

ETHYL OLEATE PRODUCTION BY MEANS OF PERVAPORATION-ASSISTED ESTERIFICATION USING HETEROGENEOUS CATALYSIS

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Abstract - Pervaporation-assisted esterification of oleic acid and ethanol was investigated by means of heterogeneous acid catalysis with the aim of increasing the ethyl oleate yield. The experimental strategy comprised kinetic tests with Amberlyst 15 Wet (Rohm & Haas), the characterization of hydrophilic Pervap 1000 membrane (Sulzer) and the evaluation of the membrane-assisted reactor. Kinetic tests were carried out to study the effect of temperature, catalyst loading and ethanol/organic acid molar ratio for the esterification of oleic acid and ethanol. The ester yield and initial reaction rate were used as response. The hydrophilic poly(vinyl alcohol) membrane was able to remove water from the reaction medium and, hence, the ester yield was increased. The potential of coupling esterification and pervaporation was demonstrated, with a two-fold increase in the reaction yield of ethyl oleate.

Keywords: Pervaporation; Esterification; Heterogeneous catalysis; Oleic acid; Membrane-assisted reactor.

INTRODUCTION

The coupling of reaction and separation has become a current trend in the chemical industry in order to obtain more efficient processes and lower energy consumption. A classical example is the production of esters, which are traditionally obtained by reacting an organic acid and an alcohol in the presence of mineral acids, the homogeneous catalyst. A major drawback in such reactions is the limit established by the thermodynamic equilibrium, which requires the addition of a separation step to remove one of the products and, thus, shift the equilibrium towards the ester production (Lipnizki *et al.*, 1999). A large excess of one reactant leads to equilibrium displacement, although separation costs are increased. Distillation is industrially used to accomplish the separation of ethyl and propyl esters,

but trace water hydrolyses the product and decreases its purity, quality and usability (Wynn, 2001). Pervaporation, a membrane process, is one of the most promising approaches to perform this task because it allows a very selective water removal from the reaction medium combined with lower energy requirements (Néel, 1995). By comparing distillation and pervaporation-assisted processes, it was found that the latter decreases the energy input by 75%, with less than 50% in investment and operating costs (Waldburger and Widmer, 1996).

The application of pervaporation to reversible reactions such as esterification has been studied in a number of recent papers (Tanaka *et al.*, 2001; Gonçalves *et al.*, 2004; Benedict and Parulekar, 2006; Sanz and Gmehling, 2006) in which hydrophilic membranes are used to remove water and thereby increase the ester yield. To enhance the

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process efficiency, many efforts have been made to prepare membranes exhibiting higher selectivities, higher permeabilities and better chemical resistance (Yeom and Lee, 1996; Chemseddine and Audinos, 1996; Kita *et al.*, 1995; Shao and Huang, 2007). The development of more stable membranes is a challenge that must be faced in order to increase the industrial acceptance of pervaporation-based processes (Zhu *et al.*, 1996).

Homogeneous catalysts, such as the mineral acids used in esterification, usually cause corrosion problems. Moreover, the addition of a neutralization stage after the reaction is complete increases the operational costs and the catalyst consumption. In the last few years, ion exchange resins with strong acid sites and large specific area have proven to be an attractive alternative to the conventional catalysts. They have been used as acid catalysts in a large range of applications, allowing the use of milder conditions (Tesser *et al.*, 2005; Xu and Chuang, 1996; Pouilloux *et al.*, 1999). In addition, they can be regenerated and reused (Malshe and Sujatha, 1997). However, the application of these heterogeneous catalysts to the esterification of large chain organic acids is still scarce in the literature, especially for fatty acid esters.

Kita *et al.* (1988) studied the pervaporation-assisted esterification of acetic and oleic acids with ethanol using a poly(ether imide) membrane and *p*-toluene sulfonic acid as catalyst. Almost complete conversion was obtained. The hybrid process was also used to evaluate the reaction of propionic acid with 1-propanol and 2-propanol (David *et al.*, 1991 a and b). The results showed an increase from 70 to 90% in ester conversion at 323 K. The authors developed a mathematical model to address the effect of process parameters such as temperature, reactant molar ratios and membrane surface area to reaction volume ratio. Okamoto *et al.* (1993) investigated the ethyl oleate production with *p*-toluene sulfonic acid as catalyst and two kinds of hydrophilic non-porous membranes at temperatures above 360 K. The authors presented a model in which kinetic and permeation flux equations were combined. In a concise approach, Bagnell *et al.* (1993) proposed the esterification of acetic acid with *n*-butanol at room temperature using Nafion[®] tubes both as catalyst and pervaporation membrane. *N*-butyl acetate production was raised from 70 to 95% as a result of water removal.

Pervaporation-assisted lipase-catalyzed esterification of oleic acid has also been investigated (Kwon *et al.*, 1998; Kwon and Rhee, 1998; Dormo *et al.*, 2004). The enzyme has to be immobilized on an appropriate

support that retains the essential hydration shell of the lipase, which is one of the most difficult steps of the process. In addition, water and alcohol content can change the catalyst activity completely since lipase is very sensitive to these chemicals (Koszorz *et al.*, 2004).

Although an increase in ethyl oleate yield would appear to be a difficult task, the investigation of an alternative route to run the reaction is a current trend, specially when the application of the ester that is produced is considered. Besides being widely used as lubricants, ethyl and methyl esters of fatty acids have been increasingly used as biodiesel in order to replace the fossil fuels (Garcia *et al.*, 2008; Lopez *et al.*, 2008; Tapanes *et al.*, 2008). Much effort has been concentrated on the alkaline transesterification of vegetable oils in order to produce biodiesel (Cervero *et al.*, 2008). However, this route is technically and economically viable only when the free acid and moisture contents are low. In the case of vegetable oils used in frying processes, for example, the traditional route fails. Therefore, the investigation of an alternative route to decrease the free fatty acid and water contents of oils in the synthesis of biodiesel can make the process feasible and increase biodiesel availability and usability.

Hence, the aim of this work was the evaluation of the production of ethyl esters from oleic acid by pervaporation-assisted esterification, using a sulfonic acid resin as catalyst. The advantage of the coupled process is an increase in the ester yield under milder operating conditions. This is a strategic area, since it is one of the steps in the development of biodiesel. The synthesis of these high value-added fatty acid esters can provide economical benefits and environmental protection.

EXPERIMENTAL

Materials and Chemicals

Ethanol (99%, Vetec[®]) and oleic acid (77%, Merck[®]) were purchased and used without further purification. The organic acid impurities were other fatty acids of lower molecular weight. They were not expected to cause significant changes in either the catalytic activity or the permeation behavior. Amberlyst 15 Wet (A15), generously supplied by Rohm & Haas[®], and Pervap 1000 (Sulzer[®]) were used as catalyst and membrane, respectively. The hydrophilic membrane is based on a crosslinked poly(vinyl alcohol) layer coated onto a polyacrylonitrile substrate.

Kinetic Tests

Regarding the catalytic tests with oleic acid, the effect of temperature, A15 loading and reactant molar ratios on ester yield were addressed. The temperature was investigated from 323 to 343 K, while catalyst loading was varied from 20 to 60 g/L and ethanol/oleic acid molar ratio was studied from 0.5 to 2. A15 pre-conditioned in ethanol was also investigated. To perform this conditioning, catalyst beads were swollen in ethanol for 12 hours at room temperature. In order to compare different operating conditions, the corresponding equilibrium conversion was experimentally determined.

Membrane Characterization

The characterization of the commercial membrane was accomplished through pervaporation of equimolar mixtures of oleic acid/ethanol and oleic acid/ethanol/water. Equimolar mixtures have high acid content, which could damage the membrane due to the reaction between the fatty acid and the hydroxyl groups of PVA.

Tests were performed at 343 K during 4 hours. Feed samples were collected every hour for analysis, whereas permeate was withdrawn at the end of the experiment.

Pervaporation-Assisted Esterification

Pervaporation-assisted esterification of oleic acid and ethanol using A15 as catalyst was performed to investigate the increase in the ester yield as a result of water removal. Operational conditions of the coupled test were set at 333 K, 60 g/L of A15 and ethanol/oleic acid molar ratio of 6. Feed flow rate in the permeation

cell was 30 L/h and the ratio of membrane area to reaction volume was $0.18 \text{ cm}^2/\text{cm}^3$.

The experimental apparatus is schematically presented in Figure 1. Catalyst beads were added to the reactor in a kind of basket to avoid friction between them and the reaction vessel. The stirring speed in this vessel was 1400 rpm in all experiments. Feed was pumped from the reactor into the separation unit at a flow rate of 30 L/h. A 45 cm^2 area membrane was fixed in this unit. Retentate returned to the reactor. The entire system was thermally insulated, including the membrane cell. The temperature was measured inside the reactor and after the separation unit by a thermometer. The temperature difference was negligible. Liquid nitrogen (N_2) was used to recover permeate. The permeate pressure was lower than 3 mbar.

Chemical Analysis

The oleic acid content was determined by potentiometric titration according to the ASTM D664 method. The sample was dissolved in a solution of toluene, isopropyl alcohol and water and titrated with alcoholic potassium hydroxide using a Mettler Toledo® DL 50 automatic titrator, with a DG 113 glass electrode. In the catalytic tests, ethanol, ethyl oleate and water contents were quantified by a material balance based on the consumption of oleic acid. The water and ethanol concentrations in the permeate were measured by gas chromatography on a CP-Poraplot-Q® column ($10 \text{ m} \times 0.32 \text{ mm} \times 10 \mu\text{m}$) with helium as the carrier gas. The adopted conditions were: oven temperature 423 K, injector and detector temperatures 473 K, column pressure 30 kPa, carrier flow rate 1.5 mL/min. Ethyl oleate content in the permeate stream was neglected.

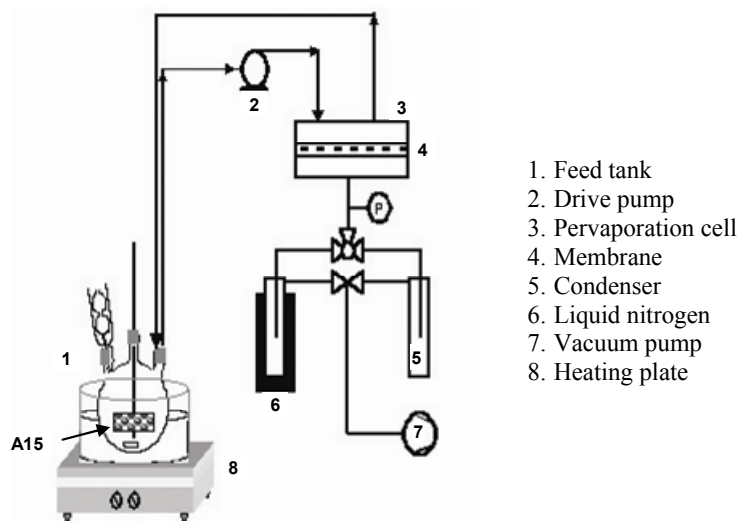


Figure 1: Experimental apparatus for pervaporation-assisted esterification test.

RESULTS AND DISCUSSION

Membrane Characterization

Pervaporation tests were conducted to evaluate the performance of Pervap 1000 with the acid solution. The oleic acid concentration profile in the feed mixture as a function of time is presented in Figures 2 and 3 for the oleic acid/ethanol and oleic acid/ethanol/water solutions, respectively. The operating conditions were 343 K, no catalyst, equimolar ratio between the chemicals, membrane surface to solution volume ratio of $0.23 \text{ cm}^2/\text{cm}^3$, feed flow rate equal to 30 L/h.

It could be seen that the oleic acid concentration decreased with time for the system without added water (Figure 2). This can be understood in terms of the reaction of the free fatty acid with ethanol, since the content of oleic acid in the permeate was low. On the other hand, for the ternary system, oleic acid/ethanol/water, the organic acid concentration increased with time. This behavior was ascribed to water permeation through the membrane, as the latter was hydrophilic. Although just a slight difference in acid concentration was observed in the feed — the values changed within 0.1-0.2 mol/L —, the tendency was clearly present. Total fluxes and permeate chemical composition for both systems are presented in Table 1. Since there was no chemical affinity between ethyl oleate and the membrane, the permeation rate of this ester was negligible.

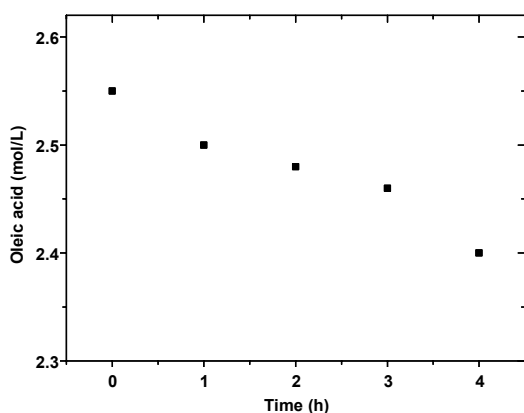


Figure 2: Oleic acid concentration as a function of time in the pervaporation feed stream for an ethanol/oleic acid equimolar mixture.

For the mixture of oleic acid and ethanol, it could be seen that water constituted 99.6 wt.% of the permeate and the oleic acid concentration was just 0.3 wt.%, which indicated that oleic acid did not permeate significantly through the membrane, but rather reacted with ethanol to form ethyl oleate and water. In other words, 8% of the oleic acid was converted into ester as a result of the water removal by pervaporation, even without catalyst. This result clearly showed the effect of pervaporation, since no reaction was observed for the system without this separation step under the same operating conditions.

For the oleic acid/ethanol/water system, however, the oleic acid concentration increases with time because water was preferentially removed from feed stream. No reaction was observed probably due to the negative effect of the large water excess in the feed stream.

Upon analysing Table 1, one can observe that the permeate flux was significantly increased by water addition to the system. It was also noticeable that the presence of water on the feed side changed the permeate composition. More specifically, water increased ethanol permeation and reduced the oleic acid transport through the membrane. This could be explained by the swelling of the membrane in water, which probably favored ethanol permeation by a drag effect. The evidence for such a phenomenon was the ratio between water and ethanol in the permeate for the oleic acid/ethanol and oleic acid/ethanol/water systems, 830 and 31, respectively.

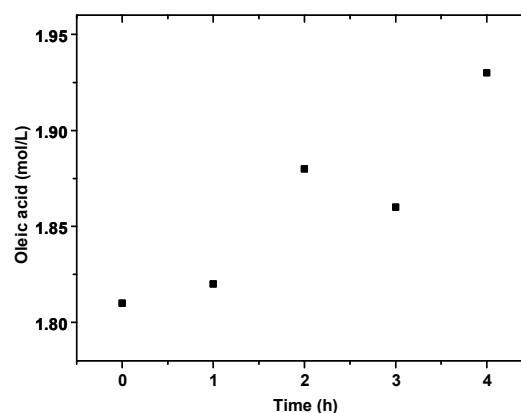


Figure 3: Oleic acid concentration as a function of time in the pervaporation feed stream for an ethanol, oleic acid and water equimolar mixture.

Table 1: Permeate flux and chemical composition in pervaporation tests.

System	Total flux ($\text{g}/\text{m}^2 \cdot \text{h}$)	Permeate chemical composition (wt. %)		
		Water	Ethanol	Oleic acid
Oleic acid/ethanol	30	99.55	0.12	0.33
Oleic acid/ethanol/water	110	96.91	3.08	< 0.01

At the end of the experiments, no visible degradation of Pervap 1000 was observed and the membrane retained its good transport and selectivity properties. The permeate flux of a water/ethanol mixture 5:95 in weight was 215 g/h.m², with a selectivity of 120 at 25°C and 4 hours. This indicated that the membrane can still be used to remove water from the reaction medium.

Kinetic Tests for Oleic Acid

Catalytic tests were performed in order to evaluate the kinetics of the oleic acid esterification. Tests conducted at 303 K showed no reaction during the 4 hours of the experiment. Thus, the temperature range was increased, taking into account the fact that fatty acids usually decompose at relatively low temperatures. For oleic acid, the limiting temperature is 353 K (Weast, 1985). The effects of A15 loading and conditioning in ethanol, as well as the reactant molar ratio, were also evaluated in order to identify the best operating condition to perform the pervaporation-assisted esterification tests.

Ethanol Conditioning of A15

Since the reaction rate at 303 K was nil, tests were carried out with A15 pre-conditioned in ethanol for 12 hours to verify whether the adsorbed water could reduce the catalyst activity. It should be pointed out that the catalyst was used in its wet form, in which the water content was 50.3 wt%. The evolution of the ethyl oleate conversion with time using A15 pre-conditioned in ethanol is presented in Figure 4. This run was performed with 20 g/L of A15. The dashed line corresponds to the equilibrium conversion.

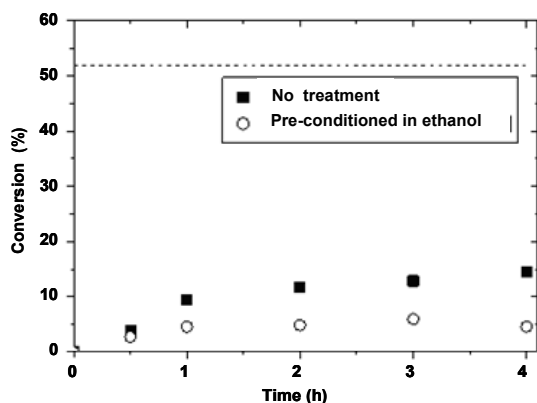


Figure 4: Amberlyst 15 pre-conditioned in ethanol. Operating conditions: temperature = 343 K, A15 = 20 g/L, molar ratio ethanol/oleic acid = 1.

The ethyl oleate conversion systematically decreased with the alcohol-conditioned A15 catalyst. This behavior can be understood in terms of preferential adsorption of ethanol onto catalytic sites and the consequent spatial exclusion of oleic acid, thereby reducing A15 activity. This result is in agreement with the literature (Pouilloux *et al.*, 1999), in which an ion exchange resin swollen in glycerol and oleic acid was used and higher activity and selectivity were found for the free fatty acid.

Since the activity of A15 decreased in alcoholic medium, further experiments were conducted with the catalyst in its wet form. Even though this condition may be worse than with dry resin, since water can decrease the reaction rates, it was chosen here because the swelling in oleic acid must be slower than in ethanol.

Reactant Molar Ratio

The effect of ethanol/oleic acid molar ratio on the ester conversion is presented in Figure 5. The molar ratio was varied from 0.5 to 2 in order to evaluate the behavior of the excess of one of the reactants on the reaction rate. It is well known that the addition of an excess of reactant, usually the alcohol, can displace the equilibrium of esterification reactions.

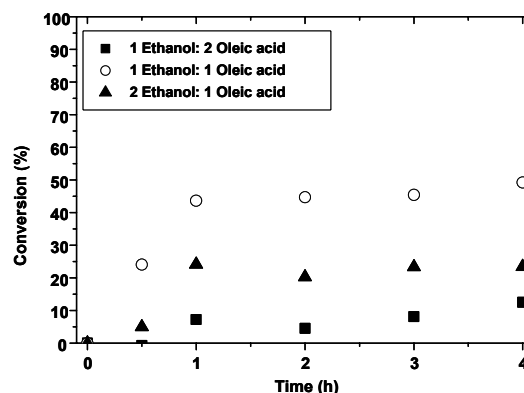


Figure 5: Ethanol/oleic acid molar ratio effect on ethyl oleate conversion. Operating conditions: temperature = 343 K, A15 = 40 g/L.

Within the range investigated, an equimolar ratio led to the highest conversion. This was not expected, since most of esterification systems show an increase in reaction rate when a large excess of one reactant is used (Wynn, 2001). However, in this case, an excess of oleic acid probably caused resistance of the reactants to the catalyst surface, since the medium viscosity was very high, whereas an excess of

ethanol decreased catalytic activity, because it was preferentially adsorbed onto the sites.

Taking into account the results obtained for the ethanol-conditioned catalyst and the reactant molar ratio, there seems to be a competition of the organic acid and the alcohol for the catalytic sites. This provides some insight about the reaction mechanism, suggesting that both reactants should be adsorbed on the catalyst surface. As a result, an equimolar alcohol to acid ratio would represent the fastest reaction kinetics, which is very interesting economically, since no excess reagent must be recovered at the end of the process. Based on these results, the catalytic tests to address the effect of A15 loading and temperature were investigated for an equimolar reactant ratio.

Catalyst Loading

The catalyst loading effect was evaluated from 20 to 60 g/L at 343 K with an equimolar ratio between reactants. The results are presented in Figure 6, in which the dashed line corresponds to equilibrium conversion, which was experimentally determined.

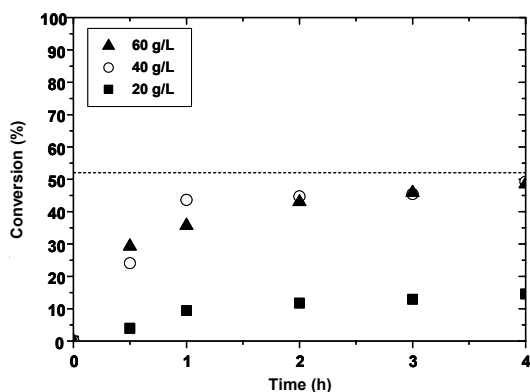


Figure 6: Effect of A15 load on ethyl oleate yield. Operating conditions: temperature = 343 K, molar ratio ethanol/oleic acid = 1.

When the catalyst loading was varied from 20 to 40 g/L, the ester conversion increased as a result of the higher amount of acid sites to drive the reaction. However, further increase in A15 to 60 g/L did not bring about any changes in the ester yield. Perhaps this result can be explained by the existence of mass-transfer resistance to adsorption of the chemicals on the catalyst surface, which was the limiting rate of the process. Another explanation for the results is the increase in the initial water content in the reaction mixture. Since water is one of the products of the

reversible reaction, the increase in its initial concentration, due to the higher catalyst loading, caused the reaction to be slower.

The investigation of better catalysts and the improvement of the hydrodynamic conditions could lead to an increase in the reaction rate. However, this was beyond the scope of the present study.

Temperature

The effect of the temperature on ethyl oleate yield was investigated from 323 to 343 K. The temperature range was limited because no reaction was observed below 313 K or above 353 K, where the fatty acid decomposes at atmospheric pressure. The results are presented in Figure 7.

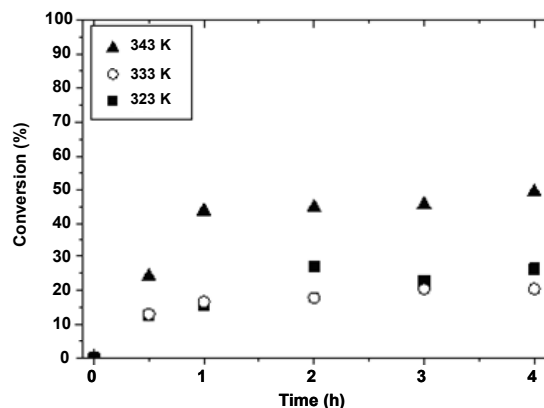


Figure 7: Temperature effect on the ethyl oleate yield. Operating conditions: A15 = 40 g/L, molar ratio ethanol/oleic acid = 1.

The ester yield was very similar for 323 and 333 K, which can be ascribed to the quite low reaction rates and the small difference between the temperatures. As the consequence, the experimental deviation was probably very high and the effect of a temperature increase from 323 to 333K was not observed. However, when the temperature was raised to 343 K, the ester conversion increased significantly. These results can be explained by the hydrodynamic conditions of the reacting medium. The increase in temperature favored the diffusivity of the reactants, causing higher ester yields.

The apparent activation energy for the system was estimated to be 5.8 kcal/mol, assuming the validity of the Arrhenius equation. The value is very low, especially when compared to that reported in the literature for the same system (Okamoto *et al.*, 1993), namely, 15 kcal/mol. This is further evidence that, under these operating conditions, the esterification was diffusion-limited.

Although the heterogeneous-catalysed esterification reaction has been intensively studied, the mechanism by which the reaction proceeds is still a controversial matter. Common kinetic models used to describe the catalytic data comprise the pseudo-homogeneous approach as well as the Eley-Rideal theory (Liu *et al.*, 2006). Because our purpose was the investigation of the coupled system, no attempts to adjust a model were made.

Based on the previous results and assuming that there are no interactions between the variables investigated, the best operational conditions were 343 K, 40 g/L of A15 and an equimolar ratio of the reactants. Attempts to improve reaction rates further may still be useful since there is a trade-off within the range of each variable. For instance, an increase in temperature may cause acid degradation; the use of higher loads of A15 proved to be inefficient, and an excess of one reactant decreases reaction rates. The investigation of the stirring speed would be another choice, especially to verify the range of the diffusion-limited system. However, as our purpose here was the evaluation of the coupled system, such approaches were not tested here.

Pervaporation-Assisted Esterification

The effect of water removal on the ethyl oleate yield was investigated by coupling a pervaporation unit with the reactor. Initially, the operating condition used was an equimolar ratio of reactants at 343 K. The A15 loading was varied from 20 to 60 g/L. However, no increase in the ethyl oleate yield was observed. The most plausible explanation for these results was the evaporation and loss of ethanol from the feed stream.

Alternatively, new tests were performed at an

ethanol/oleic acid ratio equal to 6, in order to avoid a high viscosity of the feed solution, and a temperature of 333 K, to minimize evaporation losses. The ester yields for the experiments with and without the pervaporation step are presented in Figure 8.

At the beginning of the test, it was observed that the conversion degree was lower in the coupled system. This might be explained by ethanol swelling and permeation through the commercial membrane, which significantly changes the alcohol/oleic acid ratio. However, ester conversion increased and surpassed the equilibrium limit as a result of water removal. Ethyl oleate conversion reached 50% in 24 hours, a value that is two fold higher than the equilibrium value (23%). At times longer than 24 h, it was not possible to increase the ester yield further because the reaction rate was very slow, as evidenced by the fluxes shown in Figure 9.

As expected, the water permeation flux decreases with time on account of the decreasing driving-force, but ethanol and oleic acid fluxes were almost constant. Pervap 1000 membrane showed good selectivity to water when exposed to the reaction mixture. As a result, it can be clearly seen that the pervaporation-assisted reactor increased the ester yield two-fold, which evidences the potential application of the technique.

It is worth noting that the operating conditions used in this work were milder than the ones commonly used in the literature, in which supercritical CO₂, organic solvents and higher temperatures are commonly adopted (Isayama and Saka, 2008; Izci and Bodur, 2007). Our alternative route to decrease the free fatty acid and moisture content of vegetable oils showed the feasibility of ethyl oleate production at 333 K and atmospheric pressure.

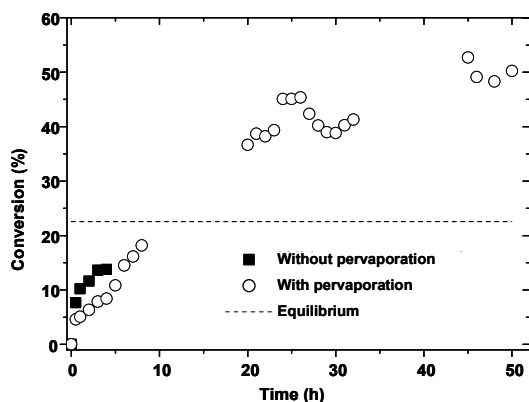


Figure 8: Comparison between ethyl oleate yields for the reaction with and without pervaporation. Operating conditions: temperature = 333 K, A15 = 60 g/L, ethanol/oleic acid molar ratio = 6, S/V = 0.18 cm²/cm³, feed flow rate = 30 L/h.

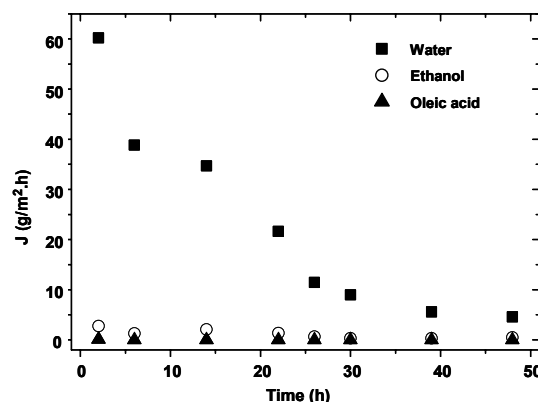


Figure 9: Oleic acid, ethanol and water fluxes as a function of time for the pervaporation-assisted reactor.

It should be pointed out that an increase in the ratio between membrane area and reaction volume could impart higher conversion values, since this parameter affects the rates of water production and removal from the reacting mixture. The investigation of better conditions to perform the pervaporation-assisted esterification of oleic acid and ethanol can make the use of this alternative route for the synthesis of biodiesel feasible.

CONCLUSION

The Pervap 1000 membrane showed high selectivity to water in the ethanol/oleic acid/water/ethyl oleate system. Pervaporation of the oleic acid/ethanol mixture showed that 8% of the acid was converted into ethyl oleate as a result of water removal, since there was no reaction without pervaporation.

Amberlyst 15 Wet has proven to be a good catalyst for esterification of oleic acid and ethanol. However, the study of better hydrodynamic conditions to perform the reaction between oleic acid and ethanol could increase the reaction rate.

The coupling of pervaporation with the esterification reaction was an efficient method for shifting the equilibrium towards ethyl oleate production. In fact, the ester yield was raised by a factor of two, surpassing the equilibrium limit. These results indicated that the hybrid process is a promising technique and can potentially be used to drive esterification under mild operating conditions. Concerning the synthesis of biodiesel, the coupled system can be used as a pre-treatment stage or even as an alternative to transesterification when the free-fatty acid and water contents of vegetable oils are high.

ACKNOWLEDGEMENTS

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NOMENCLATURE

A15	Amberlyst 15 Wet (Rohm & Haas), used as acid catalyst
Pervap 100	Poly(vinyl alcohol) hydrophilic membrane (Sulzer)
J	Flux through the membrane, in g/h.m ²

REFERENCES

- Bagnell, L., Cavel, K., Hodges, A. M., Mau, A. W. H., Seen, A. J., The use of catalytically active pervaporation membranes in esterification reactions to simultaneously increase product yield, membrane permselectivity and flux. *Journal of Membrane Science*, 85, No. 3, 291 (1993).
- Benedict, D. J., Parulekar, S. J., Pervaporation-assisted esterification of lactic and succinic acids with downstream ester recovery. *Journal of Membrane Science*, 281, No. 1-2, 435 (2006).
- Cervero, J. M., Coca, J., Luque, S., Production of biodiesel from vegetable oils. *Grasas y Aceites*, 59, No. 1, 76 (2008).
- Chemseddine, B., Audinos, R., Use of ion-exchange membranes in a reactor for esterification of oleic acid and methanol at room temperature. *Journal of Membrane Science*, 115, No. 1, 77 (1996).
- David, M. O., Gref, R., Nguyen, T. Q., Neel, J., Pervaporation-esterification coupling, part I: basic kinetic model, *Chemical Engineering Research and Design*, 69, No. 4, 335 (1991a).
- David, M. O., Nguyen, T. Q., Neel, J., Pervaporation-esterification coupling, part II: modelling of the influence of different operating parameters. *Chemical Engineering Research and Design*, 69, No. 4, 341 (1991b).
- Dormo, N., Belafi-Bako, K., Bartha, L., Ehrenstein, U., Gubicza, L., Manufacture of an environmental-safe biolubricant from fused oil by enzymatic esterification in solvent-free system. *Biochemical Engineering Journal*, 21, No. 3, 229 (2004).
- Garcia, C. M., Teixeira, S., Marciniuk, L. L., Schuchardt, U., Transesterification of soybean oil catalyzed by sulfated zirconia. *Bioresource Technology*, 99, No. 14, 6608 (2008).
- Goncalves, F. D., Borges, L. E. P., Borges, C. P., Synthesis of ethyl acetate by coupling a heterogeneous catalytic system with a pervaporation unit. *Separation Science and Technology*, 39, No. 7, 1485 (2004).
- Figueiredo, K. C. S., Study on pervaporation-assisted catalytic esterification of organic acids. M. Sc. Dissertation, Federal University of Rio de Janeiro (2004).
- Isayama, Y., Saka, S., Biodiesel production by supercritical process with crude bio-methanol prepared by wood gasification. *Bioresource Technology*, 99, No. 11, 4775 (2008).
- Izci, A., Bodur, F., Liquid-phase esterification of acetic acid with isobutanol catalyzed by ion-exchange resins. *Reactive & Functional Polymers*, 67, No. 12, 1458 (2007).

- Lipnizki, F., Field, R. W., Ten, P. K., Pervaporation-based hybrid process: a review of process design, applications and economics. *Journal of Membrane Science*, 153, No. 2, 183 (1999).
- Liu, Y. J., Lotero, E., Goodwin Jr., J. G., A comparison of the esterification of acetic acid with methanol using heterogeneous versus homogeneous acid catalysis. *Journal of Catalysis*, 242, No. 2, 278 (2006).
- Lopez, D. E., Goodwin, J. G., Bruce, D. A., Furuta, S., Esterification and transesterification using modified-zirconia catalysts. *Applied Catalysis A-General*, 399, No. 1, 76 (2008).
- Kita, H., Horii, K., Ohtoshi, Y., Tanaka, K., Okamoto, K. I., Synthesis of a zeolite NaA membrane for pervaporation of water-organic liquid-mixtures. *Journal of Materials Science Letters*, 14, No. 3, 206 (1995).
- Kita, H., Sasaki, S., Tanaka, K., Okamoto, K.-i., Yamamoto, M., Esterification of carboxylic acid with ethanol accompanied by pervaporation. *Chemical Letters*, 12, 2025 (1988).
- Koszorz, Z., Nemesothy, N., Ziobrowski, Z., Belafibako, K., Krupiczka, R., Influence of pervaporation process parameters on enzymatic catalyst deactivation. *Desalination*, 162, No. 1-3, 307 (2004).
- Kwon, S. J., Rhee, J. S., On-off dewatering control for lipase-catalyzed synthesis of n-butyl oleate in n-hexane by tubular type pervaporation system. *Journal of Microbiology and Biotechnology*, 8, No. 2, 165 (1998).
- Kwon, S. J., Song, K. M., Hong, W. H., Rhee, J. S., Removal of water produced from lipase-catalysed esterification in organic solvent by pervaporation. *Biotechnology and Bioengineering*, 46, No.4, 393 (1995).
- Malshe, V. C., Sujatha, E. S., Regeneration and reuse of cation-exchange resin catalyst used in alkylation of phenol. *Reactive and Functional Polymers*, 35, No.3, 159 (1997).
- Néel, J., Pervaporation, in Noble, R. W., Stern, S. A. (eds.), *Membrane Separations Technology: Principles and Applications*. Vol. 2, Elsevier, New York, p. 143 (1995).
- Okamoto, K.-i., Yamamoto, M., Otoshi, Y., Semoto, T., Yano, M., Tanaka, K., Kita, H., Pervaporation-aided esterification of oleic acid. *Journal of Chemical Engineering of Japan*, 26, No. 5, 475 (1993).
- Pouilloux, Y., Abro, S., Vanhove, C., Barrault, J., Reaction of glycerol with fatty acids in the presence of ion-exchange resins – preparation of monoglycerides. *Journal of Molecular Catalysis A: Chemistry*, 149, No. 1-2, 243 (1999).
- Sanz, M. T., Gmehling, J., Esterification of acetic acid with isopropanol coupled with pervaporation, part I: kinetics and pervaporation studies. *Chemical Engineering Journal*, 123, No.1-2, 1 (2006).
- Shao, P., Huang, R. Y. M., Polymeric membrane pervaporation. *Journal of Membrane Science*, 287, No. 2, 162 (2007).
- Tanaka, K., Yoshikawa, R., Ying, C., Kita, H., Okamoto, K.-i., Application of zeolite membranes to esterification reactions. *Catalysis Today*, 67, No. 1-3, 121 (2001).
- Tapanes, N. C. O., Aranda, D. A. G., Carneiro, J. W. D., Antunes, O. A. C., Transesterification of *Jatropha curcas* oil glycerides: theoretical and experimental studies of biodiesel reaction. *Fuel*, 87, No. 10-11, 2286 (2008).
- Tesser, R., Di Serio, M., Guida, M., Nastasi, M., Santacesaria, E., Kinetics of oleic acid esterification with methanol in the presence of triglycerides. *Industrial Engineering Chemistry Research*, 44, No. 21, 7978 (2005).
- Waldburger, R. M., Widmer, F., Membrane reactors in chemical production processes and the application to the pervaporation-assisted esterification. *Chemical Engineering Technology*, 19, No. 2, 117 (1996).
- Weast, R. C., *Handbook of chemistry and physics*. CRC Press Inc., Boca Raton (1985).
- Wynn, N., Pervaporation comes of age. *CEP Magazine*, 97, No. 10, 66 (2001).
- Xu, Z. P., Chuang, K. T., Kinetics of acetic acid esterification over ion exchange catalysts. *The Canadian Journal of Chemical Engineering*, 74, No.4, 493 (1996).
- Yeom, C., Lee, K., Pervaporation separation of water-acetic acid mixtures through poly(vinyl alcohol) membranes crosslinked with glutaraldehyde. *Journal of Membrane Science*, 109, No. 2, 257 (1996).
- Zhu, Y., Minet, R. G., Tsotsis, T. T., A continuous pervaporation membrane reactor for the study of esterification reaction using a composite polymeric/ceramic membrane. *Chemical Engineering Science*, 51, No. 17, 4103 (1996).