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Kinetic Study for the Reactive System of Lactic Acid Esterification with Methanol: Methyl Lactate Hydrolysis Reaction

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The hydrolysis of methyl lactate catalyzed by an acidic cation-exchange resin, Amberlyst 15, is presented in this work. The kinetic experiments were carried out in a stirred tank batch reactor. The effects of catalyst loading, temperature, and feed composition were investigated. The reaction modeling was carried out by correlating the experimental kinetic data obtained for the esterification (previously reported) and the hydrolysis reactions simultaneously. Three models were essayed, the quasi-homogeneous, the Langmuir–Hinshelwood, and the Eley–Rideal models. Because of the high nonideality of the reaction mixture, the kinetics were expressed in terms of activities. The activity coefficients were calculated by using the group contribution method UNIFAC. The quasi-homogeneous model was found to represent the esterification and hydrolysis reactions over Amberlyst 15 fairly well.

Introduction

Lactic acid is a very useful chemical intermediate because of the two functional groups, acid and hydroxyl, in its molecule. In the last years, lactic acid has been attracting growing attention as a monomer for the manufacture of biodegradable plastics,¹ where a high purity of this reactant is important. Among the methods for purification, the esterification of lactic acid with a suitable alcohol and subsequent hydrolysis of the purified ester is widely accepted as highly efficient.^{2–5} This complex process can be carried out by reactive distillation unit. The technology of reactive distillation offers a large number of advantages over the conventional sequential approach of reaction and separation.⁶

For the correct design of a reactive distillation column, kinetic and thermodynamic studies are needed. The kinetics of the esterification of lactic acid with methanol, catalyzed by the cation-exchange resin Amberlyst 15, were reported in a previous publication.⁷ The effects of different kinetic variables were evaluated and modeled. Here, the hydrolysis of methyl lactate, the reverse reaction, has been investigated and the hydrolysis and esterification experimental data, all together, have been correlated to provide a general model. Different models based on the homogeneous and heterogeneous approaches were tested to represent the kinetic behavior of the system. These models were expressed as a function of the activities of the components instead of mole fractions in order to take into account the nonideality of the reaction mixture, which is usually fairly strong in aqueous mixtures.⁸ The activity coefficients were determined by the group contribution method UNIFAC.

In most of the esterification equilibrium reaction studies found in the literature, the kinetic models are

obtained from only esterification reaction kinetic data.^{2,7–11} Only some works consider both esterification and hydrolysis reaction kinetic data simultaneously. This is the case of the work published by Choi et al.,³ who reported the esterification of lactic acid with methanol and the corresponding hydrolysis catalyzed by a gel-type resin, Dowex 50W-X8, as a solid catalyst, although they did not take into account the nonideality of the reactive liquid mixture.

Experimental Section

(i) Materials. *S*-(–)-Methyl lactate was supplied by Acros (Belgium) with a reported purity of 97%. After it was purified by vacuum distillation, a purity of 99.9 wt % was obtained as determined by gas chromatography (GC). The water used was twice distilled. In a previous work,¹² some physical properties of the pure components were measured and compared with values reported in the literature. A strong cation-exchange resin, Amberlyst 15 (Supelco), was used as a solid catalyst. This resin was washed several times with distilled water before use and dried at 95 °C to avoid desulfonation, which takes place over 120 °C. Its total exchange capacity was 4.9 mequiv of H⁺ (g of dry resin)^{–1}.

(ii) Procedure. The kinetics of methyl lactate hydrolysis in the liquid phase were determined in a stirred batch reactor that was previously described in detail.⁷ This reactor was filled with distilled water and the catalyst and was heated to the desired reaction temperature. The second reactant, methyl lactate, was added into the reactor through a thermostatic funnel connected directly to one of the necks of the reactor, after reaching the reaction temperature. For a kinetic experience, the end of the addition of methyl lactate was considered to be the starting time of the reaction. The course of the reaction was followed by determination of the composition of small samples extracted from the reaction mixture at regular time intervals.

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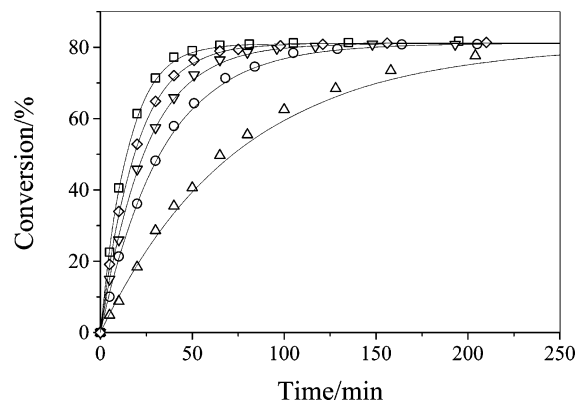


Figure 1. Conversion versus time for the methyl lactate hydrolysis ($T = 353.15$ K, $R_{W/ML} = 15$) catalyzed by different amounts of Amberlyst 15 expressed as mass fraction (Δ , 1.1%; \circ , 2.5%; ∇ , 3.5%; \diamond , 4.5%; \square , 6.0%). The continuous lines represent the results of the QH model.

Some sorption experiments were carried out to evaluate the sorption of different molecules on the catalyst surface. These experiments were carried out by following the procedure proposed by Pöpkén et al.¹³

(iii) Sample Analysis. Samples were analyzed using a Hewlett-Packard 6890 GC. The GC was equipped with series-connected thermal conductivity and flame ionization detectors using helium (99.999% pure) as the carrier gas. The GC column was a 25 m \times 0.25 mm bonded-phase fused-silica capillary column. The oven was operated at variable-programmed temperature, from 353 to 493 K at a rate of 40 K min^{-1} . The injector and detectors were at 503 and 533 K, respectively. 1,2-Propanediol was used as the internal standard.

The amount of lactic acid in the samples was also determined by titration with a standard sodium hydroxide solution using phenolphthalein as the indicator. No significant differences were observed between the lactic acid composition obtained by GC and this method.

Results and Discussion

(i) Reaction Kinetic Experimental Results. Several kinetic experiments were carried out for the heterogeneously catalyzed hydrolysis of methyl lactate. The effects of catalyst loading, reaction temperature, and initial reactant molar ratio on the reaction kinetics were determined. It was found in a previous kinetic study of the esterification reaction,⁷ that a stirrer speed of 500 rpm was enough to ensure the absence of external mass-transfer limitations. Thus, for the hydrolysis reaction, all of the experiments were carried out at 500 rpm. Regarding the internal diffusion resistance, it can usually be neglected for reactions catalyzed by Amberlyst resins.¹¹ In fact, no effect of the resin size was found on the esterification kinetics;⁷ therefore, to perform the hydrolysis kinetic experiments in this work, the resin was used as received, without further sieving.

The reaction rate, based on the amount of the dried catalyst, was obtained from eq 1, in which the differential term was calculated as the slope of the curves resulting from fitting of the conversion data against time through a fifth-degree polynomial.^{7,14,15}

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

Effect of Catalyst Loading. Figure 1 shows the effect

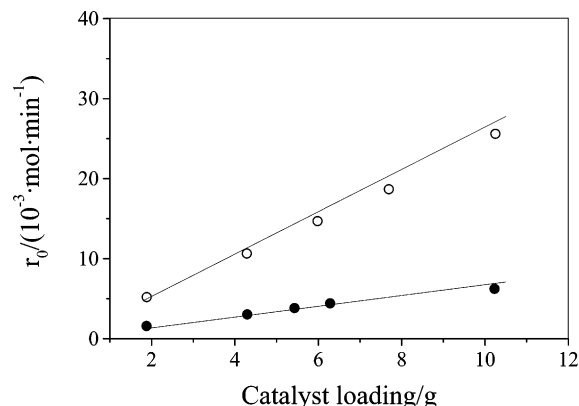


Figure 2. Initial reaction rate versus catalyst loading for the methyl lactate hydrolysis (\circ ; $T = 353.15$ K, $R_{W/ML} = 15$) and for the reverse esterification⁷ (\bullet ; $T = 353.15$ K, $R_{M/LH} = 3$). The continuous lines represent the results of the QH model.

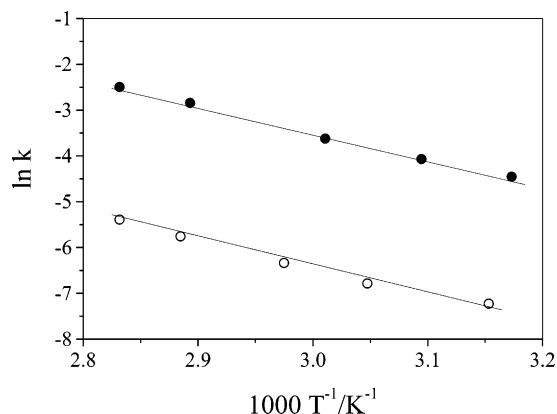


Figure 3. Arrhenius plot for the methyl lactate hydrolysis (\circ ; mass fraction of catalyst = 2.5%, $R_{W/ML} = 15$) and for the reverse esterification⁷ (\bullet ; mass fraction of catalyst = 2.5%, $R_{M/LH} = 3$). The continuous lines represent the results of the QH model.

of the catalyst concentration on reactant conversion. The catalyst loading was varied from 1.1% to 6%. It can be observed that the chemical equilibrium was reached faster with increasing catalyst concentration. Figure 2 shows a linear relationship between the initial reaction rate (r_0), expressed as moles per minute, and the catalyst loading, confirming that the process is controlled by the reaction on the catalyst surface, as was found when considering only the esterification reaction.⁷

Effect of the Reaction Temperature. The hydrolysis experiments were carried out at different temperatures from 317.15 to 353.15 K. As the reaction temperature increased, the reaction kinetics were faster, but equilibrium conversions were nearly the same in the range of temperatures studied in this work. The Arrhenius plot is presented in Figure 3.

Effect of the Reactant Molar Ratio. Several hydrolysis experiments were carried out at different initial reactants molar ratios (from $R_{W/ML} = 1$ to 54). The effect of this molar ratio is shown in Figure 4, where it can be observed that the equilibrium conversion increased with the initial reactant molar ratio.

(ii) Reaction Kinetic Modeling. To obtain a general model able to reproduce the esterification and hydrolysis kinetics with one only set of parameters, the data obtained from the hydrolysis experiments carried out in this work were correlated, together with the esterification experimental data obtained in a previous work.⁷ Parameters for the different models were estimated by

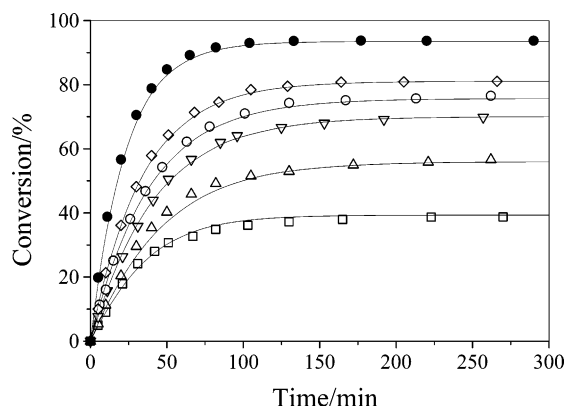


Figure 4. Conversion versus time for the methyl lactate hydrolysis ($T = 353.15$ K, catalyst mass fraction = 2.5%) for different initial reactant molar ratios, $R_{W/ML}$ (\square , 1; \triangle , 2; ∇ , 7; \circ , 10; \diamond , 15; \bullet , 54). The continuous lines represent the results of the QH model.

minimizing the sum of the residual squares (SRS) between the experimental and calculated reaction rates (eq 2) through the simplex Nelder method.

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

The kinetic models with the parameters obtained from data correlation were integrated by using the fourth-order Runge–Kutta method to recalculate the evolution of methyl lactate weight fractions with time. Calculated and experimental methyl lactate weight fractions were compared through the mean relative deviation (MRD) as indicated in eq 3.

$$MRD = \frac{1}{n} \left(\sum_{\text{all samples}} \left| \frac{W_{ML,calc} - W_{ML,exp}}{W_{ML,exp}} \right| \right) \times 100 \quad (3)$$

Three different models were used for experimental data reduction, a quasi-homogeneous (QH) model and two adsorption-based models, i.e., Langmuir–Hinshelwood (L–H) and Eley–Rideal (E–R) models. The QH model is based on the Helfferich approach¹⁶ that considers catalysis of liquid-phase reactions by ion-exchange resins similar to homogeneous catalysis by dissolved electrolytes. This model provides a good description for those systems where one of the reactants or the solvent is highly polar and swells the resin, facilitating the access of the reactants to the sulfonic acid groups.¹⁷ When adsorption effects are important, the L–H and E–R models are often used. Assuming that the process is controlled by the reaction on the catalyst surface, the L–H model considers the reaction to take place between two adsorbed molecules and the E–R model between one adsorbed molecule and one nonadsorbed molecule.

A general equation for the different models considered in this work can be written (eq 4), where $n = 0$ for the

$$-r' = \frac{k_e \exp\left(-\frac{E_{A,e}}{RT}\right) a_{LH} a_M - k_h \exp\left(-\frac{E_{A,h}}{RT}\right) a_{ML} a_W}{\left(1 + \sum_i k_i a_i\right)^n} \quad (4)$$

QH model, $n = 1$ for the E–R model, and $n = 2$ for the L–H model. The nonideality of the liquid phase was taken into account by using the activity coefficients, as

Table 1. Results of the Correlation to Equation 5 of the Adsorption Equilibrium Experimental Data Obtained for the Nonreactive Binary Systems Methanol + Water, Methanol + Methyl Lactate, and Water + Lactic Acid at 303.15 K

Adsorbed Mass per Catalyst Mass $m^S/m_{\text{cat}} = 0.38$	
Adsorption Equilibrium Constants	
$k_W = 5.7126$	$k_{ML} = 0.6211$
$k_M = 5.0071$	$k_{LH} = 0.5648$

calculated by UNIFAC, to calculate the activities of the components in the reaction mixture.

For the L–H adsorption-based approach, the adsorption constants were obtained by two different procedures. According to the first procedure, the adsorption constants for water and methanol were estimated in the correlation of the experimental kinetic data, together with the four kinetic parameters (i.e., activation energies and preexponential factors for the esterification and hydrolysis reactions). The adsorption of lactic acid and methyl lactate molecules was considered to be negligible in comparison with the most polar molecules, water and methanol. According to the second procedure, the adsorption constants were obtained from independent adsorption experiments and only the four kinetic parameters were estimated. The adsorption experiments were carried out for three of the nonreactive binary systems involved in the quaternary reactive system considered in this work, i.e., methanol + water, methanol + methyl lactate, and water + lactic acid. To obtain the adsorption constants for the different molecules in a binary system, the relation proposed by Pöppken et al.¹³ (eq 5) assuming Langmuir-type adsorption, based on mass, has been used, where m_0 is the initial weight of

$$\frac{m_0(w_1^0 - w_1^L)}{m_{\text{cat}}} = \frac{m^S}{m_{\text{cat}}} \frac{(k_1 a_1 w_2^L - k_2 a_2 w_1^L)}{1 + k_1 a_1 + k_2 a_2} \quad (5)$$

liquid, w_1^0 is the initial weight fraction of component 1 in the mixture, m_{cat} is the catalyst mass in contact with the liquid mixture, and w_i^L are the equilibrium weight fractions in the solution.

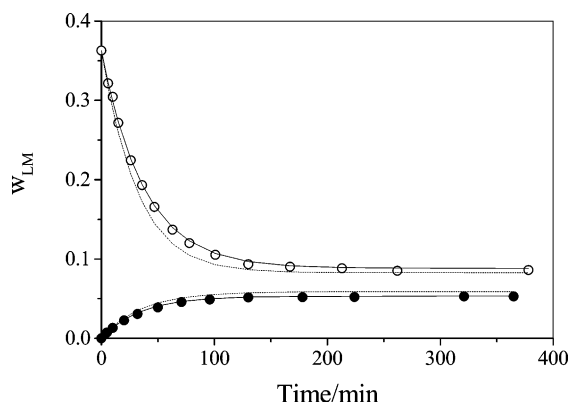
Some experiments¹³ carried out to obtain the mass of the pure components adsorbed per unit mass of catalyst (m^S/m_{cat}) showed that this value can be considered nearly constant for all of the binary systems. For the binary system water + lactic acid, the presence of poly(lactic acid) was taken into account. The simplex Nelder method was used to estimate the adsorption constants and the ratio m^S/m_{cat} from the experimental adsorption equilibrium data. The results, presented in Table 1, show that adsorption is much stronger for the most polar molecules, water and methanol, than for the methyl lactate and lactic acid molecules, supporting the previous assumption of considering the adsorption constants of these two last molecules to be negligible.

Table 2 lists the parameters obtained from the correlation of the experimental kinetic data to the models QH, L–H, and E–R, along with the SRS between experimental and calculated reaction rates and the MRD between experimental and calculated methyl lactate weight fractions.

The QH model, considering the nonideality of the liquid mixture, provides a quite good description for this reactive system, with only four parameters. This model has often been used successfully to describe esterifica-

Table 2. Adjustable Parameters Estimated from Simultaneous Correlation of the Methyl Lactate Hydrolysis and Reverse Esterification Kinetic Data to the QH, L-H, and E-R Models

model	$k_e^0/(\text{mol g}^{-1} \text{min}^{-1})$	$E_{A,e}/(\text{kJ mol}^{-1})$	$k_h^0/(\text{mol g}^{-1} \text{min}^{-1})$	$E_{A,h}/(\text{kJ mol}^{-1})$	k_M	k_W	SRS	MRD/%
QH	1.16×10^6	48.52	1.65×10^5	50.91			2.26×10^{-6}	4.90
QH(ideal)	8.88×10^7	48.68	3.79×10^7	49.92			5.82×10^{-6}	12.04
L-H ^a	7.89×10^7	49.51	8.72×10^6	51.35			3.03×10^{-6}	5.82
L-H(ideal) ^a	2.62×10^6	49.21	7.30×10^5	49.18			4.95×10^{-6}	12.98
L-H	1.39×10^7	46.42	4.71×10^6	51.61	3.91	3.91	3.24×10^{-6}	6.62
E-R	9.36×10^6	49.39	2.52×10^6	53.77	4.52	4.98	2.47×10^{-6}	5.46

^a Adsorption constants in Table 1.**Figure 5.** Mass fraction of methyl lactate as a function of time for the methyl lactate hydrolysis reaction (○; $R_{W/ML} = 10$, $T = 353.15$ K, mass fraction of catalyst = 2.5%) and for the reverse esterification reaction⁷ (●; $R_{M/LH} = 2$, $T = 353.15$ K, mass fraction of catalyst = 2.5%). The solid lines represent the QH model considering the nonideality of the reaction mixture, and the dashed lines represent the QH model considering the reaction mixture to be ideal.**Table 3. Activation Energies for the Lactic Acid Esterification with Methanol (M) and Butanol (n-B)^a**

reaction	catalyst	$E_A/(\text{kJ mol}^{-1})$	literature
HL + M ↔ ML + W	Amberlyst 15	$E_{A,e} = 48.52$	this work
		$E_{A,h} = 50.91$	this work
	Amberlyst 15	$E_{A,e} = 48.67$	Sanz et al. ⁷
	Amberlyst 15	$E_{A,e} = 46.50$	Seo and Hong ²
	Dowex 50W-X8	$E_{A,e} = 48.98$	Choi et al. ³
HL + n-B ↔ BL + W	Amberlyst 15	$E_{A,e} = 48.06$	Choi et al. ³
		$E_{A,e} = 48$ (dioxane as the solvent)	Dassy et al. ²⁰
		$E_{A,h} = 64$ (dioxane as the solvent)	Dassy et al. ²⁰
		$E_{A,e} = 46.5$ (toluene as the solvent)	Dassy et al. ²⁰

^a HL ≡ lactic acid; ML ≡ methyl lactate; BL ≡ butyl lactate; W ≡ water.

tion reactions catalyzed by ion-exchange resins.^{2,18,19} The continuous solid lines in Figures 1–5 represent the results obtained by integration of the QH model by the Runge–Kutta method. The L–H model, in which the adsorption constants were obtained from independent adsorption experiments, gives also a good representation of the kinetic experimental data.

Table 3 shows the values of the activation energies obtained in this work through the QH model for the esterification and hydrolysis reactions, and some values found in the literature for similar reactive systems, for comparison. The high values found for the activation energy support a surface reaction rate-controlled process and the absence of external and internal mass-transfer resistances.

The L–H model, based on independent adsorption experiments, and the QH model were expressed in terms of mole fractions as well as in terms of activities.

The results of the correlation obtained for the two cases are also reported in Table 2 as L–H(ideal) and QH(ideal) models. In both cases, it was observed that the assumption of ideal behavior of the liquid mixture results in larger errors in comparison with those obtained when nonideality was taken into account. This result can also be observed in Figure 5, where two kinetic experiments, one for the esterification reaction and another for the hydrolysis reaction, have been represented, together with the kinetic results predicted by the QH model when considering the liquid mixture to be ideal and nonideal.

The largest deviations of the models, when the experimental kinetic data were reproduced, were found for the esterification kinetics at different initial reactant molar ratios. Troupe and Kobe^{4,5} pointed out that the mechanism of esterification of lactic acid changes when using high reactant molar ratios and proposed different kinetic equations according to the values of such ratios.

The composition of the reactant mixture has been reported to have an influence also on the equilibrium constant obtained from experimental data for the esterification kinetics.^{4,5,21,22}

All of these considerations suggest that a better description of the esterification reactive systems could be obtained by including some functionality of the initial reactant mole ratios in the models.

(iii) Equilibrium Constant. The equilibrium constant of the reaction in this work, in terms of activity, is defined as indicated by eq 6.

$$K_a = K_x K_\gamma = \frac{x_{ML} x_W \gamma_{ML} \gamma_W}{x_{LH} x_M \gamma_{LH} \gamma_M} \quad (6)$$

Most of the hydrolysis kinetic experiments carried out in this work, and the esterification kinetics previously reported,⁷ lasted long enough for chemical equilibrium to be reached, which allowed us to calculate the equilibrium constant, K_x , in both cases by using eq 6. The activity coefficients for the components in the reaction mixture were calculated by the group contribution method UNIFAC.

A traditional approach was used to obtain the dependence of the equilibrium constant with temperature as indicated by eq 7.

$$\ln K_a = -2.60 - \frac{-1954.2}{T} \quad (7)$$

The usual plot of $\ln K_a$ vs $1/T$ allows one to compute the reaction enthalpy as indicated by the van't Hoff equation. The standard enthalpy of the reaction considered in this work resulted to be $\Delta H_r^\circ = -16.23$ kJ mol⁻¹, which is very close to the value obtained from the enthalpy of formation of the individual components.

The parameters in this equation have been obtained by simultaneous correlation of the equilibrium constants

obtained from the hydrolysis and esterification kinetic experiments, and therefore the equation represents the influence of temperature on the equilibrium constant in a global manner.

Conclusions

The kinetic behavior of the methyl lactate hydrolysis catalyzed by Amberlyst 15 has been experimentally studied. The hydrolysis rate has been found to increase with temperature and catalyst loading. The equilibrium conversion increased with the initial molar ratio ($R_{W/ML}$). Different kinetic models have been tested to correlate the kinetic experimental data of the methyl lactate hydrolysis and the reverse esterification reactions simultaneously in order to obtain a general model. Taking into account the nonideality of the liquid mixture, by calculation of the activity coefficients through UNIFAC, provided a better description of this reactive system than when the reaction mixture was considered to be ideal. The QH model gives a good representation for the kinetic behavior of the global system; therefore, this model can be used for the design of a reactive distillation system to purify lactic acid.

Acknowledgment

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Nomenclature

a = activity

$E_{A,e}$ = apparent activation energy for the esterification reaction

$E_{A,h}$ = apparent activation energy for the hydrolysis reaction

K = equilibrium constant

k_e^0 = preexponential factor for the esterification reaction

k_h^0 = preexponential factor for the hydrolysis reaction

k = adsorption coefficient

n = number of experimental data

n_0 = initial mole number of methyl lactate

R = gas constant, J mol⁻¹ K⁻¹

r' = reaction rate, mol (g of catalyst)⁻¹ min⁻¹

$R_{W/ML}$ = initial molar ratio of water/methyl lactate

$R_{M/LH}$ = initial molar ratio of methanol/lactic acid

T = temperature, K

t = time, min

W = catalyst weight, g

w = weight fraction

X = conversion

x = molar fraction

γ = activity coefficient

Subscripts

calc = calculated values

exp = experimental values

W = water

LH = lactic acid

M = methanol

ML = methyl lactate

Literature Cited

- (1) Lipinsky, E. S.; Sinclair, R. G. Is Lactic Acid a Commodity Chemical? *Chem. Eng. Prog.* **1986**, Aug, 26.
- (2) Seo, Y.; Hong, W. H. Kinetics of Esterification of Lactic Acid with Methanol in the Presence of Cation Exchange Resin Using a Pseudo-Homogeneous Model. *J. Chem. Eng. Jpn.* **2000**, 33, 128.
- (3) Choi, J. I.; Hong, W. H.; Chang, H. N. Reactions Kinetics of Lactic Acid with Methanol Catalyzed by Acid Resins. *Int. J. Chem. Kinet.* **1996**, 28, 37.
- (4) Troupe, R. A.; Kobe, K. A. Kinetics of Methanol–Lactic Acid Reaction. Reaction with 44% Technical Acid. *Ind. Eng. Chem.* **1950**, Jul, 1403.
- (5) Troupe, R. A.; Kobe, K. Kinetics of methanol–lactic acid reaction. Reaction with 85% Acid. *Ind. Eng. Chem.* **1950**, May, 801.
- (6) Taylor, R.; Krishna, R. Modelling Reactive Distillation. *Chem. Eng. Sci.* **2000**, 55, 5183.
- (7) Sanz, M. T.; Murga, R.; Beltran, S.; Cabezas, J. L.; Coca, J. Autocatalyzed and Ion-Exchange Resin-Catalyzed Esterification Kinetics of Lactic Acid with Methanol. *Ind. Eng. Chem. Res.* **2002**, 41, 512.
- (8) Lee, M. J.; Chiu, J. Y.; Lin, H. M. Kinetics of Catalytic Esterification of Propionic Acid and *n*-Butanol over Amberlyst 35. *Ind. Eng. Chem. Res.* **2002**, 41, 2882.
- (9) Xu, Z. P.; Chuang, K. T. Kinetics of Acetic Acid Esterification over Ion Exchange Catalysts. *Can. J. Chem. Eng.* **1996**, 74, 493.
- (10) Lee, M. J.; Wu, H. T.; Lin, H. M. Kinetics of Catalytic Esterification of Acetic Acid and Amyl Alcohol. *Ind. Eng. Chem. Res.* **2000**, 39, 4094.
- (11) Liu, W. T.; Tan, Ch. S. Liquid-Phase Esterification of Propionic Acid with *n*-Butanol. *Ind. Eng. Chem. Res.* **2001**, 40, 3281.
- (12) Sanz, M. T.; Calvo, B.; Beltrán, S.; Cabezas, J. L. Vapor–Liquid Equilibria at (33.33, 66.66, and 101.33) kPa, and Densities at 298.15 K for the System Methanol + Methyl Lactate. *J. Chem. Eng. Data* **2002**, 47, 1003.
- (13) Pöpkén, T.; Götze, L.; Gmehling, J. Reaction Kinetics and Chemical Equilibrium of Homogeneously and Heterogeneously Catalyzed Acetic Acid Esterification with Methanol and Methyl Acetate Hydrolysis. *Ind. Eng. Chem. Res.* **2000**, 39, 2601.
- (14) Cunill, F.; Iborra, M.; Fité, C.; Tejero, J. Conversion, Selectivity, and Kinetics of the Addition of Isopropanol to Isobutene Catalyzed by a Macroporous Ion-Exchange Resin. *Ind. Eng. Chem. Res.* **2000**, 39, 1235.
- (15) Subramanian, C.; Bhatia, S.; Liquid-Phase Synthesis of Methyl *tert*-Butyl Ether Catalyzed by Ion Exchange Resin. *Can. J. Chem. Eng.* **1987**, 65, 613.
- (16) Helfferich, F. *Ion Exchange*; McGraw-Hill Book Company: New York, 1962.
- (17) Chakrabarti, A.; Sharma, M. M. Cationic Ion Exchange Resins as Catalyst. *React. Polym.* **1993**, 20, 1.
- (18) Jiménez, L.; Garvín, A.; Costa-López, J. The production of Butyl Acetate and Methanol via Reactive and Extractive Distillation. I. Chemical Equilibrium, Kinetics and Mass-Transfer Issues. *Ind. Eng. Chem. Res.* **2000**, 41, 6663.
- (19) Steinigeweg, S.; Gmehling, J. *n*-Butyl Acetate Synthesis via Reactive Distillation: Thermodynamic Aspects, Reaction Kinetics, Pilot-Plant Experiments, and Simulation Studies. *Ind. Eng. Chem. Res.* **2002**, 41, 5483.
- (20) Dassy, S.; Wiame, H.; Thyron, F. C. Kinetics of the Liquid-Phase Synthesis and Hydrolysis of Butyl Lactate Catalysed by Cation Exchange Resin. *J. Chem. Technol. Biotechnol.* **1994**, 59, 149.
- (21) Bart, H. J.; Reidetschläger, J.; Schatka, K.; Lehmann, A. Kinetics of Esterification of Levulinic acid with *n*-Butanol by Homogeneous Catalysis. *Ind. Eng. Chem. Res.* **1994**, 33, 21.
- (22) Kashkarova, I. B.; Rozhnov, A. M.; Verevkin, S. P. Chemical Equilibrium in the Isoamylenes–Butyric Acid–*tert*-Amyl Butyrate Reaction System. *Russ. J. Appl. Chem.* **1994**, 67, 1305.

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