Thermodynamic Equilibrium and Reaction Kinetics for the Esterification of Lactic Acid with Ethanol Catalyzed by Acid Ion-Exchange Resin

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The heterogeneous catalysis of lactic acid (88 wt %) esterification with ethanol in the presence of Amberlyst 15-wet was studied for catalyst loading of 1.2—3.9 wt %, initial molar ratio of reactants of 1.1—2.8, and temperature from 50 to 90 °C. In this work a methodology based on the UNIQUAC model was developed to determine the thermodynamic equilibrium constant since in the literature there is inconsistency concerning the temperature dependence of the thermodynamic equilibrium constant. A simplified Langmuir—Hinshelwood kinetic model was used to predict the experimental data. The proposed rate law is \( r = k_c(\alpha_{Eth}a_{La} - a_{Eth}a_W/K)/(1 + K_{Eth}a_{Eth} + K_{W}a_{W})^2 \); the kinetic parameters are the preexponential factor, \( k_c = 2.70 \times 10^7 \) mol·g\(^{-1}\)·min\(^{-1}\), and the activation energy, \( E_a = 49.98 \) kJ/mol. The equilibrium reaction constant is \( K = 19.35 \exp(-515.13/T (K)) \) with reaction enthalpy 4.28 kJ/mol. The model reasonably predicts the kinetic experimental data, and it will be very useful to apply to the design and optimization of industrial hybrid reactive separation processes.

1. Introduction

Petroleum (“black gold”) is at the heart of today’s economics and political problems. It is a finite resource, and the use of petrochemical solvents has several implications for the environment. Therefore, the replacement of traditional petroleum-derived solvents is one of the major challenges that the industry has been facing. The lactate esters derived from bio-based organic acids fall into the category of green solvents and are promising replacements for halogenated petroleum-based solvents in a wide range of applications. Ethyl lactate is a green solvent derived, for example, from processing corn or sugar crops, and it is so benign that the U.S. Food and Drug Administration approved its use in food products. It is biodegradable and could replace a range of environment-damaging halogenated and toxic solvents, including carcinogenic methylene chloride, and toxic ethylene glycol ethers and chloroform, which will result in a much safer workplace.

Lactic acid has a wide range of applications in the food (preservative and flavor), cosmetic, pharmaceutical, textile, and leather industries, but for that it must be highly pure. Lactic acid contains a hydroxyl group adjacent to the carboxylic acid and because of its bifunctional nature undergoes intermolecular esterification in aqueous solutions above 20 wt % to form linear dimer and higher oligomer acids:

\[
2\text{La}_1 \leftrightarrow \text{La}_2 + \text{W} \quad (\text{lactic acid dimer formation})
\]

\[
\text{La}_1 + \text{La}_2 \leftrightarrow \text{La}_3 + \text{W} \quad (\text{lactic acid trimer formation})
\]

\[
\vdots
\]

\[
\text{La}_1 + \text{La}_{n-1} \leftrightarrow \text{La}_n + \text{W} \quad (\text{lactic acid oligomer formation})
\]

with \( n \geq 2 \), where

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For an aqueous solution with 88 wt % lactic acid, the molar percentages of the monomer (La₁), dimer (La₂), and trimer (La₃) are about 43.5, 9.2, and 1.8 mol %, respectively, with about 45 mol % water. A 20 wt % aqueous solution of lactic acid is constituted only by monomer and water, with the monomer molar percentage being about 5.6 mol %. However, the percentage of lactic acid and ethyl lactate oligomers is less than 5% at equilibrium, and the use of an aqueous solution with a high lactic acid concentration is desirable to produce ethyl lactate on an industrial scale by means of a continuous hybrid process such as reactive pervaporation, reactive chromatographic processes, and others.

The kinetics of ethyl lactate production has been studied since 1957, but lately has deserved more attention since it is a green solvent and an alternative to the traditional petroleum-derived solvents. Troupe and Dimilla studied the esterification reaction between lactic acid and ethanol using sulfuric acid as catalyst. However, this kind of homogeneous catalyst may be the origin of a lot of problems, because of their miscibility with the reaction medium, which causes separation problems; in addition, strong acid catalysts lead to corrosion of the equipment. The replacement of homogeneous catalysts by heterogeneous catalysts is gaining importance due to their ecofriendly nature. Besides being noncorrosive and easy to separate from the reaction mixture, the heterogeneous catalyst can be used repeatedly over a prolonged period without any difficulty in handling and storage. Many solid-acid catalysts have been used, such as acid-treated clays, heteropolyacids, iodine, MCM-41, zeolite-T membrane, Smopex-101, HY zeolite, zeolite beta, and ZSM-5. However, ion-exchange resins are the most commonly used solid catalysts and they have been proved to be effective in liquid-phase esterification. Since heterogeneous catalysis is clearly advantageous, some studies have been already performed for the esterification of lactic acid with ethanol. Zhang and co-workers studied the kinetics of esterification of lactic acid (20 wt %) with ethanol catalyzed by five different cation-exchange resins. They proposed a simplified mechanism based on the Langmuir–Hinshelwood model to describe the kinetics behavior. Delgado et al. also investigated the esterification of lactic acid with ethanol and the hydrolysis of the ethyl lactate in the presence of a commercial cation-exchange resin; an aqueous lactic acid solution of 20 wt % and a mechanism based on the Langmuir–Hinshelwood model to describe the kinetics was used. This esterification with/without a solid catalyst (Amberlyst XN-10(11)) was also investigated by Benedict and collaborators. A kinetic model based on concentrations to describe the behavior of the reaction between an 88 wt % lactic acid solution with ethanol was used. The presence of oligomers was not mentioned in their work. In Tanaka and co-workers studies about this esterification, the presence of oligomers was considered and the reactions were described by simple nth-order reversible rate expressions based on the species concentration. Three different solutions of lactic acid (20, 50, 88 wt %) were used in the esterification reaction with ethanol in Asthana and collaborators’ work. The presence of oligomers was also taken into account, and a similar model based on the species concentration was used to describe the reaction kinetics.

In spite of the number of kinetic studies available in the literature, the thermodynamic equilibrium of the reaction in the liquid phase has not been clearly studied, and some of the authors do not report the values of the equilibrium constant. In some works, different equilibrium constants based on concentration (Kₑ) at the same temperature are reported. The authors of those studies have concluded that the equilibrium constant Kₑ varies significantly with the initial molar ratio of the reactants, being less sensitive to the temperature. However, the thermodynamic equilibrium constant defined as a function of the species liquid activities, which is only temperature dependent, is not presented in their works. In order to overcome the lack of thermodynamic data, Delgado and coauthors have studied the vapor–liquid reactive equilibria for ethyl lactate synthesis, and they have proposed the following expression to describe the reaction equilibrium constant:

$$\ln(K) = 7.893 - \frac{2431.2}{T(K)}$$ (1)

Nevertheless, they have found some difficulties in measuring the vapor-phase composition, which significantly affects the experimental values of the experimental equilibrium constant, leading to high deviations between experimental values and those predicted by eq 1, as shown in Figure 1.

This work was undertaken to obtain the reaction equilibrium and kinetic data for the synthesis of ethyl lactate in the liquid phase, avoiding the vaporization of all species by working at 6 bar (helium pressurization). The pressure influence on the value of the equilibrium constant is negligible for this system for the temperature and pressure operating range, as it can estimated by the correction factor Kₑ. Therefore, the thermodynamic equilibrium constant was estimated by the UNIQUAC method and the esterification reaction catalyzed by the ion-exchange resin Amberlyst 15-wet was described by a simple activity based kinetic model, which will be applied in the modeling of some reactive separation processes, such as membrane reactors. In this work a high lactic acid concentration was used with the
1.2 mm, an ion-exchange capacity of 4.7 mequiv of H

divinylbenzene, with particle diameters varying between 0.3 and

This resin is a bead-form macroreticular polymer of styrene and

commercial strong-acid ion-exchange resin named Amberlyst

Tanaka et al.6 and Asthana et al. 5 studies. However, in the final

lactate oligomers represents less than 5% according to the

industrial process. The presence of oligomers was neglected,

objective of maximizing the ethyl lactate productivity for an

process. The presence of oligomers was neglected, since at equilibrium the total amount of lactic acid and ethyl lactate oligomers represents less than 5% according to the Tanaka et al.6 and Asthana et al.5 studies. However, in the final section of this paper the presence of oligomers will be addressed.

2. Experimental Section

2.1. Chemicals and Catalyst. The chemicals used were ethanol (>99.9% in water), lactic acid (>85% in water), and ethyl lactate (>98% in water) from Sigma-Aldrich (U.K.). A commercial strong-acid ion-exchange resin named Amberlyst 15-wet (Rohm & Haas) was used as catalyst and adsorbent. This resin is a bead-form macroreticular polymer of styrene and divinylbenzene, with particle diameters varying between 0.3 and 1.2 mm, an ion-exchange capacity of 4.7 mequiv of H⁺/g of dry resin, and an inner surface area of 53 m²/g. According to Ihm et al.28 only 4% of the active sites are located at the macropores (surface of the microspheres) and the other 96% are inside gel polymer microspheres. Since the water adsorbed on the catalyst surface decreases the reaction kinetics, because it is one of the reaction products, it was necessary to guarantee anhydrous resin. For that, the resin was washed several times with deionized water and dried at 90°C until the mass remained constant. This method is of value for the reuse experiments, since water is abundantly present due to the lactic acid solution.

2.2. Experimental Setup. The experiments were carried out in a glass-jacketed 1 dm³ autoclave (Büchi, Switzerland), operating in a batch mode, mechanically stirred at 600 rpm, equipped with pressure and temperature sensors and with a blow-off valve (Figure 2). The temperature was controlled by a thermostated ethylene glycol/water solution (Lauda, Germany) that flows through the jacket of the reactor and feed vessel. To maintain the reacting mixture in liquid phase over the whole temperature range, the pressure was set at 0.6 MPa with helium. The lactic acid solution was charged into the reactor and heated to the desired reaction temperature. The dry catalyst was placed in a basket at the top of the stirrer shaft. Ethanol was heated to the desired temperature in the feed vessel and then charged to the reactor by opening the on/off valve. The agitation was immediately turned on and the basket of catalyst fell down in the reactorsolution. This time is considered to be the starting time of the esterification reaction. One of the outlets of the reactor was connected directly to a liquid sampling valve (Valco, USA), which injects 0.2 μL of pressurized liquid to a gas chromatograph.

2.3 Analytical Method. All the samples were analyzed in a gas chromatograph (Chrompack 9100, Netherlands) using a fused silica capillary column (Chrompack CP-Wax 57 CB, 25 m × 0.53 mm i.d., d₁ = 2.0 μm) to separate the compounds and a thermal conductivity detector (TCD 903 A) to quantify it. The column temperature was programmed with a 1.5 min initial hold at 110°C, followed by a 50°C/min ramp up to 190°C and holding for 8.5 min. The injector and detector temperatures were maintained at 280 and 300°C, respectively. Helium N50 was used as the carrier gas with a flow rate 10.50 mL/min. In order to analyze the lactic acid and ethyl lactate oligomers at equilibrium, a HPLC system from Gilson (France) using an ICSep ION-300 column held at 20°C was used. A 0.0085 N H₂SO₄ solution was used as mobile phase (0.4 mL/min), and species were quantified by a refractive index detector.

3. Thermodynamic Equilibrium Results

The experiments to measure the equilibrium constant were done in a temperature range of 323–363 K. At each temperature different experiments were performed using different initial molar ratios (R₁₉₀/Lₐ = 1.0 to R₂₁₀/Lₐ = 2.8) and different masses of catalyst (2.3–6.0 wt %) (see Table 1). All the experiments lasted long enough to ensure that the equilibrium was reached.

3.1. Thermodynamic Equilibrium Constant. In its most general form the chemical equilibrium constant (K) for a reaction is given by

\[
K = \exp\left(\frac{-\Delta G^\circ}{RT}\right) = \prod_i \alpha_i^{x_i} \tag{2}
\]

where \(\Delta G^\circ\) is the reaction standard free Gibbs energy, \(R\) is the ideal gas constant, \(T\) is the absolute temperature, \(\alpha_i\) is the activity of species \(i\), and \(x_i\) is its stoichiometric coefficient in the reaction.

For the esterification reaction, occurring in the liquid phase at low pressure

\[
K = \frac{a_{Eth}a_{W}}{a_{Eth}a_{La}} = \frac{x_{Eth}x_{W}}{x_{Eth}x_{La}} \frac{\gamma_{Eth}\gamma_{W}}{\gamma_{Eth}^La} = KK_y \tag{3}
\]

and are the mole fraction and the activity coefficient of each species, respectively.

The chemical equilibrium constant is only temperature dependent. From the experimental point of view, however, changing isothermically the initial mass of each reactant will give, most probably, different values for the equilibrium constant. Naturally, that is a consequence of experimental errors as well as deficiencies in the thermodynamic models used to calculate the activity coefficients. For example, as can be observed in Table 1 three different runs were carried out at 323.15 K. Estimating the activity coefficients by the UNIFAC method,29 using the relative molecular volume, the surface area, and the interaction parameters presented in Reid et al.,30 the resulting equilibrium constants are quite different: 4.126, 3.813, and 4.637, respectively, from top to bottom.

One possibility to get a single equilibrium constant value for each temperature would be to fit all the equilibrium constants using an equation of the type

\[
\ln K = a + b/T \tag{4}
\]
This, however, presents a big deficiency. In fact, using a unique value for the equilibrium constant at a given temperature, the equilibrium composition must be recalculated for each specific initial condition, which will immediately introduce changes in the magnitude of the activity coefficients.

Assuming a given value for the equilibrium constant at 323.15 K, solving eq 3 in order to the equilibrium composition involves an iterative procedure. First, all the activity coefficients must be assumed equal to 1, obtaining the equilibrium composition of an ideal solution. Then the activity coefficients can be determined using a model such as UNIQUAC or UNIFAC, and a new equilibrium composition can now be calculated. The procedure is repeated until convergence. It must be stressed that this final equilibrium composition will certainly not be the same as the one presented in Table 3, which was used to calculate the equilibrium constant and to regress the coefficients in eq 4. Therefore, this inconsistency must be avoided.

To overcome this problem, in this work it is suggested to obtain the coefficients in eq 4 that allow the calculation of the equilibrium composition as close as possible to that observed experimentally. Therefore, the coefficients were estimated minimizing the following objective function \( F_{ob} \):

\[
F_{ob} = \sum_{k} \frac{X_{k}^{exp} - X_{k}^{calc}}{X_{k}^{exp}}^2
\]

where \( X_{k}^{exp} \) and \( X_{k}^{calc} \) are the experimental and the calculated equilibrium conversions for experiment \( k \), respectively.

### 3.1.1. Activity Coefficients Estimation

In this work, instead of using the UNIFAC method, it was preferred to apply the UNIQUAC model. Indeed, there are some available experimental vapor—liquid equilibrium data involving mixtures of species involved in the reaction under study, which makes it preferable to use a correlation model instead of a pure predictive method.

Initially the parameters between ethanol and ethyl lactate were estimated based on the data published by Peña-Tejedor et al. and Vu et al. Then the parameters between water and ethyl lactate were obtained based on the data by Vu et al. Finally the parameters between lactic acid and all other species were estimated using data from the quaternary system measured by Delgado et al. The parameters were estimated minimizing the following objective function \( F_{ob} \):

\[
F_{ob} = \sum_{i} \left( \frac{y_i^{exp} - y_i^{calc}}{y_i^{exp}} \right)^2
\]

with \( i \) is the species and \( j \) is the experimental data point. It should be mentioned that the parameters between water and ethanol were found in the DECHEMA books. The interaction parameters are given in Table 2.

The average relative deviation found for the activity coefficients was 12.9%, but special difficulties were found when describing the behavior of diluted solutions, which was never the case when the chemical equilibrium experimental studies were carried out in this work.

### 3.2. Equilibrium Constant and Reaction Enthalpy for the Synthesis of Ethyl Lactate

Using the data found experimentally for the chemical equilibrium compositions in 14 different runs, at four different temperatures in the range between 323.15 and 362.87 K, the following relation for the equilibrium constant was found:

\[
\ln K = 2.9625 - 515.13/T(K)
\]
presents more difficulties to calculate accurately the activity (maximum mole fraction around 0.20), which for the model
Furthermore, the composition range is now much more restricted
librium (VLE) data as is the case for water and ethanol species.

801 database (see Table 5), it is possible to calculate
standard state enthalpy of formation. Nevertheless, the value found is in good agreement
to values given in the literature.23,24

Table 3. Experimental and Calculated Equilibrium Compositions for All Experiments Performed and Corresponding Deviation Percent

Table 4. Activity Coefficients for the Equilibrium Composition and Thermodynamic Equilibrium Constant

Table 5. Standard State Enthalpy of Formation of Different Species

801 database (see Table 5), it is possible to calculate \(-20.97 \pm 186.7 \text{kJmol}^{-1}\) for the reaction enthalpy at 298.15 K. This considerably high error (\(\pm 186.7 \text{kJmol}^{-1}\)) is mainly due to the high uncertainty in the ethyl lactate standard state of formation. Nevertheless, the value found is in good agreement to values given in the literature.23,24

3.3. Application of this Methodology to Other Works. The equilibrium compositions and equilibrium conversions of various conditions, such as catalyst loading, initial molar ratio of various conditions, such as catalyst loading, initial molar ratio

4. Kinetic Studies

The experimental results of the reaction kinetics of the esterification of lactic acid and ethanol catalyzed by the Amberlyst 15-wet resin are presented in this section. The effect of various conditions, such as catalyst loading, initial molar ratio between ethanol and lactic acid, and reaction temperature, on lactic acid conversion as a function of time is studied. This study was performed varying the condition under evaluation and keeping constant the remaining conditions, in the absence of mass transfer limitations and catalyst deactivation as shown by the preliminary studies performed.
4.1. Preliminary Studies. 4.1.1. Evaluation of External Mass Transfer Limitations (Effect of Stirring Speed). To quantify the influence of external mass transfer resistance, preliminary experiments at different stirring speeds were run. It was concluded that with a stirring speed of 600 rpm there is no limitation due to external resistance, so all further experiments were done at 600 rpm.

4.1.2. Evaluation of Internal Mass Transfer Limitations (Effect of Particle Size). Amberlyst 15-wet was separated by particle size, and three classes with different diameters were obtained: $0.425 \text{ mm} < d_p < 0.5 \text{ mm}$, $0.5 \text{ mm} < d_p < 0.6 \text{ mm}$, and $0.6 \text{ mm} < d_p < 0.85 \text{ mm}$. Kinetic experiments were performed using the three classes obtained and, also, unsieved resin. No significant internal diffusion limitations were found; therefore, the unsieved resin was used for the following kinetic experiments performed in this work. This is in agreement with several works performed with this kind of resin and type of reaction.\textsuperscript{20,24,25,35}

4.1.3. Evaluation of Catalyst Deactivation (Effect of Catalyst Reusability). The Amberlyst 15-wet catalyst reusability was studied at 344.05 K. The resin was reused up to three times. First, a reaction was carried out using fresh catalyst. Then the catalyst used was separated from the reaction mixture by filtration, washed several times with deionized water, and dried at 90 °C until the mass remained constant, and the catalyst was charged again to the reactor. A new esterification reaction was performed using the same conditions that the first one used, and so on. The lactic acid conversion as a function of time was analyzed, and the three conversion histories are presented in Figure 5. As can be seen, no significant changes were observed. The resin activity was kept the same in the three runs. However, each experiment was performed using fresh Amberlyst 15-wet catalyst. Dixit and Yadav\textsuperscript{36} studied the reusability of Amberlyst 15-wet in the alkylation reaction of $o$-xylene with styrene, and they observed a drastic reduction in the conversion of styrene due to the direct deposition of the byproducts on the active sites and the loss of accessibility of the active sites due to pore blockage. Thus, it can be concluded that the catalytic activity of the resins depends on its interaction with the reaction medium.

4.2. Kinetic Model. The esterification reactions have been described using different models, such as pseudohomogeneous, Eley–Rideal, and Langmuir–Hinshelwood (L–H).\textsuperscript{21,35,37–39} However, the L–H model has been considered the most appropriate model for the reaction between lactic acid and ethanol.\textsuperscript{24,25} Therefore, the model developed is based on an L–H mechanism and it considers the following steps:

\[
\text{ethanol and lactic acid adsorption:} \quad \text{Eth} + S \xrightleftharpoons[][K_{\text{Eth}}]{\text{Eth-S}} \quad \text{La} + S \xrightleftharpoons[][K_{\text{La}}]{\text{La-S}}
\]

Figure 3. (a) Experimental and calculated equilibrium molar fractions of ethanol and water species. (b) Experimental and calculated equilibrium molar fractions of ethyl lactate and lactic acid species.

Figure 4. Experimental and calculated equilibrium conversion. Data collected from Troupe and Dimilla,\textsuperscript{4} Benedict et al.,\textsuperscript{21} Delgado et al.,\textsuperscript{25} and this work.

Figure 5. Effect of the Amberlyst 15-wet reusability on conversion of lactic acid history at 344.05 K for a molar ratio of ethanol to lactic acid of 1.82 using 2.4 wt % Amberlyst 15-wet catalyst with an average particle diameter of 0.685 mm and stirrer speed of 600 rpm.
surface reaction between the adsorbed species of ethanol and lactic acid:

\[ \text{Eth} \cdot S + \text{La} \cdot S \xrightleftharpoons[K_i]{\text{K}_{\text{Eth}} \cdot \text{S}} \text{EL} \cdot S + W \cdot S \]

desorption of ethyl lactate and water:

\[ \text{EL} \cdot S \xrightarrow{\text{K}_{\text{Eth}} \cdot \text{S}} \text{EL} + S \]
\[ W \cdot S \xrightarrow{\text{K}_{\text{Water}} \cdot \text{S}} W + S \]

The surface reaction is assumed to be the controlling step, with the other steps remaining in equilibrium. Multicomponent Langmuir adsorption isotherms, written in terms of activities, are assumed to describe the adsorption behavior of the components of the reaction mixture in the surface of the resin. Taking into account the above considerations, the following rate expression, written in terms of activities of components, due to the nonideality of the reaction mixture, is obtained:

\[
r = k_c \frac{a_{\text{Eth} \cdot \text{La}} - a_{\text{EL} \cdot \text{W}}}{K} (1 + \sum_{i=\text{Eth}} w_i K_{s,i} a_i)^2
\]

(8)

where \(k_c\) is the kinetic constant, \(K_{s,i}\) is the adsorption constant for species \(i\), and \(K\) is the equilibrium reaction constant.

In order to reduce the number of optimization parameters, only those components that had the strongest adsorption were taken into account. It was considered that the most polar molecules, water and ethanol, have the strongest adsorption strengths on the Amberlyst 15-wet surface, so the adsorption of lactic acid and that of ethyl lactate were therefore neglected. This consideration is corroborated by several works on adsorption strengths on the Amberlyst 15-wet surface, so the adsorption of water and ethanol, have the strongest adsorption taken into account. It was considered that the most polar molecules, water and ethanol, have the strongest adsorption strengths on the Amberlyst 15-wet surface, so the adsorption of lactic acid and that of ethyl lactate were therefore neglected.

Thus, the simplified rate expression used to describe the experimental data is

\[
r = k_c \frac{a_{\text{Eth} \cdot \text{La}} - a_{\text{EL} \cdot \text{W}}}{K} (1 + K_{s,\text{Eth}} a_{\text{Eth}} + K_{s,\text{W}} a_{\text{W}})^2
\]

(9)

In this kinetic model (eq 9) there are three parameters to be estimated, the kinetic constant \((k_c)\) and the two adsorption parameters \((K_{s,\text{Eth}}\) and \(K_{s,\text{W}}\), instead of five if the rate equation (8) was used to describe the experimental data.

The temperature dependence of the kinetic constant was fitted with the Arrhenius equation:

\[
k_c = k_{0,c} \exp\left(-\frac{E_s}{RT}\right)
\]

(10)

where \(E_s\) is the reaction activation energy, \(k_{0,c}\) is the preexponential constant, \(R\) is the gas constant, and \(T\) is the temperature.

The temperature dependence of the adsorption equilibrium constants were fitted with

\[
K_s = K_{0,s} \exp\left(-\frac{\Delta H_s}{RT}\right)
\]

(11)

where \(K_{0,s}\) is the constant for eq 11 and \(\Delta H_s\) is the adsorption enthalpy.

### 4.2.1. Parameter Estimation from Experimental Data

The mass balance in the batch reactor for a component \(i\), in liquid phase, at constant temperature is given by

\[
\frac{dn_i}{dt} = V_i w_{\text{cat}} r_{ii}
\]

(12)

where \(n_i\) is the number of moles of component \(i\), \(t\) is the time, \(w_{\text{cat}}\) is the mass of catalyst, and \(r\) is the reaction rate expressed in moles of \(iI\) (mass of catalyst - min).

The number of moles of component \(i\) \((n_i)\) as a function of the conversion \(X\) of the limiting reactant \((l)\) is

\[
n_i = n_{i,0}\left(\frac{R_{ii} + v_{l} X_{l,w}}{R_{ii}^{0}}\right)\]

(13)

where \(n_{i,0}\) and \(v_{l}\) are, respectively, the initial number of moles and the stoichiometric coefficient of the limiting reactant and \(R_{ii}\) is given by

\[
r_{ii} = \frac{n_{i,0}}{n_{l,0}}
\]

(14)

where \(n_{l,0}\) is the initial number of moles of component \(l\).

Introducing eq 13 into eq 12, we get

\[
\frac{dX}{dt} = \frac{|v_{l}| w_{\text{cat}} r_{ii}}{n_{l,0}}
\]

(15)

with the initial condition: \(t = 0; X = 0\).

The differential equation (15) combined with the suggested rate expression, eq 9, was solved numerically with the DASOLV integrator implemented in gPROMS (general PROcess Modeling System), version 3.0.3, which is a commercial package from Process Systems Enterprise. For all simulations a tolerance equal to \(10^{-5}\) was fixed. The estimation of the unknown parameters \((E_s, k_{0,c}, K_{0,\text{Eth}}, K_{0,\text{W}}, \Delta H_{\text{Eth}}, \Delta H_{\text{W}})\) was carried out using the “Parameter estimation in gPROMS” that attempts to determine the values for the parameters, in order to maximize the probability that the mathematical model will predict the values obtained from experiments. Assuming independent, normally distributed measurement errors, \(e_{ik}\), with zero means and standard deviations, \(\sigma_{ik}\), this maximum likelihood goal can be captured through the following objective function:

\[
\Phi = \frac{N}{2} \ln(2\pi) + \frac{1}{2} \min_{\theta} \left\{ \sum_{i=1}^{N} \sum_{k=1}^{M} \ln(\sigma_{ik}^2) + \frac{X_{ik} - X_{ik}^0}{\sigma_{ik}^2} \right\}
\]

(16)

where \(N\) is the total number of measurements taken during the experiments \((N = 290)\), \(\theta\) is the set of model parameters to be estimated \((\theta = 6)\), \(NE\) is the number of experiments performed \((NE = 15)\), \(NM\) is the number of measurements of the conversion in the \(i\)th experiment, \(\sigma_{ik}^2\) is the variance of the \(i\)th measurement of the conversion in experiment \(i\) \((\sigma^2 = 1.83 \times 10^{-3})\), \(X_{ik}^0\) is the \(i\)th measured value of conversion in experiment \(i\), and, finally, \(X_{ik}\) is the \(i\)th (model-) predicted value of conversion in experiment \(i\). The quality of the model fit was tested through the mean relative deviation (MRD) between the calculated conversion values \((X_{\text{calc}})\) and the experimental ones \((X_{\text{exp}})\) (see eq 17).

\[
\text{MRD} = \frac{1}{N} \left\{ \sum_{i} \frac{|X_{\text{calc}} - X_{\text{exp}}|}{X_{\text{exp}}} \right\} \times 100\%
\]

(17)
4.3. Modeling and Discussion of Results. The simplified \( L-H \) model (eq 9) was used to describe the kinetic behavior of the esterification of lactic acid with ethanol using Amberlyst 15-wet as catalyst. In order to obtain the unknown parameters, at least two different experiments (different initial molar ratios) were performed for each temperature, which varied from 323.15 to 363.15 K. The values of the optimized parameters along with the MRD value are presented in Table 6. A value of MRD between experimental and calculated conversions of 6.8% was obtained.

As mentioned before in section 4.2, the Arrhenius equation was used to fit the kinetic behavior of the esterification of lactic acid with ethanol using Amberlyst 15-wet as catalyst. In order to obtain the unknown parameters, at least two different experiments (different initial molar ratios) were performed for each temperature, which varied from 323.15 to 363.15 K. The values of the optimized parameters along with the MRD value are presented in Table 6. A value of MRD between experimental and calculated conversions of 6.8% was obtained.

4.3.1. Effect of Catalyst Loading. The catalyst loading was varied from 1.2 to 3.9 wt % (weight of catalyst/total weight of reaction mixture), keeping the rest of the experimental conditions similar. The effect of the catalyst loading on the esterification reaction between lactic acid and water is shown in Figure 7. As may be observed, the reaction rate increases with the percentage of Amberlyst 15-wet. This was expected since the increase of catalyst implies an increase in the number of active sites available for the reaction.

4.3.2. Effect of Initial Molar Ratio of Reactants. To study the effect of the initial molar ratio of reactants \( R_{Eth/La} \) on the conversion of lactic acid, this condition was varied from 1.1 to 2.8, as presented in Figure 8. It can be seen that the equilibrium conversion increases with the increase of the initial molar ratio of ethanol to lactic acid and that the equilibrium is achieved faster for upper initial molar ratio values.

It may be observed from Figure 8 that the experiments are initially well predicted by the model (until about 120 min), and due to the methodology developed in this work, the equilibrium is also well described. However, there is a transient state (between 120 min and the equilibrium) where the model fails to describe the experiments, being more significant for higher values of the initial molar ratio between ethanol and lactic acid.

4.3.3. Effect of Reaction Temperature. The effect of reaction temperature is shown in Figure 9. The reaction rate increases with the reaction temperature. The same effect is noticed on the equilibrium conversion. Once again, it can be noticed that, in the transient state, the model predicts higher conversion of lactic acid values than those obtained experimentally.

4.3.4. Effect of Lactic Acid and Ethyl Lactate Oligomers. The proposed model shows a kinetic behavior with two limiting

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{0,c} ) (mol \cdot g^{-1} \cdot min^{-1})</td>
<td>2.70 \times 10^7</td>
</tr>
<tr>
<td>( E_a ) (kJ \cdot mol^{-1})</td>
<td>49.98</td>
</tr>
<tr>
<td>( K_{0,W} )</td>
<td>15.19</td>
</tr>
<tr>
<td>( \Delta H_W ) (kJ \cdot mol^{-1})</td>
<td>-99.85</td>
</tr>
<tr>
<td>( K_{0,Eth} )</td>
<td>1.22</td>
</tr>
<tr>
<td>( \Delta H_{Eth} ) (kJ \cdot mol^{-1})</td>
<td>-29.95 \times 10^2</td>
</tr>
<tr>
<td>MRD (%)</td>
<td>6.84</td>
</tr>
</tbody>
</table>
situations: (a) first slope at the beginning of the experiment, corresponding to the initial reaction rate; (b) final plateau, corresponding to the reaction equilibrium.

However, experimentally, it seems that there are three limiting situations, where the first and third are the same as the ones described by the proposed model, but the transient state is represented by a line with a very small slope. This could be due to the presence of the lactic acid oligomers and, consequently, ethyl lactate oligomers that where formed. To confirm this assumption, an evaluative modeling study was made considering the presence of oligomers using the kinetic model and the parameters reported by Tanaka et al.6

Analyzing the simulated kinetic curve for the ethyl lactate monomer, here denominated just as ethyl lactate, one can conclude a behavior similar to the experimental results shown in this work, where there are three limiting steps:

(a) The first limiting step is the initial conversion of lactic acid oligomers in ethyl lactate oligomers, but the kinetic rate is much higher for the monomers than for the dimers and trimers. Therefore the experiments are initially well predicted.

(b) The second step is the transient state, where the ethyl lactate monomer concentration increases slowly, since several reversible reactions are occurring and the equilibrium is shifted toward lactic acid monomer formation and consequently ethyl lactate monomer. In this transient step, first the dimer concentrations of lactic acid and ethyl lactate decrease due to their hydrolysis, and then the same happens to the trimers that are converted into dimers and finally again into monomers, until the equilibrium is reached.

(c) Last is the reaction equilibrium: when all the reversible reactions are in equilibrium, the total amounts of lactic acid and ethyl lactate oligomers are less than 0.4%. Therefore, the experiments are well predicted at the equilibrium since the oligomer presence is negligible.

The transient behavior, where the hydrolyses of dimers and trimers of lactic acid and ethyl lactate are dominant to produce the ethyl lactate monomer, is even more noticeable for higher values of initial molar ratio of ethanol/lactic acid, as is shown in Figure 11b. This is due to the fact that the excess of ethanol benefits more the ethyl lactate dimer formation as shown in Figure 11b, which will be further hydrolyzed, and the lactic acid dimer formed will be converted into lactic acid monomer, which will be finally converted into ethyl lactate monomer. Nevertheless, in the equilibrium composition the excess of ethanol leads to smaller amounts of oligomers (2.4 mol % in the case of \( R_{Eth/La} = 1 \) and 0.4 mol % in the case of \( R_{Eth/La} = 3 \)).

4.3.5. Effect of Polar Species. The activity of the resin varies with the polarity of the reaction medium, since it influences

Figure 10. (a) Molar fraction histories of the compounds: ethyl lactate monomer, ethanol, lactic acid monomer, and water. \( T = 363.15 \) K and \( R_{Eth/La} = 3 \). The kinetic model and the parameters used were taken from Tanaka et al.6 (b) Molar fraction histories of the oligomers: ethyl lactate dimer, ethyl lactate trimer, lactic acid dimer, and lactic acid trimer. \( T = 363.15 \) K and \( R_{Eth/La} = 3 \). The kinetic model and the parameters used were taken from Tanaka et al.6

Figure 11. (a) Molar fraction histories of ethyl lactate and lactic acid for different initial molar ratios. \( T = 353.15 \) K. The kinetic model and the parameters used were taken from Tanaka et al.6 (b) Molar fraction histories of ethyl lactate dimer for different initial molar ratios. \( T = 353.15 \) K. The kinetic model and the parameters used were taken from Tanaka et al.6
the number of available sulfonic groups and their acidity.\textsuperscript{22} The polarity of the medium, mainly due to the water and alcohol concentrations, can affect the reaction rate in two ways:

(i) The more adsorbed species (water and alcohol) inhibit the others to adsorb onto the active sites.

(ii) Water can ionize, solvate, and dissociate the acidic protons of the sulfonic groups, depending on their concentration; when the sulfonic sites are completely dissociated, the reaction occurs in the liquid phase as in the case of homogeneous catalysis.\textsuperscript{43}

In this case, the reaction medium has a high water concentration: besides the water initially present in the reaction due to the lactic acid solution, more water is being formed during the course of the esterification of lactic acid with ethanol. Although the kinetic model proposed in this work has taken into account the inhibitory effect caused by adsorption, it does not consider the remaining effects that could be due to the presence of water or ethanol. Therefore, this could also be a reason for the deviations between the experimental results and those predicted by the kinetic model in the transient stage. Françoisse and Thyrion\textsuperscript{44} studied the ETBE synthesis catalyzed by Amberlyst 15. In that study the influence of ethanol on the reaction rate was taken into account. A kinetic model to describe the behavior of the reaction for low and high ethanol concentrations was developed. However, this case is different from the one presented in this work, since the most adsorbed component was ethanol and there was no water as reaction product. They used a nonpolar solvent (n-pentane), and the other reactant (isobutene) was also nonpolar. In the case under study, besides ethanol there is also lactic acid concentrated solution that has a high water content. Therefore, at the beginning of the reaction there are three polar species competing for the acid sites; it was observed that the initial kinetic rate increases with the ethanol concentration until a plateau, which was not the behavior observed in the ETBE kinetics. Most works about the esterification reaction of ethanol and lactic acid consider that water and ethanol are the most adsorbed species, which supports our kinetic model assumptions.\textsuperscript{24,25} Moreover, in a later work from Dassy et al.\textsuperscript{45} for the esterification of lactic acid with butanol catalyzed by Amberlyst 15, the authors did not observe different mechanisms for high and low alcohol concentrations, and similar to our model, they neglected the presence of oligomers and only considered the water adsorption.

The proposed model describes quite well the experimental data up to 80% of the equilibrium conversion as well as the equilibrium stage, which are the most important to apply to a hybrid reactive separation technology.

5. Conclusions

The equilibrium composition for the liquid-phase reaction of ethyl lactate synthesis catalyzed by the acid ion-exchange resin Amberlyst 15-wet was measured in the temperature range 50–90 °C, at 6 bar. The thermodynamic equilibrium constant estimated by the UNIQUAC method was \( K = 2.9625 \times 515.13/T \) (K) and the average reaction enthalpy was 4.28 kJ/mol\textsuperscript{-1} in that temperature interval. This relation was also successfully applied to describe the equilibrium compositions of other published studies; better prediction was found for systems where high concentrations of lactic acid were used.

Because of the strong nonideality of the liquid reaction mixture, the reaction rate model was formulated in terms of activities. The rate-controlling step for the esterification reaction between lactic acid and ethanol, heterogeneously catalyzed by Amberlyst 15-wet was the surface reaction, since external and internal mass resistances were insignificant for the temperature range 50–90 °C. The catalyst reusability was also studied, and catalyst deactivation was not verified until three usages of the same resin sample.

A three-parameter model based on a Langmuir–Hinshelwood rate expression was proposed to describe the experimental kinetic results: \( r = k_i (a_{Eth,La} - a_{Eth,La}^o)/(1 + K_{Eth,La} + K_{EthEth} + K_{Eth,La}^o)\); the model parameters are \( k_i = 2.70 \times 10^7 \exp(-6011.55/T) \) (K), \( K_{Eth} = 15.19 \exp(12.01/T) \) (K), and \( K_{Eth,La} = 1.22 \exp(359.63/T) \) (K). The agreement between experimental and simulated results was good for the following operating conditions: catalyst loading from 1.2 to 3.9 wt %, initial molar ratio of reactants from 1.1 to 2.8, and temperature from 50 to 90 °C.

Acknowledgment

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Notation

\( a \) = liquid phase activity
\( d_p \) = pellet diameter (nm)
\( d_l \) = film thickness (μm)
\( E_a \) = apparent reaction activation energy (J mol\textsuperscript{-1})
\( K \) = equilibrium reaction constant
\( K_e \) = equilibrium constant based on molar fractions
\( K_a \) = equilibrium constant based on activity coefficients
\( K_s \) = equilibrium adsorption constant
\( k_i \) = kinetic constant (mol g\textsuperscript{-1} min\textsuperscript{-1})
\( k_{0,i} \) = preexponential factor (mol g\textsuperscript{-1} min\textsuperscript{-1})
\( K_{Eth} \) = constant for eq 17
\( MRD \) = mean residual deviation
\( n \) = number of moles (mol)
\( N \) = total number of measurements taken during the experiments
\( NE \) = number of experiments performed
\( NM \) = number of measurements of the conversion in experiment \( i \)
\( \Delta H_a \) = enthalpy of adsorption (J mol\textsuperscript{-1})
\( \Delta H_{f,a}^o \) = standard enthalpy of formation (J mol\textsuperscript{-1})
\( \Delta G^o \) = standard Gibs energy of reaction (J mol\textsuperscript{-1})
\( R \) = gas constant (J mol\textsuperscript{-1} K\textsuperscript{-1})
\( r \) = reaction rate (mol g\textsuperscript{-1} min\textsuperscript{-1})
\( R_{Eth,La} \) = initial molar ratio of ethanol to lactic acid
\( t \) = time coordinate (min)
\( T \) = temperature (K)
\( X \) = conversion of the limiting reactant \( x \) molar fraction
\( w_{cat} \) = mass of dry catalyst (g)
\( \chi_{Eth}^i \) = kth (model-) predicted value of conversion in experiment \( i \)
\( X_{Eth}^i \) = kth measured value of conversion in experiment \( i \)

Greek Symbols

\( \nu \) = stoichiometric coefficient
\( \gamma \) = activity coefficient
\( \theta \) = set of model parameters to be estimated
\( \sigma_{i,j}^2 \) = variance of the kth measurement of conversion in experiment \( i \)
\( \bar{\sigma}^2 \) = average of variance

Subscripts

\( 0 \) = initial value
Eth = ethanol
La = lactic acid
EL = ethyl lactate


(34) DIPPR 801. Thermophysical Properties Database; 1998.


