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Research Article

Ion-exchange Resin Catalyzed Esterification of Lactic Acid with Isopropanol: a Kinetic Study

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Abstract

The kinetic behavior of esterification of lactic acid with isopropanol over an acidic cation exchange resin, Amberlyst 15, was studied under isothermal condition. Isopropyl lactate synthesized in this reaction is an important pharmaceutical intermediate. The experiments were carried out in a stirred batch reactor in the temperature range of 323.15 to 353.15 K. The effect of various parameters such as temperature, molar ratio and catalyst loading was studied. Variation in parameters on rate of reaction demonstrated that the reaction was intrinsically controlled. Kinetic modeling was performed using Eley-Rideal model which acceptably fits the experimental data. The activation energy was found to be 22.007 kJ/mol and frequency factor was 0.036809 $l^2\ g^{-1}\ mol^{-1}\ min^{-1}$ for forward reaction. The value of entropy for the forward reaction was found to be 182.317 $J\ K^{-1}\ mol^{-1}$. © 2011 BCREC UNDIP. All rights reserved

Keywords: Heterogeneous catalysis; Esterification; Lactic acid: Ion exchange resin; Amberlyst-15

Esterification is a well-known process and a number of industrially important chemicals such as methyl, ethyl and butyl esters, alkyl t-butyl ethers (MTBE and ETBE) are produced using such reactions [1,2]. Esterification is very widely understood and extensively used reaction, especially in the pharmaceutical, chemical industries such as solvents of paints, adhesives, plasticizers, flavors and fragrances, pesticides and emulsifiers, perfumery, food industries and in the preparation of biodiesel from lower quality feedstock [3,4]. Derivatives of some esters are useful as chemical intermediates and monomers for resins and high molecular weight polymers [5].

Esterification of carboxylic acids with alcohols in presence of acid catalysts has been extensively investigated. Typical homogenous catalysts like H_2SO_4, HCl and $ClSO_3OH$ are used but due to their miscibility with the reaction medium, separation becomes a problem, hence ion exchange resins are preferred over homogeneous acids due to ease of product separation and catalyst recovery [6]. The drive to develop green processes has led to the development of solid acid catalysts to a significant increase in research activities both in academic and industrial sections. These materials can replace the corrosive liquid acids currently used in many industries [7].Therefore heterogeneous catalyst become an attractive alternative catalyst which is non-polluting, non corrosive and has long activity life. Scientific literature contains some reports on the use of heterogeneous acid catalysts

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for esterification. The most popular solid acid catalysts used to produce esters have been ion-exchange organic resins, such as amberlyst 15, Amberlyst 35, Amberlyst 36, Dowex 50 W etc [8-15].In the recent years a lot of studies were subjected to ion-exchange resins, which are distinguished among solid-state catalysts by their reactivity and selectivity. They are also relatively cheap and could be reused many times [9-16]

Lactic acid and their esters are used in food industry for preservation and flavoring purposes, as well as in the pharmaceutical and cosmetic industries [9]. Sanz et al [17, 18] studied the ion exchange resin catalyzed esterification of lactic acid with methanol and ethanol and reported that Amberlyst 15 is most suitable catalyst for the reaction. Zang et al [19] investigated the esterification of lactic acid with ethanol in the presence of five different cation exchange resins. Their investigations indicated that pseudo homogeneous second order model was the most appropriate model to describe the kinetic behavior. Studies on esterification reaction of lactic acid with isopropanol has been done by Yadav et al [3] over Amberlyst 36 at higher molar ratios of reactants (i.e. lactic acid to iso-propanol upto 1:44).

They also studied the application of different heterogeneous catalyst such as Amberlyst 15, Indion 130, Amberlite-120, Dowex 50 W, and Filtrol-44. Amongst these Amberlyst 15, Amberlyst 36 and Indion-130 were observed to be most effective. By using the large excess of one of the reactants the reaction yield of other compound can be enhanced but because of the presence of the large excess of one of the reactant, the recovery of the product and the reactant becomes more expensive [18].

The present study aims at to provide insight into the kinetics of the esterification of lactic acid with isopropanol over amberlyst 15 at low molar ratios and compare the results with data available for higher molar ratios [3] and to investigate the effect of reaction temperature, catalyst loading and molar feed ratio.

2. Experimental

2.1. Chemicals and Catalysts

All chemicals used in the study were obtained from the reputed firms. Lactic acid (Qualigens fine chemicals, Mumbai), 2-Propanol (Qualigens fine chemicals, Mumbai), Ion exchange resin, Amberlyst 15 (Roam and Hass, Pennsylvania, USA), Sodium Hydroxide (s.d. fine chemicals ltd., Boisar), Phenolphthalein indicator, (Qualigens fine chemicals, Mumbai)

2.2. Apparatus and Procedure

Reaction kinetics was studied in a three-necked glass reactor of 500 ml capacity operating in a batch mode. A reflux condenser was used to avoid the loss of volatile compounds. The catalyst was suspended in the reaction mixture with the help of stirrer. A simple pretreatment was given to the catalyst to convert it to acid form. The catalyst was initially washed with distilled water four to five times and was dried at ambient conditions for 4-5 hrs. Further the catalyst was washed by dipping in 0.1 N hydrochloric acid solution for half an hour. This solution was then filtered to separate the catalyst and dried at atmospheric conditions for about 48 hrs. In all the experiments, a known amount of lactic acid and the catalyst were charged into the reactor and heated to the desired temperature. Temperature inside the reactor was controlled within the accuracy of ±0.5 K. All of the reactants charged in the reactor were volumetrically measured. The progress of the reaction was followed by withdrawing samples at regular intervals, small enough to consider them negligible compared to the volume of the reaction mixture.

2.3. Analysis

To measure the concentration of unreacted acid in the reaction mixture, each sample was analyzed volumetrically by 1 N NaOH as titrant and phenolphthalein as an indicator.

3. Results and Discussion

The esterification reaction of lactic acid with isopropanol was studied in a batch reactor in the presence of acidic ion exchange resin catalyst; Amberlyst 15.The kinetics of esterification of lactic

Table 1. Experimental conditions and range of fractional conversion obtained

S.no.	*Reaction Temperature (K)*	*Molar Ratio (M)*	*Catalyst Loading (kg/m³)*	*Range of Conversion X_A*
1	323 to 353	1.5	11.84	0.12 to 0.30
2	353	1.5	4.73 to 11.84	0.12 to 0.36
3	353	1 to 3	11.84	0.15 to 0.42

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acid was studied at different temperatures from 323-353 K, different molar ratios (M i.e. molar ratio of isopropanol to lactic acid) and varying the catalyst loading as given in table 1.

3.1. Kinetics

Esterification of lactic acid with iso-propanol can be represented as:

$$\underset{\text{(Lactic acid)}}{CH_3CHOHCOOH} + \underset{\text{(Isopropanol)}}{(CH_3)_2CHOH} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{\text{(Isopropyl lactate)}}{CH_3CHOHCOO(CH_3)_2CH} + \underset{\text{(Water)}}{H_2O} \quad (1)$$

Reaction mechanism for this reaction can be well studied by Eley-Rideal model [20] that is the reaction takes place between adsorbed molecules of alcohol and the molecules of acid in bulk solutions. The adsorption of ester is reported to be negligible [20-22].Hence the rate equation is:

$$\frac{dX_A}{dt} = \frac{k_1 C_{A0}(w/V)[(1-X_A)(M-X_A)-(X_A(N+X_A)/K_e)]}{1+K_B C_{A0}(M-X_A)+K_W C_{AO}(N+X_A)} \quad (2)$$

As stated in the literature the value of K_B, K_w were found to be negligible for esterification of lactic acid with lower alcohols [3, 23].

As in absence of any product initially N=0, Equation 2 reduces to

$$\frac{dX_A}{dt} = k_1 C_{AO}(w/V)\left[(1-X_A)(M-X_A) - \frac{X_A^2}{K_e}\right] \quad (3)$$

Putting $k_1 C_{A0} (w/V) = k$ in equation 3 and then integrating the equation:

$$\left[\frac{\tanh^{-1}\dfrac{K_e(M-2X_A+1)+2X_A}{\sqrt{K_e}\sqrt{K_e(M+1)^2+4M}}}{\dfrac{\sqrt{K_e(M-1)^2+4M}}{2\sqrt{K_e}}}\right] = kt + C$$

Which can be written as:

$$Y=kt+C \quad (4)$$

where

$$Y = \left[\frac{\tanh^{-1}\dfrac{K_e(M-2X_A+1)+2X_A}{\sqrt{K_e}\sqrt{K_e(M+1)^2+4M}}}{\dfrac{\sqrt{K_e(M-1)^2+4M}}{2\sqrt{K_e}}}\right]$$

The value of C at t=0 , X_A=0

$$C = \frac{2\sqrt{K_e}\tanh^{-1}\left[\dfrac{K_e(M+1)}{\sqrt{K_e}\sqrt{K_e(M-1)^2+4M}}\right]}{\sqrt{K_e(M-1)^2+4M}}$$

3.2 Effect of catalyst loading on reaction

The catalyst loading was varied from 4.73 kg/m^3 to 14.21 kg/m^3 (of the reaction mixture), which corresponds to 1 to 3 % (Weight/volume) of reaction mixture at a temperature of 353.15 K and molar ratio, M of 1.5. Fig.1 illustrates the variation in fractional conversion (X_A) of lactic acid for different catalyst loading at specified temperature. Fractional conversion was found to be increasing with the increase in catalyst loading. Equilibrium conversion increases with increase in catalyst loading which could be due to more number of available acid sites for the reaction. For reactions catalyzed by the amberlyst series resins, the intraparticle diffusional resistances are usually negligible [20].

Thus typical second order rate equation was used as given in Equation (4) to find the values of rate constant k. Fig 2.shows the plot of Y vs. time at different catalyst loading is straight line and the slope of these lines gives the rate constant. The rate constants thus calculated at different catalyst loading were plotted with catalyst loading (w) as shown in Fig.3. It is seen that the rate is linearly proportional to w (weight of the catalyst) which is in accordance with the observation reported in [3, 20, and 22].

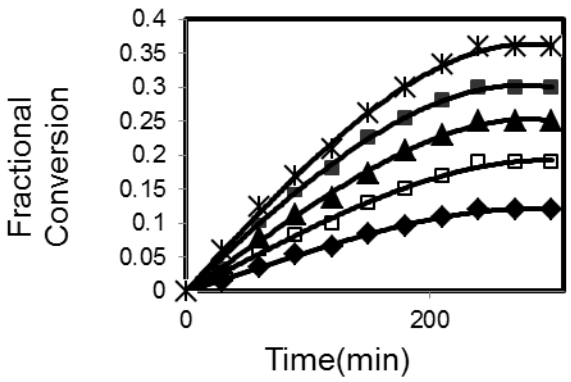

Figure 1. Lactic acid conversion vs. time for different catalyst loading of Amberlyst 15, ♦4.73 kg/m^3, □ 7.11 kg/m^3, ▲9.47 kg/m^3, ■,11.84 kg/m^3 , ¤ 14.21 kg/m^3 (Temperture:353 K and M=1.5)

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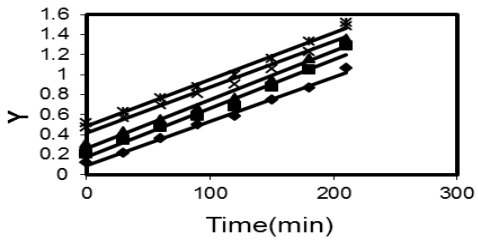

Figure 2. Effect of catalyst loading. Y vs.time (min), ♦4.73 kg/m³, □, 7.11 kg/m³, ▲9.47 kg/m³, ■,11.84 kg/m³ , ¤ 14.21 kg/m³ (Temperture:353 K and M=1.5)

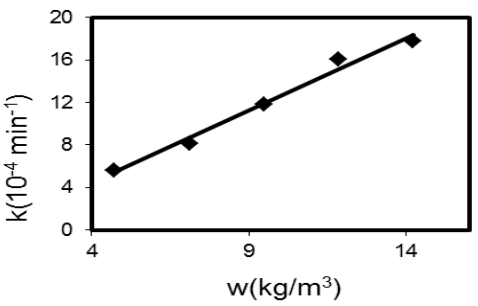

Figure 3. Reaction rate constant (k) vs. catalyst loading (w) for reaction of lactic acid with isopropanol at temperature 353 K and M=1.5

Table 2. Rate constant values at different temperature

Temperature (K)	*Rate Constant k_1 ($l\ mol^{-1}\ g^{-1} min^{-1}$)*
323.15	1.058×10^{-5}
333.15	1.235×10^{-5}
343.15	1.588×10^{-5}
353.15	2.117×10^{-5}

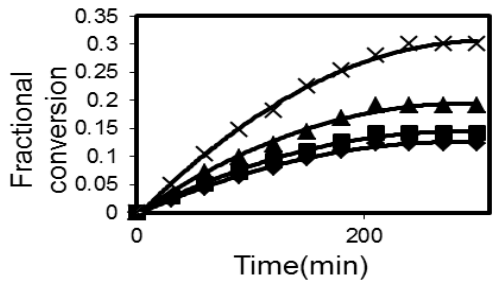

Figure 4. Lactic acid conversion versus Time for different temperatures for 11.84 kg/m³ catalyst loading at M=1.5, x 353K; ▲ 343 K; ■ , 333 K; ♦ 323 K

3.3 Effect of Temperature

To study the effect of the temperature is important since it is useful in calculating the activation energy of the reaction. The effect of temperature on conversion under otherwise similar conditions was studied in the range of 323.15 to 353.15 K (Fig.4). Lui and Tan [21] have reported that ester conversion is dependent on the temperature and conversion increases with the increase in temperature. The plots Y vs. time gives a straight line as shown in Fig 5 and the rate constants for forward reaction at different temperatures were calculated using whole data and the values are tabulated in table 2. Temperature dependency of the specific reaction rate constant was expressed in terms of Arrhenius equation, which follows,

$$k_1 = k_o \exp\left(\frac{-E_1}{RT}\right) \quad (5)$$

Where, k_o = Frequency factor; E_1 = Activation energy, and R = Gas constant ($8.314\ JK^{-1}mol^{-1}$)

For the linear plot of –ln k_1 versus to 1000/T Fig.6, activation energy (E_1) and frequency factor (k_o) for the forward reaction was determined. E_1 was found to be 22.0079 kJ/mol and k_0 was found to be $3.681*10^{-2}\ l^2 g^{-1} mol^{-1} min^{-1}$. The increase in the value of the equilibrium constant with an increase in temperature indicates that the reaction is endothermic in nature. Reaction enthalpy (ΔH°) and reaction entropy (S°) for forward reaction were obtained from Equation (6) by plotting ln K against 1000/T [7].

$$\ln K = \frac{\Delta H^0}{RT} + \frac{\Delta S^o}{R} \quad (6)$$

Where K = equilibrium constant, R = universal gas constant. The positive value of enthalpy suggests that the esterification reaction is endothermic in nature. The linear plot yields $\Delta S^o = 182.317\ J\ K^{-1}\ mol^{-1}$ and $\Delta H^o = 70.022\ kJ\ mol^{-1}$

3.4. Effect of molar ratio

The initial molar ratio of lactic acid to isopropanol was varied from 1 to 3 for the esterification reaction at a catalyst loading of 11.84 kg/m³ at 353 K. As can be seen from Fig 7 that the equilibrium conversion increases with the initial reactant molar ratio. From this figure it can be

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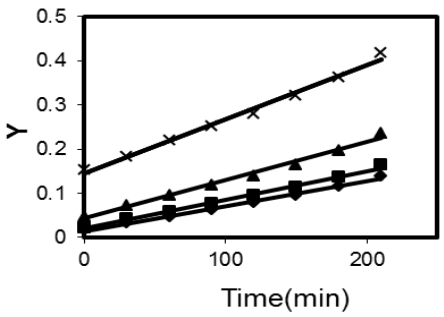

Figure 5. Y versus Time for different temperatures for 11.84 kg/m^3 catalyst loading at M=1.5, × 353K; ▲343 K; ■ 333 K; ♦ 323 K

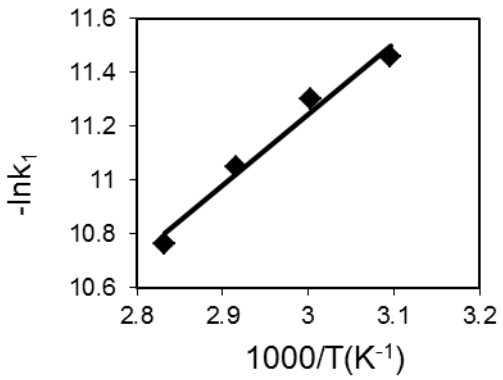

Figure 6. Arrhenius plot of ln k_1 vs. 1000/T, M=1.5(LA: IP), catalyst loading 11.84 kg/m^3)

observed that equilibrium conversion for molar ratio M=1 is 15 % which increases up to 42% for molar ratio M =3. In Fig 8 the conversions obtained at lower initial reactant molar ratios for the esterification reactions of lactic acid with isopropanol was compared with conversions reported in the literature at higher molar ratios [3].The use of large excess of one of reactants the reaction yield is increased but due to presence of large excess of one of the reactant, the recovery of the product and cost of the reactant increases, so trade off between the cost recovery and conversion has to be addressed.

The experimental data was fitted in the Equation (2) and the values of K_B and K_W were found to be negligible. The experimented values of fractional conversion were compared with the values calculated from the Equation (4) taking k= $k_0e^{-E/RT}$ as shown in Fig 9. The predicted values of X_A are in close agreement with the experimental values within the range of experimental error.

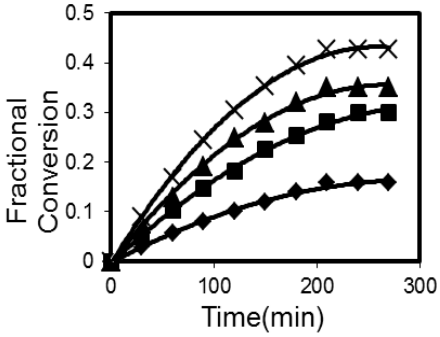

Figure 7. Lactic acid conversion versus Time for different molar ratios for 11.84 kg/m^3 catalyst loading at 353 K, × 3; ▲ 2; ■ 1.5; ♦ 1

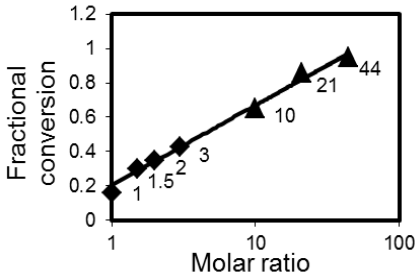

Figure 8. Fractional conversion (X_A) versus molar ratio at temperature 353 K. ▲ [3] (at catalyst loading of 27.27 (kg/m^3)), ■ (present experimental values at catalyst loading of 11.84 (kg/m^3))

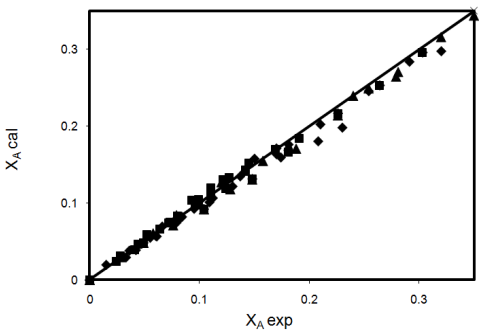

Figure 9. Fitting calculated to experimental data for Esterification of lactic acid with isopropanol over Amberlyst 15 as catalyst. ▲; molar ratio (1to 3)at 11.84 kg/m^3 catalyst loading and 353 K temperature, ■ ;Temperature(323 to 353 K) at 11.84 kg/m^3 and 1.5 molar ratio , ♦,Catalyst loading(4.73 to 14.21 kg/m^3) at 353 K and 1.5 molar ratio

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4. Conclusions

Kinetic behavior has been investigated experimentally for the synthesis of isopropyl lactate using Amberlyst 15 as a catalyst. The experimental data were obtained in a batch reactor within the temperature range (323.15 K to 353.15 K). Reaction entropy and enthalpy for the esterification of lactic acid with isopropanol over Amberlyst 15 at different temperatures were found to be ΔS^o = 182.317 $JK^{-1}mol^{-1}$ and ΔH^o = 70.022 $kJmol^{-1}$. Activation energy and frequency factor for the forward reaction were found to be 22.0079 kJ/mol and 0.036809 $l^2\ g^{-1}\ mol^{-1}min^{-1}$ respectively. The reaction is endothermic in nature. The reaction kinetics was well represented by Eley-Rideal model. The reaction rate increased with the increasing temperature of the reaction, weight of the catalyst, and molar ratio. The experimental work showed that esterification of lactic acid with isopropanol can successfully be carried out at low molar ratio also.

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Notations

k_1	Rate constant for esterification reaction
C_{A0}	Initial concentration of lactic acid (mol/lt)
M	Molar ratio
X_A	Fractional conversion
w	Weight of the catalyst (kg/m^3)
V	Volume of the reaction mixture(litre)
K_e	Equilibrium rate constant
K_w	Adsorption rate constant for water
K_B	Adsorption rate constant for alcohol
ΔH^o	Enthalpy of the reaction($kJmol^{-1}$)
ΔS^o	Entropy of the reaction($JK^{-1}mol^{-1}$)
k_0	Frequency factor($l^2\ g^{-1}\ mol^{-1}min^{-1}$)
E_1	Activation energy ($kJmol^{-1}$)

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