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Autocatalyzed and Ion-Exchange-Resin-Catalyzed Esterification Kinetics of Lactic Acid with Methanol

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The esterification kinetics of lactic acid with methanol without addition of catalyst and catalyzed by ion-exchange resins are presented in this work. The effect of catalyst type, stirrer speed, catalyst size, catalyst loading, initial reactant ratio, and temperature on reaction kinetics was evaluated. Experimental reaction rates were correlated by some models based on homogeneous and heterogeneous (dual- and single-site mechanisms) approaches. Nonideality of the liquid phase was taken into account by using activities instead of mole fractions. Prediction of the activity coefficients was made by UNIFAC. Parameters of the different models were obtained by the simplex search method.

Introduction

Lactic acid is the simplest hydroxycarboxylic acid with an asymmetric carbon atom. It can be produced from biomass, coal, petroleum, or natural gas liquids. Polymers and copolymers of lactic acid are known to be environmentally compatible because of their degradability into harmless products, which makes them desirable as substitutes of petrochemical polymers. Some of the applications of these polymers are focused toward the market for prosthetic devices, pesticide formulation, plastic production, etc.[1] For their production, highly purified monomeric lactic acid is needed.

Purification of lactic acid is conventionally obtained by liquid–liquid extraction, steam distillation, calcium salt formation followed by re-release of the acid, and reverse osmosis.[2] However, such purification procedures are somehow difficult because of the low volatility of lactic acid (122 °C at 1661.73 Pa), its affinity to water, its tendency to self-polymerize, etc. An alternative purification process for lactic acid aqueous solutions is to obtain some of its esters, much more volatile than lactic acid itself, and, once purified, hydrolyze them back into lactic acid. Such processes may be carried out by catalytic distillation.

Catalytic distillation offers some advantages over conventional processes where reaction and purification are carried out separately. Some of them are the reduction of capital and operating costs, high selectivity, reduced energy uses, and reduction or elimination of solvents.[3] Its major disadvantage is that chemical reaction has to show significant conversion at distillation temperature.[4]

The work presented in this paper is part of a wider project whose aim is the design of a catalytic distillation column for lactic acid production. To do so, it is necessary to have information on phase and reaction equilibria, reaction rates, adsorption equilibria for heterogeneous catalysts, selectivity, etc. In this paper, the esterification kinetics of lactic acid with methanol, without addition of catalyst and heterogeneously catalyzed, are particularly considered. A comparison of several acid ion-exchange resins was made, with Amberlyst 15 dry, a macroreticular resin, being chosen for further kinetic studies. The use of ion-exchange resins as solid catalysts offers many advantages over homogeneous acid catalysts. They allow mechanical separation from the liquid reaction mixture by filtration or decantation, present high selectivity, and can be used in continuous processes.[5] Some other authors have previously studied lactic acid esterification using alcohols and/or catalysts different from those used in this work.[6–8]

The experimental reaction rates obtained in this work were correlated by some models based on homogeneous and heterogeneous (dual- and single-site mechanisms) approaches. Nonideality of the liquid phase was taken into account by using activities instead of mole fractions, and the activity coefficients were predicted through the group contribution method UNIFAC. Parameters of the different models were obtained by the simplex search method.

Experimental Section

(i) Materials. An aqueous lactic acid solution (20%) and methyl *S*-(−)-lactate (97%) were supplied by Acros (Belgium). The amount of monomeric lactic acid in the purchased solution was determined by boiling it in a measured excess of sodium hydroxide and back-titrating. The amount of polymerized lactic acid was low enough to consider it negligible. Methanol of 99.9% purity was supplied by Lab-Scan (Ireland).

The water content of the commercialized products was measured by Karl–Fisher titration with a Mitsubishi Kasei model CA-20.

Four different strong ion-exchange resins were tested: Dowex 50W8x and Dowex 50W2x supplied by Acros (Belgium) and Amberlyst 36 and Amberlyst 15 dry from Aldrich. The ion-exchange capacity of these

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resins was close to 4.9 mequiv g^{-1} in all cases. Amberlyst 15 dry was the resin selected for studying the influence of different parameters on the esterification kinetics. This resin suffers gradual desulfonization at temperatures higher than 120 °C; therefore, when it was reused, it was dried at 99 °C after washing it with distilled water in order to eliminate poisoning or fouling. Reused resin had the same catalyst activity as the fresh one. However, fresh resin was used in each run.

(ii) Apparatus and Procedure. Reaction kinetics were studied in a four-necked jacketed reactor of 500 mL capacity operating in batch mode. A reflux condenser avoided loss of volatile compounds. The temperature inside the reactor was controlled within ±0.5 K. The ion-exchange resin was suspended in the reaction mixture by magnetic stirring.

The commercial aqueous lactic acid solution and the catalyst were charged into the reactor and heated to the desired temperature. The required amount of methanol and the water necessary to simulate a fermentation broth were added through a thermostated funnel connected directly to one of the necks of the reactor. The end of this addition was taken as zero time for a run. All of the reactants charged in the reactor were gravimetrically measured. The progress of the reaction was followed by withdrawing samples—small enough to consider them negligible compared to the volume of the reaction mixture—at regular time intervals.

(iii) Analytical Methods. Two types of analyses were carried out for quantification of the reaction mixtures: (1) by titration with a standard sodium hydroxide solution using phenolphthalein as the indicator and (2) by gas chromatography with a Hewlett-Packard (6890) gas chromatograph (GC) equipped with series-connected thermal conductivity and flame ionization detectors that allowed one to detect water and the rest of the components in the same run. The GC column was a 25 m × 0.25 mm bonded-phase fused-silica capillary column. The injector and detectors were at 503 and 533 K, respectively. The oven was operated at variable-programmed temperature, from 353 to 493 K. 1,2-Propanediol was used as the internal standard. Helium, 99.999% pure, was used as the carrier gas. No significant differences at the 95% confidence level were found between both types of analyses when applying the statistical t test.

Results and Discussion

The experimental results of the reaction kinetics of the noncatalyzed and catalyzed esterification of lactic acid with methanol are presented in this section. Data reduction was made by using different kinetic models according to the following procedure: Reaction rates were calculated by the differential methods as proposed by Cunill et al.[9] and Subramanian and Bhatia.[10] Conversion data were fitted as a function of time through a fifth-degree polynomial, whose slope allowed one to calculate the reaction rate. In the case of the heterogeneously catalyzed reaction, eq 1 was used.

$$r = \frac{n_0}{W}\left(\frac{dX}{dt}\right) \tag{1}$$

Nonideality of the liquid phase was taken into account by using the activity of the components.[11-15] The UNIFAC group contribution method was used for the estimation of activity coefficients.[16] The equilibrium
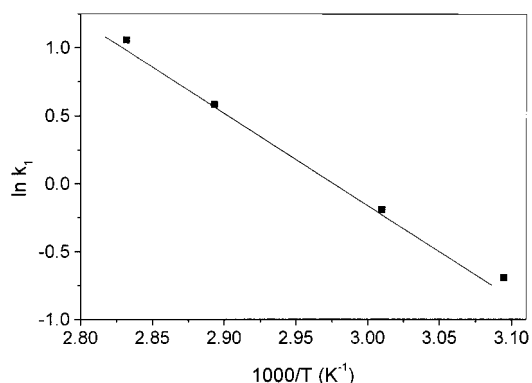
Figure 1. Arrhenius plot for the esterification of lactic acid with methanol. The reaction was carried out with an initial methanol/lactic acid ratio of $R_{M/LH} = 3$. The continuous line represents the kinetics predicted by the autocatalysis model where $\alpha = 1$.

constant was calculated from the component concentrations at equilibrium through eq 2.

$$K_{eq} = \left(\frac{a_{ML}a_W}{a_{LH}a_M}\right)_{eq} = \left(\frac{x_{ML}x_W}{x_{LH}x_M}\right)_{eq}\left(\frac{\gamma_{ML}\gamma_W}{\gamma_{LH}\gamma_M}\right)_{eq} = K_x K_\gamma \tag{2}$$

In the temperature range studied, no side reactions were observed, as was previously pointed out by Choi et al.[7] and Seo and Hong.[8] Different models have been used to describe the kinetic behavior of the reaction without addition of catalyst and catalyzed by ion-exchange resins. The estimation of the parameters for the different models was performed by minimizing the sum of squared residuals between the experimental and calculated reaction rates (eq 3) through the simplex algorithm.

$$SRS = \sum_{\text{all samples}} (r_{exp} - r_{calc})^2 \tag{3}$$

The so-called improved Euler's numerical method[17] was used for integrating the different equations that describe the kinetic model with the previously determined parameters. Experimental results were then compared with those of the model prediction through the values of the mean relative deviation (MRD) between experimental and calculated weight fractions (eq 4).

$$MRD = \frac{1}{n}\left(\sum_{\text{all samples}}\left|\frac{w_{ML,calc} - w_{ML,exp}}{w_{ML,exp}}\right|\right) \times 100 \tag{4}$$

(i) Homogeneous Autocatalyzed Reaction. The lactic acid esterification with methanol without addition of a catalyst was studied at different temperatures. The experimental results are presented in Figure 1 as the Arrhenius plot of the reaction rate constant. Although no external catalyst was added to this reaction, it may be catalyzed by lactic acid itself because it is generally catalyzed by acids. Pöpken et al.[4] proposed the following kinetic equation to model this type of reaction according to the autocatalysis mechanism:

$$r = n_0\frac{dX}{dt} = k_1° \exp\left(-\frac{E_{A,1}}{RT}\right)a_{LH}^\alpha\left(a_{LH}a_M - \frac{a_{ML}a_W}{K_{eq}}\right) \tag{5}$$

where α can take the values of 0.5 or unity when the autocatalysis mechanism is assumed to take place via

Table 1. Adjustable Parameters of the Autocatalysis Model for the Esterification of Lactic Acid with Methanol without Addition of External Catalyst: Preexponential Factor of the Esterification Reaction, $k_1°$, and Activation Energy, $E_{A,1}$

| exponent α	$k_1°$ (mol min^{-1})	$E_{A,1}$ (kJ mol^{-1})	SRS	MRD (%)
0.5	1.730×10^8	57.38	9.81×10^{-8}	6.54
1.0	6.024×10^8	56.45	5.12×10^{-8}	3.48
1.03	7.164×10^8	56.61	5.14×10^{-8}	3.05
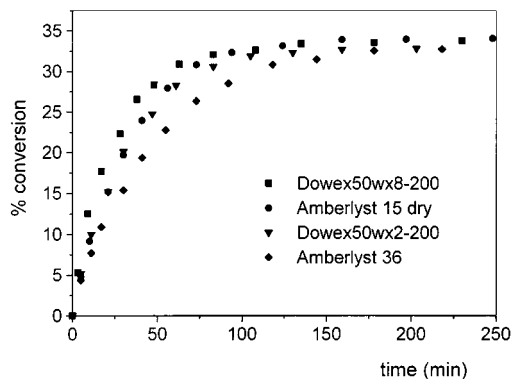
Figure 2. Conversion versus time for the esterification of lactic acid with methanol catalyzed with different resins. The reaction was carried out with an initial methanol/lactic acid ratio of $R_{M/LH}$ = 3, a temperature of 353 K, and a stirrer speed of 500 rpm. The catalyst loading was 2.5% (w/w) in all cases.

the solvated protons of the dissociated acid or via the molecular acid, respectively.[4] The results obtained for the parameters of eq 5 are presented in Table 1. When α = 1, the experimental kinetics are better reproduced by the model than when α = 0.5, indicating that the molecular lactic acid is more likely to be catalyzing the reaction than the dissociated acid. A value of the activation energy of $E_{A,1}$ = 56.45 kJ mol^{-1} was obtained. This value was similar to the value $E_{A,1}$ = 57 kJ mol^{-1} reported by Seo and Hong.[8] Data reduction was also made by considering α to be an adjustable parameter, which led to the best correlation giving a value of α close to unity.

(ii) Ion-Exchange-Catalyzed Reaction. The effects of variables such as catalyst type, stirring speed, catalyst size, catalyst loading, molar ratio of reactants, and temperature on the reaction kinetics were studied.

(a) Effect of Catalyst Type. A comparison of the catalyst behavior of four different commercial ion-exchange resins on the basis of the same catalyst loading is shown in Figure 2. Experiments were carried out under identical conditions except for the type of catalyst. Amberlyst 36 showed the lowest acid activity and Dowex 50W8x the highest. When the activity and cost of the resins assayed were taken into account, Amberlyst 15 was chosen for further studies.

(b) External Mass-Transfer Resistance. To evaluate the external mass-transfer resistance, the esterification reaction was carried out at different stirrer speeds, from 60 to 700 rpm, while keeping the rest of the reaction conditions similar. The results are presented in Figure 3. A paired sample comparison was made in order to test differences between all of the data sets considered two by two. No significant differences at the 95% confidence level were found by applying the statistical *t* test for the runs between 300 and 700 rpm, indicating that external mass-transfer resistance was not important. In the run at 60 rpm, on the contrary,
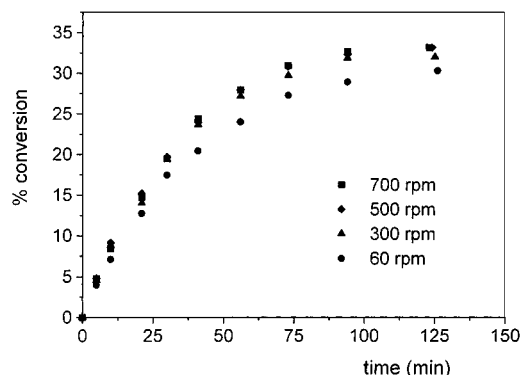
Figure 3. Conversion versus time for the esterification of lactic acid with methanol catalyzed with Amberlyst 15 dry at different stirrer speeds. The reaction was carried out with an initial methanol/lactic acid ratio of $R_{M/LH}$ = 3 and a temperature of 353 K. The catalyst loading was 2.5% (w/w) in all cases.

Table 2. Size Distribution of Amberlyst 15 Dry

| diameter range (mm)	wt %	diameter range (mm)	wt %
<0.250		0.850−1	16.86
0.250−0.500	19.73	>1	16.24
0.500−0.850	47.17		

external mass-transfer presents certain resistance to the global process. All further experiments were performed at 500 rpm to ensure that the reaction rate was not limited by external diffusion. This result agrees with that of Chakrabarti and Sharma,[5] who indicate that external diffusion does not usually control the overall rate in the reactions catalyzed by ion-exchange resin unless the agitation speed is very low or the reaction mixture is very viscous.

(c) Internal Diffusion. To evaluate the intraparticle diffusion effect, the commercial Amberlyst 15 resin was screened into five different size ranges, as shown in Table 2. Different runs were carried out with each of the fractions obtained. Two different molar ratios of methanol/lactic acid ($R_{M/LH}$ = 1 and 3) at 353 K were assayed. A paired sample comparison was made for every possible pair of data sets. No significant differences at the 95% confidence level were found in the reaction rate for the different catalyst sizes, which allowed one to conclude that internal mass transfer could be considered negligible in the particle size range used in this work. Unsieved resin was used for all further experiments.

(d) Effect of Catalyst Loading. Catalyst loading was varied from to 1.1 to 6% (w/w; weight of catalyst/total weight of reactants). The effect of the catalyst concentration may be observed in Figure 4. The higher the catalyst loading, the sooner the equilibrium was reached because of the increase of the total number of acid sites available for the reaction. It was observed that the initial reaction rate, expressed as moles per minute, was a linear function of the catalyst loading. Such linearity is shown in Figure 5.

(e) Effect of the Reactant Molar Ratio. The initial molar ratio of methanol to lactic acid was varied from $R_{M/LH}$ = 0.5 to 5 while keeping the rest of the experimental conditions similar. The results obtained are presented in Figures 6 and 7. As may be observed, the equilibrium conversion increases with the initial molar methanol/lactic acid ratio, although it appears to reach a limit (Figure 7) which would correspond to a resin saturated by the alcohol molecules. Similar behavior has
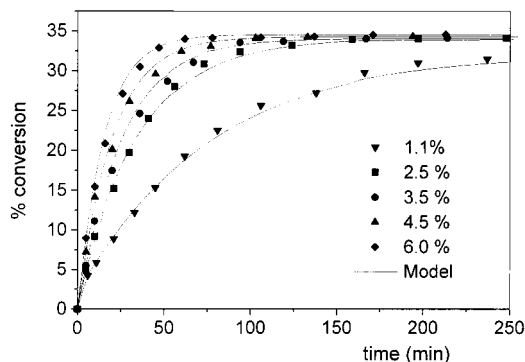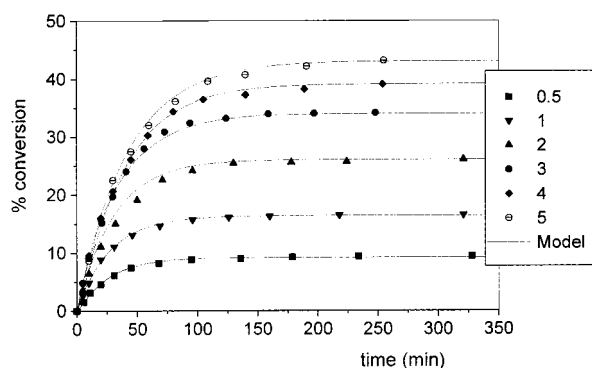
Figure 4. Conversion versus time for the esterification of lactic acid with methanol catalyzed with different amounts of Amberlyst 15 dry. The reaction was carried out at 353 K, with a stirrer speed of 500 rpm and an initial methanol/lactic acid ratio of $R_{M/LH} = 3$. The continuous lines represent the results of the L−H model.
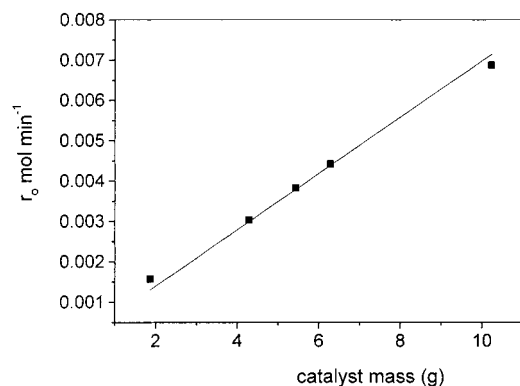

Figure 5. Initial reaction rate as a function of the mass of catalyst for the esterification of lactic acid with methanol catalyzed with different amounts of Amberlyst 15 dry. The total weight of reactants was 170 g in all cases. The reaction conditions are given in the caption of Figure 4. The continuous line represents the results of the L−H model.
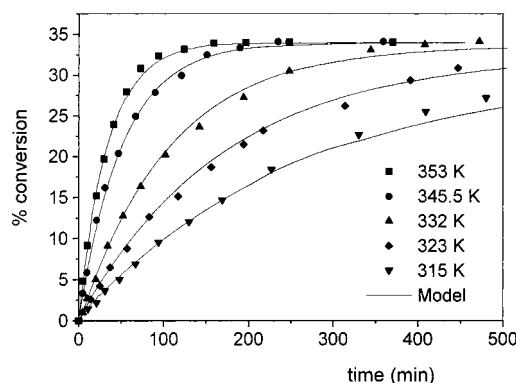

Figure 6. Conversion versus time for the esterification of lactic acid with methanol for different initial methanol/lactic acid ratios, $R_{M/LH}$. The reaction was catalyzed with 2.5% (w/w) of Amberlyst 15 dry at 353 K and a stirrer speed of 500 rpm. The continuous lines represent the results of the L−H model.

been previously observed in the lactic acid esterification with butanol.[6]

(f) Effect of the Reaction Temperature. Figure 8 shows the effect of the reaction temperature on conversion. The reaction rate increased with the reaction temperature, although the concentrations at equilibrium were nearly equal at all temperatures studied. Choi et al.[7] found similar results. The heat of reaction for many esterification reactions is very small or even zero; therefore, the equilibrium constant is essentially temperature independent.[18] The preexponential factors and
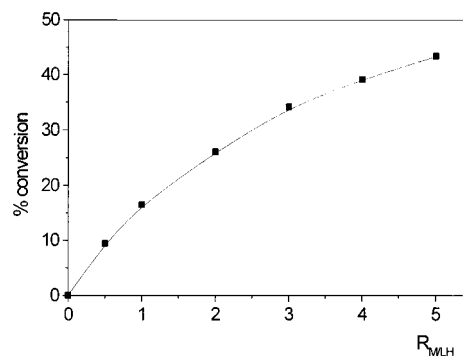
Figure 7. Equilibrium conversion versus initial methanol/lactic acid ratio, $R_{M/LH}$, for the catalyzed esterification of lactic acid with methanol. The reaction conditions are specified in the caption of Figure 6. The continuous line is to a guide for the eye.

Figure 8. Conversion versus time for the catalyzed esterification of lactic acid with methanol at different temperatures. The reaction was catalyzed with 2.5% (w/w) of Amberlyst 15 dry, with a stirrer speed of 500 rpm and an initial methanol/lactic acid ratio of $R_{M/LH} = 3$. The continuous lines represent the results of the L−H model.
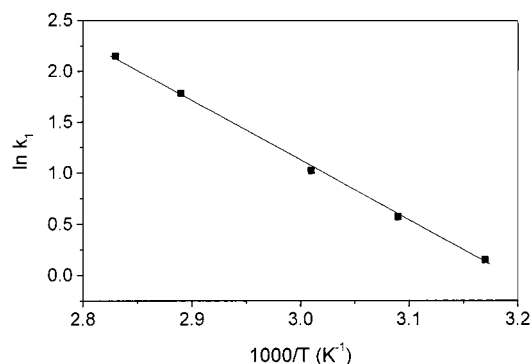
Figure 9. Arrhenius plot of the resin-catalyzed esterification of lactic acid with methanol. The reaction conditions are indicated in the caption of Figure 7. The continuous line represents the results of the L−H model.

the activation energy were estimated together with the rest of the kinetic model parameters in the process of data reduction. Figure 9 shows the Arrhenius plot of the reaction rate constant.

(g) Kinetic Modeling. Three different models have been used for the description of the kinetic behavior of the heterogeneously catalyzed esterification reaction: the quasi homogeneous approach (QH), the Langmuir−Hinselwood model (L−H), and the Eley−Rideal (E−R) mechanism.[13] The QH model assumes complete swelling of the polymeric catalyst in contact with polar solvents, leading to an easy access of the reactants to the active sites. This model can be derived from the L−H model considering that none of the components is strongly

Table 3. Adjustable Parameters of the L−H, E−R, and QH Models for the Catalyzed Esterification of Lactic Acid with Methanol: Preexponential Factor for the Forward Reaction, $k_1°$, Activation Energy, $E_{A,1}$, and Adsorption Coefficients for Methanol and Water, k_M and k_W

model	$k_1°$ (mol g^{-1} min^{-1})	$E_{A,1}$ (kJ mol^{-1})	k_M	k_W	SRS	MRD (%)
L−H	1.310×10^8	48.67	11.38	8.18	2.06×10^{-8}	2.72
L−H	9.927×10^6	44.69		5.37	1.28×10^{-7}	5.68
E−R	1.063×10^7	48.63	13.55	5.30	2.07×10^{-8}	4.95
E−R	3.834×10^6	45.42		9.83	8.66×10^{-8}	7.05
QH	7.592×10^5	47.24			6.30×10^{-8}	4.90

adsorbed. The L−H and E−R mechanisms consider the ion-exchange resins as a solid porous catalyst where reaction at the catalyst surface was assumed to control the overall process. The E−R model is applied when the reaction occurs at the catalyst surface between one adsorbed reactant and one nonadsorbed reactant, while the L−H mechanism considers the possibility of adsorption of all reagents. In both models the adsorption of the most polar molecules, water and methanol, was considered to be stronger than the adsorption of lactic acid and methyl lactate, which, in comparison, were considered negligible. A general expression for the three models considered can be written as eq 6, where $n = 2$ for the L−H model, $n = 1$ for the E−R model, and $n = 0$ for the QH model.

$$r = k_1° \exp\left(-\frac{E_{A,1}}{RT}\right) \frac{\left(a_{LH} a_M - \dfrac{a_{ML} a_W}{K_{eq}}\right)}{(1 + k_W a_W + k_M a_M)^n} \quad (6)$$

The adjustable parameters obtained for the three models are presented in Table 3 along with the sum of residual squares resulting from the minimization process and the mean relative deviation between experimental and calculated weight fractions. All of the models fit the experimental data without high errors, even the simple QH model, with only two adjustable parameters, represents the experimental observations with a MRD < 5%. This was expected because the polarity of the reaction medium is fairly high. The activation energy obtained for the three models was very similar and close to the values found in the literature 48.987[7] and 46.5 kJ mol^{-1}.[8] The high value of the activation energy supports the assumption that the overall process is controlled by the reaction at the surface of the catalysts. The model represented in the graphs included in this work is the L−H model because it presented the lowest MRD.

Conclusions

To design a catalytic distillation process, experiments on reaction rates for heterogeneous catalysts must be done. In this work, autocatalyzed and heterogeneously catalyzed lactic acid esterification with methanol has been studied.

Consideration of autocatalysis of the reaction by molecular lactic acid provided the best description of the homogeneous reaction mechanism.

Amberlyst 15 was found to be a good catalyst for this reaction. Internal and external mass transfer were easily avoided. The reaction rate increased with temperature and catalyst loading. The equilibrium conversion increased as the methanol/lactic acid ratio increased. Three kinetic models (QH, L−H, and E−R) were used for data reduction. The QH model represents the experimental data fairly well as expected for a higly polar mixture. The high value of the apparent activation energy supports the assumption that the reaction in the catalyst surface was the rate-controlling step.

Nomenclature

a = activity
$E_{A,1}$ = apparent activation energy, kJ mol^{-1}
K_{eq} = equilibrium constant
$k_1°$ = preexponential factor for the esterification reaction, mol g^{-1} min^{-1}
k_M = adsorption coefficient for methanol
k_W = adsorption coefficient for water
MRD = mean relative deviation between experimental and calculated methyl lactate weight fractions, %
n = number of experimental data (as exponent: parameter of the heterogeneous model)
n_0 = initial mole number of lactic acid
R = gas constant, J mol^{-1} K^{-1}
r = reaction rate (homogeneous reaction, mol min^{-1}; heterogeneous reaction, mol g^{-1} min^{-1})
$R_{M/LH}$ = initial molar ratio of methanol/lactic acid
SRS = minimum sum of residual squares resulting in the fitting procedure
T = temperature, K
t = time, min
W = catalyst weight, g
w = weight fraction
X = conversion
x = molar fraction
α = parameter that takes into account the lactic acid autocatalysis in the homogeneous kinetic reaction
γ = activity coefficient

Subscripts

calc = calculated values
exp = experimental values
LH = lactic acid
M = methanol
ML = methyl lactate
W = water

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