Chem Res.*, 50, 1989–1996 (2011).
- (68) H. Li, S. Yu, F. Liu, C. Xie, and L. Li, Synthesis of dioctyl phthalate using acid functionalized ionic liquid as catalyst, *Catal Commun.*, 8, 1759–1762 (2007).
- (69) U. Dorosz, N. Barteczko, P. Latos, K. Erfurt, E. Pankalla, and A. Chrobok, Highly efficient biphasic system for the synthesis of alkyl lactates in the presence of acidic ionic liquids, *Catalysts*, 10, 37 (2020).
- (70) M. Przepis, K. Matuszek, A. Chrobok, M. Swadźba-Kwaśny, and D. Gillner, Inexpensive and tuneable protic ionic liquids based on sulfuric acid for the biphasic synthesis of alkyl levulinates, *J Mol Liq.*, 308, 113166 (2020).
- (71) C. Chiappe and S. Rajamani, Structural effects on the physico-chemical and catalytic properties of acidic ionic liquids: an overview, *Eur J Org Chem.*, 2011, 5517–5539 (2011).
- (72) K. Matuszek, A. Chrobok, F. Coleman, K. R. Seddon, and M. Swadźba-Kwaśny, Tailoring ionic liquid catalysts: structure, acidity and catalytic activity of protonic ionic liquids based on anionic clusters, [(HSO₄)(H₂SO₄)_x]⁻ (x = 0, 1, or 2), *Green Chem.*, 16, 3463–3471 (2014).
- (73) B. H. Huang, Y. F. Wang, K. Zhang, Y. X. Fang, and B. L. Zhou, Synthesis of pyrrolidonium acidic ionic liquids and their catalytic activity for esterification of acetic acid and butanol, *Chinese J. Catal.*, 28, 743 (2007).
- (74) D. J. Tao, J. Wu, Z. Z. Wang, Z. Lu, Z. Yang, and X. Chen, SO₃H-functionalized brønsted acidic ionic liquids as efficient catalysts for the synthesis of isoamyl salicylate, *RSC Adv.*, 4, 1–7 (2014).

