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Kinetic Study of Aluminum – Alginate Catalyzed Esterification of Lactic Acid with 1-Butanol

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Aluminum-alginate catalyst prepared from aluminum chloride and inexpensive biopolymer sodium alginate is used in lactic acid esterification with 1-butanol. Effect of initial reactant molar ratio, catalyst loading and reaction temperature on the acid conversion is investigated. Maximum conversion of about 81.2% was achieved after 6 h of reaction at 85°C with initial 1-butanol-to-lactic-acid molar ratio of 5 and catalyst loading of 1%w/v. Experimental kinetic data are correlated by pseudo-homogeneous model using UNIFAC to describe non-ideality of the reaction components. Satisfactory agreement between the experimental and calculated data is achieved. The specific rate and equilibrium constant for this reaction are reported.

Keywords : Esterification, 1-Butanol, Lactic acid, Sodium alginate, Butyl lactate

INTRODUCTION

Lactic acid is a commodity chemical utilized in several applications including in food, agricultural, chemical and pharmaceutical industries. It is also used as an important raw material for the manufacture of biodegradable polymers such as polylactic acid and its copolymers, which could be alternative materials to conventional petroleum-based polymers. The acid can be produced by either chemical synthesis or by fermentation. The latter has become more attractive because production of pure optical isomer of lactic acid can be realized by selecting the proper strain of microorganism. Recovery of the acid from fermentation broth, however, presents numerous challenges due to the dilute and complex natures of the broth. Several separation and purification techniques have been investigated to overcome this difficulty. Amongst those, a reactive distillation process employing simultaneous catalyzed esterification of lactic acid and separation of lactate ester, which will later be hydrolyzed back into its acid form, has

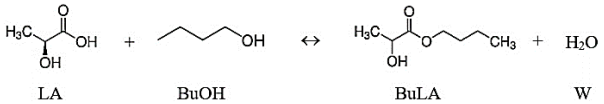
shown remarkable viability in lactic acid purification. Accordingly, many researchers have conducted experiments to investigate catalytic esterification of lactic acid with various alcohols. Su *et al.*, (2013) developed and optimized reactive distillation process to minimize the cost for lactic acid recovery from fermentation broth by esterification and hydrolysis with different alcohols. The results suggest that the process using butanol is economically preferred if short payback period is to be achieved.

Zhang *et al.*,(2013) studied the esterification of oleic acid with alcohols using a new heterogeneous acid catalyst prepared from inexpensive aluminum chloride and biopolymer sodium alginate. The aluminum-alginate catalyst showed high catalytic activity in esterification of oleic acid. It can be applied to the esterification reaction of fatty acids with various carbon chain lengths.

In this work, aluminum-alginate catalyst is used in the esterification of lactic acid with 1-butanol. Effect of reaction variables on conversion of lactic acid are examined. Experimental kinetic data is simulated by pseudo-homogeneous model with non-ideal assumption. Specific rate and rate constant of this reaction are reported.

THEORY AND KINETIC MODELING

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



In order to incorporate the non-ideality of liquid phase components into the reaction kinetics, reaction rate law is expressed in terms of activity of reaction component i (a_i) following a pseudo-homogeneous model as shown in Eq. (1).

$$-r_{LA} = \left(\frac{N_{A0}}{m_{cat}}\right)\frac{dX_{LA}}{dt} = k\left(a_{LA}a_{BuOH} - \frac{a_{BuLA}a_{H_2O}}{K_e}\right) \quad (1)$$

where $-r_{LA}$ is the reaction rate (mol·g^{-1}·min^{-1}), N_{A0} is number of moles of lactic acid initially charged into the reactor, m_{cat} is catalyst mass (g), X_{LA} is lactic acid conversion, t is reaction time (min), k is specific rate or rate constant (mol·g^{-1}·min^{-1}) and K_e is equilibrium constant. Activity of each reaction component is determined using UNIFAC model.

Both specific rate and rate constant are temperature dependent. The former relates to the activation energy (E_A) of the reaction by Arrhenius equation in Eq. (2).

$$k = A\exp\left(-\frac{E_A}{RT}\right) \quad (2)$$

where A is pre-exponential factor (mol·g^{-1}·min^{-1}), T is absolute temperature (K) and R is the gas constant (J·mol^{-1}·K^{-1}). The equilibrium constant is calculated from the component activity at equilibrium using Eq. (3).

$$K_e = \left(\frac{a_{BuLA}a_{H_2O}}{a_{LA}a_{BuOH}}\right)_{eq.} = \left(\frac{x_{BuLA}x_{H_2O}}{x_{LA}x_{BuOH}}\right)_{eq.}\left(\frac{\gamma_{BuLA}\gamma_{H_2O}}{\gamma_{LA}\gamma_{BuOH}}\right)_{eq.} \quad (3)$$

where x_i and γ_i are mole fraction and activity coefficient of component i, respectively, at equilibrium.

The kinetic parameters of the models are obtained by minimizing sum of squared residuals (SSR) between the experimental ($X_{\exp}$) and the calculated (X_{cal}) conversion of experiment j as shown in Eq. (4) through the non – linear least square method.

$$SSR = \sum_{j=1}^{M} \left(X_{\exp,j} - X_{cal,j} \right)^2 \quad (4)$$

EXPERIMENT

Materials

Lactic acid with concentration of 88 %wt and 1-butanol are purchased from Carlo Erba. Aluminum chloride ($AlCl_3$) powder of 98.5% purity and technical grade sodium alginate are from Acros.

Catalyst Preparation

Aluminum (III)-alginate is synthesized using the procedure described by Qiuyun *et al.*, (2013) with slight modification. Approximately, 2 g of sodium alginate is added to 100 mL of deionized water. The liquid is stirred until a clear viscous solution is achieved. A hundred milliliters of 0.1 M $AlCl_3$ solution is added stepwise into the viscous solution at room temperature. The solution is left to equilibrate for 2 h before it is mixed with 100 ml of deionized water. The liquid is then evaporated out using a rotary evaporator at 105°C and 300 mbar for 1.5 h. Finally, the aluminum-alginate granules are oven-dried at 60°C for 3 h. This catalyst is denoted as ALA catalyst.

Kinetic Study of Latic Acid Esterification

A kinetic study of lactic acid esterification with 1-butanol is performed in a 100 mL glass vessel equipped with a thermometer and a magnetic stirrer. The reaction temperature is controlled by a thermostatic oil bath. Weighed amount of lactic acid and the catalyst is firstly charged into the reactor and heated to the desired temperature. Once that is attained, a known amount of preheated 1-butanol at the same temperature is added. This time is considered as a starting point of the reaction. The liquid samples of 0.01 mL are carefully pipetted out from the reactor at different time intervals. The concentration of non-reacted lactic acid is analyzed by titration with the standard 0.01 M NaOH solution. Every experiment is carried out for 6 h.

RESULTS AND DISCUSSIONS

Effect of Catalyst Loading

Effect of catalyst loading on conversion of lactic acid is investigated at 75°C and initial 1-butanol-to-lactic-acid molar ratio of 5:1 with the catalyst loading of 0.25, 0.50 and 1.00 %w/v. The result is shown in **figure 1**. Rate of reaction is found to increase with the catalyst loading but nearly the same equilibrium conversion is achieved in every experiment.

Effect of Initial 1 – Butanol – to – Lactic – Acid Molar Ratio

Esterification is a reversible reaction, and using excess quantity of the alcohol

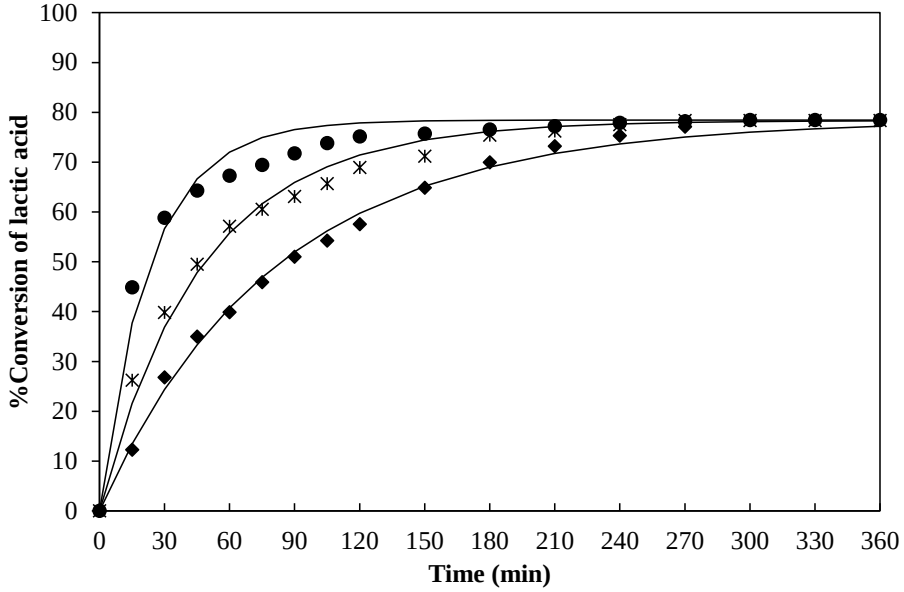


Fig. 1: Effect of catalyst loading on conversion of lactic acid at 75°C and intial 1-butanol-to-lactic-acid molar ratio of 5:1: (◆) 0.25%w/v; (✳) 0.5%w/v; (●)1%w/v. Solid lines indicate the calculation values.

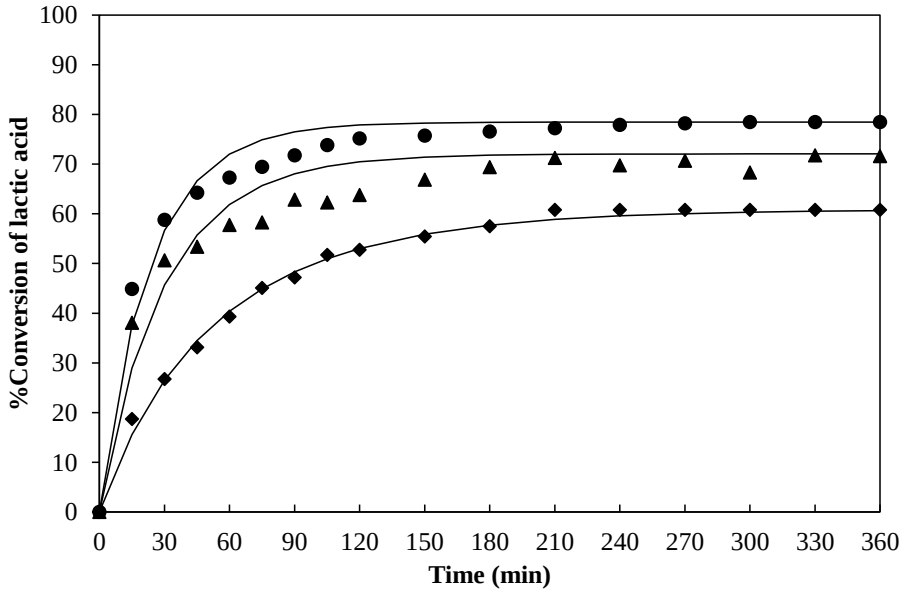


Fig. 2: Effect of initial 1-butanol-to-lactic-acid molar ratio on conversion of lactic acid at 75°C and 1% w/v catalyst loading: (◆)1:1; (▲)3:1; (●) 5:1. Solid lines indicate the calculation values.

can drive the reaction equilibrium toward the formation of ester product. In this work, effect of initial 1-butanol-to-lactic-acid molar ratio of 1:1, 3:1 and 5:1 on lactic acid conversion is studied. The reaction is carried out at 75°C using 1%w/v of catalyst loading. As shown in **figure 2**, lactic acid conversion is increased with increasing reactant molar ratio.

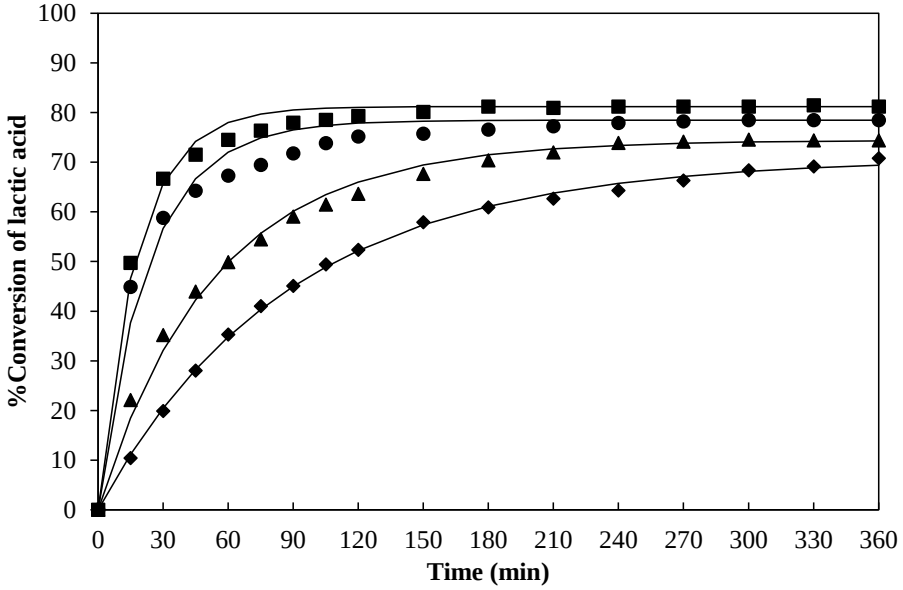


Fig. 3: Effect of reaction temperature on conversion of lactic acid at 1-butanol-to-lactic-acid molar ratio of 5:1 and catalyst loading of 1%w/v: (◆)55°C; (▲)65°C; (●)75°C; (■)85°C. Solid lines indicate the calculation values.

Table 1. Kinetic parameters for esterification of lactic acid with 1-butanol catalyzed by ALA catalyst.

Reaction condition			k	K_e	SSR	R^2
85	5	1	0.0536	2.7771	0.0058	0.9911
75	5	1	0.0410	2.2812	0.0169	0.9722
65	5	1	0.0165	1.7477	0.0044	0.9940
55	5	1	0.0093	1.3998	0.0008	0.9989
75	3	1	0.0379	2.5707	0.0333	0.9581
75	1	1	0.0343	2.2036	0.0022	0.9957
75	1	0.50	0.0397	2.2602	0.0074	0.9903
75	1	0.25	0.0451	2.2532	0.0042	0.9956

Effect of Temperature

Effect of reaction temperature on conversion of lactic acid is studied in the range of 55 to 85°C using 1-butanol-to-lactic-acid molar ratio of 5:1 and catalyst loading of 1 %w/v. The result is in **figure 3**, which clearly shows substantial increase of the reaction rate with the increase of reaction temperature. Equilibrium conversion of lactic acid is found to be dependent of the reaction temperature as well. This is likely due to the endothermic nature of esterification reaction, which is confirmed from value of the activation energy explicated in the next section.

Kinetic Modeling

The experimental kinetic data of esterification of lactic acid with 1-butanol are correlated by pseudo-homogeneous model with non-ideal assumption in order to determine the specific rate and the equilibrium constant. As shown in **Table 1**, small value of SSR and value of

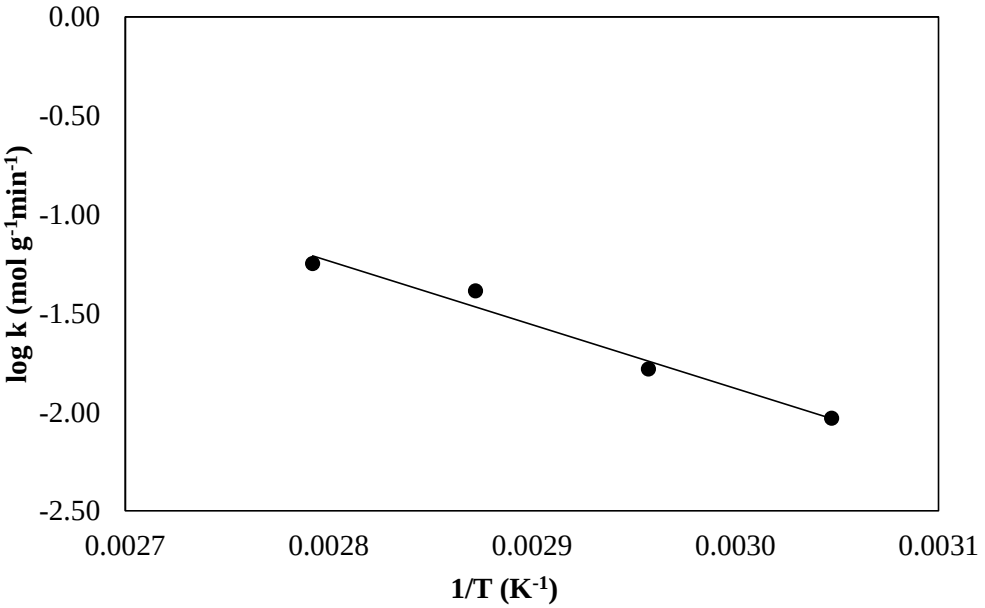


Fig. 4: Arrhenius plot for ALA catalyzed esterification of lactic acid with 1-butanol

coefficient of determination (R^2) closed to unity indicates good agreement between the experimental and the calculated conversion. Slight variation in value of equilibrium constant at 75°C is observed, which may be due to error in component analysis caused by phase separation in water+lactic acid+1-butanol mixtures reported by Chawong *et al.*, (2015). This issue has been mentioned in the study concerning esterification of fatty acid as well (Hassan and Vinjamur, 2013).

Plotting $\log k$ versus $1/T$ at constant initial 1-butanol to lactic acid molar ratio and catalyst loading gives a straight line as shown in **figure 4**. Slope and intercept of the plot are used to calculate the pre-exponential factor and the activation energy of this ALA-catalyzed reaction. The values obtained are 6.35 x 10^7 mol·g^{-1}·min^{-1} for pre-exponential factor and 61.80 kJ·mol^{-1}·K^{-1} for activation energy of the reaction.

CONCLUSION

Esterification of lactic acid with 1-butanol catalyzed by aluminium-alginate (ALA) catalyst is studied. Effect of reaction temperature, initial 1-butanol-to-lactic-acid molar ratio, as well as catalyst loading on lactic acid conversion is elucidated. The ALA catalyst appears to be effective for this reaction. The pseudo-homogeneous model with non-ideal assumption is able to describe the reaction kinetic with satisfactory agreement. The pre-exponential factor and activation energy for this reaction are found to be 6.35 x 10^7 mol·g^{-1}·min^{-1} and 61.80 kJ mol^{-1}K^{-1}, respectively.

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