



# Highly efficient tetrafluoroethylene recovery for batch polymerization system: Membrane preparation and process development



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## ABSTRACT

In tetrafluoroethylene (TFE) batch polymerization,  $H_2$  is utilized to stabilize pressure and control reaction degree. TFE lost in the purge can account for about 6.0% of the loaded monomer. In this work, membrane-based separation system was presented to effectually reduce TFE loss. Polyimide asymmetric membrane with  $J_{H_2}$  up to 196 GPU and  $\alpha_{H_2/TFE}$  higher than 1680 was developed for the separation. A pseudo-steady process was customized to sufficiently complete TFE recovery within the 30-min idle period after batch polymerization. With the procedure that  $H_2$ -enriched permeate is compressed back into the reactor, it is succeeded to overcome the limits that the purge is gradually falling in pressure and the TFE-enriched stream is hazardous in compression. In this instance, TFE recovery ratio was increased to about 90%. For a 5.0-kt/a TFE polymerization unit, the investment for the separation system is about  $2.56 \times 10^5$  USD, the running payout is less than  $4.35 \times 10^4$  USD/a, and meanwhile the annual gross profit can be up to  $3.126 \times 10^6$  USD. On the whole, gas membrane separation is a promising technique to reduce TFE loss in the batch polymerization processes.

## 1. Introduction

Polytetrafluoroethylene resin, in virtue of its chemical inertness and desirable properties such as the hydrophobic and the electrical insulating abilities, has been widely utilized in many fields, e.g., energy, chemical, environmental, mechanical, aerospace and biological industries [1–6]. However, fluorinated polymers are very expensive due to the scarce raw material and the difficult monomer synthesis [7–9]. In this instance, tetrafluoroethylene (TFE) loss in polymerization processes should be given our most careful attention.

TFE polymerization can be happened over a wide pressure range. High reaction pressure offers an advantage over low pressure in enhancing reaction rate and consequently obtaining the eligible polymer with high molecular weight in a much shorter time [10]. For batch polymerization widely used in industry, it is inevitable that the reaction pressure is decreasing gradually. In this instance, the charging with inert gases, e.g.,  $CO_2$ ,  $N_2$ , and  $H_2$ , is widely employed to mitigate the attenuation in pressure [11–13]. With the advantage that  $O_2$  hazardous to TFE reaction can be eliminated by Pt catalysis thoroughly and facilely,  $H_2$  is much more appropriate as the charging medium.

TFE remaining in the batch polymerization, subject to the reaction degree, would be discharged along with the inert gases. According to the data from Dongyue Group Ltd., the largest fluorinated material base

in China, TFE content in the exhaust gas can be up to 64% in volume, which results in a TFE loss accounting for about 6.0% of the loaded monomer. In order to recycle the unreacted monomer conveniently in liquid state, cryogenic condensation is settled after the polymerization in industrial plants. Nevertheless, TFE has a normal boiling point as low as  $-75.9$  °C. Under the usual liquefaction condition at  $-30$  °C and real-time pressure, TFE recovery ratio is lower than 20%. In addition, water existing in the exhaust gas and TFE oligomerization in the compression make the cryogenic recovery system complicated and unreliable. In order to concentrate TFE efficiently and sufficiently, the practical technique independent on phase transition is demanded urgently.

Gas membrane separation, not involving heat exchange and mobile separating reagent for phase transition, has been widely attempted either to substitute or to assist the cryogenic operation in the last three decades [14–17]. For instance, the vapor-gas separation systems with rubbery membranes have become the standard units to enhance  $C_2H_4$  and  $C_3H_6$  recovery after shallow condensation in petroleum and chemical industries [18–20]. In consequence, gas membrane separation might be an promising technique to avoid the key problems encountered in cryogenic recovery process for TFE batch polymerization. In addition, considering the significant difference in molecule size,  $H_2$  and TFE are expected to be separated efficiently with the glassy membranes. In glassy, rigid polymers, e.g., polysulfone,

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polyetherketone and polyimide, gas selective permeation is mainly dependent on molecular size [21,22]. In this instance, the small components in the purge stream, i.e.,  $H_2$ , should be much more permeable than the heavy species in the purge, i.e., TFE monomer.

In the present work, Matrimid 5218, a commercial polyimide material, by virtue of its high  $H_2$  separation ability,  $P_{H_2} = 24$  Barrer and  $\alpha_{H_2/CH_4} = 111$ , was selected and fabricated as the asymmetric membrane to assess  $H_2/TFE$  separation ability [22]. Considering that TFE is much larger than  $CH_4$  in critical volume (TFE,  $0.1720 \text{ m}^3/\text{kmol}$ ;  $CH_4$ ,  $0.0990 \text{ m}^3/\text{kmol}$ ), it is expected that  $\alpha_{H_2/TFE}$  would be much higher. Afterwards, the pseudo-steady membrane separation system was customized to achieve TFE recovery sufficiently within the 30-min idle period after batch polymerization. In this design, the limitations that the purge is gradually falling in pressure and the TFE-enriched stream is hazardous in compression were emphatically considered to develop a robust system.

## 2. Problem statement

After launching its first PTFE synthesis plant in 2002, Dongyue Group Ltd. has been the largest manufacturer in the world nowadays with the total scale up to 35 kt/a. The main technique adopted in Dongyue Group is batch polymerization, in which  $H_2$  is charged to maintain pressure. The purge condition and the requisite for TFE recovery are described as follows.

TFE polymerization scale is about 5000 t/a for a single unit, which is accomplished by repetitive reaction for 900 times. The purge after each reaction is about 330 kg, in which TFE molar fraction is about 64.0% and moisture concentration is about 0.1%. According to the reaction condition, the purge stream is released with the initial pressure at 2.0 MPaG and the ultimate pressure lower than 0.05 MPaG. Nevertheless, mechanical compression should be avoided for those streams enriched in TFE monomer, because TFE is reactive and hazardous in attacking and heating situation.

The integral cycle for TFE polymerization is 8 h, in which the reaction would last for 7 h and the auxiliary work should be finished in 1 h. In this instance, the time remained for TFE recovery is no more than 0.5 h. In addition, it is better that TFE in the purge is recovered in liquid status with the available refrigerant at  $-35 \text{ }^\circ\text{C}$ , owing to the condition for filling monomer into reactor.

## 3. Membrane preparation and characterization

### 3.1. Composite membrane preparation

The commercial Matrimid 5218 polyimide, with the chemical structure exhibited in Fig. 1, was purchased from Huntsman (Basel, Switzerland) and utilized as received. Its asymmetric composite membranes, with the ultrathin and dense selective layer to conduct highly selective and permeable gas separation, would be fabricated in the pilot scale.

The casting solution was prepared by dissolving non-solvent n-BuOH (9.0 wt%) and Matrimid 5218 (15.0 wt%) in dehydrated N-methyl-2-pyrrolidone (NMP), referring to the experimental data in the literature [23]. After vacuum degassing, the solution was spreading evenly on the non-woven fabric in air with RH < 20% at  $25 \text{ }^\circ\text{C}$  using the pilot scale membrane casting machine. The minimal distance from the

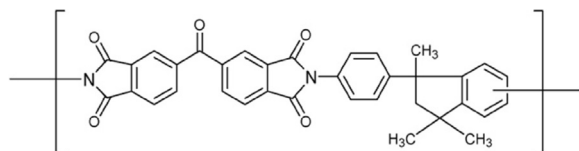


Fig. 1. Chemical structure of Matrimid 5218 polyimide for gas separation membrane.

non-woven fabric to the casting knife is about  $200 \mu\text{m}$ . The coagulation bath was filled with renewal deionized water at  $20 \text{ }^\circ\text{C}$ . The air gap between casting knife and water surface is  $0.25 \text{ m}$  in the machine, and then the casting speed was optimized as  $4 \text{ m/min}$  so that solvent can be vaporized properly to make the selective layer ultrathin and dense. The obtained membranes were immersing in an aqueous bath at least 24 h to remove solvents sufficiently.

The pinhole defects existing on the selective layer would seriously impair membrane separation performance [24,25]. The initial membranes would be coated with PDMS solution to eliminate the defects according to Henis-Tripodi method [26,27]. Sylgard-184 PDMS (MW  $\approx 22,000$ ), together with its exclusive cross-linking agent and catalyst, was purchased from Dow Corning (USA). Its pentane solution was prepared with 3.0 wt% concentration. Before the coating process, the initial membranes were dried in a vacuum oven at  $110 \text{ }^\circ\text{C}$  for 24 h. During the coating procedure, a slight trans-membrane pressure difference was applied to facilitate PDMS penetration. After the coating process, the membranes were resettled to finish the cross-linking in an oven at  $50 \text{ }^\circ\text{C}$  for 12 h.

In order to demonstrate the defect blocking action, membrane surface structure before and after PDMS was characterized via a high-resolution FE-SEM (NOVA NanoSEM 450, USA), as shown in Fig. 2. On the initial asymmetric membrane surface, we have found three minute spots likely to be the defects. According to the scale, their average diameter is about  $50 \text{ nm}$ . After dip-coating by the dilute PDMS solution, membrane surface morphology is uniform and all the defects have been eliminated apparently. This composite structure is beneficial to achieve high perm-selectivity.

### 3.2. Membrane microstructure characterization

Membrane sectional morphology was characterized via a regular SEM (KYKY-2800B, Beijing, China) and a high-resolution FE-SEM (NOVA NanoSEM 450, USA), as exhibited in Fig. 3. The asymmetric composite membrane could be distinctly divided into three layers. The cross-section bulk, acting as the supporting layer, is sponge-like with well-interconnected porous framework to decrease gas flowing resistance. The cross-section outer edge is the selective layer, which is dense but ultrathin with the thickness much less than  $0.5 \mu\text{m}$  to decrease permeation resistance. It should be emphasized that the real dense layer thickness cannot be simply measured by the SEM images, and then we would calculate it according to the intrinsic permeability and the tested permeance in the following. The outermost side is the PDMS coating layer, which is partially penetrated into the selective layer to block these pinhole defects. On the whole, such an asymmetric cross-section structure should be positive to ensure the membrane with gas processing capacity high enough to perform the separation of interest.

### 3.3. Membrane performance tests

In order to test membrane properties, a pilot-scale plate-and-frame module was assembled with two membrane leaves in the cell, as shown in Fig. 4. The cavity diameter is  $16.0 \text{ cm}$  and the total effective area utilized in the test is about  $400 \text{ cm}^2$ . Gas permeation tests with pure  $O_2$  and  $N_2$  were conducted at first in the lab to examine whether the prepared membranes are defect-free. Pure gas permeation rates, as a function of feed pressure, have been given in Fig. 5. Accordingly, the ideal selectivity between  $O_2$  and  $N_2$  is about 6.4 for the prepared membranes, very close to the intrinsic properties of Matrimid 5218, which is confirmed to be 6.8 in the literature [28,29]. The deviation between them can be attributed to the concurrent permeation through polyimide selective layer and the defects cured with PDMS. By dividing the intrinsic permeability with the tested permeance of  $O_2$  ( $1.7$  Barrer vs.  $19.3$  GPU), the real dense layer thickness is probably less than  $0.1 \mu\text{m}$ , which is much thinner than the thickness observed by SEM

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