# The Esterification of Oleic Acid with Ethanol Accompanied by Membrane Separation

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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

$$R^1-\overset{O}{\overset{\|}{C}}-OH \quad + \quad R^2-OH \quad \rightleftarrows \quad R^1-\overset{O}{\overset{\|}{C}}-O-R^2 \quad + \quad H_2O$$
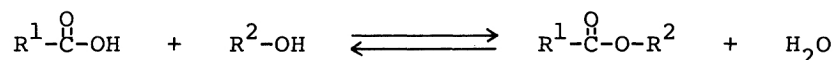
one of the reactants in excess or by removal of water formed. In practice, a large
excess of alcohol has been used to shift
the equilibrium in favor of the ester
synthesis and to improve the efficiency
of conversion of acid to ester. The use
of membranes for removal of water result-
ing in favorable chemical equilibrium
shift has not been reported except those
in two patents,[1,2] in which pervaporation
was used as a membrane separation system.

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
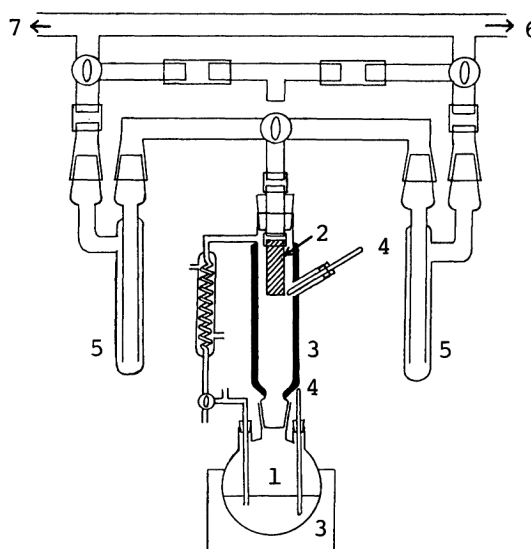ethanol accompanied by membrane separation

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.

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 method[3,4] in order to obtain
the microporous structure on its outer surface. The pore size distribution of the
microporous membrane determined by the BET method[3] 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

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 $kg\ m^{-2}h^{-1}$	α [a]
Polyimide A[b]	1	0.02	440
B[c]	1	1.43	6
C[c]	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.

permeated gaseous mixture was col-
lected 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 2. Permeability(P), diffusivity(D), and solubility(S) coefficients of
water vapor in and through polyimide films at 50 °C[a]

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

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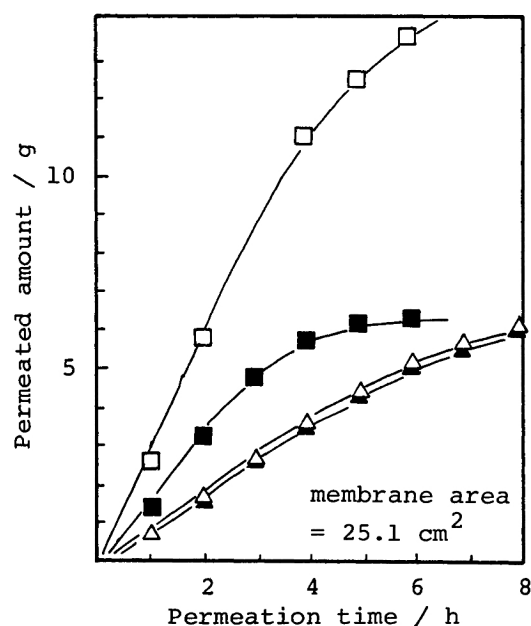b) Calculated from the relation of P=D·S .

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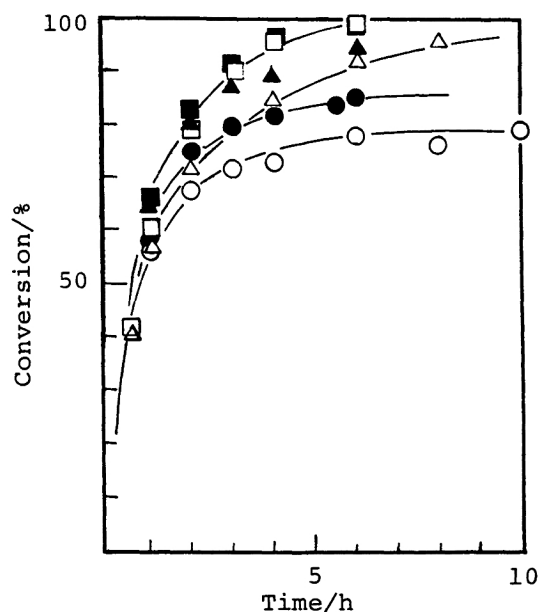permeate and (closed symbols) per-
meated amount of water.

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:(○,●) with-
out 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
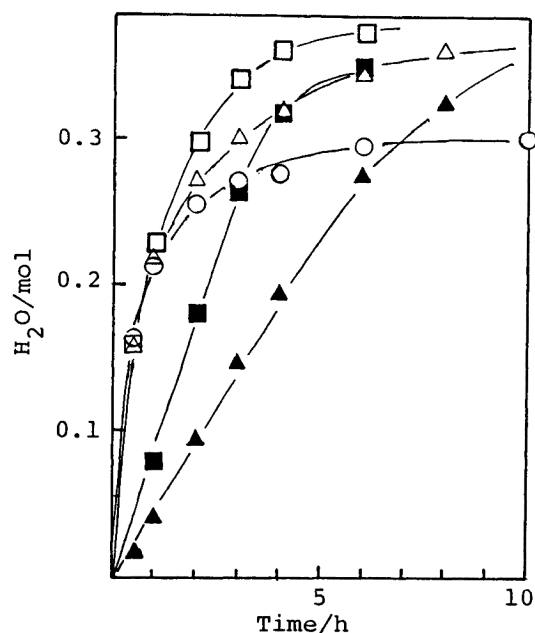
membrane B. The permeated amount of
water becomes constant at about 6 and 10
hours for the membrane B and C, respec-
tively, which suggests that all of the
oleic acid was esterified and a large
portion of water generated by the esteri-
fication was permeated until that time.
Figure 3 shows the effect 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 equi-
librium in favor of the ester formation
and a conversion greater than the equi-
librium 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

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

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.

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