

Ethyl Lactate Synthesis using A15 resin as Catalyst/Adsorbent: Kinetic and Adsorption Studies

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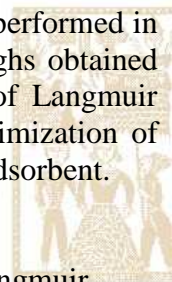
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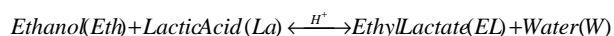
ABSTRACT – The heterogeneous catalysis of lactic acid (88 wt. %) esterification with ethanol in presence of Amberlyst 15-wet was studied. A simplified Langmuir-Hinshelwood kinetic model was used to predict the experimental data. The effect of the catalyst loading, initial molar ratio between ethanol and lactic acid and reaction temperature on lactic acid conversion as function of time was studied. Binary adsorption experiments were performed in the fixed bed in absence of reaction at 298.15 K. The experimental breakthroughs obtained were used to determine the multicomponent adsorption equilibrium isotherm of Langmuir type. The results obtained will be very useful to apply for the design and optimization of industrial hybrid reactive separation process using Amberlyst 15-wet as catalyst/adsorbent.

KEYWORDS: Ethyl lactate, kinetics, esterification, adsorption, Amberlyst 15, Langmuir isotherm.



1. INTRODUCTION

Petroleum (“black gold”) has been revealed like one of the biggest economics and politics problems of the actuality. It is a finite resource and the use of petrochemical solvents has several implications on the environment. Therefore, the replacement of traditional petroleum derived solvents is a big challenge. Ethyl lactate is a green solvent derived, for example, from processing corn, and is a promising replacement for halogenated petroleum-based solvents in a wide range of applications. It can be used as food additive, perfumery, flavour chemicals and solvent (Tanaka *et al.*, 2002). The ethyl lactate synthesis comprises a liquid-phase reversible reaction between ethanol and lactic acid, wherein water is a sub-product:



All esterification reactions occur in acid medium, they are self-catalyzed by the acid involved in the reaction. But, the kinetics of the self-catalyzed reaction is too slow and the use of homogenous or heterogeneous catalyst is advantageous. The kinetics of ethyl lactate production has been studied since 1957 (Troupe and Dimilla, 1957), but lately has deserved more attention since it is a green solvent and an alternative to the traditionally petroleum derived solvents. Troupe and Dimilla (1957) studied the esterification reaction between lactic acid and ethanol using sulphuric acid as catalyst. However, this kind of homogeneous catalysts may origin a lot of problems, because their miscibility with the reaction medium, which causes separation problems; in addition, strong acid catalysts leads to corrosion of the equipment. The replacement of homogeneous catalysts by heterogeneous catalysts is gaining importance due to their ecofriendly nature. Besides being non-corrosive 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. In this case, the chosen catalyst was the sulfonic acid ion exchange resin Amberlyst 15-wet (Rohm and Haas). This resin is of great interest for use in reversible reactions, since it can act as catalyst and as selective adsorbent (Kawase *et al.*, 1996; Mazzotti *et al.*, 1996; Silva and Rodrigues, 2002; Gandi *et al.*, 2006). Therefore the production of Ethyl Lactate in a chromatographic reactor using this resin is very attractive. However, it is necessary to have information about the kinetics and also about the adsorption. So, this work was undertaken to obtain the kinetic model that describe the synthesis of the ethyl lactate in the liquid phase and to determine the multicomponent adsorption equilibrium isotherm of Langmuir type over the A15 resin. These results will be very useful to apply in the modelling of some reactive separation processes, such as a fixed-bed reactor.

2. EXPERIMENTAL SECTION

2.1 Chemicals and Catalyst

The chemicals used were ethanol (>99.9% pure), lactic acid (>85% pure) and ethyl lactate (>98% pure) 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 diameter varying between 0.3 to 1.2 mm, an ion exchange capacity of 4.7 meq H⁺/g of dry resin and inner surface area of 53 m²/g. 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 deionised water and dried at 90 °C until the mass remains constant.

2.2 Experimental set-up

2.2.1 Batch Reactor set-up (kinetic studies)

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. The temperature was controlled by 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 0.6MPa with helium.

2.2.2 Fixed Bed set-up (Adsorption studies)

The experiments were performed in a laboratory-scale jacketed glass column that was maintained at constant temperature (293.15 K), through a thermostatic bath; at atmospheric pressure. The column was packed with the resin Amberlyst 15-wet (Rohm and Haas). It has an ion exchange capacity of 4.7 eq H⁺/kg of dry resin and inner surface area of 53 m²/g.

2.3 Analytical method

All the samples were analysed in a gas chromatograph (Chrompack 9100, Netherlands) using a fused silica capillary column (Chrompack CP-Wax 57 CB, 25 m x 0.53 mm ID, df = 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 held for 8.5 min. The injector and detector temperature was maintained at 280 °C and 300 °C, respectively. Helium N50 was used as the carrier gas with flowrate 10.50 ml/min.

3. Kinetic Studies

The experimental results of the reaction kinetics of the esterification of lactic acid and ethanol catalyzed by the A15 resin are presented in this section. The effect of the catalyst loading, initial molar ratio between ethanol and lactic acid and reaction temperature on lactic acid conversion as function of time is studied. This study was performed in absence of mass transfer limitations and catalyst deactivation. A three-parameter model (see Equation 1) based on a Langmuir-Hinshelwood rate expression; using activity coefficients from the UNIQUAC method is proposed (Pereira *et al.*, 2008).

$$r = k_c \frac{a_{Eth} a_{La} - \frac{a_{EL} a_W}{K}}{(1 + K_{s,Eth} a_{Eth} + K_{s,W} a_W)^2} \quad (1)$$

With:

$$K_c = 2.70 \times 10^7 \exp(-6011.55/T(K)) \quad (2)$$

$$K_W = 15.19 \exp(12.01/T(K)) \quad (3)$$

$$K_{Eth} = 1.22 \exp(359.63/T(K)) \quad (4)$$

Where, a_i is the activity for specie i , k_c is the kinetic constant, $K_{s,i}$ is the adsorption constant for species i and K is the equilibrium reaction constant.

In Figures 1, 2 and 3 experimental and simulated results are shown. It can be seen that the proposed kinetic law predicts well the time evolution of the lactic acid conversion for different masses of catalyst (A15), for different initial molar ratio of reactants and for different temperatures.

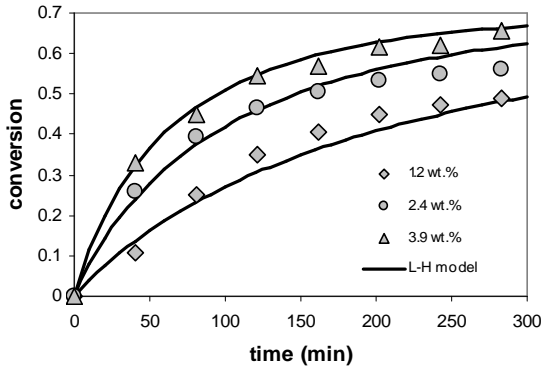


Figure 1- Effect of catalyst loading on the conversion of lactic acid history for a molar ratio of ethanol to lactic acid of 1.82 at 353.49 K.

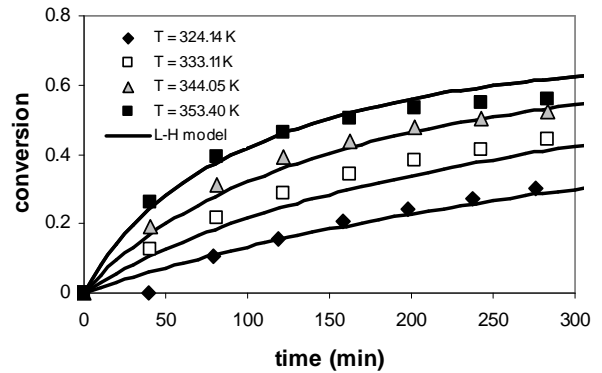


Figure 3- Effect of the reaction temperature on the conversion of lactic acid history for a molar ratio of ethanol to lactic acid of 1.82.

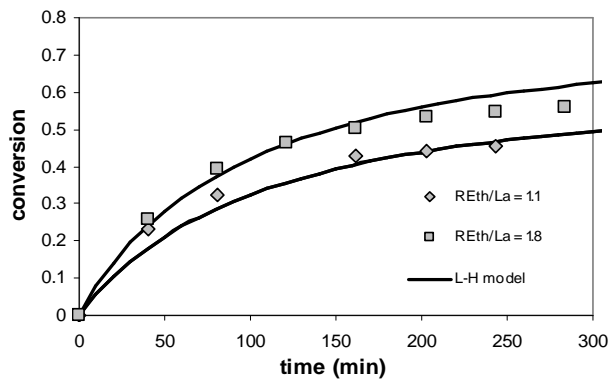


Figure 2- Effect of initial molar ratio of ethanol to lactic acid on the conversion of lactic acid history at 353.40 K.

4. Adsorption Results

As the resin A15 acts simultaneously as adsorbent and as catalyst, in order to have information on the adsorptive equilibrium alone it is necessary to perform experiments with non reactive binary mixtures. So, the breakthrough curves of ethanol, lactic acid, ethyl lactate and water were measured in the absence of reaction. The resin was saturated with a certain component A and then the feed concentration of component B was changed stepwise. The possible binary mixtures to run the breakthrough experiments in absence of reaction are ethanol / water, ethyl lactate / ethanol and lactic acid / water. The experiments were performed at 293.15 K and the concentration histories of the different pairs are presented in Figures 4, 5 and 6.

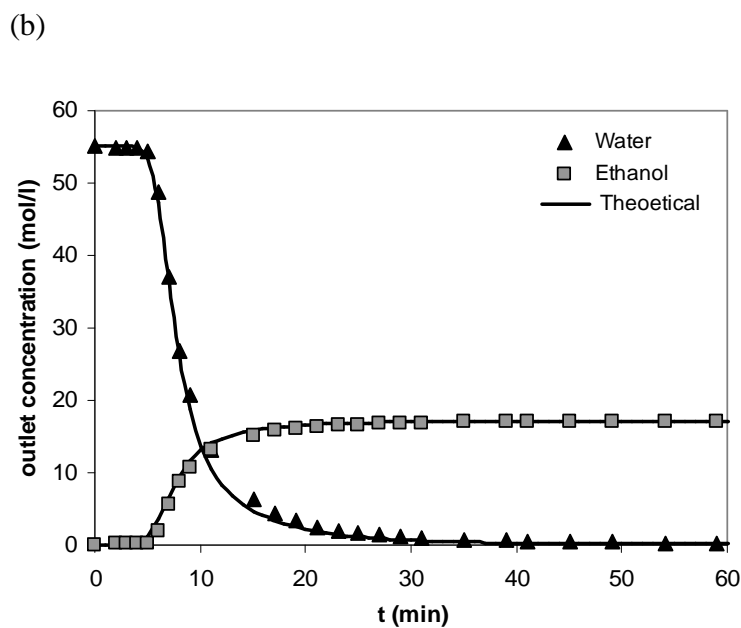
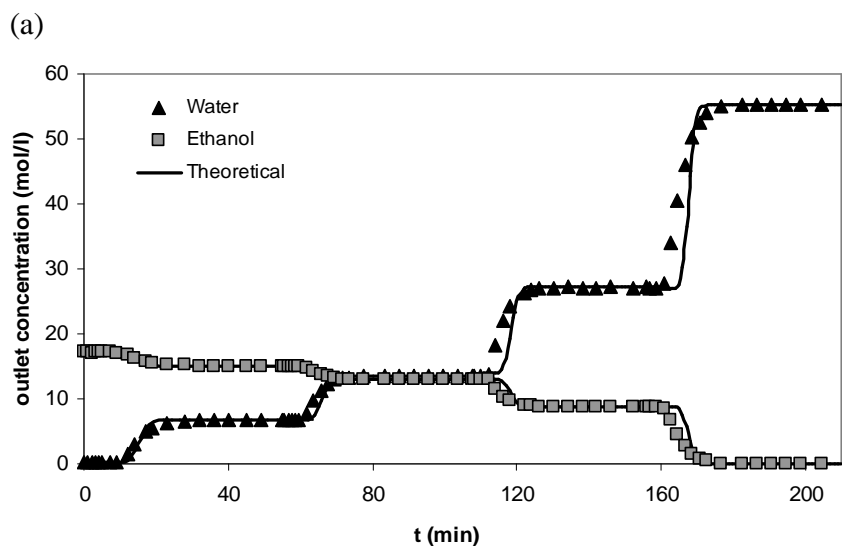
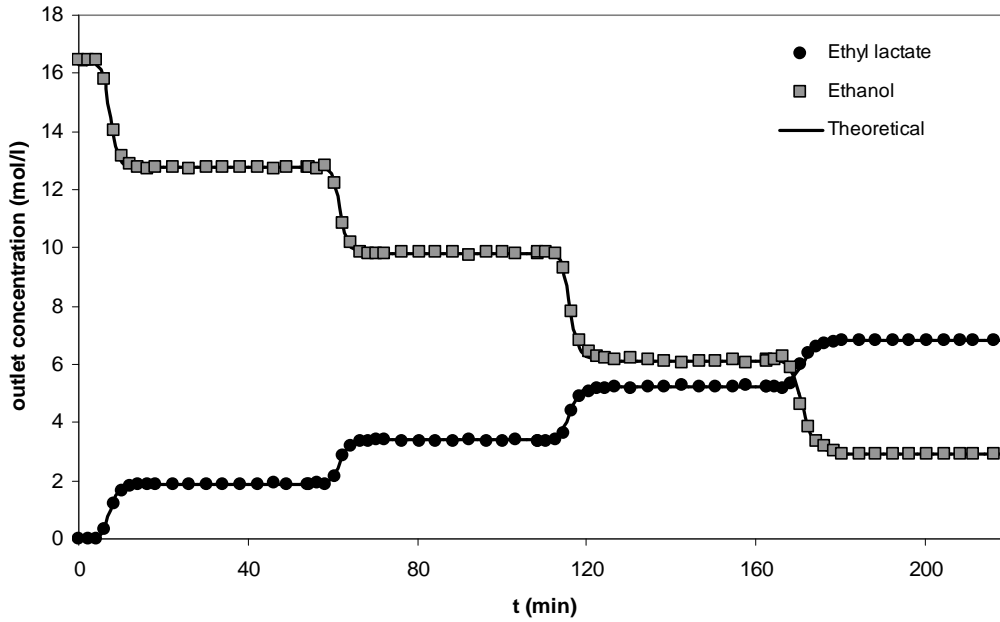


Figure 4- Breakthrough experiments: outlet concentration of ethanol and water as a function of time; $Q = 5 \text{ mL} / \text{min}$; $T = 293.15 \text{ K}$; (a) water displacing ethanol; Bottom up flow direction; (b) ethanol displacing water; Top-down flow direction.

(a)



(b)

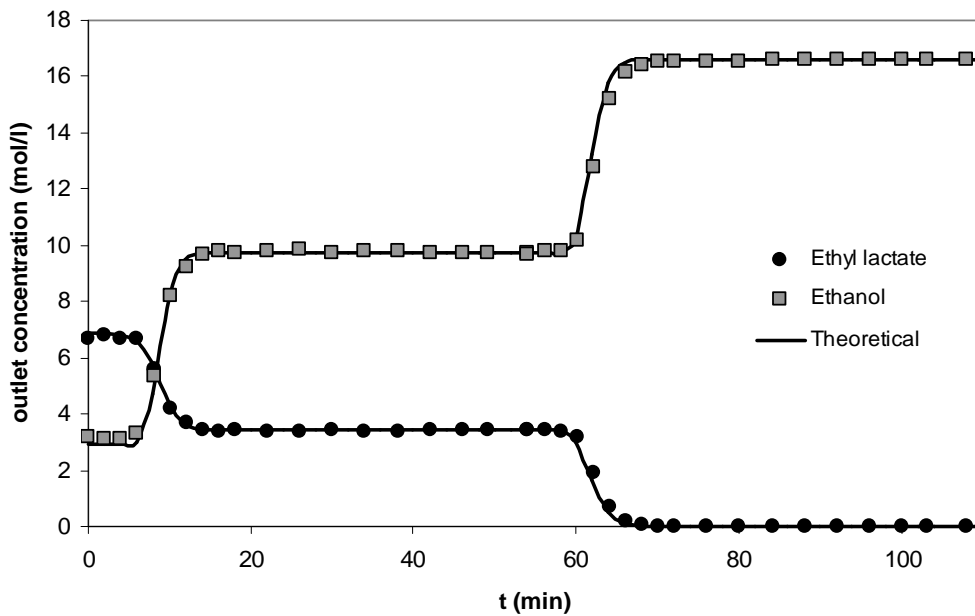


Figure 5- Breakthrough experiments: outlet concentration of ethanol and ethyl lactate as a function of time; $Q = 5 \text{ mL} / \text{min}$; $T = 293.15 \text{ K}$; (a) ethyl lactate displacing ethanol; Bottom up flow direction (b) ethanol displacing ethyl lactate; Top-down flow direction.

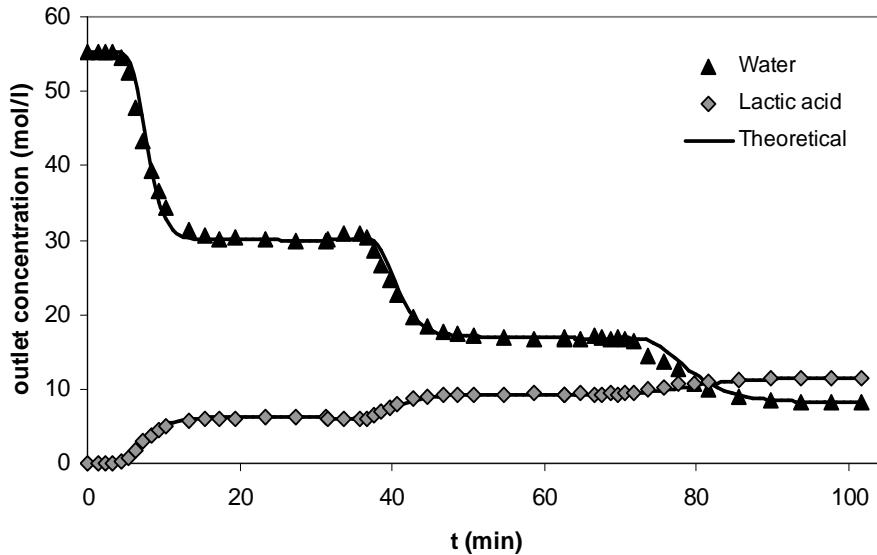


Figure 6- Breakthrough experiments: outlet concentration of water and lactic acid as a function of time; $Q = 5 \text{ mL} / \text{min}$; $T = 293.15 \text{ K}$; Lactic acid displacing water; Bottom up flow direction.

The adsorption parameters of the multicomponent adsorption equilibrium isotherm of Langmuir type (Equation 5) were optimized by minimizing the difference between experimental and theoretical number of moles adsorbed/desorbed for all the adsorption experiments and they are presented in Table 1.

Langmuir Adsorption equilibrium isotherm to component i :

$$q_i = \frac{Q_i K_i \bar{C}_{p,i}}{1 + \sum_{j=1}^n K_j \bar{C}_{p,j}} \quad (5)$$

Where Q_i , and K_i represent the total molar capacity per unit volume of resin and the equilibrium constant for component i ,

respectively, and n the total number of components.

Table 1- Adsorption parameters over A15 resin at 298.15 K.

Component	Q (mol/l _{real solid})	K (l/mol)
Ethanol	6.704	5.443
Lactic acid	5.225	4.524
Ethyl lactate	3.421	1.117
Water	21.57	15.35

The preferentially adsorbed component by the resin A15 is water and the weakest adsorbed one is ethyl lactate. This could be seen analyzing the concentration front of ethanol in Figures 7a and 7b. In the first case it has a dispersive character and in the second one the ethanol concentration front is self-sharpening.

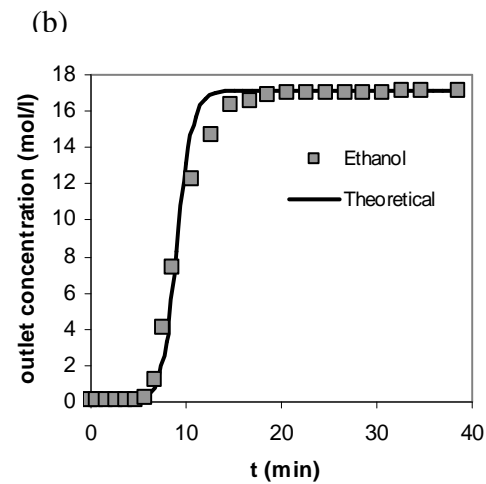
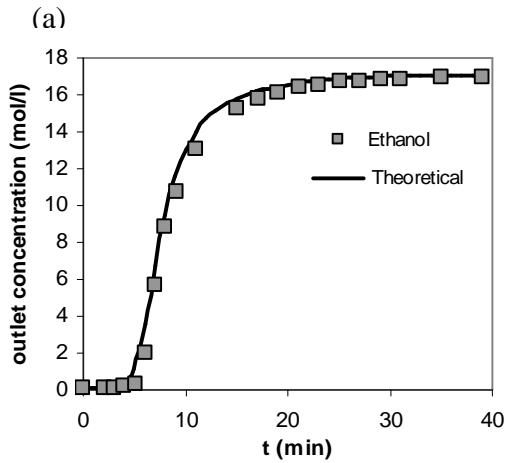


Figure 7- Outlet concentration of ethanol as a function of time; $Q = 5 \text{ mL/min}$; $T = 293.15 \text{ K}$; top-down direction flow; a) ethanol displacing water; b) ethanol displacing ethyl lactate.

5. Conclusions

A three-parameter model based on a Langmuir-Hinshelwood rate expression was proposed to describe the experimental kinetic results:

$$r = k_c (a_{Eth} a_{La} - a_{EL} a_W / K) / (1 + K_{Eth} a_{Eth} + K_W a_W)^2$$

; and the model parameters are

$$K_c = 2.70 \times 10^7 \exp(-6011.55 / T(K)),$$

$$K_W = 15.19 \exp(12.01 / T(K))$$

$$\text{and } K_{Eth} = 1.22 \exp(359.63 / T(K)).$$

The agreement between experimental and simulated results was good for the following operating conditions: catalyst loading from 1.2 wt. % to 3.9 wt. %, initial molar ratio of reactants from 1.1 to 1.8 and temperature from 50 °C to 80 °C.

Adsorption experiments in absence of reaction at 20 °C were performed and used to obtain the adsorption parameters, by minimizing the difference between experimental and theoretical number of moles adsorbed/desorbed. It was observed that the preferentially adsorbed component by the resin A15 is water and the weakest adsorbed one is ethyl lactate.

6. References

- Gandi, G. K.; Silva, V. M. T. M.; Rodrigues, A. E. Synthesis of 1,1-dimethoxyethane in a fixed bed adsorptive reactor. *Industrial and Eng. Chem. Res.*, v. 45, p. 2032-2039, 2006.
- Kawase, M.; Suzuki, T. B.; Inoue, K.; Yoshimoto, K.; Hashimoto, K. Increased esterification conversion by application of the simulated moving-bed reactor. *Chem. Eng. Sci.*, v. 51, p. 2971-2976, 1996.
- Mazzotti, M.; Kruglov, A.; Neri, B.; Gelosa, D.; Morbidelli, M. A continuous chromatographic reactor: SMBR. *Chem. Eng. Sci.*, v. 51, p. 1827-1836, 1996.
- Pereira, C. S. M.; Pinho, S. P.; Silva, V. M. T. M.; Rodrigues, A. E. Thermodynamic Equilibrium and Reaction Kinetics for the Esterification of Lactic Acid with Ethanol Catalyzed by acid ion exchange resin. *Ind. Eng. Chem. Res.*, v. 47, p. 1453-1463, 2008.
- Silva, V. M. T. M.; Rodrigues, A. E. Dynamics of a fixed-bed adsorptive reactor for synthesis of diethylacetal. *AIChE Journ.*, v. 48, p. 625-634, 2002.



Tanaka, K.; Yoshikawa, R.; Ying, C.; Kita, H.; Okamoto, K.-i. Application of zeolite T membrane to vapor-permeation-aided esterification of lactic acid with ethanol. *Chem. Eng. Sci.* v. 57, p. 1577-1584, 2002.

Troupe, R.A. and Dimilla E. Kinetics of the Ethyl Alcohol-Lactic Acid Reaction. *Ind. Eng. Chem.*, v. 49, p. 847, 1957.