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# Membrane-based air separation for catalytic oxidation of isolongifolene

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ABSTRACT

Oxygen-enriched air (OEA) from membrane-based air separation has been widely used in the industrial field in the past two decades. Isolongifolenone, an oxygenated derivative of isolongifolene, is an important perfume ingredient in the perfumery industry. In this paper, the OEA produced by the membranes was employed as oxidant to convert isolongifolene into isolongifolenone with cobaltous acetate as catalyst. The effects of the reaction conditions on the conversion and the yield were investigated thoroughly. It was found that the conversion of isolongifolene increased with the oxygen concentration of the OEA and the reaction temperature. The maximum yield was obtained under the conditions of the oxygen concentration of 33.1% and the temperature of 60 °C. Both the conversion and the yield increased with the flux of OEA. In addition, the solvent-free reaction process not only facilitated the catalyst recovery, but also minimized the effluent discharge.

## 1. Introduction

The separation, purification or enrichment of gases is usually carried out by cryogenic drying, adsorption or other methods. In the last 20 years, membrane separation of gases had gained wide acceptance due to low capital cost, compact size, modular configuration, and low energy requirements [1]. Air separation represents one of the first applications of membrane technology in the field of gas treatment. A potential giant market exists for oxygen-enriched air (OEA) (25–40% $O_2$) and relative high-purity oxygen product (>90%) [2,3]. OEA has been applied widely in the industrial field including chemical processing, hazardous waste destruction, biotechnology, aircraft propulsion, new engines and fuel combustion system for the improvement of process efficiency [2–9].

Isolongifolene, a bridged tricyclic sesquiterpene with trisubstituted double bond, is obtained mostly from the isomerization of longifolene that is found abundantly in turpentine oil of Himalayan pine and Pinus massoniana. Oxygenated derivatives (ketone and oxide) of isolongifolene have occupied vintage place in modern perfume industry because of their extremely rich woody and floral odor [10–13]. Isolongifolenone, one of the important derivatives, has also been found more effective in repelling ticks and deterring feeding mosquitoes than DEET (diethyltoluamide) that is used most widely as an insect repellent [14]. Most of the reported processes for the oxidation of isolongifolene to produce isolongifolenone are homogeneous reactions employing traditional oxidant such as air, oxygen, metal oxidants and t-butyl hydroperoxide [14–16]. These reactions usually result in complex mixtures of epoxide, alcohol, ketone and lactone, since the longifolene system is prone to rearrangement or overoxidation [11,12]. The separation of the desired product from the mixture becomes more difficult due to the great similarity of the chemical and physical properties of these oxygenated derivatives. Therefore, it is necessary to enhance the selectivity by the modification of catalyst, oxidant, reaction medium, and temperature and so on. In addition, particularly important for green chemistry, the great challenges are the introduction of the solvent-free technologies to minimize the amounts of effluent and facilitate the catalyst recovery.

In this paper, the PDMS/PSF (Polydimethylsiloxane/Polysulfone) composite membranes capable of producing high fluxes of OEA with moderate concentration of oxygen (25–40%) were prepared, and the influence of the pre-evaporation time of the PSF substrate membrane on the permeation performance of the composite membranes were investigated. The OEA produced by the composite membranes was used to substitute air for the conversion of isolongifolene into isolongifolenone utilizing cobaltous acetate as catalyst in the solvent-free reaction process. Besides, the effects of the oxygen concentration, the flux of OEA and the reaction temperature on the conversion and the yield were studied thoroughly.

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## 2. Experimental

### 2.1. Membrane separation unit

#### 2.1.1. Materials

PSF and PDMS were purchased from Shanghai Chemical Plant and Shanghai Synthetic Resin Company, China, respectively. The solvent *n*-heptane, N-methy-2-pyrrolidinone (NMP), the curing agent tetraethyl orthosilicate (TAOS) and the catalyst dibutyltin dilaurate (DBTDL) were obtained from Shanghai Chemical Agents Company and used without further purification. Compressed air used in the permeation experiments and the gases of oxygen concentration above 40% were provided by Nanjing Tongguang Special Gas Company and used as received.

#### 2.1.2. Membrane preparation

PSF membranes were fabricated using the solution casting technique as follows. The PSF polymer was dissolved in the NMP thoroughly to get 17 wt% solution. Stirred for 24 h and filtered, the casting solution was moved into the vacuum oven to remove the dissolved air. The aged casting solution was then cast onto a smooth glass plate to give wet film with thickness of 100 μm by mayor stick. The wet film was kept in a clean room with appropriate atmosphere (25 °C, 53%RH) for a pre-determined time, and then immerged into coagulation bath of deionized water to complete the phase inversion. The finished membranes were rinsed with fresh deionized water and dried in the vacuum oven.

The PDMS/PSF composite membranes were prepared as follows: the PSF membranes were placed on the surface of water in advance as the substrate, and then the PDMS casting solutions consisting of 1–2 wt% PDMS with appropriate ratio of TAOS and DBTDL in *n*-heptane were poured onto them. Evaporated at ambient temperature for 6 h, the composite membranes were removed into the vacuum oven of 60 °C for another 6 h to complete the cross-linking.

#### 2.1.3. Permeation experiment

The gas permeabilities of these composite membranes were evaluated using constant pressure-variable method. The PDMS/PSF composite membranes were mounted in a stainless steel membrane cell offering an effective permeation area of 64 $cm^2$. The upstream side of the cell was pressurized with compressed gas cylinders equipped with pressure regulators to control the upstream pressure and the permeate side was kept open to the atmosphere. The steady-state permeation fluxes were measured from the gas flow meter, and the oxygen concentrations in the permeated streams were determined using a portable oxygen analyzer produced by the Shanghai Leici instruments company, China.

### 2.2. Catalytic oxidation of isolongifolene

Isolongifolene was achieved by the acid-catalyzed rearrangement of longifolene and the multiple distillations in laboratory-scale packed columns. Cobaltous acetate as the catalyst was activated by heat treatment. Reactions were carried out in a three-necked bottle equipped with a magnetic stirrer and a sampling system. In a typical run, mixture of isolongifolene (20 g, 0.1 mol) and catalyst (1 g, 0.004 mol) was stirred at the pre-determinate temperature controlled by the oil-bath, then the oxygen-enriched air produced by PDMS/PSF complex membranes was introduced for 12 h, and sampling was taken every 2 h. The quantitative analysis of the reaction oil was carried out by Agilent 6890N gas chromatograph (GC) equipped with FID detector and automatic gas sample injection module. The GC separation was achieved using an OV-101 (100% Dimethylpolysiloxane) fused-silica capillary column (25 m × 0.32 mm i.d., 0.25 μm film thickness), with temperature program: 120 °C, 4 °C/min up to 160 °C; 160 °C, isothermal, 1 min; 20 °C/min up to 230 °C; and 230 °C, isothermal, 1 min. The samples were analyzed three times to obtain duplicate data.

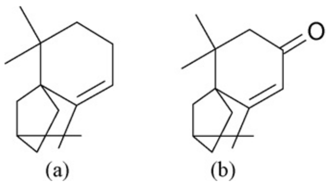

**Fig. 1.** The structure of isolongifolene (a) and isolongifolenone (b).

After the reaction, the catalyst was removed from the cooled reaction oil by centrifugation, then washed with cyclohexane and weighed. The filtrate was distilled under reduced pressure, then two main distillation cuts I (b.p. 103–105 °C/0.93 kPa) and II (b.p. 105–150 °C/0.93 kPa) were collected, finally the residual was kept without further separation. Cut I was the unreacted isolongifolene, and cut II was identified as the isolongifolenone (shown in Fig. 1) by IR (PerkinElmer 783), NMR (Bruker AV-300) and GC-MS (Micromass GC-TOF).

Isolongifolenone: IR ($cm^{-1}$): $\nu$ 1665, l363, 1265, 1170, 1125, 1080, 920, 890, 820; MS (*m*/*z*, %): 218[$M^+$] (35), 203(16), 189(12), l75(100), 161(52), 147(60), 133(23), 119(43), 105(24), 91(29), 77(17), 69(15), 55(18); $^1H$ NMR($CDCl_3$, 300 MHz): δ, 0.94(3H, s, $-CH_3$), 1.05 (3H, s, $-CH_3$), 1.08(3H, s, $-CH_3$), 1.14(3H, s, $-CH_3$), l.20–2.35 (9H, m, $-CH_2$, –CH), 5.65(1H, s, =CH); $^{13}C$ NMR($CDCl_3$, 300 MHz): 24.26, 24.50, 25.29, 25.69, 26.91, 27.76, 34.36, 36.59, 43.88, 46.44, 49.83, 58.52, 116.78, 183.72, 200.10. The data are consistent with those reported in Refs. [13,14].

## 3. Results and discussion

### 3.1. Performance of the PDMS/PSF complex membranes

The trends that the permeation flux and the oxygen content in the permeated stream varied with the operation pressure were shown in Figs. 2 and 3. It could be noted that the pre-evaporation time of PSF substrate membrane had an important effect on the permeation performance of the composite membranes. When the pre-evaporation time of PSF substrate membranes was less than one minute, the higher permeation fluxes were attained, but the oxygen concentrations in the permeated stream were lower than others. In addition, at moderate operation pressure, the oxygen concentrations dropped sharply accompanied by rapid augments in flux. The above results indicated that the membranes with less pre-evaporation time had poor separation selectivity and mechani-

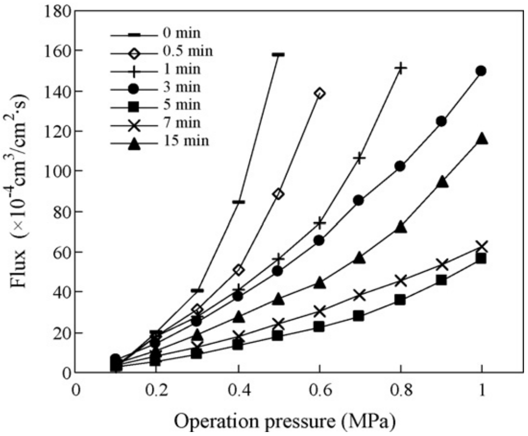

**Fig. 2.** Effect of feed pressure on the permeation flux at different per-evaporation time.

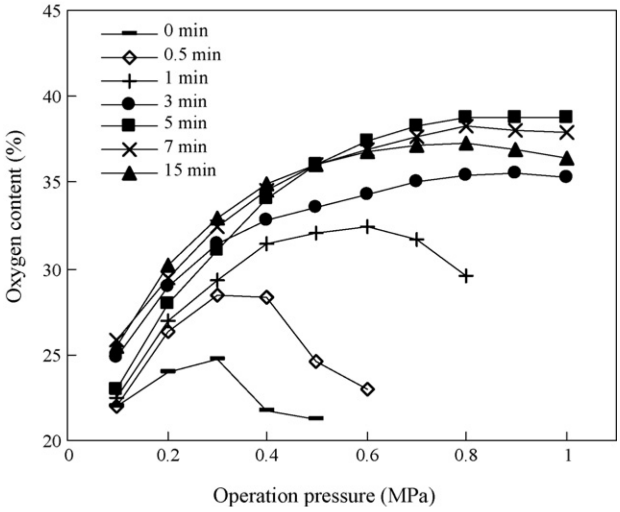

**Fig. 3.** Effect of feed pressure on the oxygen concentration in the permeate at different per-evaporation time.

cal intensity. When the pre-evaporation time increased from 1 min to 15 min, the flux descended and then ascended, and the contrary trend was found for the oxygen content in the permeated stream at the same pressure. It is generally believed that for the PDMS coating gas separation membranes, the PDMS layer was used to plug up the defects in the dense skin layer of PSF membrane and force the gas to permeate through the polymer matrix in the skin layer. The membrane morphology was determined by the phase separation process, and the structure of the skin layer decided the gas separation performance [17–19]. The extension of the evaporation time could make the skin layer denser and thicker, leading to the increase of the gas permeating resistance and the drop of the flux. However, the denser and thicker skin layers of the PSF substrate membranes were prone to enhance the selectivity of the composite membranes, resulting in the rise of the oxygen content in the permeated stream. In addition, it was noticeable that when pre-evaporation time were extended over 5 min, contrary to the expectation, the flux increased with pre-evaporation time at the pressure over 0.6 MPa, and the corresponding oxygen content in the permeate dropped. One possible reason responsible for the phenomena was that when the wet films were exposed to the humid ambience excessively, much water vapor were absorbed in the surface of the wet film and induced the interior solvent diffuse outward. It leaded to the variation of the surface polymer composition, which finally influenced the phase separation process in the coagulation bath.

Therefore, an assumption could be made that there was an optimal evaporation time range in the membrane preparation process. In this experiment, the high oxygen concentration with the appropriate flux was obtained when the pre-evaporation time of PSF substrate membrane in the range of 3–5 min. Fig. 3 also showed that the maximum oxygen concentration in the permeated stream approached 40% for the membranes with a pre-evaporation time of 5 min.

In the following three months experimental period, the steady permeated flux and selectivity indicated that these composite membranes had the favorable mechanical integrity and durability.

## 3.2. Catalytic studies

In the reactions of oxidation of isolongifolene, a free radical chain mechanism is proposed which involves the formation of allylic hydroperoxides that typically decompose to several products. The role of the catalyst is generally explained in terms of catalysis of the decomposition of the allylic hydroperoxide intermediates which facilitates the initiation of the free radical chain mechanism. In cobalt-catalyzed oxidations of alkenes, a competition between the abstraction of the allylic hydrogen to give allylic oxidation products and the addition of the alkylperoxy radical to the double bond resulted in epoxide products. A strong preference exhibited by isolongifolene for allylic oxidation over epoxidation can be explained by the high reactivity of the allylic hydrogen in this molecular toward the abstraction [13,15].

In the experiments, the recovery rate of catalyst was around 98%. To determine the amount of catalyst dissolved in the reaction mixture, after the removal of catalyst by centrifugation, one experiment was carried out in which the filtrate was stirred for further 6 h while oxygen-enriched air was provided to react with it, but the augment of conversion was not observed finally. It implied that no significant amount of catalyst was dissolved in the mixture, and the loss of catalyst probably took place in the multiple washing operations.

### 3.2.1. Effects of reaction time on the conversion and the selectivity

Under the conditions of the flux of 37.5 ml/min and reaction temperature of 60 °C, the variations of the conversion of isolongifolene and the selectivity of isolongifolene to isolongifolenone with the reaction time at the different oxygen concentration were shown in Fig. 4. It could be seen that the conversion increased and then slowed down with the reaction time, and it increased with the oxygen concentration in the feed gases at the same reaction time. The selectivity did not changed obviously with the reaction time, but it dropped sharply with the increase in the oxygen concentration when the oxygen concentration was over 50%. The results indicated that the proper oxygen concentration could restrain the chain reaction to some extent and avoid the further oxidation.

### 3.2.2. Effects of oxygen concentration

Fig. 5 presented the variation of the conversion and the yield with the oxygen concentration. With the increase in the oxygen concentration at the constant flux of 37.5 ml/min and the temperature of 60 °C, an obvious growth of conversion was observed, and the yield of main product isolongifolenone showed an interesting trend that ascended and then descended with the oxygen concentration. The maximum yield was attained at the oxygen concentration of 33.1%. When the oxygen concentration in feed gas was high enough, more oxygen was dissolved in the solution and activated into free di-radical molecular under the conditions of ray or heat. At the same time, the born oxygen free radical induced more isolongifolene molecular into allyl radical, resulting in the acceleration of the reaction process. On the other hand, the allyl radical was prone to the rearrangement reaction, and the appearance of more by-products decreased the yield of the desired product. Therefore, in order to obtain high yield, the oxygen concentration in the feed gas should be in the range of 31–40% as shown in Fig. 5. It was interesting that the range of oxygen concentration just fell into the field of oxygen-enriched air produced by membrane air separation. The results implied that the application of the composite membranes in the preparation of isolongifolenone was feasible.

### 3.2.3. Effect of the flux of OEA

The conversion and the yield at various fluxes with the oxygen concentration of 33.1% and the temperature of 60 °C were shown in Fig. 6. The results indicated that the conversion and the yield increased with the flux, and the increment slowed down when the flux was over 40 ml/min. For the gas–liquid–solid heterogeneous reaction system, the dissolution of the oxygen and its diffusion to the surface of solid catalyst in the solution were the control steps when the concentration of the dissolved oxygen was lower.

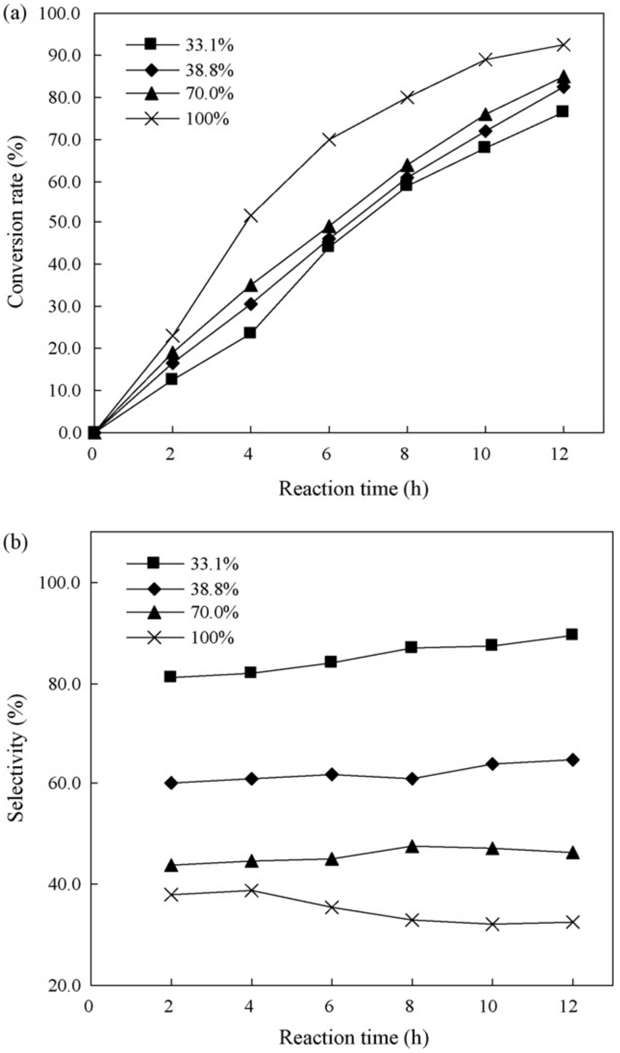

**Fig. 4.** Variation of conversion and selectivity with reaction time at the gas flux of 37.5 ml/min and the reaction temperature of 60 °C.

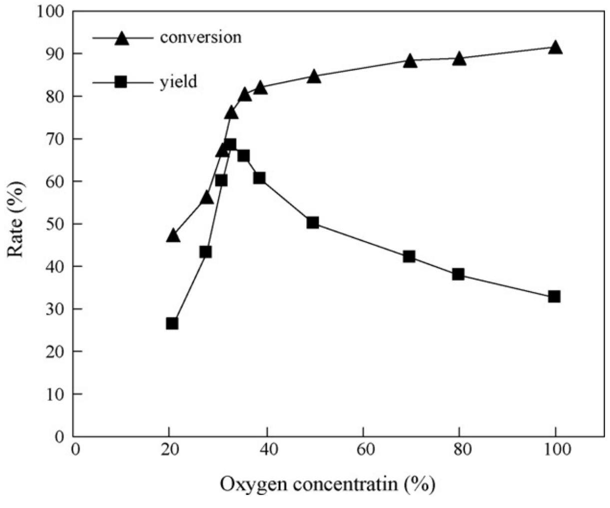

**Fig. 5.** Effect of oxygen concentration on the conversion and the yield at the gas flux of 37.5 ml/min and the reaction temperature of 60 °C.

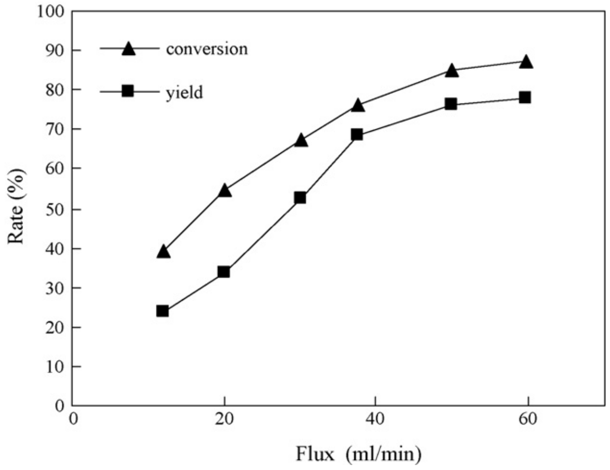

**Fig. 6.** Effect of the flux on the conversion and the yield at the oxygen concentration of 33.1% and the reaction temperature of 60 °C.

The increment of the feed flux could raise the concentration of dissolved oxygen and accelerate the mass transfer. When the mass transfer speed was much higher than the reaction speed, the reaction process was controlled by the kinetics. The further increment of the flux would not speed the reaction remarkably. In addition, since the large flux required more membrane areas and higher operation pressure, and the excessive gases were released rather than reacted, resulting in the additional power consumption. Therefore, the feasible flux was found to be less than 60 ml/min in this experiment scale.

### *3.2.4. Effect of reaction temperature*

In order to explore the gross effects of the reaction temperature on the reaction, the conversion and the yield at different reaction temperature were investigated with the constant oxygen concentration of 33.1% and the fixed flux of 37.5 ml/min. The results in Fig. 7 indicated that the conversion increased rapidly with the temperature, and the yield reached the maximum of 68.5% at 60 °C. For the free radical-induced catalysis process, the high temperature was prone to activate the oxygen molecular into the free di-radical molecular more rapidly, resulting in the acceleration of the reaction process. Meanwhile the presence of more isolongifolene allyl radical can cause other reactions and decrease the yield of isolongifolenone. To obtain the higher yield, the reaction temperature should be controlled around 60 °C.

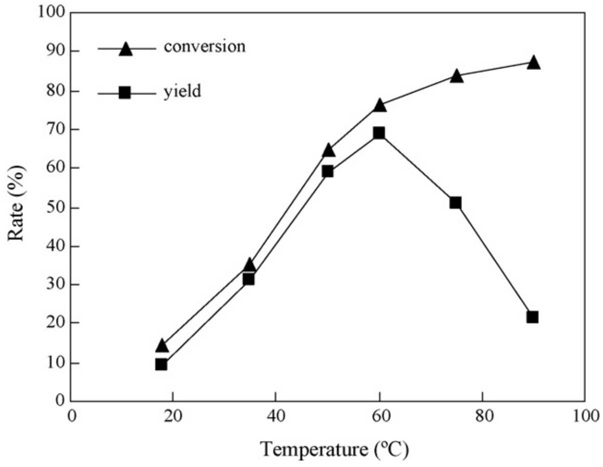

**Fig. 7.** Effect of the temperature on the conversion and yield at the oxygen concentration of 33.1% and the gas flux of 37.5 ml/min.

**Table 1**
Conversion and yield in various reaction mediums.

| Serial | Solvent | Oxidant | Gas flux (ml/min) | Temperature (°C) | Time (h) | Conversion rate (%) | Yield rate of isolongifolenone (%) |
|---|---|---|---|---|---|---|---|
| 1[a] | Acetic anhydride | Air | 200 | 60 | 12 | 84.3 | 60.1 |
| 2[a] | Ethyl acetate | Air | 200 | 60 | 12 | 57.7 | 45.6 |
| 3[a] | Benzene | Air | 200 | 60 | 12 | 22.9 | 12.9 |
| 4[a] | Cyclohexane | Air | 200 | 60 | 12 | 17.0 | 10.9 |
| 5 | None | Air | 37.5 | 60 | 12 | 47.2 | 26.1 |
| 6 | None | $27.5\%O_2$ | 37.5 | 60 | 12 | 56.1 | 43.0 |
| 7 | None | $31.0\%O_2$ | 37.5 | 60 | 12 | 67.5 | 59.8 |
| 8 | None | $33.1\%\ O_2$ | 37.5 | 60 | 12 | 76.5 | 68.5 |
| 9 | None | $33.1\%\ O_2$ | 60 | 60 | 12 | 87.5 | 78.0 |
| 10 | None | $38.3\%O_2$ | 37.5 | 60 | 12 | 82.3 | 60.3 |
| 11 | None | $50\%\ O_2$ | 37.5 | 60 | 12 | 85.1 | 50.2 |

*Note*: [a]Data from the literature [14], in which isolongifolene 50 g reacted with organic cobalt salt 1 g.

### 3.2.5. *Effects of reaction medium on the conversion and the yield*

The conversion and the yield under the various reaction mediums were compared in Table 1. It can be seen that the higher conversions were obtained in the polar solvent mainly due to the solvents acetic anhydride and ethyl acetate participating in the reaction, but the appearance of more by-products reduced the yield of isolongifolenone [15]. In the non-polar solvent benzene and cyclohexane, both the conversion and the yield were lower due to the poor dispersion of isolongifolene in the solvents. For the solvent-free reaction process in this paper, the conversion and the yield were lower when air was used as the oxidant. Correspondingly, the higher conversion and yield were obtained when the OEA produced from the PDMS/PSF composite membranes were employed as oxidant to replace air (shown in Table 1). Especially for the oxygen concentration of 33.1%, the results were attractive even compared with the reaction process containing acetic anhydride. The results indicated that the solvent-free process had good oxidation selectivity using OEA as oxidant. The method also avoided the potential pollution of the product perfume by the peculiar smell of the organic solvent mentioned above. In addition, the facile recovery of catalyst represented another attractive feature of the developed process.

## 4. Conclusions

The PDF/PDMS composite membranes were prepared to separate air in the paper and showed a good oxygen enrichment performance. The effects of the pre-evaporation time of the PSF substrate membrane on the permeation performance of the composite membranes were investigated, and the optimal pre-evaporation time should be in the range of 3–5 min in this experiment, with the oxygen concentration in the permeated stream approaching 40%. The oxygen-enriched air produced from the PSF/PDMS composite membranes was applied in the catalytic oxidation of isolongifolene to produce isolongifolenone. The results indicated that the conversion increased with the oxygen concentration, the feed flux and the reaction temperature. The yield reach the maximum of 78.0%, and the corresponding conversion of 87.5% in the case of the oxygen concentration of 33.1% and the flux of 60 ml/min at 60 °C. These implied that the application of OEA was beneficial to the preparation of isolongifolenone from isolongifolene oxidation. In addition, the environmentally friendly catalytic process of the inexpensive cobalt as the catalyst, the innoxious OEA as the oxidant, and solvent-free conditions is significant practical advantages.

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