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Kinetic study for esterification of lactic acid with ethanol and hydrolysis of ethyl lactate using an ion-exchange resin catalyst

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Abstract

The esterification of lactic acid with ethanol and the hydrolysis of the corresponding ester, ethyl lactate, have been studied in the presence of the commercial cation-exchange resin Amberlyst 15. The influence of different operating parameters such as stirrer speed, catalyst particle size, initial reactant molar ratio, reaction temperature and catalyst loading, has been examined. Additionally, the adsorption constants for the four components on Amberlyst 15 were determined by performing adsorption experiments between two non-reacting species. The values found for the adsorption constants follow the order: water > ethanol > lactic acid > ethyl lactate. Experimental kinetic data of the esterification and the hydrolysis reactions were correlated simultaneously with the Langmuir–Hinshelwood (LH) and pseudo-homogeneous (PH) models. The activity coefficients were calculated according to the UNIQUAC model. The LH model gave the best agreement with the kinetic experimental data. The activation energy of esterification and hydrolysis reactions were found to be 52.29 and 56.05 kJ mol^{-1}, respectively.

Keywords: Esterification; Hydrolysis; Lactic acid; Ethyl lactate; Chemical equilibrium

1. Introduction

Food industry generates large volumes of carbohydrates which can be substrates for bioconversion to valuable products such as lactic acid and its derivates. Lactic acid and their esters can be used in the food industry for preservation and flavoring purposes, as well as in the pharmaceutical and cosmetic industries. Lactic acid is also used as a monomer for the manufacture of biodegradable polymers as substitutes for conventional petrochemical polymers. Fermentation-derived lactic acid requires extensive purification operations [1]. Esterification of lactic acid with lower alcohols, such as methanol, ethanol, isopropanol and butanol, can be used as a method to obtain highly purified lactic acid from fermentation broths. The volatile lactate ester produced can be separated from the reactive mixture and hydrolyzed back to pure lactic acid and the corresponding alcohol that can be recovered and reused [2].

In previous work, our research group studied the catalyzed esterification of lactic acid (20 wt.%) with methanol [3] and the hydrolysis of the methyl lactate [4]. Analysis of the experimental data showed that the pseudo-homogeneous (PH) model represented the esterification and hydrolysis kinetics over Amberlyst 15 fairly well.

Kinetic studies on the esterification of lactic acid with ethanol are scarce in the literature and usually the hydrolysis of ethyl lactate is not included. Troupe and Dimilla [2] studied this esterification reaction in the presence of sulfuric acid as homogenous catalyst. In their experiments lactic acid of 85 and 44 wt.% analytical grade was used. They studied the effect of reaction temperature, amount of catalyst and initial reactant molar ratio. Based on their results they suggested that the mechanism of reaction changed above an initial reactant molar ratio ($n_{\mathrm{EtOH}}/n_{\mathrm{HL}}$) of 4. Zhang et al. [5] investigated the esterification of lactic acid (80 wt.%) with ethanol in the presence of five different cation-exchange resins. They found that the Langmuir–Hinshelwood (LH) model based on the selective adsorption of water and ethanol on the catalyst was the most appropriate model to describe the kinetic behavior. Engin et al. [6] carried out also the esterification of lactic acid with ethanol over hetero-poly-acid supported on ion-exchange resins (Lewatit® S100) showing higher activities than the resin itself. They used lactic acid 92 wt.% and the hydrolysis reaction of lactoyllactic acid (the linear dimer of lactic acid) was taken into account.

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Nomenclature

a	activity
E_A	apparent activation energy (kJ mol^{-1})
k	adsorption coefficient
k_e	forward reaction rate constant (mol min^{-1} g^{-1})
k^o	pre-exponential Arrhenius factor (mol min^{-1} g^{-1})
K_{eq}	thermodynamic equilibrium constant
m_{cat}	mass of catalyst (g)
MRD	mean relative deviation
n	number of experimental data
n_i	moles of component i
O.F.	objective function
r	reaction rate (mol g-cat^{-1} min^{-1})
R	gas constant (kJ mol^{-1} K^{-1})
t	time (min)
T	absolute temperature (K)
w	mass fraction
x	mole fraction

Greek symbols

γ	activity coefficient
ν	stoichiometric coefficient

Subscripts

e	esterification reaction
eq	equilibrium
i, j	components
calc	calculated value
exp	experimental value
HL	lactic acid
EL	ethyl lactate
EtOH	ethanol
W	water

Several studies have also been performed based on hybrid processes combining reaction and pervaporation [7–9]. Shifting the equilibrium towards product formation, higher conversions than the equilibrium conversion were obtained.

In this work, the esterification of lactic acid with ethanol and the hydrolysis of the corresponding ester, ethyl lactate, both over Amberlyst 15, have been investigated. Dilute solutions of lactic acid were used in the esterification experiments in order to avoid the presence of polymers of high molecular weight. Because of the two functional groups, acid and hydroxyl, lactic acid can suffer intermolecular esterification [10]. Dilute lactic acid solutions containing about 20 wt.% lactic acid correspond mainly to monomer lactic acid and water. Polylactic acid of different chain lengths is formed in aqueous solutions of higher concentration due to the self-esterification process. Several experiments have been carried out to analyze the influence of the stirrer speed, catalyst size, catalyst loading, initial reactant molar ratio and temperature on the forward and the backward reactions. To provide a general kinetic model, experimental esterification and hydrolysis kinetic data were correlated altogether by using different models based on homogeneous and heterogeneous approaches. To take into account the non-ideality of the liquid mixture, activities were used instead of mole fractions. The activity coefficients were calculated by the UNIQUAC equation. Additionally, some esterification kinetics of lactic acid with ethanol were carried out at different temperatures without the addition of catalyst.

2. Experimental

2.1. Materials

Ethyl lactate was supplied by Aldrich with a reported purity of 99 wt.%. Ethanol of 99.9 wt.% purity was purchased from Lab-Scan. Water was nanopure. An aqueous lactic acid solution (20 wt.%) was obtained from Acros. The amount of polymerized lactic acid was considered negligible after being determined by back titration [4]. The purity of the chemicals was checked by gas chromatography (GC). All of them were used without further purification.

The strongly acidic ion-exchange resin, Amberlyst 15, with an exchange capacity of 4.75 mequiv H^+/g of dry catalyst (Rohm & Haas) was used as catalyst. The resin was washed several times before use with distilled water and dried at 353.15 K until the mass remained constant.

2.2. Kinetic measurements

The kinetics of esterification of lactic acid with ethanol and of ethyl lactate hydrolysis were carried out in a thermostated stirred batch reactor of 500 mL capacity. The equipment and procedure have already been described in detail elsewhere [3]. For the esterification reaction, the aqueous lactic acid solution and Amberlyst 15 were charged into the reactor and heated to the desired reaction temperature. Ethanol was heated separately up to the desired temperature and fed to the reactor, through a thermostated funnel connected to one of the necks of the reactor. This time was considered to be the starting time of the reaction. In the case of the hydrolysis reaction, water and catalyst were heated together in the reactor and ethyl lactate was heated separately and added to the reactor after reaching the reaction temperature. The temperature in the reactor was kept constant within ±0.5 K. The kinetic reaction was conducted by withdrawing samples at regular time intervals that were analyzed by gas chromatography.

2.3. Sorption equilibrium experiments

Some sorption experiments were performed for three of the binary non-reactive mixtures to take into account the sorption of the different reactants on the Amberlyst 15 surface. The experiments were carried out by following the procedure proposed by Pöpken et al. [11]. Among the four non-reactive binary systems, only three independent binary adsorption experiments can be carried out since lactic acid is obtained as aqueous solution.

Binary samples of known weight composition were contacted with a certain amount of Amberlyst 15 (12 wt.%) in 50 mL glass flasks at 303 K. This mixture was stirred in an orbital shaker

(Grant-OLS 200), where the temperature was maintained with an accuracy of ±0.5 K. The establishment of sorption equilibrium was ensured by checking the liquid phase composition. It was observed that the equilibrium was reached in a very short time, however, the samples were kept for more than 24 h in the orbital shaker and after that, they were analyzed by gas chromatography.

2.4. Sample analysis

All kinetic and adsorption samples were analyzed by gas chromatography using an HP 6890 chromatograph equipped with series-connected thermal conductivity detector (TCD) and flame ionization detector (FID). Helium, with a purity higher than 99.99 wt.%, was used as the carrier gas. The GC column was a bonded-phase fused-silica capillary column of 30 m × 0.25 mm. The injector and detectors were kept at 523.15 and 533.15 K, respectively. The oven temperature was controlled from 363.15 to 473.15 K. The amount of lactic acid was also determined by titration using phenolphthalein as indicator.

3. Kinetic model

Esterification reactions catalyzed by ion-exchange resins can be described by using different kinetic models based on homogeneous and heterogeneous approaches. The pseudo-homogeneous model has been successfully used in high polar reaction media [4,12,13] where a complete swelling of the polymeric catalyst can be assumed, leading to an easy access of the reactants to the active sites. However, the PH model does not take into account the sorption effect into the resin of the different species in the reactant medium. The Langmuir–Hinshelwood and the Eley–Rideal (ER) mechanisms include sorption effects in their kinetic model. The basic idea of the Langmuir–Hinshelwood mechanism is that all reactants are adsorbed on the catalyst surface before chemical reaction takes place. Castor González and Fair [14] proposed an empirical kinetic expression, based on Langmuir–Hinshelwood model assuming that water is adsorbed on the resin following an exponential distribution (modified LH model). The ER model is applied when the reaction takes place between an adsorbed and a non-adsorbed reactant. In this work the kinetic data of the esterification of lactic acid with ethanol and the hydrolysis of ethyl lactate were correlated simultaneously by using the PH and LH models. Among the different heterogeneous approaches the LH model was chosen based on the results found in the literature for this kind of reaction [3,5]. The modified LH model was not studied in order not to have an additional kinetic parameter. A general kinetic expression can be written as:

$$r = \frac{1}{m_{\text{cat}}}\frac{1}{\nu_i}\frac{dn_i}{dt} = \frac{k_e(a_{\text{HL}}a_{\text{EtOH}} - (a_{\text{EL}}a_{\text{W}}/K_{\text{eq}}))}{\left(1+\sum_i k_i a_i\right)^n} \tag{1}$$

where m_{cat} is the catalyst mass, ν_i the stoichiometric coefficient of the ith component, n_i the number of moles of the ith component, t the time, k_e the forward reaction rate constant, k_i the adsorption constant of the ith component, a_i the activity of the ith component, K_{eq} the equilibrium constant and the exponent is $n = 2$ for the LH model and $n = 0$ for the PH model. An Arrhenius-type temperature dependence for the reaction constant was used:

$$k_e = k_e^o \exp\left(\frac{-E_{A,e}}{RT}\right) \tag{2}$$

where k_e^o is the pre-exponential Arrhenius factor, E_A the activation energy, R the gas constant and T is the absolute temperature.

The non-ideality of the liquid phase was considered by using activities instead of mole fractions. The activity coefficients of the components in the liquid phase were calculated by using the UNIQUAC equation. For the non-reactive binary systems UNIQUAC parameters were taken from the literature [15,16]. In the case of the reactive binary systems, vapor liquid equilibrium (VLE) data were predicted by UNIFAC, and the estimated data were used to obtain the UNIQUAC parameters [17]. In the case of the binary system water (1) + lactic acid (2) new UNIQUAC parameters were obtained by using previously reported experimental VLE data [18] and the lactic acid vapor pressure provided by the simulation Software Aspen Plus [16]. The resulting parameters for this system were $\Delta u_{12} = -39.61$ K and $\Delta u_{21} = 155.18$ K.

The equilibrium constant was calculated from the component composition at equilibrium:

$$K_{\text{eq}} = \left(\frac{a_{\text{EL}}a_{\text{W}}}{a_{\text{HL}}a_{\text{EtOH}}}\right)_{\text{eq}} = \left(\frac{x_{\text{EL}}x_{\text{W}}}{x_{\text{HL}}x_{\text{EtOH}}}\right)_{\text{eq}}\left(\frac{\gamma_{\text{EL}}\gamma_{\text{W}}}{\gamma_{\text{HL}}\gamma_{\text{EtOH}}}\right)_{\text{eq}} \tag{3}$$

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

The kinetic parameters of the PH and LH models were obtained by reduction of the experimental kinetic data to Eq. (1), minimizing the following objective function (O.F.):

$$\text{O.F.} = \frac{\sum_{\text{all samples}}|x_{\text{EL,exp}} - x_{\text{EL,calc}}|}{n_{\text{samples}}} \times 100 \tag{4}$$

by using the Simplex–Nelder–Mead method [19]. The differential equation was solved numerically with a fourth order Runge-Kutta method.

The quality of the fit was evaluated through the mean relative deviation (MRD):

$$\text{MRD} = \frac{\sum_{\text{all samples}}|(x_{\text{EL,exp}} - x_{\text{EL,calc}})/x_{\text{EL,exp}}|}{n_{\text{samples}}} \times 100 \tag{5}$$

The subscripts ‘exp’ and ‘calc’ in Eqs. (4) and (5) are referring to the experimental and calculated mole fraction of ethyl lactate for each experimental kinetic data (n_{samples}).

4. Results and discussion

4.1. Homogeneous esterification

The esterification of lactic acid with ethanol was performed at different temperatures (358.15–328.15 K) without the addition of Amberlyst 15. In this case, the reaction is catalyzed by lactic acid itself. To take into account the autocatalytic effect of the carboxylic acid in homogeneous esterification reactions, Pöpken

Table 1
Parameters of the kinetic model for the homogeneous esterification of lactic acid with ethanol without external catalyst

Exponent, α	k_e^o (mol g^{-1} min^{-1})	$E_{A,e}$ (kJ mol^{-1})	O.F.	MRD (%)
0.5	8.354×10^8	62.50	0.028	4.99
1	5.298×10^8	64.44	0.030	5.46

et al. [11] proposed the following kinetic equation:

$$\frac{1}{\nu_i}\frac{dn_i}{dt} = k_e^o \exp\left(-\frac{E_{A,e}}{RT}\right) a_{HL}^{\alpha}\left(a_{HL}a_{EtOH} - \frac{a_{EL}a_W}{K_{eq}}\right) \tag{6}$$

All terms in Eq. (6) have the same meaning as in Eq. (1). The exponent α can take different values according to the autocatalytic mechanism [11]. If catalysis is assumed to take place via the solvated protons of the dissociated carboxylic acid, $\alpha = 0.5$, whereas $\alpha = 1$ if catalysis is assumed via the molecular acid.

The kinetic parameters of this model were obtained by minimizing the objective function in Eq. (4), using the Simplex–Nelder–Mead [19] method and solving the differential equation numerically with a fourth order Runge-Kutta method. The quality of the fit was evaluated through the mean relative deviation (Eq. (5)). These kinetic parameters are presented in Table 1. Slightly better results were obtained when $\alpha = 0.5$. The activation energy of the auto-catalyzed esterification reaction resulted to be 62.50 kJ mol^{-1}.

The Arrhenius plot of the reaction rate constant for the homogeneous esterification reaction is presented in Fig. 1. The reaction rate constants calculated by the model are included as lines.

4.2. Sorption experiments

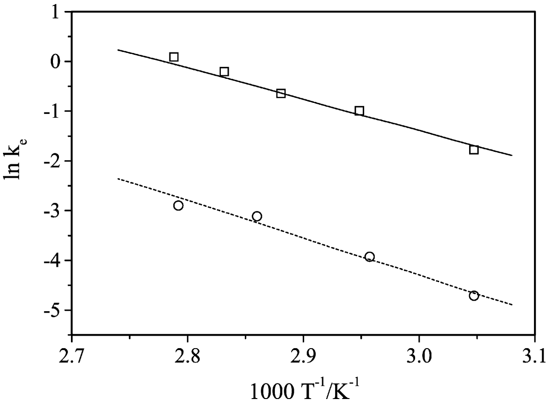

Fig. 1. Arrhenius plot of the esterification of lactic acid with ethanol ($n_{EtOH}/n_{HL} = 3$). Auto-catalyzed reaction (○). The dashed line represents the results of the autocatalysis model ($\alpha = 0.5$). Reaction catalyzed by 2.5 wt.% Amberlyst 15 (□). The continuous line represents the results of the LH model.

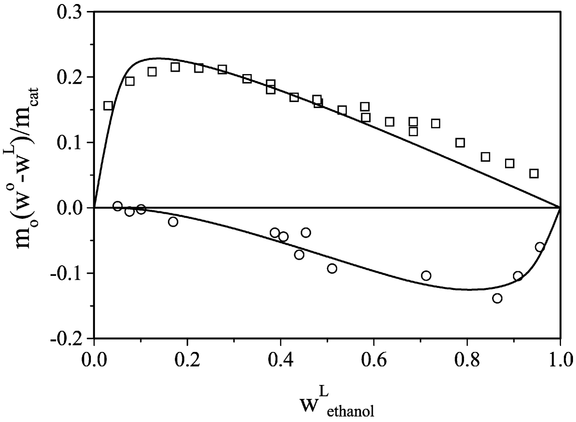

Fig. 2. Adsorption equilibrium for the non-reactive binary systems ethanol + water (○) and ethanol + ethyl lactate (□) on Amberlyst 15 at 303.15 K. The lines represent the results of Eq. (7).

The adsorption constants for the LH model were obtained from independent sorption experiments as it has been described in the Section 2. In this case a better extrapolation capability of the model can be reached [11]. The sorption experiments were performed for three of the four binary non-reactive systems involved in the esterification of lactic acid with ethanol, i.e., ethanol + water, ethanol + ethyl lactate and water + lactic acid. The results obtained are presented in Figs. 2 and 3. The following expression proposed by Pöpken et al. [11] was used to obtain the sorption constants assuming Langmuir-type adsorption:

$$\frac{m_o(w_1^o - w_1^L)}{m_{cat}} = \frac{m_s}{m_{cat}}\frac{(k_1a_1w_2^L - k_2a_2w_1^L)}{1 + k_1a_1 + k_2a_2} \tag{7}$$

where m_o is the initial weight of liquid mixtures, m_{cat} the catalyst mass, w_1^o the initial weight fraction of component 1, w_i^L the weight fraction at equilibrium of the ith component, k_i the adsorption constant for the ith component and m_s/m_{cat} is the total amount of adsorbed components per unit of catalyst mass. Based on swelling experiments of Amberlyst 15 in pure components the ratio m_s/m_{cat} was assumed to be constant for all binary mixtures studied in this work. In the case of the binary system water + lactic acid the presence of lactoyllactic acid was taken into account. The sorption constants for the components involved in this system as well as the ratio m_s/m_{cat} were obtained by using the Simplex–Nelder–Mead [19] method and are presented in Table 2. It can be observed that water was adsorbed most strongly followed by ethanol, lactic acid and ethyl lactate. Similar results were obtained by Zhang et al. [5]. Through FTIR experiments they proved that water was adsorbed much stronger on the resin surface than lactic acid and ethyl lactate

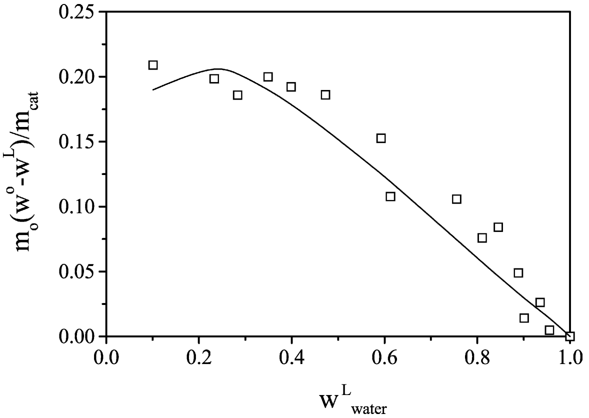

Fig. 3. Adsorption equilibrium for the non-reactive binary system water + lactic acid (□) on Amberlyst 15 at 303.15 K. The line represents the results of Eq. (7).

Table 2
Results of the correlation of the non-reactive binary adsorption equilibrium on Amberlyst 15 at 303.15 K

Adsorbed mass per catalyst mass	
m_s/m_{cat}	0.3600
Adsorption equilibrium constants	
k_w	8.2421
k_{EtOH}	5.0193
k_{EL}	0.1270
k_{HL}	0.5121

for the macroporous resin D002. Zhang et al. [5] also found by kinetic experiments that the adsorption coefficient of water was greater than that of ethanol over the catalyst NKC and D002, suggesting that water was adsorbed more strongly than ethanol on the active sites of the catalyst.

4.3. *Mass transfer resistance*

Preliminary experiments were carried out to evaluate the influence of the different mass transfer resistances. First of all, the stirrer speed was varied between 100 and 235 rpm to study the external mass transfer resistance. The experiments showed that in the range considered in this work, there was little effect of the stirrer speed in the reactor on the overall reaction rate. This conclusion agrees with the work of Chakrabarti and Sharma [20] who established that external diffusion does not control the overall reaction rate unless the agitation speed is very low or the viscosity of reactant mixture is very high. To ensure the absence of external mass transfer resistance, the kinetic experiments in this work were performed at 185 rpm.

To investigate the internal diffusion, the Amberlyst 15 was screened into several different particle sizes [3]. Different runs were carried out in the particle range between 250 mm and the maximum particle size of Amberlyst 15. No significant differences were found for the different catalyst sizes, and unsieved resin was used for the following kinetic experiments in this work. This result agrees with Liu and Tan [21] who pointed out that intra-particle diffusion resistance is usually negligible for most of the reactions catalyzed by the Amberlyst series resins.

4.4. *Ion-exchange catalyzed reaction*

A set of kinetic experiments was performed for the esterification of lactic acid with ethanol and the hydrolysis of ethyl lactate catalyzed by Amberlyst 15. The effect of catalyst loading, initial reactant molar ratio and reaction temperature on the esterification and hydrolysis kinetics was analyzed.

4.4.1. *Effect of temperature*

The study of the effect of the temperature is very important since it is useful to calculate the activation energy of the reaction. Kinetic experiments were performed in a temperature range from 328.15 to 358.65 K for the esterification reaction and from 328.15 to 360.15 K for the hydrolysis reaction. Typical results are shown in Fig. 4. It can be seen that the reaction rate increases with increasing reaction temperature. However, the equilibrium conversion was nearly equal in the range of temperatures considered in this work. In general, in most esterification reactions, the equilibrium constant is a weak function of the temperature because of the small value of the heat of reaction. The same behavior was observed in the reaction of lactic acid with methanol [3]. A value for the activation energy of 52.29 kJ mol^{-1} was found in the fitting procedure to the LH model for the esterification reaction of lactic acid with ethanol. The high value of the activation energy confirms that there is no mass transport limitation. Fig. 1 shows the Arrhenius plot of the reaction rate constant together with the rate constant for the homogeneous esterification. Zhang et al. [5] obtained activation energies for the esterification reaction of 51.58 and 52.26 kJ mol^{-1} for the resins D002 and NKC, respectively. In all cases, the catalyst reduces the activation energy of this reaction that was found to be 62.50 kJ mol^{-1} when no external catalyst was used (see Section 4.1). An activation energy of 56.05 kJ mol^{-1} was obtained for the hydrolysis of ethyl lactate.

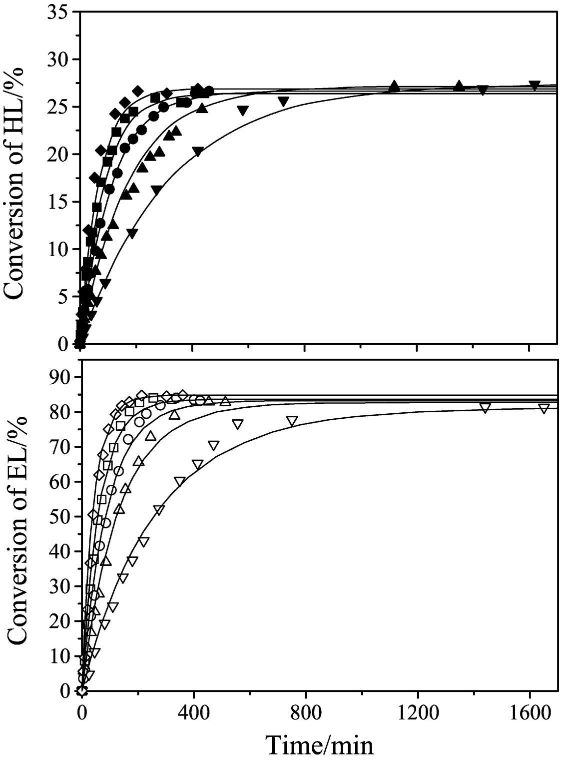

Fig. 4. Conversion vs. time at different temperatures for the esterification reaction (catalyst loading = 2.5 wt.%, $n_{EtOH}/n_{HL} = 3$): (▼), 328.15 K; (▲), 339.15 K; (●), 347.15 K; (■), 353.15 K; (♦), 358.65 K; and for the hydrolysis reaction (catalyst loading = 2.5%, $n_W/n_{EL} = 15$): (▽), 328.15 K; (△), 339.15 K; (◯), 346.15 K; (□), 353.15 K; (◊), 360.15 K. The continuous lines represent the results of the LH model.

4.4.2. *Effect of catalyst loading*

The catalyst loading was expressed as the weight ratio of the catalyst to the total reaction mixture. The catalyst loading was varied from 1.1 to 6 wt.% for the esterification and hydrolysis reactions. An increase in the catalyst loading leads to an increase of the reaction rate due to an increase in the total number of active

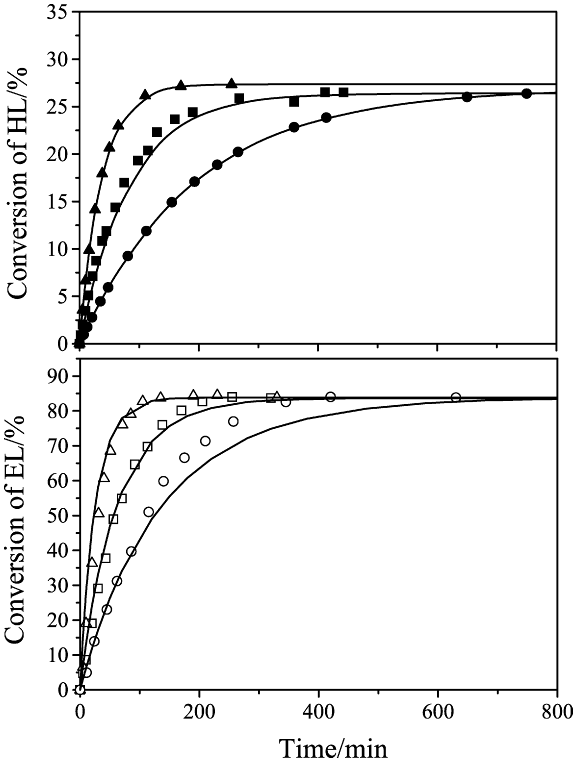

Fig. 5. Conversion vs. time at different catalyst loading, for the esterification reaction ($T = 353.15$ K, $n_{\mathrm{EtOH}}/n_{\mathrm{HL}} = 3$): (●), 1.1 wt.%; (■), 2.5 wt.%; (▲), 6 wt.%; and for the hydrolysis reaction ($T = 353.15$ K, $n_{\mathrm{W}}/n_{\mathrm{EL}} = 15$): (○), 1.1 wt.%; (□), 2.5 wt.%; (△), 6 wt.%. The continuous lines represent the results of the LH model.

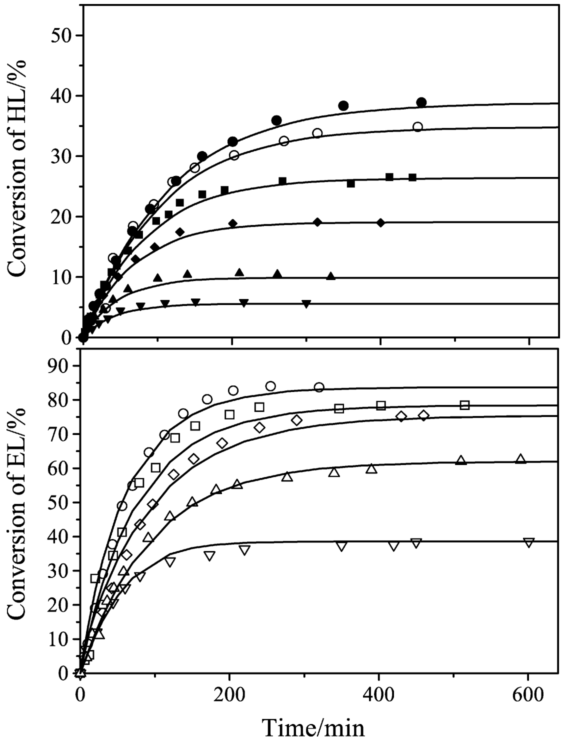

Fig. 6. Conversion vs. time at different initial reactant molar ratios ($n_{\mathrm{EtOH}}/n_{\mathrm{HL}}$) for the esterification reaction ($T = 353.15$ K, catalyst loading = 2.5 wt.%): (▼), 0.5; (▲), 1; (♦), 2; (■), 3; (○), 5; (●), 6; and for the hydrolysis reaction ($n_{\mathrm{W}}/n_{\mathrm{EL}}$) ($T = 353.15$ K, catalyst loading = 2.5 wt.%): (▽), 1; (△), 3; (◇), 7; (□), 10; (○), 15. The continuous lines represent the results of the LH model.

catalytic sites. The effect of catalyst loading can be observed in Fig. 5.

4.4.3. *Effect of initial reactant molar ratio*

The initial molar ratio of ethanol to lactic acid ($n_{\mathrm{EtOH}}/n_{\mathrm{HL}}$) was varied from 0.5 to 6 for the esterification reaction. For the hydrolysis reaction the initial molar ratio of water to ethyl lactate ($n_{\mathrm{w}}/n_{\mathrm{EL}}$) was varied from 1 to 15. As can be seen in Fig. 6 the equilibrium conversion increases with the initial reactant molar ratio. From this figure, it can be observed that the equilibrium conversion of 9% for a $n_{\mathrm{EtOH}}/n_{\mathrm{HL}} = 1$ increases up to a value of 35% for a $n_{\mathrm{EtOH}}/n_{\mathrm{HL}} = 6$. By using a large excess of one of the reactants the reaction yield of the other compound is enhanced. But, because of the presence of the large excess of one of the reactants, the recovery of the product will become more expensive. In Fig. 7 the conversions obtained at different initial reactant molar ratios for the esterification reaction of lactic acid with ethanol are compared with the conversions obtained in the case of the esterification with methanol [3]. Higher conversions were reached with the lowest alcohol. Under similar reaction conditions higher equilibrium constant, K_{x}, were obtained for methanol than for ethanol. Due to the lower values of K_{x}, the conversions reached for ethanol are lower than those for methanol.

As it has been shown previously, temperature and catalyst loading have not a great effect on the equilibrium constant (K_{x}) in the range considered in this work. However, a considerable variation has been observed by changing the initial reactant molar ratio. Similar results were obtained by Troupe and Dimilla [2]. They studied the homogeneous esterification of lactic acid with ethanol catalyzed by sulfuric acid. In their experiments, lactic acid aqueous solutions of different analytical grades ($w_{\mathrm{HL}} = 85$ and 44 wt.%) were used as reactants. In both cases, the influence of temperature or catalyst loading in the value of the equilibrium constant was minor. However, a definite trend was found with the initial reactant molar ratio. Fig. 8 shows the equilibrium constant based on concentration (K_{x}) as a function of the initial reactant molar ratio for the esterification

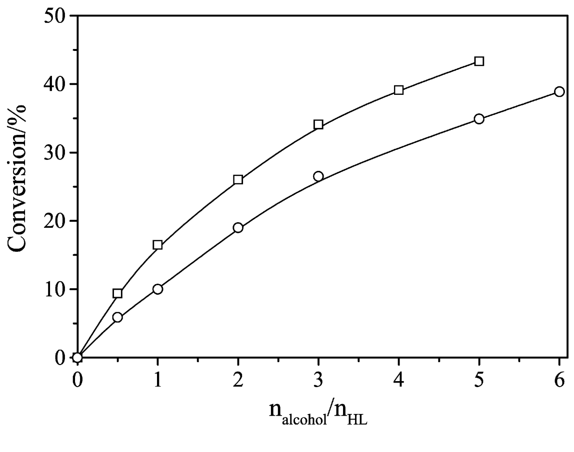

Fig. 7. Lactic acid conversion vs. initial molar reactant ratio for the esterification reaction of lactic acid with methanol (□) and ethanol (○) ($T = 353.15$ K, catalyst loading = 2.5 wt.%). The continuous line is to guide the eye.

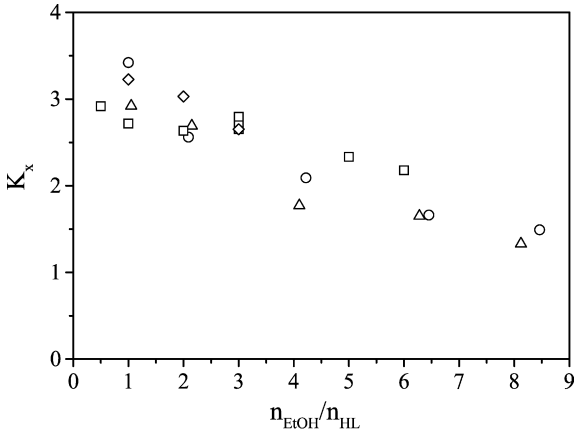

Fig. 8. Equilibrium constant based concentration at different initial molar reactant ratios (n_{EtOH}/n_{HL}) for esterification reaction for different mass fraction of lactic acid in the initial aqueous solution (w_{HL}): (□), this work, w_{HL} = 20 wt.%, T = 353.15 K, catalyst loading = 2.5 wt.%; (◇), this work, w_{HL} = 20 wt.%, T = 347.15 K, catalyst loading = 2.5 wt.%; (△), Troupe and Kobe [2], w_{HL} = 85 wt.%, T = 373.15 K, mass fraction of sulfuric acid = 0.1 wt.%; (○), Troupe and Kobe [2], w_{HL} = 44 wt.%, T = 373.15 K, mass fraction of sulfuric acid = 0.1 wt.%.

of lactic acid with ethanol. In this figure the values of the equilibrium constant for three different analytical grades of lactic acid (w_{HL} = 85, 44 and 20 wt.%) are plotted. Similar behavior was observed in the study of the esterification of lactic acid with methanol [3,22,23].

4.4.4. Kinetic modeling

The kinetic data of the esterification and the hydrolysis reactions were correlated with two different kinetic models: the pseudo-homogeneous model and the Langmuir–Hinshelwood model according to Eq. (1). The adjustable kinetic parameters obtained in the fitting procedure (k_e^o, $E_{A,e}$) are presented in Table 3 together with the value of the objective function and the mean relative deviation.

Both models were found to represent the experimental data without high errors. The low value of the MRD obtained in the case of the PH model was quite expected due to the high polarity of the reaction medium. In the kinetic study of the esterification of acetic acid with 2-propanol with different acidic cation-exchange resins [24], the PH was found to be also a competent model at predicting the esterification system, taking into account that is the less complex model. Additionally, it was [24] found that when the system was catalyzed by Amberlyst 15, the modified LH model gave a slightly higher error even compared with the PH model.

The PH model was expressed in terms of activities as well as in terms of mole fractions. From Table 3 it can be concluded that the assumption of ideal behavior of the liquid phase results in large errors. The continuous lines in Figs. 1 and 4–6 represent the results obtained with the LH model since it presents the lower value of the MRD. From these figures good agreement between experimental data and the results obtained with this model can be observed. Zhang et al. [5] also found the LH model to be suitable for predicting lactic acid esterification with ethanol.

Table 3
Parameters of the kinetic models for the ion-exchange catalyzed esterification of lactic acid with ethanol

Model	k_e^o (mol g^{-1} min^{-1})	$E_{A,e}$ (kJ mol^{-1})	O.F.	MRD (%)
PH	4.105×10^6	58.47	0.1679	7.4404
PH (ideal)	6.577×10^4	41.01	0.4223	17.0988
LH	3.844×10^7	52.29	0.1269	6.1967

5. Conclusions

The kinetics for the esterification of lactic acid with ethanol and the hydrolysis of the corresponding ester, ethyl lactate, catalyzed by Amberlyst 15 have been investigated. The effect of the reaction temperature, catalyst loading and initial reactant molar ratio was studied in a stirred batch reactor. The reaction rate has been found to increase with temperature and catalyst loading. The activation energy was reduced from 62.50 to 52.29 kJ mol^{-1} in the presence of Amberlyst 15 for the esterification reaction. The equilibrium conversion was found to increase with the initial reactant molar ratio for the esterification and hydrolysis reactions.

The pseudo-homogeneous model and the Langmuir–Hinshelwood model were used to correlate the kinetic experimental data. Independent adsorption experiments were carried out to obtain the adsorption equilibrium constants of the LH model. Water and ethanol were found to be adsorbed stronger than lactic acid and ethyl lactate. A better description of the reacting system is achieved by taking into account the non-ideality of the liquid mixture. Slightly better results were obtained for the LH model; nevertheless, due to the high polarity of the reacting medium, the PH model also provides a good agreement with the experimental kinetic data.

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