Synthesis of Ricinoleic Acid Estolides by the Esterification of Ricinoleic Acids Using Functional Acid Ionic Liquids as Catalysts

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Abstract: Estolides of ricinoleic acid (RA) have been used as lubricants and pigment dispersant in many industries. In this paper, functional acid ionic liquids (ILs) were firstly used as catalysts to prepare RA estolides by the esterification of RAs in solvent-free system. Different ILs were used as catalysts for the esterification. Effect of reaction variables (IL amount, reaction temperature and reaction time) on the esterification were also investigated and optimized using response surface methodology (RSM). Among all tested ILs, [BSO₃HMIM]TS showed the best performance for the esterification. Arrhenius equation for the esterification was $\ln V_0 = 14.897 - 7558.7/T$, and the activation energy (E_a) was 62.84 kJ/mol. A high degree of polymerization with an acid value of 48.0 ± 2.5 mg KOH/g was achieved at the optimized conditions (IL load 12%, reaction temperature 140°C, and reaction time 12 h). The effect of reaction variables on the esterification decreased in the order of catalyst loading of IL > reaction temperature > reaction time.

Key words: esterification, estolide, functional ionic liquid, ricinoleic acid, response surface methodology

1 INTRODUCTION

Estolides are kinds of linear oligomeric polyesters, which can be prepared by the esterification between carboxyl group and hydroxyl group of hydroxyl fatty acids¹⁻³). Ricinoleic acid (RA, 18:1⁹-OH¹²) is an unsaturated hydroxyl fatty acid that naturally occurs in castor oil. The estolides formed by the esterification of ricinoleic acids (RA) and their derivatives, owing to their excellent lubricities and biodegradability properties, have been used in many industries⁴⁻⁶), for example, as base stocks for lubricants and functional fluids, cutting oil base in metal processing, a viscosity controller for chocolate, an emulsifier for margarine, and pigment dispersant in paint, ink, cosmetics, etc..

According to those previous reports^{1, 7, 8}), ricinoleic acid estolides can be prepared by enzymatic esterification of RA. For example, free *Candida rugosa* lipase was used as catalyst for ricinoleic acid estolides preparation in a batch reactor¹). The estolide with an acid value (AV) of 65 mg KOH/g can be obtained at 48 h after the removal of water formed in the reaction. In order to further improve the operational stability of reaction system, immobilized *Candida rugosa* lipase was used to catalyze the esterification of RA, and an estolide with high degree of polymerization (AV,

57.5 mg KOH/g) can be obtained at 48 h in a vacuum reactor^{7, 9}).

A noncommercial immobilized *Staphylococcus xylosus* lipase 2 was also used to prepare ricinoleic acid estolide in presence or absence of organic solvent⁸). High yield of ricinoleic acid estolide ($65 \pm 4\%$) was achieved at 48 h in a solvent-free system and the presence of molecular sieves⁸). In order to effectively synthesize ricinoleic acid estolide, a bioreactor system containing immobilized lipase was used to rapidly prepare ricinoleic acid estolide with high degree of condensation⁶). However, due to the high cost of enzyme and low reaction efficiency of enzymatic reaction, more efficient methods and green catalysts for ricinoleic acid estolide preparation have attracted much attention.

Ionic liquids (ILs) are salts consisting of organic cations and inorganic or organic anions. ILs, as the novel environmental friendly catalysts, due to non-volatile, thermal stability, and easy separation, have been used as green solvents and catalysts for many reactions¹⁰⁻¹⁸). However, the information of IL as catalyst for the synthesis of ricinoleic acid estolides was not available.

In this work, various functional ILs were used as catalysts to prepare ricinoleic acid estolides in solvent-free

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Accepted March 7, 2017 (received for review February 6, 2017)

Journal of Oleo Science ISSN 1345-8957 print / ISSN 1347-3352 online

<http://www.jstage.jst.go.jp/browse/jos/> <http://mc.manuscriptcentral.com/jjocs>

Fig. 1 Synthesis of estolides by the esterification of ricinoleic acids catalyzed using ionic liquids (ILs).

system (Fig. 1). Compared with those previous reports using lipases as catalysts, ricinoleic acid estolides can be efficiently prepared using functional ILs as catalysts. And the effect of reaction variables (ILs amount, reaction temperature, and reaction time) on the preparation of ricinoleic acid estolides were also investigated and optimized using response surface method (RSM). The relationship between initial reaction rate and reaction temperature was established, and the activation energy (E_a) of the esterification was also evaluated.

2 EXPERIMENTAL

2.1 Materials

Ricinoleic acid (>97.0% (T), >70% (GC)) was purchased from Aladdin (Shanghai, China). Ionic liquids (ILs): 1-butylsulfonic-3-methylimidazolium tosylate ([BSO₃HMIM]TS), 1-butylsulfonic-3-methylimidazolium hydrogensulfate ([BSO₃HMIM]HSO₄), 1-butylsulfonic-3-methylimidazolium trifluoromethanesulfonate ([BSO₃HMIM]OTf) and 1-butylsulfonic-3-methylimidazolium hydrophosphate ([BSO₃HMIM]HPO₄) were purchased from Shanghai Cheng Jie Chemical Co. Ltd (Shanghai, China). Ethyl acetate (>99.5% purity) was purchased from Tianjin Kemiu Chemical Reagent Co. Ltd (Tianjin, China). All other solvents were analytical grade.

2.2 The esterification of RAs

The esterification of RAs were carried out in 250-mL three-necked glass flasks, equipped with a reflux condens-

er and magnetic stirrer at 500 r/min, in oil bath. In a typical run, the mixture of RA (50 g) was catalyzed by different ILs (10%, relative to the weight of RA) at 140°C. Samples were withdrawn, eluted and centrifuged, and the AV of the supernatant liquid was determined.

2.3 Measurement of the reaction extension

The degree of reaction were evaluated using acid values (AVs), which correspond to the carboxyl group concentration in the reaction mixture. In addition, the decrease in AVs can reflect the condensation of RA, which had been confirmed by HPLC¹⁾. AVs were analyzed according to AOCS Cd 3d-63 and AOCS Ca 5a-40¹⁹⁾. The AVs (mg KOH/g) of ricinoleic acid estolides were determined as follows:

$$AV = 56.1VC/W \quad (1)$$

where V and C are the consumed volume and concentration of NaOH solution, respectively. W is the weight of the sample. The initial AV (A_0) of RA is 155.8 ± 1.2 mg KOH/g.

2.4 Experimental design for RSM and statistical analysis

A Box-Behnken design for three independent parameters (ILs load, reaction temperature, and reaction time) was used to obtain the combination of values that optimizes the response (the AV of RA) within the region of the three dimensional observation space. The factors and levels selected were as follows: reaction time (2, 7, 12 h), reaction temperature (90, 120, 150°C), and IL load (0.1, 10, 19.9%).

The model evaluates the effect of each independent variable on the AV of RA. 3^k factorial tests allow efficient estimation of a second order polynomial regression. The mathematical relationship relating the reaction variables to the AV of RA can be calculated by the following quadratic polynomial equation:

$$Y = \beta_0 + \sum_{i=1}^3 \beta_i X_i + \sum_{i=1}^3 \beta_{ii} X_i^2 + \sum_{i=1}^2 \sum_{j=i+1}^3 \beta_{ij} X_i X_j \quad (2)$$

where Y is the AV of RA; X_i and X_j represent the independent variables; β_0 , β_i , β_{ii} , and β_{ij} are the constant, the linear term coefficient, the quadratic term coefficient, and the cross term coefficient, respectively. The experiments were carried out for analysis using Design Expert. For the present study, the coefficients of the model were also estimated.

All experiments were performed at least in triplicate. Results were expressed as average $\pm$ S.E.M. A two-way analysis of variance (ANOVA) was used. Statistical significance was considered at $p < 0.05$.

3 RESULTS AND DISCUSSION

3.1 Effect of different functional ILs

The acidity and solubility of ILs are relative to its anion, which depend on the activity of ILs as catalysts. Due to the

Fig. 2 Effect of various functional ILs as catalysts on the esterification of RAs. Reaction conditions: 50 g RAs, 5 g ILs (10%, relative to the weight of RAs), 120°C, and 500 r/min.

Fig. 3 Effect of reaction time on the esterification of RAs. Reaction conditions: 50 g RAs, 5 g [BSO₃HMIM]TS (10%, relative to the weight of RAs), 120°C, and 500 rpm.

high acidities, the SO₃H-functional ILs showed high activities for some esterifications²⁰⁾. In the present work, the effect of different functional ILs used as catalysts for ricinoleic acid estolides preparation were compared (Fig. 2).

As shown in Fig. 2, the activities of four functional ILs as catalysts for the esterification of ricinoleic acid decreased in the order of [BSO₃HMIM]TS > [BSO₃HMIM]OTF > [BSO₃HMIM]HSO₄ > [BSO₃HMIM]HPO₄. Among the ILs tested, [BSO₃HMIM]TS showed the highest catalytic activity, and an estolides with a high degree of polymerization (56.9 ± 2.9 mg KOH/g) was obtained in 10 h (Fig. 3). The AV of the estolide (56.9 ± 2.9 mg KOH/g) was lower than that reported previously (65 mg KOH/g)¹⁾ and reaction time (10 h) was significant shorter than those (48 h) of lipase-

Fig. 4 (A) Effect of reaction temperature on the esterification of RAs. Reaction conditions: 50 g RAs, 5 g [BSO₃HMIM]TS (10%, relative to the weight of RAs), and 500 rpm. (B) The relationship between the initial esterification rate to form RA estolides (V_0) and reaction temperature. Reaction conditions were same as Fig. 4A.

catalyzed reactions^{1,7)}. These results were attributed to the strong acidity of [BSO₃HMIM]TS^{21, 22)}, which can provide more catalytic activity sites for the esterification.

3.2 Effect of reaction temperature on the esterification

Reaction temperature can affect the mass transfer, catalytic activity and the miscibility of reaction system. The AV of RA significantly decreased with the increase of reaction temperature in 4 h (Fig. 4A). And the time that the esterification reached equilibrium shortened from >10 h of 120°C to 6 h of 160°C. When reaction temperature was 140°C, the RA estolides with an AV of 48.9 ± 0.9 mg KOH/g was achieved at 10 h, which was similar with those of 150°C (50.9 ± 1.7 mg KOH/g) and 160°C (52.0 ± 1.4 mg KOH/g). These results showed that further increase of reaction

temperature ($>140^{\circ}\text{C}$) did not lead to a significant increase of estolides formation.

The initial reaction rates (V_0 , mol/(L·min)) of the esterification to form RA estolides, defined as the initial RA estolide yield per unit time (V_0 , mol/(L·min)), were calculated from five experimental points of the yield–time profile corresponding to the first 0.5 h of the reaction (15.0% or less RA estolides yield), where the profiles were found to be approximately linear. Therefore, Arrhenius law can be described as follows:

$$\ln V_0 = \ln A - E_a/RT \quad (3)$$

where A is Arrhenius constant, E_a is the activation energy, R is gas constant, and T is absolute temperature (K). As illustrated in Fig. 4B, a plot of $\ln V_0$ versus $1/T$ shows a good linearity at the tested temperature. Arrhenius equation for the synthesis of RA estolides can be expressed as: $\ln V_0 = 14.897 - 7558.7/T$, and E_a was 62.84 kJ/mol, which is higher than other E_a values (0.97–34.5 kJ/mol) determined for the lipase-catalyzed esterifications²³.

3.3 Effect of IL load on the esterification

In order to investigate IL ([BSO₃HMIM]TS) load on the esterification, different IL load from 0.5% to 20% were used. As shown in Fig. 5, with the increase of [BSO₃HMIM]TS load from 0.5% to 10%, reaction rate increase significantly, and the minimum AV ($48.9 \pm 0.9\%$) was achieved with 10% IL load. However, a further increase in IL load did not lead to a superior degree of polymerization (low AV). In addition, an excessive IL in reaction system resulted in the increase of system viscosity, which decreased mass transfer efficiency and reaction rate. Therefore, 10% of [BSO₃HMIM]TS catalyst load was used in next experiments.

3.4 Model Fitting.

RSM is an empirical modeling technique used to evaluate the relationship between a set of controllable experimental factors and observed results. Modeling of factors and responses was performed by RSM to predict the highest possible conversion of RA. The results obtained for the models are listed in Table 1. Duplicate experiments were carried out at all design points.

The experimental values acquired from the Box-Behnken experimental design were analyzed and regressed using a quadratic polynomial equation depicted in Eq. (4):

$$\begin{aligned} \text{AV (mg KOH/g)} = & 56.34 - 25.90A - 30.25B - 12.28C + \\ & 2.88AB + 13.08AC - 2.52BC + 13.42A^2 \\ & + 31.42B^2 + 13.27C^2 \end{aligned} \quad (4)$$

The analysis of variance (ANOVA) for this model and the significance test for each regression coefficient were shown in Table 2. The quadratic polynomial regression model was

Fig. 5 Effect of [BSO₃HMIM]TS load on the esterification of RAs. Reaction conditions: 50 g RAs, 140°C , and 500 rpm.

extremely significant ($p < 0.0001$), which indicated that the model was prominent and adequate to explain the actual relationship between the AV of RA estolides and reaction variables with a high coefficient of determination ($R^2 = 0.9823$).

The relationship between the AV of RA estolides and the interaction of reaction variables can be evaluated by 3D surface plots (Fig. 6). The minimum AV of the estolides obtained appeared in reaction temperature of $>130^{\circ}\text{C}$, reaction time of >6 h, and IL load of $>10\%$. Figure 6 also showed that the influence of the variables affecting the esterification decreased in the order of IL load $>$ reaction temperature $>$ reaction time.

Figure 6A shows the mutual interaction of reaction temperature and IL load on the synthesis of ricinoleic acid estolides. The interaction of reaction temperature and IL load was the most significant. The minimum AV can be found in high temperatures ($>130^{\circ}\text{C}$) and high IL load (10–18%). And elliptical contours can be obtained between temperature with IL load, which indicated that the interaction of reaction temperature and IL load was very significant²⁴. Figure 6B shows that, compared with reaction time, the effect of reaction temperature on the synthesis of RA estolides was more significant, which can also be found from Table 2. Figure 6C shows that the mutual interaction effect of IL load and reaction time in the synthesis of RA estolides at 150°C . Low AV (<51.7 mg KOH/g) of RA can be obtained in high IL load ($>10\%$) and long reaction time (>8 h). And compared reaction time, the effect of IL load was more significant, which can be also obtained from F-values (Table 2).

3.5 Attaining optimum conditions and model verification

Reaction conditions were optimized using RSM as follows: IL load 12%, reaction temperature 140°C , and re-

Table 1 Response surface design and results of the preparation of RA estolides.

treatment No. ^a	A, temperature (°C)	B, IL load (%)	C, time (h)	AV (mg KOH/g)
1	150	19.9	7	55.3 ± 1.2
2	120	10.0	7	57.9 ± 1.7
3	120	10.0	7	55.5 ± 2.0
4	120	10.0	7	53.3 ± 1.4
5	90	10.0	2	136.6 ± 0.9
6	150	10.0	2	56.4 ± 1.7
7	120	10.0	7	60.8 ± 2.5
8	120	0.1	12	129.0 ± 2.2
9	90	19.9	7	99.1 ± 1.1
10	150	0.1	7	97.5 ± 1.4
11	90	0.1	7	152.8 ± 0.9
12	120	19.9	2	78.1 ± 1.9
13	120	19.9	12	50.9 ± 2.5
14	90	10.0	12	83.5 ± 1.7
15	120	10.0	7	54.2 ± 3.3
16	150	10.0	12	55.6 ± 2.0
17	120	0.1	2	146.1 ± 1.7

^a: Numbers were run randomly.

Table 2 Analysis of variance (ANOVA) for quadratic model for the preparation of RA estolides.

Source	Sum of squares	Degrees of freedom	Mean square	F value	P>F
Model	20801.56	9	2311.28	43.32	<0.0001
A-Temperature	5366.48	1	5366.48	100.58	<0.0001
B-ILs load	7320.50	1	7320.50	137.20	<0.0001
C-Time	1205.40	1	1205.40	22.59	0.0021
AB	33.06	1	33.06	0.62	0.4570
AC	683.82	1	683.82	12.82	0.0090
BC	25.50	1	25.50	0.48	0.5116
A ²	758.02	1	758.02	14.21	0.0070
B ²	4156.04	1	4156.04	77.89	<0.0001
C ²	741.16	1	741.16	13.89	0.0074
Residual	373.50	7	53.36		
Lack of fit	336.65	3	112.22	12.18	0.0176
Pure Error	36.85	4	9.21		
Cor Total	21175.06	16			
R ² =0.9824					

action time 12 h. Under these optimal conditions, low AV (48.0 ± 2.5 mg KOH/g) of RA was achieved, which is well accorded with the predicted result (46.6 mg KOH/g), which indicated that the model developed was accurate and reliable. Compared with the previous report (57.7 mg KOH/g

at 48 h)⁷⁾, lower AV (48.0 ± 2.5 mg KOH/g) of RA can achieved in shorter time (12 h) in the work.

Fig. 6 (A) Response surface plot of reaction temperature and IL load with reaction time 7 h in the synthesis of ricinoleic acid estolides. (B) Response surface plot of reaction temperature and reaction time with [BSO₃HMIM]TS load 10% in the synthesis of ricinoleic acid estolides. (C) Response surface plot of IL load and reaction time with 150°C in the synthesis of ricinoleic acid estolides.

4 CONCLUSION

In the work, several functional acid ionic liquids (ILs) were used as catalysts for the esterification of RA to prepare RA estolides. Among all tested ILs, [BSO₃HMIM]TS showed the best performance for the preparation of RA estolides. The interaction effect of reaction variables were studied and optimized using RSM, and reaction conditions were optimized as follows: IL load 12%, reaction temperature 140°C, and reaction time 12 h. The order affected the synthesis of RA estolides was IL load > reaction temperature > reaction time. Under these optimal conditions, the AV of ricinoleic acids was 48.0 ± 2.5 mg KOH/g, which is lower than those (57.7 mg KOH/g) of previous reports using lipases as catalysts. And reaction time (12 h) reached equilibrium in the work is one quarter of previous report (48 h). These results showed that, compared with those previous reports using lipases as catalysts, RA estolides can be efficiently prepared using functional ILs as catalysts.

Acknowledgements

The authors gratefully acknowledge financial support from Program for Science & Technology Innovation Talents in Universities of Henan Province (15HASTIT030), and Funding Scheme for Young Teachers Cultivating Program in Henan University of Technology.

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