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Ethyl lactate production via esterification of lactic acid with ethanol combined with pervaporation

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ABSTRACT

The synthesis of ethyl lactate from ethanol and lactic acid has been studied in a batch reactor combined with a pervaporation unit. The commercial acid resin Amberlyst 15 and the hydrophilic membrane PERVAP® 2201 were used in the experiments. First esterification–pervaporation experiments were performed for dilute lactic acid aqueous solutions. Results show that the yield of ethyl lactate exceeds the corresponding thermodynamic equilibrium via selective removal of water from the reaction mixture through the membrane. If the process is performed sufficiently long, near total use of lactic acid could be reached. The water production and removal rates obtained from independent reaction and pervaporation experiments were used to simulate the behavior of the coupled system. The simulation results reveal the same trend observed in the experiments. The influence of different kinetic and pervaporation parameters such as initial reactant molar ratio, amount of catalyst, temperature and the ratio of membrane area/initial volume of reaction was analyzed in terms of ethyl lactate yield. For dilute lactic acid aqueous solutions the effect of catalyst loading has been found not to have a great influence, unlike the other parameters. Additionally the effect of the initial concentration of lactic acid aqueous solution was evaluated by performing experiments with different lactic acid aqueous solutions concentrations (20, 50 and 79–81 wt%). Initial water content has a great influence since total permeation is proportional to water concentration in the reactor.

1. Introduction

Lactate acid esters are powerful high-boiling solvents that are biodegradable and non-toxic. Specifically ethyl lactate is used as food and perfumery additive, flavor chemical and solvent [1,2]. Current production of lactate esters by esterification of lactic acid with the corresponding alcohol suffers from low conversion and purity [3,4]. Esterification reactions are characterized by thermodynamic limitations on conversion. Integration of reaction and separation may involve important savings in capital as well as operating costs [5]. The integration of a pervaporation process into a conventional esterification process is attractive because offers the opportunity to shift continuously the conversion beyond the thermodynamic equilibrium conversion by removing continuously water from the chemical reactor [6]. This way, this kind of integrated process overcomes the inhibition of the thermodynamic equilibrium and therefore leads to an increased productivity.

The objective of this work was the study of the esterification of lactic acid with ethanol, catalyzed by Amberlyst 15, coupled to a pervaporation unit for water removal to improve ethyl lactate yield. Experiments have been performed in a batch reactor coupled with an external pervaporation unit using the commercial polymeric membrane PERVAP® 2201 for water removal.

Our group has already studied the kinetics of the reaction using lactic acid aqueous solutions of 20 wt% [4] as well as the pervaporation performance of the membrane PERVAP® 2201 for some of the binary mixtures involved in the esterification system and for the quaternary mixture [7,8], showing that this membrane presents high selectivity towards water. Based on these previous studies a model has been proposed to describe the integrated esterification–pervaporation process. Good agreement was obtained between experimental and simulated values; therefore this model has been used to analyze the influence of different operating parameters such as operating temperature, ratio of membrane area to initial reaction volume, initial reactant molar ratio and amount of catalyst.

In the literature some studies have been reported on esterification of lactic acid with ethanol coupled to membrane processes, but normally, only concentrated lactic acid was considered. Benedict et

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Nomenclature

a	activity
A	membrane area, m^2
F	molar permeation flux, mol min^{-1} m^{-2} (Eq. (1))
J	mass permeation flux, kg h^{-1} m^{-2}
K_{eq}	equilibrium constant
m_{cat}	mass of catalyst, g
n	number of moles
r	reaction rate, mol g^{-1} min^{-1}
t	time, min
T	absolute temperature, K
V_o	initial volume of reaction mixture, m^{-3}
w	mass fraction
EtOH	ethanol
L_1E, L_2E, L_3E	ethyl lactate and its oligomers
HL_1, HL_2, HL_3	lactic acid and its oligomers
W	water
υ	stoichiometric coefficient

al. [9,10] used concentrated lactic acid of 88 wt% using Amberlyst XN-1010 as catalyst. They determined lactic acid concentration by titration. However, this way, only the total acid content is calculated and not the monomer and other oligomers [11]. Parulekar [12] studied the efficacy of different reactor separator configurations in driving esterification to ethyl lactate formation based on the model equations reported by Benedict et al. [9]. Jafar et al. [13] considered vapour permeation to remove water from the vapour mixture allowing the ethanol to come back to the reactor in order to increase the yield of ethyl lactate, but they did not take into account the lactic acid oligomers either. Similarly, Tanaka et al. [14] studied the vapour–permeation separation with zeolite T membranes applied to esterification of concentrated lactic acid with ethanol. But the work of Tanaka et al. [14] did already consider the presence in the reactor of higher oligomers acids and their esters.

In this work the efficacy of the integrated esterification–pervaporation process for different commercial lactic acid aqueous solutions, specifically 20, 50 and 79–81 wt%, was considered. For dilute aqueous solution, less than approximately 20 wt%, composition corresponds mainly to monomeric lactic acid and water. The concentrated aqueous solutions are more complex due to self-esterification of lactic acid [15].

2. Theory: reaction–pervaporation coupled model

In the reaction–pervaporation process, the change in compounds concentration during the process is associated with the amount formed or consumed in the reaction and the amount removed by pervaporation. By performing the material balance for the reactor-pervaporation system, the following expression is obtained for each of the components in the reaction mixture:

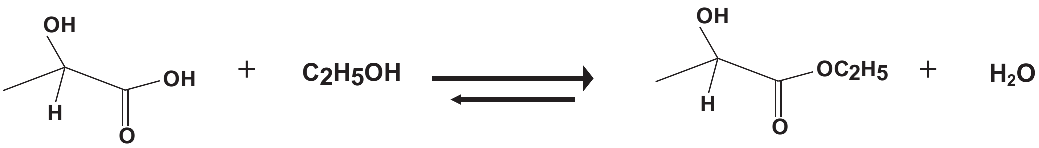
$$\frac{dn_i}{dt} = m_{cat} r_i - AF_i \tag{1}$$

where n_i is the number of moles of species i in the reactor, r_i the reaction rate of component i in the catalytic reaction (mol/g of catalyst min), m_{cat} the mass of catalyst in the reactor (g), F_i the molar permeate flux of species i (mol/min m^2) through the membrane, and A the area of the membrane (m^2).

2.1. Kinetics of the reaction

2.1.1. Dilute lactic acid aqueous solution (20 wt%)

For dilute lactic acid aqueous solutions, only the monomer has to be considered, therefore the only reaction to be considered is the esterification of monomeric lactic acid with ethanol:



The pseudohomogeneous model was used to evaluate the reaction rate for dilute lactic acid aqueous solution (20 wt%):

$$r_{L_1E} = \frac{1}{m_{cat}}\frac{1}{\upsilon_i}\frac{dn_{L_1E}}{dt} = 1.357\times10^{6} \exp\left(\frac{-55.04}{RT}\right)\cdot\left(a_{HL_1}a_{EtOH} - \left(\frac{a_{L_1E}a_W}{K_{eq}}\right)\right) \tag{2}$$

This expression was obtained by correlating the kinetic data previously reported by our work group using Amberlyst 15 as catalyst [4], and calculating the activity coefficients with the UNIQUAC parameters obtained in the study of the phase equilibrium of this esterification system [16]. The expression for the reaction equilibrium constant was obtained from previous work [16] by using kinetic data [4] and phase equilibrium data [16]:

$$\ln K_{eq} = 7.8927 - \frac{2431.2}{T(\mathrm{K})} \tag{3}$$

The pseudohomogeneous model expressed in Eq. (2) represents the previous kinetic data [4] quite well, with a mean relative deviation of 7.1 between experimental and calculated ethyl lactate mole fraction. The relationship between the reaction rates of the four components can be expressed by the stoichiometric factors:

$$r_W = r_{L_1E} = -r_{HL_1} = -r_{EtOH} \tag{4}$$

2.1.2. Lactic acid concentrated aqueous solution

Lactic acid appears generally in the form of more or less concentrated aqueous solutions. At concentrations higher than 20 wt%, lactic acid undergoes intermolecular esterification spontaneously resulting in the formation of lactoyllactic acid and higher linear oligomers acids [15]. These lactic acid oligomers react with ethanol to form oligomers esters. The set of reactions that describes lactic acid monomer esterification as well as oligomers formation and esterification are the following [14]:

$$HL_1 + EtOH \underset{k_1/K_{eq,1}}{\overset{k_1}{\rightleftarrows}} L_1E + H_2O \tag{5}$$

$$HL_2 + EtOH \underset{k_2/K_{eq,2}}{\overset{k_2}{\rightleftarrows}} L_2E + H_2O \tag{6}$$

$$HL_3 + EtOH \underset{k_3/K_{eq,3}}{\overset{k_3}{\rightleftarrows}} L_3E + H_2O \tag{7}$$

$$HL_2 + H_2O \underset{k_4/K_{eq,4}}{\overset{k_4}{\rightleftarrows}} 2HL_1 \tag{8}$$

$$HL_3 + H_2O \underset{k_5/K_{eq,5}}{\overset{k_5}{\rightleftarrows}} HL_1 + HL_2 \tag{9}$$

Asthana et al. [17] performed an exhaustive work to characterize these oligomers formation by esterification of the corresponding lactic acid oligomers catalyzed by Amberlyst 15. The kinetic parameters for all the reactions reported above have been taken from Asthana et al. [17] to simulate the behavior of these complex systems.

2.2. Rates of pervaporation

Partial flux of each component in the mixture through the membrane PERVAP® 2201 was evaluated through the expressions obtained in previous work [8], where it was shown that the water permeation flux was close to the total permeation flux. The water permeation flux (kg/hm^2) can be described by the following expression:

$$J_W = 1.19 \times 10^7 \exp\left(\frac{-49.96}{RT}\right)[\exp(2.17w_W) - 1] \tag{10}$$

The permeation flux for the other components can also be found in previous work [8].

The set of conversion equations obtained from the material balance for all the components present in the reaction mixture were solved numerically by using a fourth-order Runge–Kutta method to obtain the concentration profile for all the components in the reactor as a function of time.

3. Experimental

3.1. Materials

The pervaporation membrane used in this work was the commercial hydrophilic membrane PERVAP® 2201 supplied by Sulzer Chemtech®. The strongly acidic ion-exchange resin, Amberlyst 15, with an exchange capacity of 4.75 mequiv. H$^+$/g of dry catalyst (Rohm & Haas) was used as catalyst.

Ethyl lactate was supplied by Fluka with a reported purity of 99 wt%. Ethanol of 99.9 wt% purity was purchased from Merck. Water was nanopure. Different aqueous lactic acid solutions were used in this work. An aqueous lactic acid solution (20 wt%) was obtained from Acros. The amount of polymerized lactic acid was considered negligible after being determined by back titration. Additionally two more concentrated lactic acid aqueous solutions (50 wt% and 79–81 wt%) were obtained from Fluka. The amount of polymerized lactic acid was determined by HPLC. The purity of the rest of the chemicals was checked by gas chromatography.

3.2. Esterification–pervaporation coupled equipment

Experiments on the semi-batch pervaporation membrane reactor have been performed in the same equipment as for the pervaporation studies [7,8]. However in this case, the reactor has 2 L capacity and a frame of four stainless steel mesh catalyst baskets (i.d. = 1.9 cm and length = 4 cm) was installed on a rotating shaft. The ethanol solution was charged into the reactor and heated to the desired reaction temperature. The aqueous lactic acid solution was heated separately up to the desired temperature and fed to the reactor. The catalyst baskets were then sunken into the reaction mixture. At the same time the reaction mixture was pumped continuously through the pervaporation unit. This time was taken as the starting time for the experiments. The stainless steel permeation cell (Sulzer Chemtech®) for flat sheet membranes has an effective membrane area in contact with the feed mixture of 170 cm^2. The temperature of the feed liquid mixture was kept constant (±0.5 °C) by using a thermostat. A peristaltic pump circulated the feed and the feed flow rate was set to 0.6 L/min.

The permeate was evaporated by lowering the partial pressure on the permeate side (around 1 mbar) with the help of a vacuum pump and condensed on two parallel glass cold traps cooled by liquid nitrogen to ensure that all permeates were fully collected.

Periodically, samples were withdrawn from the reactor to follow the course of the process by determining the composition of all the components in the reactor.

3.3. Sample analysis

Permeate and feed concentrations were measured in triplicate off-line. Water, ethyl lactate and ethanol were analyzed using a Hewlett Packard (6890) gas chromatograph (GC) equipped with series connected thermal conductivity (TCD) and flame ionization (FID) detectors. Lactic acid and its oligomers (HL_2 and HL_3), and ethyl lactate and ethyl esters of oligomers acids (EL_2) were analyzed by HPLC using a Hewlett Packard 1100 series liquid chromatograph. Quantification by UV detection was made at a wavelength of 210 nm. The GC and HPLC methods have already been described in a previous work [7]. The mean relative deviation for all the components was less than 3% for sample analysis. The composition of commercial lactic acid aqueous solutions used in this work is presented in Table 1.

4. Results and discussion

Different esterification–pervaporation experiments were carried out starting from different lactic acid aqueous solutions. First of all, a 20 wt% lactic acid aqueous solution was considered. Simulation experiments were also performed to study the effect of some of the most important variables of the process such as: temperature, initial reactant molar ratio, ratio membrane area to initial volume solution and catalyst loading.

Table 1
Composition of lactic acid aqueous solutions used in this work.

Commercial lactic acid	Water	Lactic acid monomeric	Dimer	Trimer	Higher oligomers
20 wt%	75.64	24.36	–	–	–
50 wt%	50.91	45.92	3.05	0.12	–
79–81 wt%	19.13	59.86	17.71	2.82	≤0.48

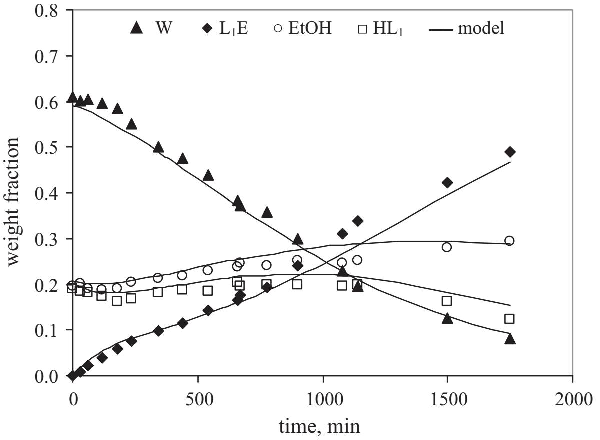


Fig. 1. Concentration profiles of reaction components for dilute lactic acid esterification with pervaporation: $n_{EtOH}/n_{HL1} = 2$, $T_{reaction} = 348.15$ K, $T_{PV} = 342.15$ K, $A/V_o = 23\ m^{-1}$, catalyst = 2 wt%. The continuous lines represent the results obtained with the model.

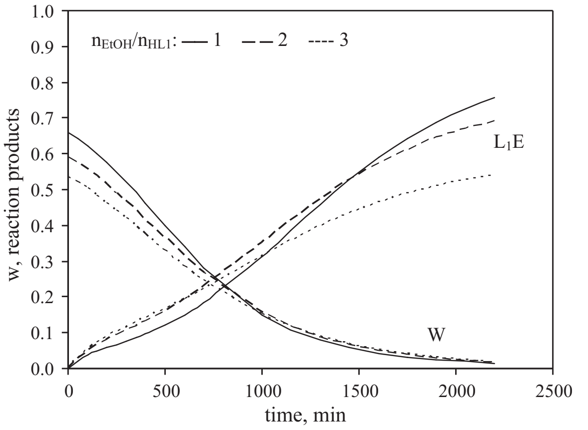


Fig. 3. Effect of the initial reactant molar ratio on the performance of the esterification–pervaporation reactor for dilute lactic acid esterification: $T_{reaction,PV} = 348.15$ K, $A/V_o = 23\ m^{-1}$, catalyst = 2 wt%.

Additionally some more esterification–pervaporation experiments were performed with two more concentrated lactic acid aqueous solutions to analyze the effect of the initial lactic acid concentration.

4.1. Esterification–pervaporation results: 20 wt% lactic acid aqueous solution

For dilute lactic acid aqueous solutions, only esterification of lactic acid monomer with ethanol has to be taken into account since the presence of higher oligomers can be considered negligible. Figs. 1 and 2 show the concentration profile (as weight fraction) of all the components in the reaction medium as a function of time for two different initial reactant molar ratios, 2 and 3 respectively. The other experimental conditions were the following: ratio of membrane area to initial reacting mixture volume, (A/V_o) 23 m^{-1}, reaction temperature, 348.15 K, pervaporation temperature, 342.15 K, and amount of catalyst, 2%.

The water concentration profile shows that water weight fraction in the reactor continuously decreases with time. In case of 20 wt% lactic acid aqueous solution esterification, initial water concentration in the reaction medium is high, around 55–60 wt%. In previous pervaporation studies it was shown that the higher the water concentration the higher the permeation flux. Consequently, at such high initial concentration, water removal rate per pervaporation is higher than its production via esterification and the water profile continuously decreases with time. As it can be observed in the ethyl lactate concentration profile, its weight fraction continuously increases with time as a consequence of shifting the conversion beyond the equilibrium conversion due to the water removal by pervaporation. The trend in the lactic acid concentration in the reactor is slightly decreasing due to its consumption to form ethyl lactate. However, despite of its consumption, ethanol concentration in the reactor tends to increase because ethanol is the excess reactant and selective removal of water further concentrates the reactants. If the process is carried out sufficiently long, near total use of lactic acid could be reached, and the reactor could contain mainly ester and alcohol reducing the effort for separation. As it was pointed out by Benedict et al. [9] ethyl lactate could be easily removed from the pervaporation retentate by distillation since ethanol and ethyl lactate do not form a zoetrope [9,16].

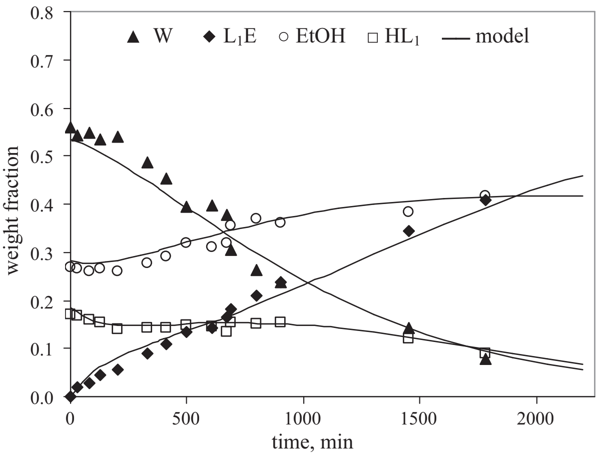


Fig. 2. Concentration profiles of reaction components for dilute lactic acid esterification with pervaporation: $n_{EtOH}/n_{HL1} = 3$, $T_{reaction} = 348.15$ K, $T_{PV} = 342.15$ K, $A/V_o = 23\ m^{-1}$, catalyst = 2 wt%. The continuous lines represent the results obtained with the model.

The continuous lines in Figs. 1 and 2 represent the results obtained with the simulation model proposed in the theory section. A comparison of the experimental concentrations with those calculated with the model proposed shows reasonably good agreement. The mean relative deviations found between experimental data and model calculations were: ethanol 5.7%, water 7.5%, lactic acid 7.1%, and ethyl lactate 12.5%. Therefore this model was used to study the influence of different operating parameters for dilute lactic acid aqueous solution in an esterification–pervaporation reactor to provide a fundamental understanding of the behavior of the membrane reactor. David et al. [18] classified these operating parameters in three groups: (1) factors which influence directly the esterification kinetics: catalyst concentration and initial reactant molar ratio (n_{EtOH}/n_{HL1}), (2) factors that influence directly pervaporation kinetics: ratio of membrane area to initial reaction volume (A/V_o), and (3) factors that influence simultaneously the esterification and pervaporation kinetics: temperature.

4.2. Effect of operating variables on PV-aided esterification

4.2.1. Effect of initial reactant molar ratio

The effect of ethanol:lactic acid initial feed molar ratio (n_{EtOH}/n_{HL1}) has been analyzed over a range of 1:1 to 3:1. The values for the other operating parameters were the following: catalyst loading, 2%, ratio membrane area to initial volume of reaction, $S/V_o = 23\ m^{-1}$ and reaction and pervaporation temperature, 348.15 K. In Fig. 3, the concentration profile of the reaction products (ethyl lactate and water) has been plotted as a function of

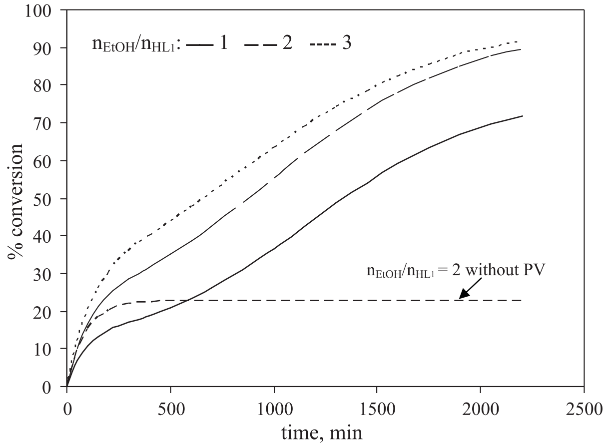


Fig. 4. Effect of the initial reactant molar ratio on conversion of the esterification–pervaporation reactor for dilute lactic acid esterification: $T_{reaction,PV} = 348.15\,K$, $A/V_o = 23\,m^{-1}$, catalyst = 2 wt%.

time. As in conventional reactors, at the beginning of the process the higher the initial reactant molar ratio, the higher the reaction rate and consequently ethyl lactate concentration in the reaction medium shows higher values. In pervaporation aided esterification process the excess reactant, ethanol, will remain in the reactor and the final ethyl lactate concentration in the reactor will be higher when working close to the stoichiometric proportion due to the dilution effect of ethanol. In Fig. 4, the conversion for the different initial feed molar ratio has been plotted as a function of time. In conventional reactors, higher equilibrium conversions were obtained by increasing the initial reactant molar ratio, but the limited reactant will never react completely [4]. In esterification–pervaporation reactors a complete conversion of one reactant is obtainable when the other reactant is in excess, no matter how small the excess is [19]. Fig. 4 also shows, for a value of initial reactant molar ratio equal to 2, the conversion reached in a conventional batch reactor. From this figure it can be clearly observed that the conversion in this kind of integrated process can go beyond the equilibrium conversion, which is the maximum conversion reached in a conventional reactor.

4.2.2. Effect of catalyst concentration

Fig. 5 shows the simulation results at different amount of catalyst in the reactor (2, 3.5 and 5.5 wt% of total initial solution mass) in the esterification–pervaporation coupled system. The values for the other operating parameters were the following: initial reactant molar ratio, $n_{EtOH}/n_{HL1} = 2$, ratio membrane area to initial volume of reaction, $S/V_o = 23\,m^{-1}$ and reaction and pervaporation temperature, 348.15 K. In previous kinetic studies, it was shown that an increase in the amount of catalyst leads to an increase in the reaction rate. This increase can be also observed in the early stage of the process, however due to the high initial amount of water in the reactor this variable is not very important in the esterification–pervaporation process of dilute lactic acid aqueous solutions.

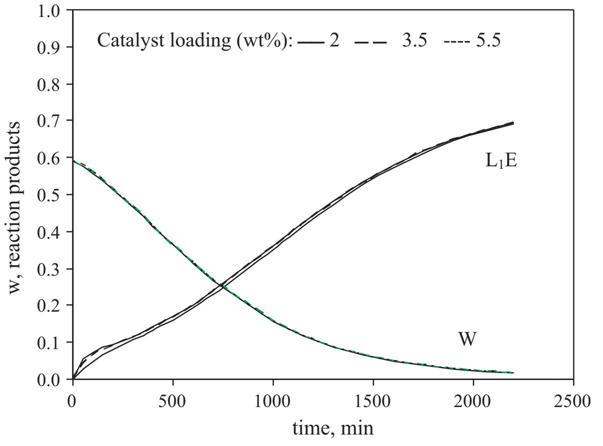


Fig. 5. Effect of the catalyst concentration on the performance of the esterification–pervaporation reactor for dilute lactic acid esterification: $n_{EtOH}/n_{HL1} = 2$, $T_{reaction,PV} = 348.15\,K$, $A/V_o = 23\,m^{-1}$.

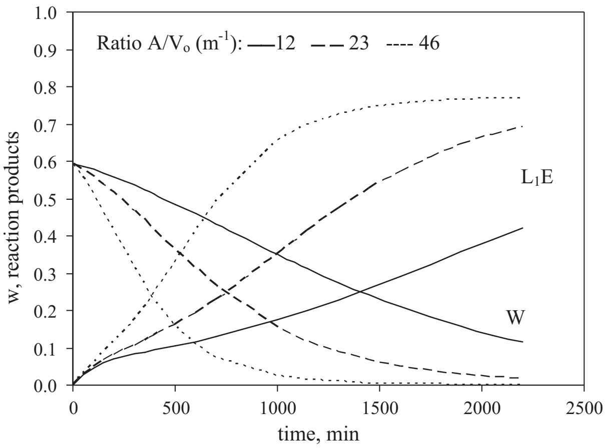


Fig. 6. Effect of the ratio A/V_o on the performance of the esterification–pervaporation reactor for dilute lactic acid esterification: $n_{EtOH}/n_{HL1} = 2$, $T_{reaction,PV} = 348.15\,K$, catalyst = 2 wt%.

4.2.3. Effect of membrane area to initial reaction volume ratio (A/V_o)

The ratio membrane area to initial reaction volume is one of the most important variables in the design of this hybrid process. Some simulations were carried out to show the influence of this parameter on the concentration profile of the reaction products (Fig. 6). This ratio has been varied over a range of 12–46 m^{-1}. The values for the rest of the operating parameters were the following: initial reactant molar ratio, $n_{EtOH}/n_{HL1} = 2$, catalyst loading, 2%, and reaction and pervaporation temperature, 348.15 K. From Fig. 6, it can be observed that at a given operating time, the higher the value of this ratio the higher the ethyl lactate concentration in the reactor, therefore higher conversions are reached. This result is obvious since water concentration in the reactor will decrease faster when the membrane area per unit of reaction volume is larger [20]. In esterification–pervaporation reactors, a low membrane permeability can be compensated by using a larger membrane area [19]. Selection of the membrane area to initial volume of reaction ratio is usually determined from an economic point of view [21].

4.2.4. Effect of reaction and pervaporation temperature

The operating temperature has a direct influence on the permeation and reaction rates. According to previous kinetic and pervaporation studies [4,7,8], an increase in temperature leads to faster reaction and pervaporation rates. In Fig. 7, the simulation results obtained at different operating temperatures (338.15, 348.15 and 358.15 K) are presented. From Fig. 7, it can be observed that water content in the reaction medium decreased rapidly when membrane permeation flux increased as a consequence of an increase in pervaporation temperature. As a result, the esterification rate increases. Consequently, at a given operating time, ethyl lactate concentration in the reactor presents higher values

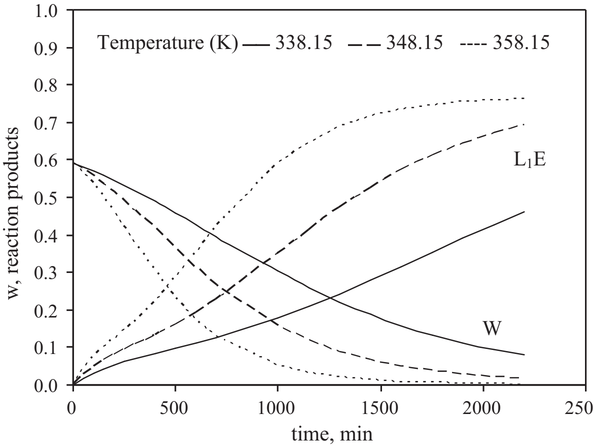


Fig. 7. Effect of the operating temperature on the performance of the esterification–pervaporation reactor for dilute lactic acid esterification: $n_{EtOH}/n_{HL1} = 2$, $A/V_o = 23\ m^{-1}$, catalyst = 2 wt%.

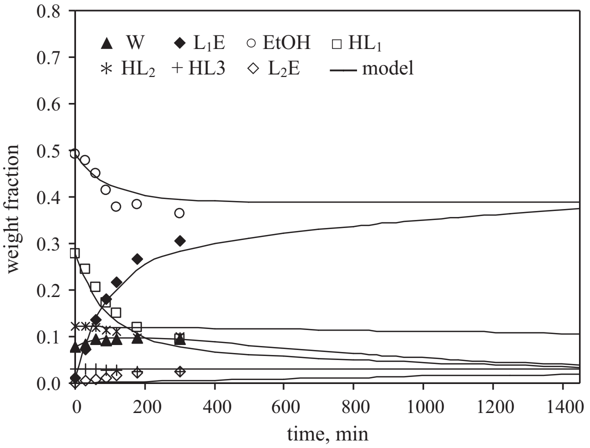


Fig. 9. Concentration profiles of reaction components for 79–81 wt% lactic acid esterification with pervaporation: $n_{EtOH}/n_{HL1} = 3.45$, $T_{reaction} = 348.15$ K, $T_{PV} = 342.15$ K, $A/V_o = 23\ m^{-1}$, catalyst = 2 wt%. The continuous lines represent the results obtained with the model.

when working at higher operating temperatures. The maximum vapour pressure that can be used as driving force in the pervaporation process will be determined by the maximum long operating temperature of the membrane PERVAP® 2201 (100 °C).

4.3. Esterification–pervaporation results with different concentrated lactic acid aqueous solutions

At concentrations higher than 20 wt%, lactic acid suffers oligomerization to yield linear oligomers acids [11]. These lactic acid oligomers react with ethanol to form oligomers esters (Section 2). Some experiences were performed with concentrated lactic acid solutions to study the effect of oligomers in the esterification–pervaporation process.

Fig. 8 presents the weight fraction of the components in the reactor as a function of time obtained for 50 wt% lactic acid esterification. At such initial lactic acid concentration, the presence of lactic acid dimer (lactoyllactic acid, HL_2) has to be taken into account as it can be appreciated in Fig. 8. The initial reactant molar ratio, n_{EtOH}/n_{HL1}, was set equal to 2. Obviously, in this case, initial water weight fraction is lower than the value obtained for the 20% lactic acid esterification. This is the reason why the decrease in water concentration in the reactor is slower than the observed in Fig. 1, since water pervaporation increases with water concentration in the reactor.

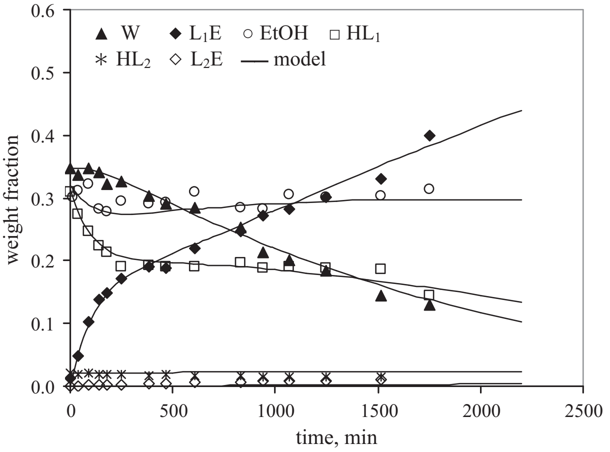


Fig. 8. Concentration profiles of reaction components for 50 wt% lactic acid esterification with pervaporation: $n_{EtOH}/n_{HL1} = 2$, $T_{reaction} = 348.15$ K, $T_{PV} = 342.15$ K, $A/V_o = 23\ m^{-1}$, catalyst = 2 wt%. The continuous lines represent the results obtained with the model.

Fig. 9 shows the concentration profile as a function of time for the different components in the reaction medium for 79–81 wt% lactic acid esterification. In this case, not only the monomer, but also the dimer and trimer of lactic acid appear in the reaction medium. The initial reactant molar ratio, n_{EtOH}/n_{HL1}, was set equal to 3.45. It must be pointed out that a maximum appears in the water concentration profile. This means that at the beginning of the process, water production by esterification is faster than its removal by pervaporation due to the low initial water content (compared to the more diluted lactic acid aqueous solutions). As the reactions proceeds, water concentration increases until a maximum in which its production by esterification is equal to its removal by pervaporation. After this maximum, water removal by pervaporation from the reaction mixture is faster than its formation and water concentration in the reactor decreases continuously. This behavior has been observed in the literature for other esterification reactions where the initial water content in the reactor was negligible [19].

The continuous lines in Figs. 8 and 9 correspond with the model proposed in the theory section. In this case, the kinetic parameters were taken from Asthana et al. [17] to characterize oligomers reactions. Predictions for component profiles show fairly good agreement with the experimental values except for the ethyl lactate dimer. Generally, deviations between experimental data and model calculations are bigger for lactic acid oligomers (HL_2 18%, HL_3 9%) and ethyl lactate dimmer (as big as 60%) than for the rest of the compounds. For ethyl lactate dimmer component big relative differences were observed between experimental and simulated results probably due to experimental errors in its determination since its weight fraction was very low in all cases.

4.3.1. Comparison of the three lactic acid aqueous solutions

For a better comparison of the esterification–pervaporation process for the different lactic acid aqueous solutions considered in this work, only simulation results are plotted in Fig. 10. The simulation conditions were set the same for the three cases: initial reactant molar ratio, $n_{EtOH}/n_{HL1} = 2$, amount of catalyst, 2 wt%, reaction and pervaporation temperature 348.15 K, and ratio membrane area to initial volume of reaction, $S/V_o = 23\ m^{-1}$. The main differences come from the fact that the initial water concentration in the reaction medium decreases as concentration of lactic acid aqueous

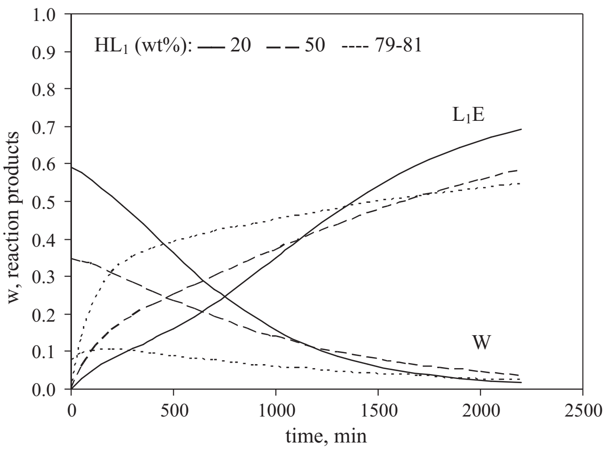


Fig. 10. Effect of lactic acid aqueous solution concentration on the performance of the esterification–pervaporation reactor: $n_{EtOH}/n_{HL1} = 2$, $T_{reaction,PV} = 348.15$ K, $A/V_o = 23\ m^{-1}$, catalyst = 2 wt%.

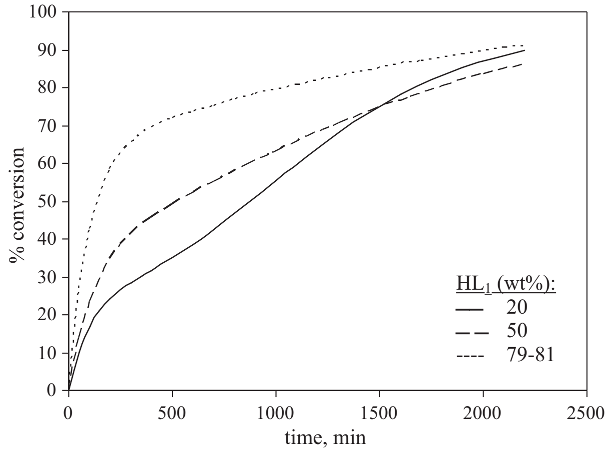


Fig. 11. Effect of lactic acid aqueous solution concentration on conversion for the esterification–pervaporation reactor: $n_{EtOH}/n_{HL1} = 2$, $T_{reaction,PV} = 348.15$ K, $A/V_o = 23\ m^{-1}$, catalyst = 2 wt%.

solution increases. This is the reason why different water profiles are observed in Fig. 10, since the higher the water concentration the larger the permeation rate through the membrane. As it was previously explained, even a maximum can be observed in the water profile corresponding to the 79–81 wt% lactic acid esterification. The initial water content in the reactor is also related to the esterification rate: initial reaction rate increases by decreasing the initial water content in the reactor. However, the final ethyl lactate concentration in the reactor will be higher for dilute lactic acid aqueous solutions since the permeability of lactic acid oligomers can be considered negligible.

In conventional esterification reactors, when water is present in the reactor, the thermodynamic equilibrium conversion will be decreased [19]. This can be appreciated during the early period of the reaction (Fig. 11). However, if the pervaporation aided-esterification process is carried out sufficiently long, the differences in conversion are minimized.

5. Conclusions

In this work, the integrated process esterification–pervaporation has been applied to lactic acid esterification with ethanol. The conversions achieved were distinctly higher than the equilibrium limited conversions reached in a conventional reactor, due to the selective removal of water from the reaction medium by pervaporation through PERVAP® 2201 membrane.

Combining esterification kinetic equations and permeation rates by pervaporation, a coupled esterification–pervaporation model has been proposed. Simulations based on this model are in good agreement with the experimental data obtained in this work. The right choice of the operating parameters has a great influence on the performance of this integrated process. Pervaporation and reaction rates are both increased with the operating temperature. The initial reactant molar ratio determines the final ethyl lactate concentration in the reactor. Obviously, when the A/V_o ratio increases, higher ester conversions are obtained. Finally, the effect of catalyst concentration has been found not to have a great influence for dilute lactic acid aqueous solutions esterification.

Since lactic acid is purchased as aqueous solutions, the effect of lactic acid concentration was analyzed. It has been shown that the initial water content in the reaction medium has a great influence in the performance of the process, since total permeation is proportional to water concentration in the reactor.

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