CHEMISTRY LETTERS, pp. 2053-2056, 1987.

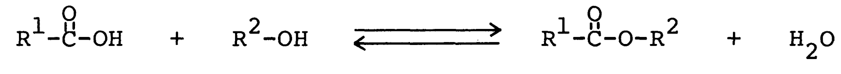
The Esterification of Oleic Acid with Ethanol Accompanied by Membrane Separation

Hidetoshi KITA, Kazuhiro TANAKA, Ken-ichi OKAMOTO,
and Masuji YAMAMOTO†

Department of Chemical Engineering, Faculty of Engineering,
Yamaguchi University, Ube, Yamaguchi 755
†Nippon Seiro Co., Ltd, Tokuyama, Yamaguchi 745

The use of water-permeable membranes for gas separation in the esterification of oleic acid with ethanol was studied. The perfect conversion due to the equilibrium shift was obtained by using a polyimide membrane for removal of water vapor generated by the esterification.

The esterification of carboxylic acids with alcohols is a reversible reaction and equilibrium ratio of reaction products to reactants in the reaction mixture is established. The reaction can be driven to the right hand side by addition of one of the reactants in excess or by removal of water formed. In practice, a large excess of alcohol has been used to shift the equilibrium in favor of the ester synthesis and to improve the efficiency of conversion of acid to ester. The use of membranes for removal of water resulting in favorable chemical equilibrium shift has not been reported except those in two patents,1,2) in which pervaporation was used as a membrane separation system.



$$R^1\text{-}\overset{\overset{O}{\|}}{C}\text{-OH} \;+\; R^2\text{-OH} \;\rightleftarrows\; R^1\text{-}\overset{\overset{O}{\|}}{C}\text{-O-}R^2 \;+\; H_2O$$

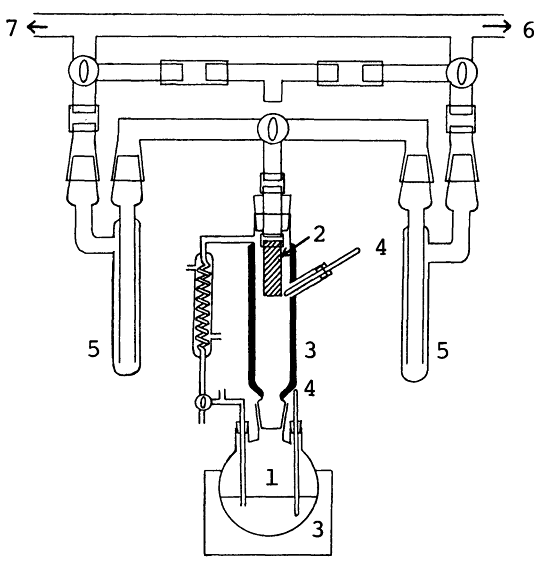


Fig. 1. A schematic diagram of the experimental apparatus: (1) reaction cell, (2) membrane, (3) heater, (4) thermometer, (5) cold trap, (6) vacuum pump, (7) pirani gauge.

In this paper, the use of water-permeable membranes for gas separation in the esterification of oleic acid with ethanol has been studied in order to shift the equilibrium and increase the conversion of the esterification by removal of water vapor from the gaseous mixture consisting of alcohol and water.

The esterification of oleic acid with ethanol accompanied by membrane separation was carried out using the apparatus depicted in Fig. 1. A porous ceramic tubing where an average pore diameter was 1 μm and the dimensions were 1 cm in diameter, 0.1 cm in thickness and 10 cm in length was used as the substrate to support a membrane. The ceramic tubing was coated with alumina membrane prepared from the hydrolyzate of aluminum isopropoxide by the sol-gel method3,4) in order to obtain the microporous structure on its outer surface. The pore size distribution of the microporous membrane determined by the BET method3) had a peak at around 2 nm pore diameter. The ceramic tubing was dipped in the solution of perfluorinated ion-exchange resin (Nafion 117), chitosan (FLONAC #250), or polyimide (Ultem). The solution coated on the ceramic tubing was dried in vacuum for one day at 65 °C. A mixture of oleic acid and ethanol with a catalytic amount of p-toluenesulfonic acid was fed to the reaction cell. The molar ratio of ethanol to oleic acid was 2:1 or 3:1. Gaseous mixture of ethanol and water generated by the esterification was refluxed and the inside of the membrane module was evacuated (13.3 Pa). The permeated gaseous mixture was collected by a trap in liquid nitrogen. The composition of the permeate was analyzed by gas chromatography. The amount of oleic acid was titrated according to the testing method for acid value of fats and oils (JIS-K-3504) and that of ethyl oleate was determined by liquid chromatography. The measurements of water vapor sorption by polyimide films were carried out at 50 °C according to the weighing method by use of the sorption apparatus equipped with a quartz spring.5)

Table 1 shows the permeation rate and separation factor of the coated membranes for the liquid mixture of water and ethanol at 85 °C. When coating time increases,

Table 1. Permeation rate (Q) and separation factor (α) of the coated membranes for water 10 mol%-ethanol 90 mol% mixture at 85 °C

Membranes	Coating times	Q kg m^{-2} h^{-1}	αa)
Polyimide Ab)	1	0.02	440
Bc)	1	1.43	6
Cc)	2	0.17	82
Chitosan	2	3.53	2
	4	0.38	12
Nafion 117	3	10.6	2
	6	4.6	3

a) Defined as concentration ratio $Y_{water}/Y_{ethanol}$ in the permeate divided by the ratio $X_{water}/X_{ethanol}$ in the feed liquid.
b) and c) Dipped in dichloroethane solution at the polyimide concentration of 8 wt% and 4 wt%, respectively.

Table 2. Permeability(P), diffusivity(D), and solubility(S) coefficients of water vapor in and through polyimide films at 50 °Ca)

Polyimide films	Supplier	Pb) 10^{-10} cm^3(STP) cm^{-1} s^{-1} cmHg^{-1}	D 10^{-8} cm^2 s^{-1}	S cm^3(STP) cm^{-3} cmHg^{-1}
Kapton-H	Du Pont	419 (5.66)	0.835 (205)	4.99 (2.76x10^{-4})
Upilex-R	Ube Ind.	180 (3.64)	0.622 (251)	2.90 (1.45x10^{-4})
Ultem	General Electric	502 (14.9)	2.20 (365)	2.28 (4.08x10^{-4})
LARC-TPI	Mitsui-Toatsu	353	0.624	5.70

a) Values in parentheses are those of H_2 at 80 °C.6)
b) Calculated from the relation of P=D·S .

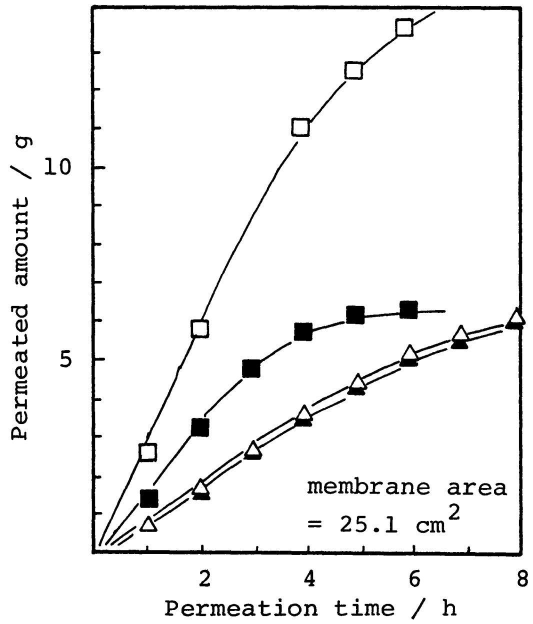


Fig. 2. The permeation behavior of two types of membranes (□,■; membrane B and △,▲; membrane C) in the esterification of oleic acid with ethanol at the molar ratio of 1:2 at 85 °C: (open symbols) total amount of the permeate and (closed symbols) permeated amount of water.

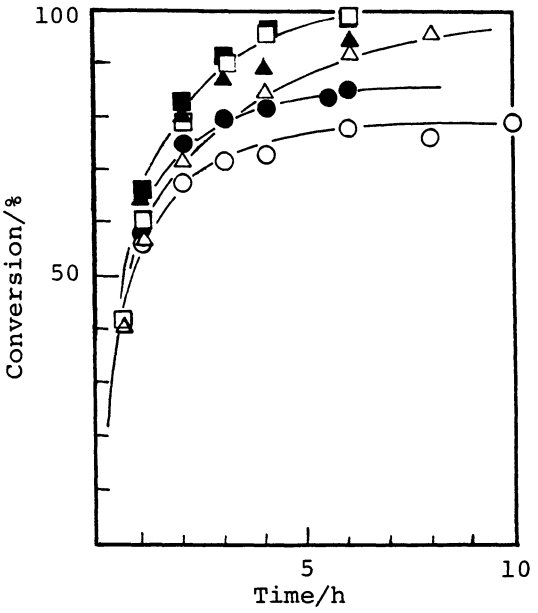


Fig. 3. Effect of membrane separation on the conversion of the esterification of oleic acid with ethanol at the molar ratio of 1:2 (open symbols) and 1:3 (closed symbols) at 85 °C: (○,●) without permeation, (□,■) membrane B, and (△,▲) membrane C.

separation factor increases but permeation rate decreases. This suggests that the pores of the microporous substrate are covered with the coated membrane and pinhole-free membrane is formed with increasing coating times. Among these water-permeable membranes, polyimide shows the highest selectivity. Permeability, diffusivity, and solubility of water vapor in and through commercially available polyimide films determined at 50 °C by the sorption measurements are listed in Table 2. Polyimide films have high permeability of water vapor in comparison with that of H_2, which can be attributed to large solubility coefficient of water vapor. It is well known that polyimide films are thermally and chemically stable. Thus, they seem to be useful in the application to the separation of the gaseous mixture generated by the esterification because of high selectivity and high-temperature stability.

In this study, two different types of polyimide membranes, i.e., membrane B and C in Table 1, were employed. The membrane B seems to have a large number of pinhole judging from high permeability and low selectivity as shown in Table 1. The permeation behavior through the two types of membranes during the course of the esterification of oleic acid with ethanol is shown in Fig. 2. For the membrane B, both water and ethanol vapor can permeate through the membrane and the permeation rate is relatively high. On the other hand, for the membrane C, water vapor can permeate specifically at the lower permeation rate than for the

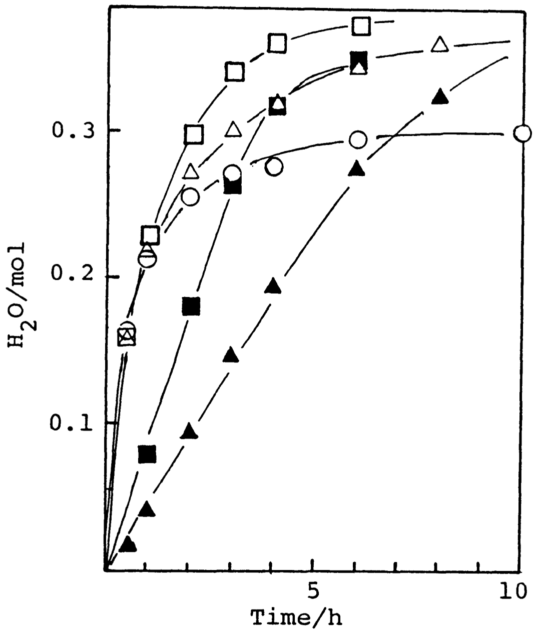


Fig. 4. Amounts of water generated by the esterification (open symbols) and those of permeated water (closed symbols) during the course of reaction: (○) without permeation, (□,■) membrane B, and (△,▲) membrane C.

membrane B. The permeated amount of water becomes constant at about 6 and 10 hours for the membrane B and C, respectively, which suggests that all of the oleic acid was esterified and a large portion of water generated by the esterification was permeated until that time. Figure 3 shows the effect of membrane separation on the conversion of oleic acid to the ester at two different molar ratios. It is evident that the removal of water by permeation shifts the equilibrium in favor of the ester formation and a conversion greater than the equilibrium value without permeation can be obtained. Changes in conversion with varying the membrane performance are also clear as shown in Fig. 3. For the case of the permeation through the membrane B, 100% conversion was obtained at about 6 hours, while for the case of C, additional time for separation was needed. Figure 4 shows the performance of two different membranes. For the case of B, amounts of water generated by the esterification rapidly increases with an increase of permeated water because of the equilibrium shift due to removal of water. For the case of C, the rate of equilibrium shift is less than that for the case of B because of the low permeation rate (Table 1), although there is no appreciable loss of ethanol due to permeation in this case.

These results suggest that if the permeation conditions are properly chosen, the perfect conversion due to the equilibrium shift can be obtained in the esterification accompanied by membrane separation. Thus, the use of membrane for separation of a reaction product in a reversible reaction seems to be an attractive method to increase the conversion of the reversible reaction resulting in a considerable reduction in the reaction time and the saving of reactants.

References

1) J. F. Jennings and R. C. Binning, U. S. Patent 2956070 (1960).
2) G. K. Pearce, Eur. Pat. Appl. EP 210055 (1987).
3) B. E. Yoldas, Am. Ceram. Soc. Bull., 54, 286 and 289 (1975).
4) B. E. Yoldas, J. Mater. Sci., 10, 1856 (1975).
5) J. Crank, "The Mathematics of Diffusion," 2nd ed, Clarendon, Oxford (1975), Chap. 10.
6) K. Tanaka, O. Yokoshi, H. Kita, and K. Okamoto, Polymer Preprints Jpn., 35, 2054 (1986).

(Received July 8, 1987)