Reaction Kinetics of Lactic Acid with Methanol Catalyzed by Acid Resins

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ABSTRACT

The esterification of aqueous lactic acid solution with methanol and its reverse reaction catalyzed by acidic cation exchange resins in the H^+ form were carried out in a batch system. The inhibiting effects of water and methanol on the resins were evaluated. The experimental data were correlated by a kinetic model that the inhibition by methanol and water was included. The reaction rate constants and the adsorption coefficients were determined from the experiments. The activity of acidic resin was compared with that of sulfuric acid as catalyst. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Lactic acid is an organic hydroxy acid whose occurrence in nature is widespread and can be produced from fermentation of carbohydrate materials at low cost. Recently, lactic acid drew new attention because of its utility as a monomer for biodegradable polymers. The synthesis of polylactide, a biodegradable polymer, requires highly purified lactic acid. However, the lactic acid solution obtained from fermentation is not purified well due to similar characteristics with water and troublesome impurities after fermentation. Lactic acid is oligomerized at high concentration to the lactyllactic acid because of two functional groups in the lactic acid molecule [1]. The vapor pressure of lactic acid is very low (14 mmHg at 122°C). Therefore, normal distillation is not applicable to the purification of lactic acid.

In order to solve these purification problems, the esterification of lactic acid with alcohol, distillation of produced volatile esters, and reverse reaction of ester to purified lactic acid were studied [2,3]. By these sequential processes highly purified lactic acid could be obtained.

The esterification of lactic acid with alcohol can be performed in a number of different ways; the choice of experimental conditions depends on the alcohol to be esterified [4]. Boiling of lactic acid with excessive alcohol under reflux had been used to prepare various esters. The reaction of lactic acid is generally catalyzed by acids such as anhydrous hydrogen chloride, sulfuric acid, or many other catalysts. The homogeneous catalyst had been used because of its advantages of low cost and high reaction rate. But the use of homogeneous catalysts causes many problems

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such as corrosion of equipment, side reactions, and removal of catalyst. The advantages of using ion exchange resin as catalyst are: no corrosion problems; no disposal of waste liquor from the reaction mixture; and no side reactions [5,6]. Also the catalyst can be easily removed and recycled from the reaction product by decantation or filtration, and continuous operation in columns is also possible.

In this article, we investigated the possibility of using acidic cation exchange resin for esterification of lactic acid with methanol and determined the rate equation including inhibiting effects applicable to the solid acidic resins.

EXPERIMENTAL

Apparatus

The reactor consisted of a three-necked Pyrex flask of 250 ml capacity fitted with a Reflux condenser, a sampling device, and a thermocouple. The temperature was controlled within ±0.1°C by circulating water from a thermostat into the cylindrical double wall of the reactor. The reaction mixture was stirred by a magnetic bar that was located in the reaction mixture and the stirring rate was controlled.

Materials

Methanol of 99.8% purity (Merck), aqueous lactic acid solution of 20 wt% acid (Janssen Chimica), and methyl lactate of 98% (Janssen Chimica) were used without further purification.

The strong acidic cation exchange resin was used as a solid catalyst. The acidic cation exchange resin in the H^+ form, DOWEX 50W, was purchased from the Sigma company. This acidic resin was a sulfonated styrene crosslinked with 8% divinylbenzene. The ion exchange capacity of the resin was determined by letting a sample of the resin in the hydrogen form be equilibrated with 5% NaCl solution and titrating with 0.1 N aqueous sodium hydroxide. The measured capacity, Q, was thus found to be 4.8 meq/(g dry resin). Before the experiments, the acidic resins were washed with deionized water and dried in a vacuum oven overnight to remove moisture completely. The resins were reused after washing with distilled water and dried.

Methods

To study the direct recovery of lactic acid obtained from fermentation, the concentration of lactic acid was diluted to the range of concentration after fermentation. In the experiments, measured weight of the aqueous lactic acid solution was supplied into the batch reactor and the temperature of the reactor was controlled by the water circulation from a thermostat. After a steady value of the desired temperature was reached, methanol and catalysts were added and the reaction mixture was mixed thoroughly. The concentration of lactic acid was analyzed by titration with standardized 0.1 N NaOH solution. The same experimental methods were used for the reverse reaction of methyl lactate with water (hydrolysis reaction).

RESULTS AND DISCUSSION

The effects of the variables such as catalyst concentration, molar ratio of reactants (M_{RE} for esterification and M_{RH} for its reverse reaction), and reaction temperature on the reaction rate were studied. The reaction rates were independent of stirring rates, which indicates that the external diffusion resistance is not significant. We also concluded that the internal mass transfer is negligible from the fact that the resin size did not affect the reaction rate.

We reused the acidic resins to test the possibility of recycling resins. The reused resins showed the same results as those of new resins with respect to the reaction rate, also, the reused resins showed the same acid equivalent as new resins. However, in experiments we used new resins for constancy of experimental conditions.

Reaction Rate

The reaction kinetics of esterification and its reverse reaction of lactic acid with methanol were already studied in the case of the sulfuric acid as a catalyst [7,8]. But when solid acidic resin was used as a catalyst, the kinetics of reaction is different from that of sulfuric acid catalyst. The effect of sorption by acidic resins should be included in the reaction rate equation. The selectivity and sorption capacity by ion exchange resins depend on the solvation characteristics of the counterion and the fixed ionic groups, the electrostatic repulsion between neighboring ionic groups, the polarity and dielectric constants of the organic solvent, and the degree of crosslinking of the resin [9]. It was found that most of sorption characteristics resulted from the presence of water and alcohol as reaction mixture [10]. So the reaction kinetics should include the inhibiting effects of water and alcohol.

When lactic acid reacts with methanol as followed, the reaction is second-order with respect to reactants [7,8].

Lactic acid + Methanol ↔ Methyl lactate + Water. From the equilibrium distribution of components between resins and bulk phase, the adsorbed amount is proportional to the concentration of the component in the bulk phase. It was reported that the adsorption inhibited the reaction [10]. Therefore, the reaction rate would be empirically expressed as following, when the catalysis of the resins is considered [10,11]

$$r = \frac{dC_{ML}}{dt} = \frac{k_f C_L C_M - k_b C_{ML} C_w}{1 + b_W C_W + b_M C_M}, \quad (1)$$

where b_M is the adsorption coefficient of methanol and b_W is the adsorption coefficient of water. The parameter values of adsorption coefficients is obtained from the experiments of reactions with ion exchange resin. The k_f and k_b are the reaction rate constants of esterification and its reverse reaction, respectively.

Comparison of Catalyst Type

We used the sulfuric acid as well as the acidic resin as the catalyst. As shown in Figure 1, the reaction rate by sulfuric acid was larger than that by acidic resin at the initial period but the conversion of the reaction using sulfuric acid was smaller as reaction time increased. The acidic resins could be compared with sulfuric acid in some aspects. The sulfuric acid is cheaper than resin in cost, but the resins can be recycled several times, and favored with its various advantages over homogeneous catalyst.

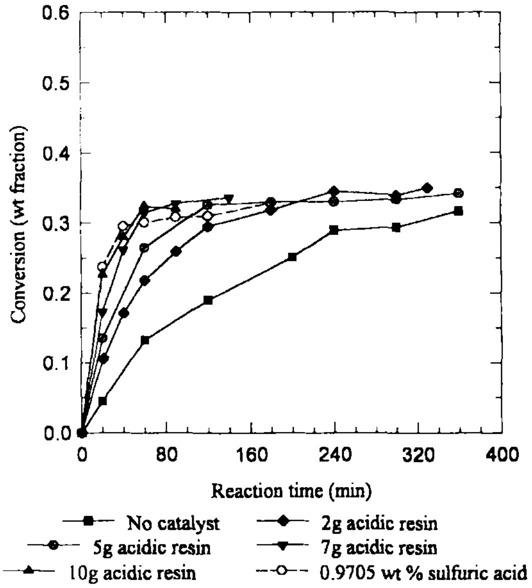

Figure 1 The esterification reaction of lactic acid with methanol (1.83×10^{-3} lactic acid mol/g, 5.49×10^{-3} MeOH mol/g, and 80°C).

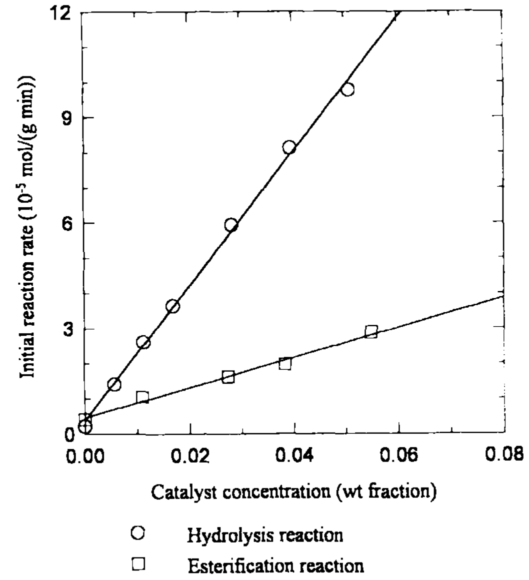

Figure 2 Initial reaction rates with respect to the resin concentration (for esterification 1.83×10^{-3} lactic acid mol/g, 5.49×10^{-3} MeOH mol/g and for hydrolysis 2.66×10^{-3} methyl lactate mol/g, 39.87×10^{-3} water mol/g, and 80°C).

Effect of Catalyst Concentration

The effect of catalyst concentration on the reaction rate of esterification of lactic acid with methanol was shown in Figures 1 and 2. When the catalyst was used, the reaction equilibrium was reached rapidly as expected. As the concentration of acidic resins was increased, the reaction rate increased. The initial reaction rates of esterification and its reverse reaction of lactic acid with methanol with respect to the resins concentration were shown in Figure 2. The initial reaction rate is proportional to the resin concentrations in both reactions. From above fact and reaction rate equation, the reaction rate constants, k_f and k_b, are the linear function of the catalyst concentration, and could be expressed with respect to the catalyst concentration

$$k_f = k_{fC} C_C + k_{fo},$$

and

$$k_b = k_{bC} C_C + k_{bo}$$

where C_c is the solid catalyst concentration. These values of parameters are calculated from experimental data as following

$$k_{fC} = 42.43 \text{ g}^2/(\text{mol min g-cat}),$$

$$k_{fo} = 0.456 \text{ g}/(\text{mol min})$$

$$k_{bC} = 17.98 \text{ g}^2/(\text{mol min g-cat}),$$

$$k_{bo} = 0.035 \text{ g}/(\text{mol min}).$$

Effect of Reaction Temperature

The reaction temperatures of both reactions were varied. The maximum reaction temperature was the boiling temperature of reaction mixture. As the reaction temperature increased the reaction rate was increased, but the concentrations of reaction mixtures at equilibrium were nearly constant at different temperatures as shown in Figure 3. The Arrhenius plot of both reactions was shown in Figure 4. From the Arrhenius plot the activation energy of esterification, E_{af}, and the value of its reverse reaction, E_{ab}, were calculated

$$E_{af} = 48.975 \text{ KJ/mol},$$

$$E_{ab} = 44.605 \text{ KJ/mol}.$$

Effect of Reactant Concentration

When the inhibiting effects of alcohol as well as water were included in the rate equation, the adsorption coefficients in the rate equation is calculated from the experimental data. To calculate the adsorption coefficients the initial reaction rates were obtained with respect to reactant concentrations [11]. For adsorption coefficient of water, b_W, the rate equation at the initial reverse reaction is modified in order to calculate b_W as follows:

$$\frac{C_{ML}C_W}{r^0} = \frac{1}{k_b} + \frac{b_W}{k_b}C_W, \qquad (2)$$

where r^0 is the initial reaction rate of the reverse reaction.

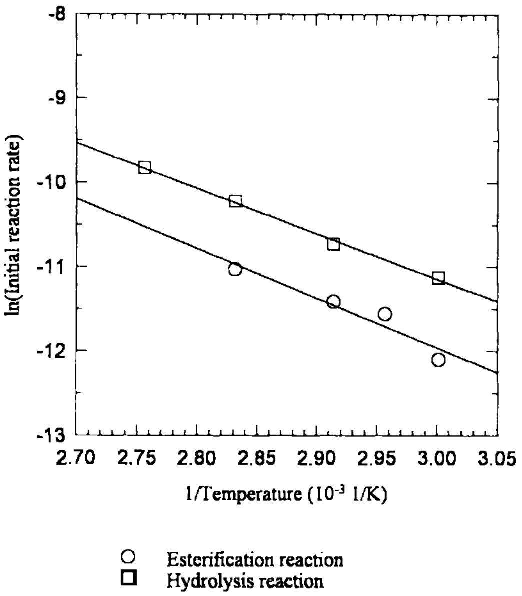

Figure 4 The Arrhenius plot of reactions (for esterification 1.83×10^{-3} lactic acid mol/g, 5.49×10^{-3} MeOH mol/g and for hydrolysis 2.66×10^{-3} methyl lactate mol/g, and 39.87×10^{-3} water mol/g).

From the slope and the intercept of this linear relation, the reaction rate constant of reverse reaction and adsorption coefficients of water are determined. Figure 5 shows that the experimental results showed the linear relation. The adsorption coefficient of water and the reaction rate constant of the reverse reaction were calculated to be $b_W = 13.09$g/mol and $k_b = 0.5176$ g/(mol min).

In order to calculate adsorption coefficient of methanol, b_M, we used the esterification reaction as

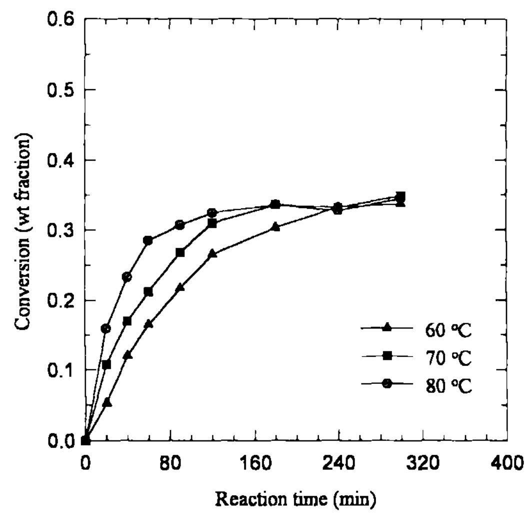

Figure 3 The effect of reaction temperature on the esterification reaction (1.83×10^{-3} lactic acid mol/g, 5.49×10^{-3} MeOH mol/g, and 5 g acidic resin).

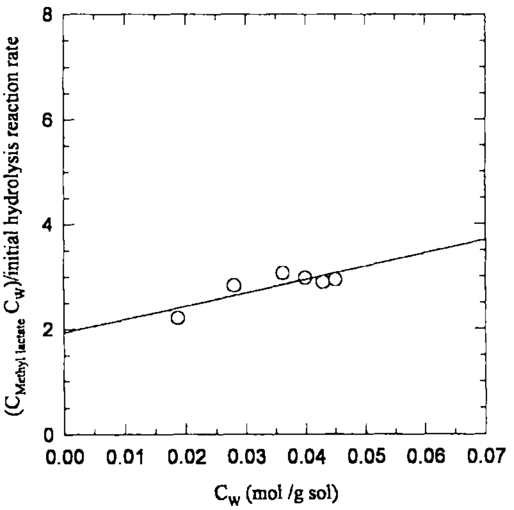

Figure 5 The adsorption coefficient of water, $\frac{(C_{Methyllactate}C_W)}{r^0} = \frac{1}{k_b} + \frac{b_W C_W}{k_b}$, where r^0 was the initial reverse reaction rate.

follows. At the initial esterification the rate equation was rearranged to

$$\frac{C_L C_M}{r^0} = \frac{1}{k_f} + \frac{b_W}{k_f} C_W + \frac{b_M}{k_f} C_M , \qquad (3)$$

where r^0 is the initial rate of the esterification. In the eq. (3), the b_M value is obtained from the curve fitting of experimental results. The value of adsorption coefficient of methanol obtained from the esterification reaction data is

$$b_M = 273.5 \text{ g/mol},$$

and reaction rate constant of esterification is calculated to be

$$k_f = 3.201 \text{ g/(mol min)}.$$

Integrated Rate Expression

The experimental results were compared with the model prediction. The Runge–Kutta method was used to integrate the rate equation with the kinetic parameters determined by experiments. As can be seen from Figure 6, a good agreement between the calculated curve with the inhibiting effect and the experimental points is observed.

CONCLUSION

The esterification and its reverse reaction of lactic acid with methanol were studied. The acidic resin in H^+ form as well as sulfuric acid were used as the catalysts. The inhibition effect of methanol as well as water in the reaction mixture was considered in the rate equation and the adsorption coefficients were calculated from experimental data. The simulated results agreed well with experimental data. Although the activity of resins is lower than that of sulfuric acid, and acidic resin is easily removed and can be reused several times.

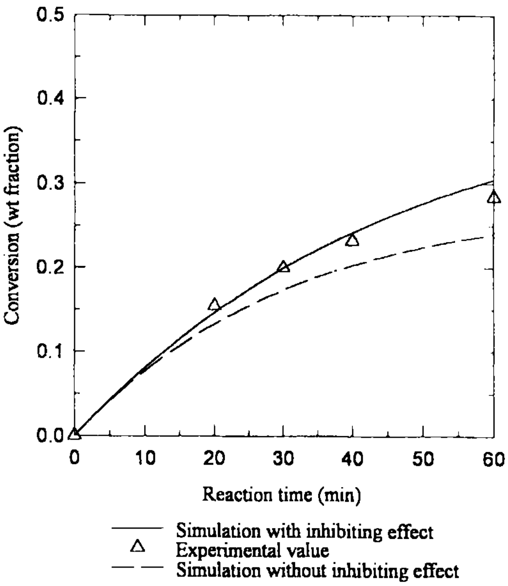

Figure 6 Experimental points and calculated curves (1.83×10^{-3} lactic acid mol/g, 5.49×10^{-3} MeOH mol/g, 5 g acidic resin, and 80°C).

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