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Aluminum alginate as a solid catalyst for esterification of lactic acid with 1-butanol

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Abstract

Aluminum-alginate (ALA) was used as a solid catalyst for esterification of lactic acid with 1-butanol at different temperature in a range of 55 to 85°C. Conversion of lactic acid was found to increase with increasing reaction temperature with the maximum conversion of 81.18% after 6 h of reaction at 85°C with 1-butanol to lactic acid molar ratio of 5 and 1%w/v of catalyst loading. The result was compared with the system using Amberlyst 15 under the same reaction condition. It was observed that ALA has a higher catalytic activity than Amberlyst 15. Experimental kinetic data were correlated by pseudo-homogeneous model with an assumption of ideal behavior. The kinetics of this reaction could be described using this model with minor errors. The activation energy for ALA-catalyzed esterification of lactic acid with 1-butanol was found to be 61.16 k J/mol.

Keywords: Esterification, Kinetic study, Lactic acid, 1-Butanol, Sodium alginate

1. Introduction

Lactic acid is an important chemical utilized in many industries. Major challenge in lactic acid production, however, is an extravagance of the acid recovery and purification cost. Reactive distillation comprising of esterification of lactic acid and hydrolysis of the lactate ester has been one of the promising process as it has lower capital cost and is able to produce highly pure lactic acid, which is the key feedstock in the production of biodegradable polymer. The interesting research was reported by Chien et al. [1], where the recovery of lactic acid from fermentation broth by esterification and hydrolysis using different alcohols was compared. The result showed that 1-butanol is the most attractive candidate, as it gives a short payback period for this process. Esterification between lactic acid and 1-butanol has, therefore, become increasingly attractive and extensive researches have been done over the years to find the most suitable solid catalyst for this reaction.

Zhang et al. [2] studied the esterification of oleic acid with alcohols using a new and easily prepared solid acid catalyst obtained from inexpensive sodium alginate and aluminum chloride. The aluminum-alginate catalyst showed high catalytic activity for esterification of oleic acid. In this work, this catalyst is used for the esterification reaction of lactic acid with 1-butanol. The kinetic data is simulated by pseudo-homogeneous model. The rate constant, equilibrium constant as well as the activation energy is also determined.

2. Materials and methods

2.1 Materials

Lactic acid with concentration of 88 %wt and 1-butanol of RPE grade with 99.9% purity were purchased from Carlo Erba. Aluminum chloride ($AlCl_3$) and sodium alginate were purchased from Acros.

2.2 Catalyst preparation

Aluminum (III)-alginate was synthesized using the procedure described by Zhang et al. [2] with slight modification. Approximately, 2 g of sodium alginate was added to 100 mL of deionized water, and the mixture was stirred until a clear viscous solution was obtained. The viscous solution was added stepwise into 100 mL of 0.1 M $AlCl_3$ solution at room temperature. The aluminum-alginate complex in the solution was left to equilibrate for 2 h. After that, 100 mL of deionized water was added into the solution. The liquid was then evaporated out using a rotary evaporator at 105°C under pressure of 300 mbar for 1.5 h. Finally, the aluminum-alginate flakes were dried in oven at 60°C for 3 h. This catalyst was denoted as ALA catalyst.

2.3 Characterization of the catalyst

The powder X-ray diffraction (XRD) patterns of the catalyst sample was performed using a Bruker D2 PHASER

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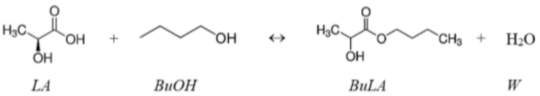
X-ray diffractometer (CuKα radiation, λ = 1.5406 Å). Patterns were recorded over goniometric (2θ) ranges from 20–80°.

2.4 Apparatus and procedure

A kinetic study of esterification of lactic acid with 1-butanol was performed in a 100 mL glass vessel equipped with a thermometer and a magnetic stirrer. The reaction temperature was maintained by an electric heating thermostatic oil bath. Amount of lactic acid and 1-butanol used in this work was 18.91 and 68.45 g, respectively. The lactic acid and 1 g of catalyst were firstly charged into the reactor and heated to the desired temperature. Once the desired temperature was attained, a known amount of preheated 1-butanol at the same temperature was added to the reactor and the time was considered as the initial reaction time. The liquid samples of 0.01 mL were carefully pipetted out from the reactor at different time intervals and the concentration of non-reacted lactic acid was analyzed by titration with 0.01 M NaOH solution.

3. Kinetic model

Esterification reaction of lactic acid (*LA*) with 1-butanol (*BuOH*) to form the butyl lactate (*BuLA*) and water (*W*) can be written as:



(1)

Assume the liquid behaves as an ideal solution, the reaction kinetics can be expressed using a pseudo-homogeneous model as follows:

$$-r_{LA} = \frac{dx_{LA}}{dt} = k\left(C_{LA}C_{BuOH} - \frac{C_{BuLA}C_W}{K_e} \right) \quad (2)$$

$$K_e = \left(\frac{C_{BuLA}C_W}{C_{BuOH}C_{LA}} \right)_{eq} \quad (3)$$

where $-r_{LA}$ is the reaction rate (mol L^{-1} min^{-1}), C_i is concentration of component *i* (mol L^{-1}), *k* is the rate constant (L mol^{-1} min^{-1}) and K_e is equilibrium constant. The kinetic parameters of the models were obtained by minimizing the sum of squared residuals (*SSR*) between the experimental (x_{exp}) and calculated (x_{cal}) mole fraction as shown in Eq. (4):

$$SSR = \sum \left(x_{\exp} - x_{cal} \right)^2 \quad (4)$$

The reaction constant is expressed using Arrhenius equation as in Eq. (5).

$$k = A\exp\left(\frac{-E_A}{RT} \right) \quad (5)$$

where A is the pre-exponential factor (min^{-1}), E_A is the activation energy (J mol^{-1}), *T* is the absolute temperature (K) and *R* is the gas constant (J mol^{-1} K^{-1}).

4. Results and discussion

4.1 Characterization of the ALA catalyst

In this study, when aluminum chloride was mixed with sodium alginate, aluminum alginate is formed immediately, as shown in Figure 1(a), indicating gelling property of the alginate. The process of gelation is the simply exchange of Al^{3+} ions for Na^+ ions. The final ALA catalyst granules is shown in Figure 1(b). It was found that the peaks at 2θ angles of approximately 31°, 45° and 56° are similar to the pure diaspore peaks reported by Zhang et al. [2], which matched with the typical aluminum oxyhydroxide particle.

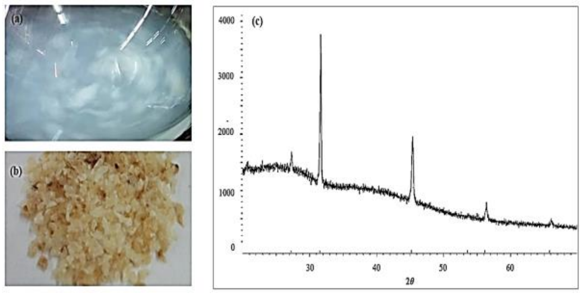


Figure 1 ALA catalyst prepared in this work; (a) ALA gelation, (b) ALA flakes, (c) XRD patterns of ALA catalyst

4.2 Catalyst performance

The performance of catalyst is very important for a reaction system since it is directly related to economical application of the process. In this study, the ALA catalyst activities was firstly tested by comparison with the commercially available catalyst Amberlyst 15. The activity of both catalysts on esterification of lactic acid with 1-butanol was compared in the reactions with temperature of 65°C and 85°C with 1-butanol to lactic acid molar ratio of 5:1 (M=5), catalyst loading of 1 %w/v and the reaction time of 6 h. The results presented in Figure 2 indicate that the ALA catalyst had higher activity than Amberlyst 15 with the conversion of 74.39% and 81.18% at the temperature of 65°C and 85°C, respectively, while the conversion when Amberlyst 15 was used was 53.19% at 65°C and was 75.17% at 85°C.

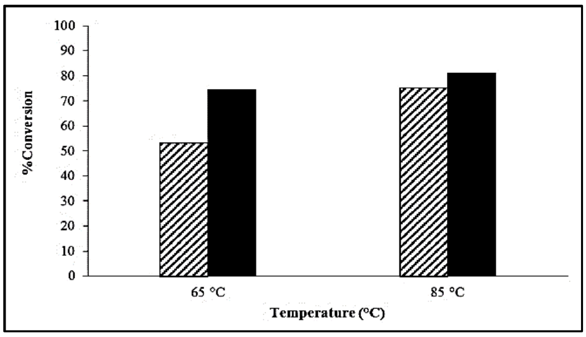


Figure 2 Comparison of conversion for esterification of lactic acid with 1-butanol using (▨) Amberlyst-15 and (■) ALA as reaction catalyst

Table 1 Kinetic parameters for esterification of lactic acid with 1-butanol using ALA and Amberlyst 15 as solid catalysts at different temperatures

Temperature (°C)	Catalyst	k (L mol^{-1} min^{-1})	K_e	*SSR*	R^2
55	ALA	0.0699	0.7866	0.0010	0.9987
65		0.1225	0.9765	0.0056	0.9922
75		0.3036	1.2700	0.0186	0.9694
85		0.4142	1.5439	0.0065	0.9900
65	Amberlyst 15	0.0241	0.9763	0.0056	0.9989
85		0.0641	1.5435	0.0151	0.9981

4.3 Effect of temperature

The reaction temperature was studied in the range of 55 to 85°C. The reaction was carried out with 1-butanol to lactic acid molar ratio of 5:1 (M=5), catalyst loading of 1 %w/v and the reaction time of 6 h. Figure 3 shows the effect of temperature on the conversion of lactic acid with ALA and Amberlyst-15 as catalysts. Since the esterification of carboxylic acid with alcohol is an endothermic reaction, the conversion is increased with the reaction temperature [3]. Similar trends were reported in the literature [4]. It can be seen from the result that the effect of temperature on the rate of 1-butyl lactate production is significant. In both catalytic systems, the reaction rate increased sharply with increasing temperature. In addition, it was found that the ALA catalyst gave the maximum conversion of 81.18% at the temperature of 85°C.

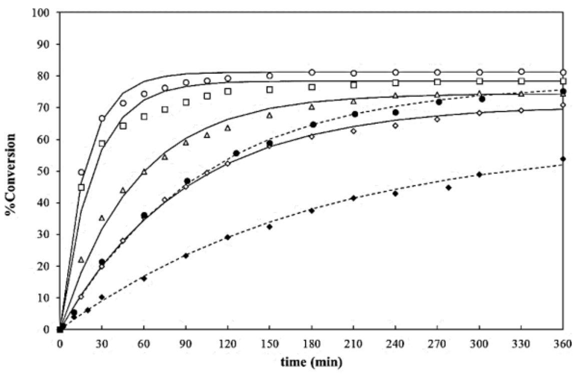


Figure 3 Effect of temperature on the conversion of lactic acid. Reaction temperature; (◊) 55°C, (∆) 65°C, (□) 75°C, (○) 85°C for ALA catalyst. (♦) 65°C, (●) 85°C for Amberlyst-15. Solid and dash lines indicated the calculated conversion of reaction with ALA and Amberlyst 15, respectively

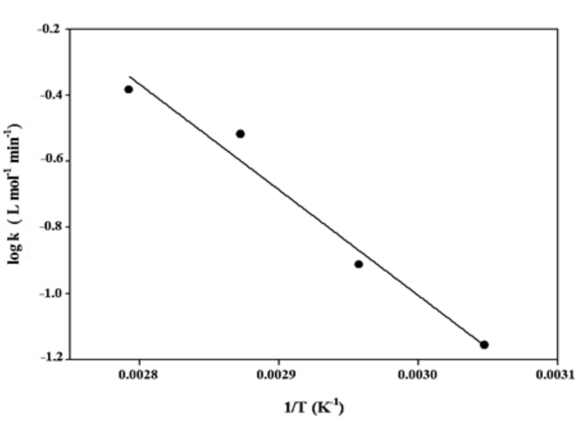


Figure 4 Arrhenius plot for ALA catalyzed esterification of lactic acid with 1-butanol

4.4 Kinetic parameters

The kinetic data of esterification of lactic acid with 1-butanol were correlated with pseudo-homogeneous model. The adjustable kinetic parameters k and K_e obtained by data fitting are shown in Table 1. It was found that both kinetic parameters increase with the reaction temperature, with the value from ALA catalyzed reaction higher than the one catalyzed by Amberlyst-15. It means that the faster reaction can be achieved over ALA catalyst. Increasing of Ke is due to high equilibrium concentration of products.

As shown in Table 1, the coefficient of determination (R^2) indicates good agreement between the experimental and the calculated conversion. It should be noted that the assumption of ideal behavior results in small errors. Taking the natural logarithm of both sides of the Arrhenius equation (Eq.5) gives:

$$\log k = \log A - \frac{E_A}{2.303RT} \tag{6}$$

A plot of log k versus $1/T$ at constant 1-butanol to lactic acid molar ratio and catalyst loading gives a straight line as shown in Figure 4. The pre-exponential factor and activation energy obtained from this work is found to be 3.7705 x 10^8 min^{-1} and 61.16 kJ/mol, respectively.

5. Conclusions

The esterification reaction of lactic acid with 1-butanol was successfully carried out over ALA solid catalyst. The reaction temperatures in the range of 55 to 85°C were investigated. It has been observed that the conversion of lactic acid increased with increasing temperature. ALA catalyst also showed better catalytic performance than Amberlyst 15. The reaction rate constant and equilibrium constant were influenced by the reaction temperature. The pseudo-homogeneous model was able to describe the kinetics of this esterification with small error. The activation energy of lactic acid esterification was found to be 61.16 kJ/mol.

6. References

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