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Flávio dos Reis Gonçalves[a]; Luiz Eduardo Pizarro Borges[a]; Cristiano Piacsek Borges[b]
[a] Instituto Militar de Engenharia/Chemical Engineering Department, Rio de Janeiro, Brazil [b] Federal University of Rio de Janeiro/COPPE—Chemical Engineering Program CT, Cidade Universitária, Rio de Janeiro, Brazil

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Synthesis of Ethyl Acetate by Coupling a Heterogeneous Catalytic System with a Pervaporation Unit

**Flávio dos Reis Gonçalves,[1,*] Luiz Eduardo Pizarro Borges,[1]
and Cristiano Piacsek Borges[2]**

[1]Instituto Militar de Engenharia/Chemical Engineering Department,
Rio de Janeiro, Brazil
[2]Federal University of Rio de Janeiro/COPPE—Chemical Engineering
Program CT, Cidade Universitária, Rio de Janeiro, Brazil

ABSTRACT

The synthesis of ethyl acetate was investigated using a heterogeneous catalyst and a pervaporation unit. Shifting the reaction equilibrium by selective water removal increased the ethyl acetate productivity. Commercial acid resin, Amberlyst 15 (Rohm and Haas), and commercial hydrophilic composite membrane, PERVAP 1000 and 1001 (Le Carbone Lorraine), were used. The effects of catalyst mass, reaction temperature, and initial reactants ratio were studied. The kinetic parameters, such as activation energy and apparent reaction order, were determined. The water

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[*] Correspondence: Flávio dos Reis Gonçalves, Instituto Militar de Engenharia/Chemical Engineering Department, Praça General Tibúrcio 80, Praia Vermelha, 22290-270, Rio de Janeiro, Brazil; E-mail: d5pizar@epq.ime.eb.br.

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production and removal rates obtained in reaction and pervaporation experiments, respectively, were used in a computational code to simulate the behavior of the coupled system. The highest conversion was observed when an initial ethanol/acetic acid molar ratio of 9 : 1 was used. At this condition, the water production was reduced turning the water removal process more selective, increasing the acetic acid conversion from 51.0% to 63.9%.

Key Words: Esterification; Ethyl acetate; Pervaporation; Acid resin; Coupled process.

1. INTRODUCTION

The classic industrial esterification process presents serious drawbacks in the reaction and separation sections. The ethyl acetate industrial process is carried out continuously in liquid phase with an excess of ethanol and a liquid acid catalyst, such as sulfuric acid. Therefore, many additional steps are needed, such as acid separation, neutralization, and discarding. The removal of the water by-product of the reaction is normally done by azeotropic distillation with benzene or toluene. This process, besides presenting high environmental risk, is energy intensive, as the alcohol excess must be separated for recycling.

As an alternative, the use of a heterogeneous catalyst can improve the process by eliminating acid recovery and reducing the steps of product purification. In order to obtain high yield, the catalyst bed can be coupled with a separation unit continuously removing the reaction water. In another way, a pervaporation unit can be combined with distillation to reduce the number of stages in the distillation column, rendering a much more compact and efficient process.

Pervaporation process coupled to chemical reactors has been evaluated in certain reversible reactions to increase the productivity by shifting the reaction equilibrium. An example is the work of Bagnell et al.[1] where a pervaporation unit with Nafion® membranes was used with the reactions of acetic acid and methanol or acetic acid and *n*-butanol as indicated in Fig. 1. The authors mentioned an increase from 73 to 77 wt% and from 70 to 95 wt% in the final concentration of methyl acetate and butyl acetate, respectively.

This work studies the coupling of a heterogeneous esterification reactor to a pervaporation unit for water removal in the reaction of ethanol and acetic acid. The objective is to present a solution to the problems observed in the industrial process. The Amberlyst 15 (Rohm and Haas) acid resin was evaluated in reaction, while the commercial PERVAP 1000 and 1001

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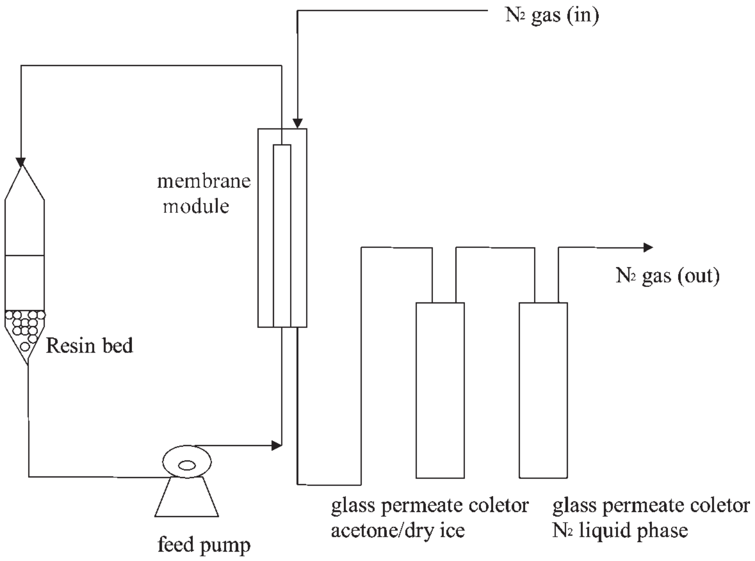

Figure 1. Heterogeneous reactor coupled to a pervaporation unit.

(Le Carbone Lorraine) hydrophilic membranes were used in pervaporation tests. The behavior of the coupled systems (reaction and pervaporation) was investigated through simulation.

2. THEORY

2.1. Esterification Reaction

The homogeneous catalysts generally used in esterification are strong mineral acids, such as sulfuric or hydrochloric acid. These acids give good conversions but favor the formation of alkyl chlorides, dehydration of alcohols, isomerization, and polymerization, reducing the selectivity towards the ester formation. Lewis acids, such as boron trifluoride, may also be used as an alternative. Organic acids, such as benzene sulfonic or paratoluene sulfonic acid, are also widely used in this process to minimize corrosion.[2]

Acid resins present similar acid forces compared to these homogeneous catalysts and can be an interesting substitute in etherification or esterification reactions. The resins exhibit good activity and high selectivity, minimizing parallel reactions. The catalyst separation step is eliminated as a fixed bed

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rector is used, with the additional advantage of a smaller reactor volume. Furthermore, it is not necessary to neutralize the reaction medium at the end of the reaction. The use of acid resins also reduces corrosion in the process equipment, such as reactors, piping, valves, and columns. In general, these resins consist of sulfonated styrene–ethylvinylbenzene copolymers.[3]

The main disadvantages of the resins are a low specific area and deactivation of the active sites due to the loss of sulfonic groups, which, however, may be regenerated with a sulfuric acid solution.[4]

Different authors had studied the acetic acid esterification using acid resins as catalyst, with both methanol[5,6] and ethanol.[7] These works were basically concerned with the determination of kinetics parameters to be used in reactive distillation system simulations.

2.2. Pervaporation Process

Pervaporation is a membrane process where the compounds permeate selectively through the membrane from the liquid phase to the vapor phase due to a partial pressure gradient. Usually, the liquid in the feed side is slightly above the atmospheric pressure, while the permeate side is kept under vacuum. The transport mechanism can be divided into three main steps: selective sorption at the feed side; selective diffusion through the membrane matrix; and desorption to vapor phase at the permeate side. Therefore, the separation is determined by differences of solubility and diffusivity of each compound present in the feed solution in the membrane material.

Normally, the pervaporation process efficiency is characterized by the selectivity and the permeate flux. The former can be defined as a concentration ratio of compounds in the permeate and in the feed solutions and denominated as separation factor (α) or enrichment factor (β). When dealing with multicomponent solutions, it is simpler to use the ratio of each component concentration in the permeate by its concentration in the feed solution, as described in Eq. (1).

$$\beta = \frac{y_i}{x_i} \tag{1}$$

where y_i and x_i are the concentrations of component "i" in the permeate and in the feed, respectively.

The permeate flux through the membrane can be described using the Fick diffusion equation. However, the frequent nonideality of the membrane phase leads to strong concentration dependence for the diffusion coefficient, as well as the phenomenon of fluxes coupling. Consequently, a number of

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semi-empirical relationships were proposed similar to that shown in Eq. (2.)[8]

$$J_i = \frac{D_{o,i}}{\ell}[\exp(\gamma C_i^m) - 1] \tag{2}$$

where $D_{o,i}$ is the diffusivity of component "i" at infinity dilution, C_i^m is its concentration in the membrane matrix, γ is the plasticization coefficient, and ℓ is the membrane thickness.

In order to obtain higher permeate fluxes, the membranes used in industrial applications show an anisotropic morphology, i.e., a thin and dense region that is responsible by the selectivity, and other porous region where the pore size increases gradually. The porous region, also called support layer, gives mechanical stability to the upper dense region. In commercial membranes applied to pervaporation each region is made of different materials and they are nominated composite membranes.

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3. EXPERIMENTAL DETAILS

3.1. Materials

The hydrophilic membranes were kindly supplied by Le Carbone Lorraine and nominated PERVAP 1000 and 1001. These membranes are based on a thin cross-linked polyvinylalcohol skin layer deposited onto a porous polyacrylonitrile film reinforced by a non-woven polyester ethyl alcohol, ethyl acetate, and acetic acid, in analytical grade, and distilled water were used to prepare feed solutions. The Amberlyst 15 resin, supplied by Rohm and Haas, was used as the acid catalyst. This resin presents appreciable specific area (45 m^2/g) and is macroporous.

3.2. Reaction Apparatus

Two set ups are used to study the kinetic behavior of the esterification reaction. In the first one, the feed is kept inside a tank immersed in a thermostatic bath and circulated by a peristaltic pump (Masterflex) through a stainless steel tubular reactor, Fig. 2. The Amberlyst resin was held inside this reactor by a steel sieve (mesh 35) and glass wool to avoid any catalyst losses. In the other reaction system, a mechanical stirrer stirs the feed and resin together in a round flask at a constant temperature. In both systems, samples are taken periodically and analyzed by gas chromatography (Chrompack 9000) using a Porapak Q packed column and a thermal conductivity detector.

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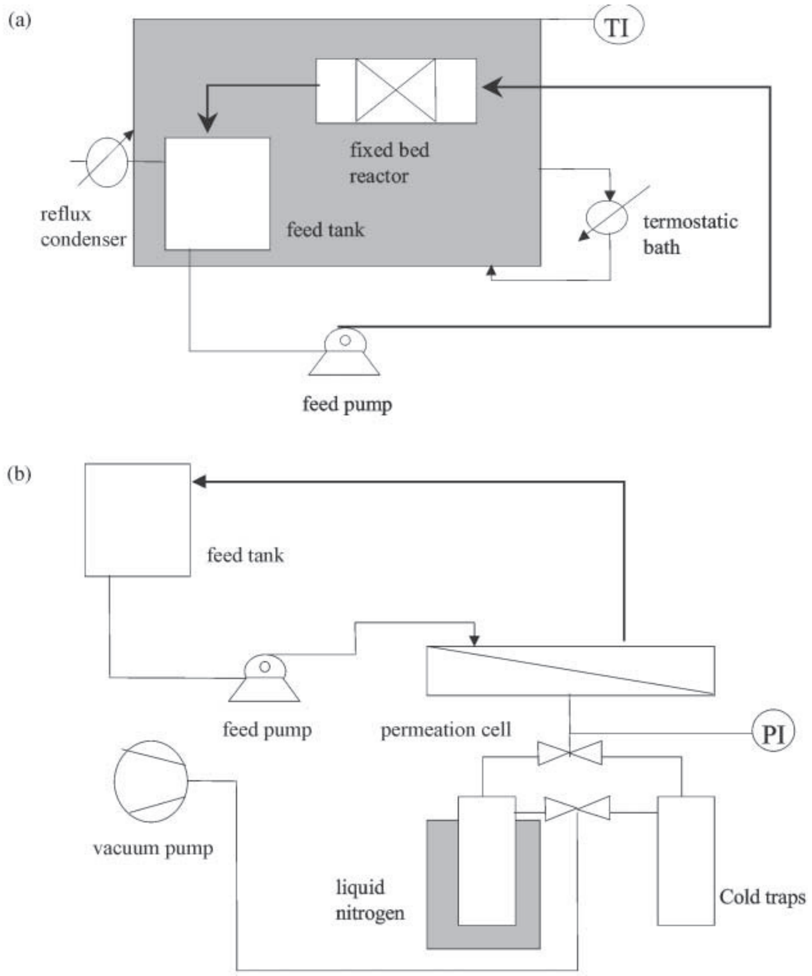

Figure 2. Experimental set ups: (a) reaction system with recycle; (b) pervaporation unit.

3.3. Pervaporation Unit

The feed solution is circulated through two stainless steel permeation cells by a gear pump (Verder) and a vacuum pump (Sargent Wells) is used to maintain a low pressure at the permeate side. The pressure at the permeate side in all experiments was below 3 mbar. The permeate is collected in cold traps and cooled with liquid nitrogen. The set up has two traps that could be used alternately, allowing a

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continuous operation. Figure 2 shows the setup schematically. The feed solution and the permeate are sampled periodically and analyzed by gas chromatography.

4. RESULTS AND DISCUSSION

4.1. Chemical Reaction

The effect of the external mass transfer on the resin particle was investigated for the system with feed recirculation. For these experiments, a bed porosity of 0.41 was estimated, using the bed dimensions (diameter $= 1.05\,\mathrm{cm}$ and length $= 2.75\,\mathrm{cm}$) and the resin density (0.77 g/mL). The experiments were developed using 250 mL of reaction volume, 1.0 g of resin, and a molar feed ratio of 9 : 1 (ethanol : acetic acid), at 70°C. The feed flow rates employed were 0.44, 0.30, and 0.14 mL/sec, corresponding to superficial velocities of 14.0, 9.6, and 4.4 cm/sec, respectively.

The ethyl acetate concentration profiles (see Fig. 3), measured during these experiments presented a sensible augmentation with the flow rate increase until a value 0.30 mL/sec, stabilizing and indicating that the limitations due to external mass transfer are not important for greater values.

In parallel, the difference in ethyl acetate concentration between the bulk liquid phase and the catalyst surface was estimated to verify whether the kinetic regime hypothesis was valid in those operation conditions. Thus, due to the high ethanol concentration, the mixture was considered pseudobinary (ethanol/ethyl acetate). The molecular diffusivity was estimated using the Wilke–Chang equation.[9] The correlation of Wilson and Geankoplis[10] was used for the K_L estimation. The concentration difference was estimated in the range of 10^{-5} mol/L, indicating that there are no limitations due to external mass transfer, and confirming the experimental results.

The effect of the catalyst mass was studied only in the stirred reactor. Tests were conducted for a reaction volume of 100 mL with a feed molar ratio of 9 : 1 (ethanol : acetic acid), at 60°C and a stirring speed above 1000 rpm. The production rates were derived from ethyl acetate concentration evolution data, integrating an adjusted function for a certain time interval. Figure 4 presents the results obtained for different catalyst mass.

A linear relation was observed between the mass of catalyst and the ethyl acetate production rate. With no catalyst, the acetic acid auto catalyzes the reaction, responding to an ethyl acetate production of approximately 0.001 mol/sec, at 60°C. This result is in agreement with the results obtained by Xu and Chuang.[5]

The activation energy was evaluated for both reaction systems, (see Fig. 5). The activation energies values are very similar—15.88 kcal/mol (system with recycle) and 15.92 kcal/mol (stirred system)—reinforcing the fact that the

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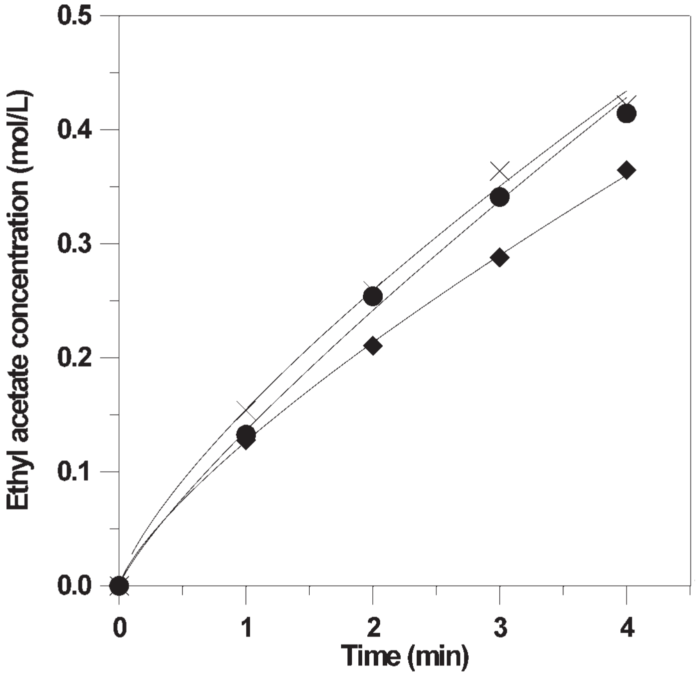

Figure 3. Effect of superficial velocity on ethyl acetate concentration profile. Initial molar ratio of ethanol : acetic acid = 9 : 1, 70°C, catalyst mass = 1 g, reaction volume = 250 mL. Superficial velocity: ×, 14.0 cm/sec; ●, 9.6 cm/sec; ◆, 4.4 cm/sec.

global reaction is processed in the kinetic regime. These numbers are comparable to the value of 13.87 kcal/mol obtained by Xu and Chuang[5] for the esterification of acetic acid with methanol using the same resin. The effectiveness factors were calculated from the Thiele modulus using the diameter and density of the Amberlyst 15 resin ($d = 0.16$ cm, $\rho = 0.77$ g/mL), and the reaction rate constant ($k = 3.51 \times 10^{12}$ mol/dm^3/sec), resulting in a value of 0.99, similar to that obtained by Xu and Chuang.[5]

The effect of the initial concentration of reagents was studied in both reactors. The reactions with mechanical stirring were carried out at 60°C, with a volume of 100 mL, using 1.0 g of catalyst and stirring speed above 1000 rpm. The molar ratios of ethanol : acetic acid used were 1 : 1 5 : 1, and 9 : 1. Similar tests were conducted with the system with recycle, with the same molar reagent ratio and resin mass, but with a volume of 250 mL and a feed flow rate of 0.30 mL/sec, at 70°C.

The results obtained for the ethyl acetate concentration profile, in both systems, are presented in Fig. 6.

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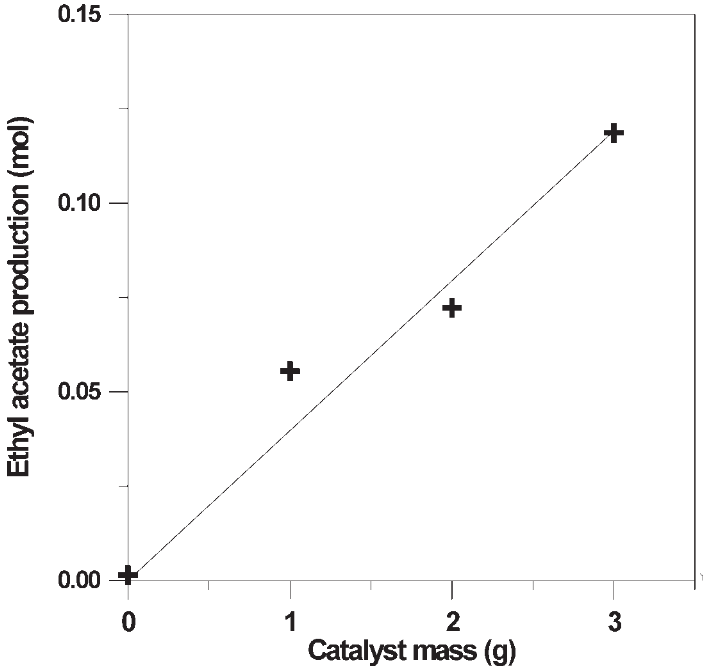

Figure 4. Effect of catalyst mass on production rate of ethyl acetate. Initial molar ratio of ethanol : acetic acid = 9 : 1, 70°C, reaction volume = 250 mL.

These results indicate an increase in the ethyl acetate production with the acetic acid initial concentration. The experiments conducted in the reactor with recycle were used to estimate the apparent order of the reaction. Figure 7 shows the relationship between the initial reaction rate and the initial acetic acid concentration. The fitted curve indicates an apparent reaction order of 1, confirming once again the low influence of mass transfer phenomena.

4.2. Pervaporation

The PERVAP 1001 and 1000 membranes were evaluated at 70°C using an initial feed solution with 85 wt% of ethanol and 5 wt% of water, acetic acid, and ethyl acetate. This composition was chosen to operate the process in conditions near those of the reaction system. The results are presented in Figs. 8 and 9 for Pervap 1001 and 1000, respectively.

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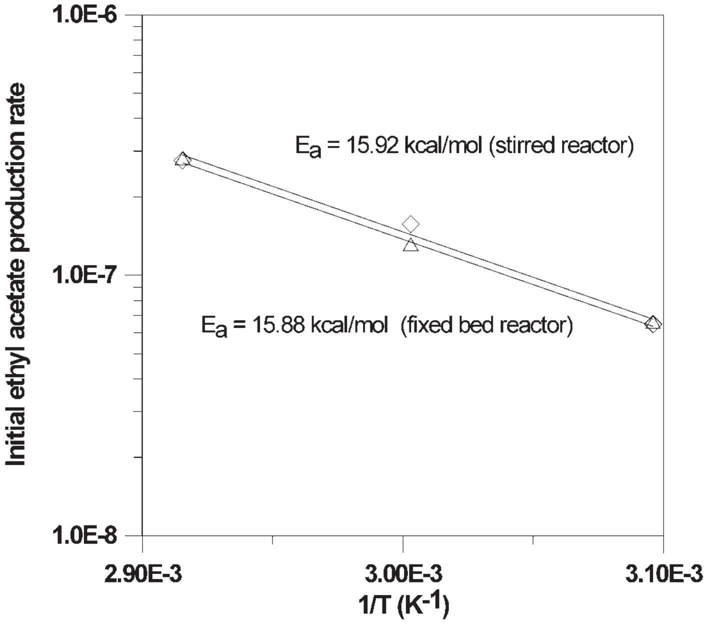

Figure 5. Effect of reaction temperature on ethyl acetate production rate and the activation energy in the reaction systems investigated. Initial molar ratio of ethanol : acetic acid = 9 : 1, catalyst mass = 1 g, reaction volume = 250 mL. *Key:* ◇, stirred reactor, △, fixed bed reactor.

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Both membranes showed to be water selective as indicated by its higher flux when compared to the other components. The pervaporation experiments were carried out for more than 12 hr, allowing the evaluation of the feed composition influence on the permeate flux.

From Figs. 8 and 9, it may be observed that both, water and ethanol concentrations, have a trend to diminish in the feed solution. The membrane PERVAP 1000 is more selective, but presents a lower permeate flux. For this membrane, the composition of other components has changed very little during water removal.

4.3. Coupled System Simulation

As suggested by Néel,[8] the effect of water removal from reaction medium was simulated using a mass balance for water in system, which is

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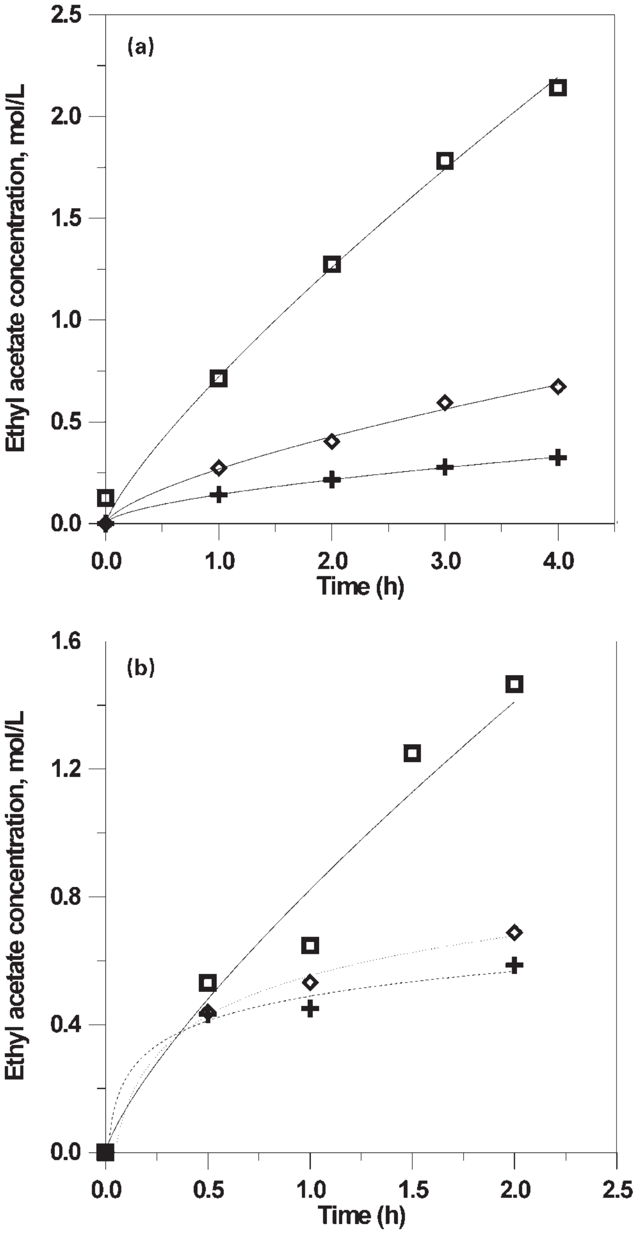

Figure 6. Effect of the initial molar ratio of reactants on the concentration profile of ethyl acetate in fixed bed reactor: (a) catalyst mass = 1 g, reaction volume = 250 mL, 70°C; (b) catalyst mass = 1 g, reaction volume = 100 mL, 60°C.

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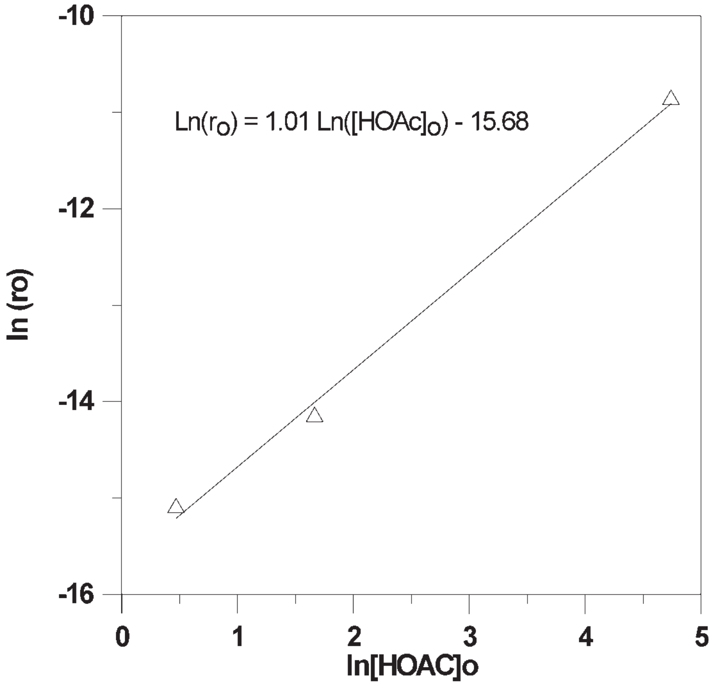

Figure 7. Determination of the apparent reaction order for acetic acid. Catalyst mass = 1 g, reaction volume = 250 mL, 70°C.

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produced by the reaction and preferentially removed by pervaporation. The reaction systems and pervaporation unit data were adjusted to represent the water production and removal rates as a function of water concentration in the medium. Table 1 presents the parameters of the fitted equations.

The simulation was carried out for the coupled system for initial ethanol : acetic acid molar ratios of 9 : 1 and 5 : 1. Table 2 presents the main results obtained using PERVAP 1000 and 1001 membranes, reaction volume of 250 mL, and catalyst mass of 1 g.

It is interesting to observe in Table 2, the equilibrium shift effect of coupling the pervaporation unit to the reaction system. It is clear that the conversion of acetic acid to ethyl acetate is higher and intensified for ethanol : acetic acid initial molar ratio of 9 : 1. This result can be understood taking into account the lower water production rate at this condition, which leads to lower water concentration in the reaction medium increasing the pervaporation selectivity.

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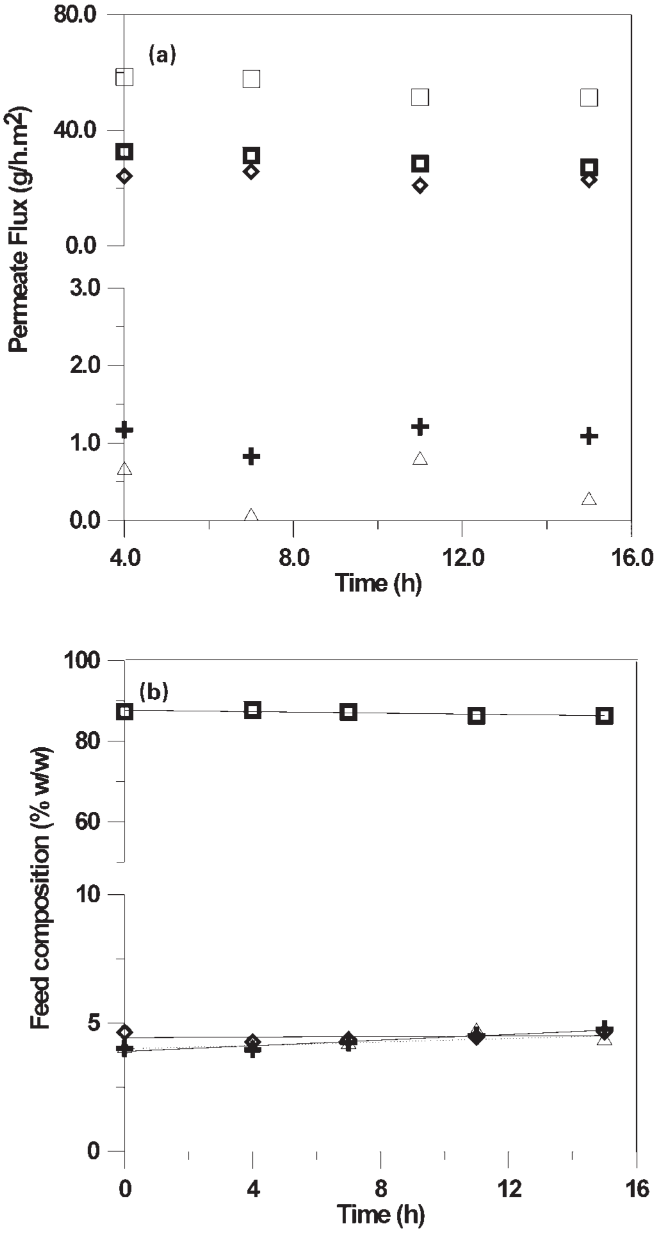

Figure 8. Permeate fluxes and feed composition during pervaporation experiments with PERVAP 1001 membrane. (a) Permeate fluxes; (b) feed composition evolution. *Key:* □, total permeate flux; □, ethanol; ◇, water; +, ethyl acetate; △, acetic acid.

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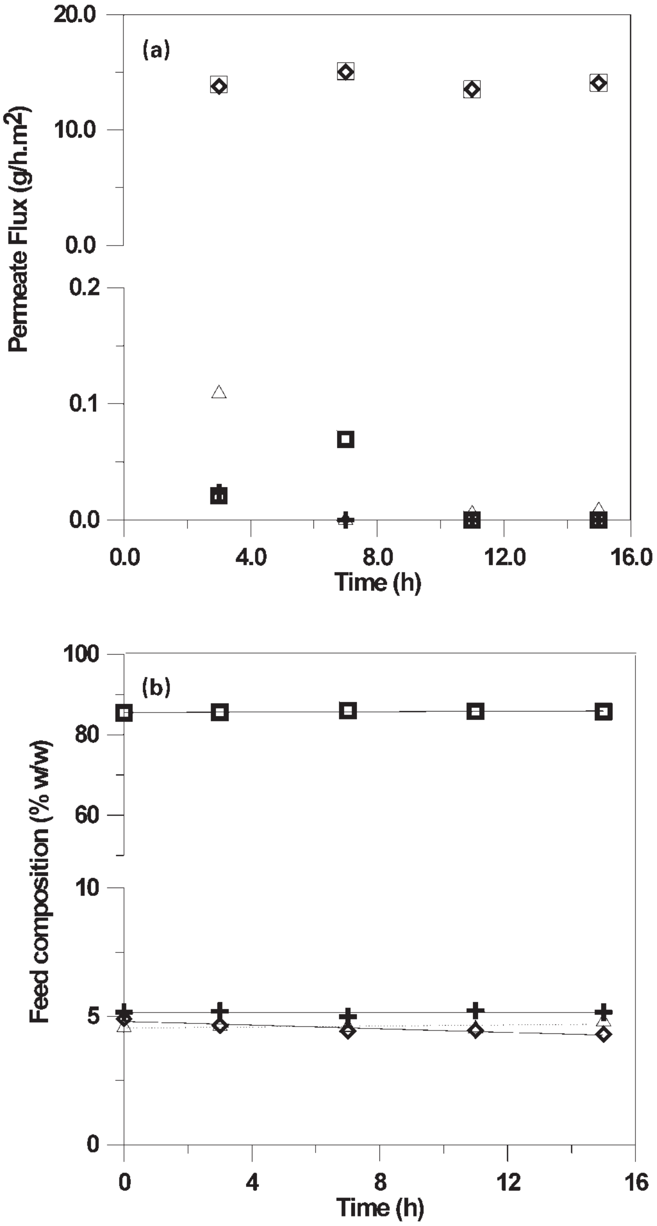

Figure 9. Permeate fluxes and feed composition during pervaporation experiments with PERVAP 1000 membrane. (a) Permeate fluxes; (b) feed composition evolution. *Key:* □, total permeate flux; □, ethanol; ◇, water; +, ethyl acetate; △, acetic acid.

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Table 1. Fitted functions for water production and removal rates.

Chemical reaction (0.004 g/mL, 70°C)		Pervaporation $(S/V) = 0.16\,\text{cm}^{-1}$	
Initial molar ratio (ethanol : acetic acid)	Production rate (mol/mL sec)	Membrane (PERVAP)	Permeate flux (mol/cm^2 sec)
9 : 1	$6.3 \times 10^{-9}[H_2O]^{-0.68}$	1000	$1.09 \times 10^{-8}[H_2O]$
5 : 1	$2.4 \times 10^{-8}[H_2O]^{-0.53}$	1001	$1.87 \times 10^{-8}[H_2O]$

Table 2. Effect of coupling a pervaporation unit on the conversion of acetic acid.

	Acetic acid conversion[a]		
		With pervaporation[b]	
Initial molar ratio (ethanol : acetic acid)	Without pervaporation	PERVAP 1000	PERVAP 1001
9 : 1	51.0	58.5	63.9
5 : 1	59.0	64.8	68.9

[a] Conversion at a reaction time of 20 hr.
[b] $S/V = 1\,\text{cm}^{-1}$.

5. CONCLUSION

The activation energies obtained in both reactor systems investigated and the apparent reaction order, estimated close to the unit, indicate that the chemical reaction was conducted in kinetic conditions. A linear relationship between the catalyst mass and the reaction rate was also observed, as well as an auto catalytic effect of the acetic acid.

Commercial hydrophilic membranes PERVAP 1001 and 1000 had been operated in same conditions in the reaction system. The PERVAP 1000 membrane was more water selective; however, it presents a lower permeate flux.

The simulation of the coupled system indicates that the water removal leads to higher reactant conversion, as expected. The water composition in the reaction medium shows a great effect on the process performance. Higher water production provides higher swelling of the membrane and lower selectivity reducing the ethyl acetate production.

6. ACKNOWLEDGMENTS

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