NOTE

Pervaporative Introduction of Organic Vapors into High-Pressure Gas Feeds

GUNAIDI DJOEKITA, DE Q. VU, WILLIAM J. KOROS

Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas 78712-1062, USA

INTRODUCTION

Better understanding is needed of the effect of organic vapor impurities on commercial polymeric membrane performance in natural gas processing streams. The presence of these hydrocarbon impurities (C6 and higher) in the process stream, even in minute concentrations, has been suspected to cause membrane performance declines in field applications (personal communication).[1–3] Studies have found that cellulose acetate membranes have high tolerance (with no loss in flux or CO_2/CH_4 selectivity) for such contaminants as benzene, toluene, and xylene in natural gas streams (personal communication).[4] Nevertheless, the intrinsic selectivity of these materials is too low to prevent significant hydrocarbon loss into the permeate.

For glassy polymeric membranes with intrinsically higher CO_2/CH_4 selectivity, one study cites harsh performance declines in the range of 50% reduction in CO_2/CH_4 selectivity for polyimide films because of saturated concentrations of toluene or n-hexane in mixed gas feeds of CO_2/CH_4.[5] Because of the recent emergence of these high-performance glassy polymeric membranes for commercial applications in natural gas processing, the effects of organic vapor impurities in gas feeds need to be understood better.

Currently, very few studies have considered the effects of organic vapor impurities on high-performance glassy polymeric membranes[5] and carbon membranes.[6,7] Moreover, experimental studies of polymeric membranes in this area have only examined exposure effects in flat-sheet membrane film form. This note describes an experimental apparatus that permits gas permeation studies with varying concentrations of organic vapor impurities. Their controlled introduction into the gas stream uses a pervaporation technique with a flat-sheet silicone rubber membrane. The impurity introduction system is illustrated by application in the study of the effects of organic vapor exposure on asymmetric hollow fiber minimodules.

MATERIALS AND METHODS

Single-Fiber and Multi-Fiber Minimodule Construction

Construction of the single-fiber and multi-fiber minimodules used in the high-pressure permeation system is described in detail in the Appendix.

High-Pressure Permeation System with Organic Vapor Introduction

The permeation testing system for the single-fiber and multi-fiber minimodules is shown in Figure 1. The method of introducing organic vapor into the feed gas stream relies on pervaporation. The main component for the pervaporation is a Millipore® high-pressure 316 stainless steel 47-mm filter holder (Model XX4504700; Millipore, Bedford, MA). Inside the filter holder is a very fine wire cloth impregnated with silicone rubber, as shown in Figure 2. The mesh wire cloth (F. P. Smith Wire Cloth Co., Northlake, IL) is woven with fine weaves of stainless steel wire (500×500 mesh count, 0.0010″ wire diameter, 25 μm width opening) to give 25.0% open area. Utilization of this wire cloth membrane is described in this section.
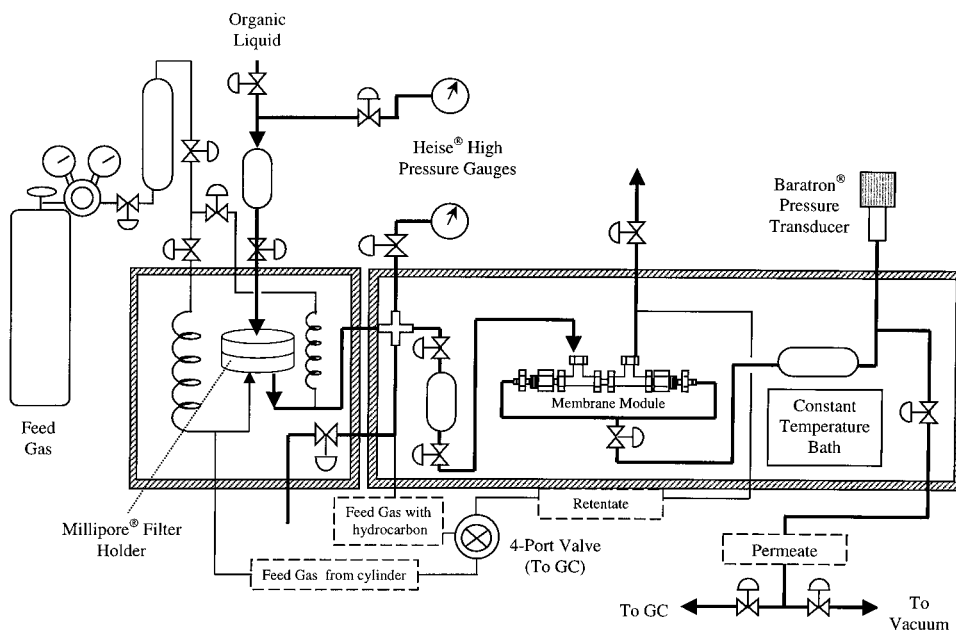
Figure 1   High-pressure permeation system with organic vapor introduction.

The feed gas stream sweeps adjacent to the membrane surface, entraining organic vapor. This system is similar to pervaporation systems used for the removal of organic impurities from a liquid stream.[8,9] In contrast to these systems, the process described herein provides for a method to control the amount of organic vapor entrained by a feed gas stream.

The poly(dimethyl siloxane), i.e., silicone rubber, is formed by mixing the silicone rubber compound (RTV615A) with the silicone curing agent (RTV615B) (GE Silicones, Waterford, NY) [1 part RTV615B per 10 parts RTV615A (by weight)]. After mixing, the mixture is degassed under vacuum for approximately 1–2 h. Next, the mixture is poured onto a section of the very fine wire cloth (approximately 16 cm^2) placed on a poly(tetrafluoroethylene) (PTFE) dish. The PTFE surface provides easy removal upon curing. The silicone rubber-impregnated wire cloth is cured overnight in a vacuum oven under heat (100°C). Another method to remove entrapped bubbles and produce thinner films is dissolving the mixture in n-hexane before pouring into the wire cloth.

In Figure 2, the organic hydrocarbon liquid is held in the upper compartment of the filter holder and contacts the silicone rubber-impregnated wire cloth. The very fine wire cloth provides mechanical strength to the silicone rubber as it swells because of the organic liquid. Early silicone rubber membranes (without wire cloth impregnation) ruptured in the filter holder because of excessive swelling from contact with the organic liquid. The silicone rubber-impregnated wire cloth has been shown to be effective in maintaining membrane integrity without rupturing.

The filter holder is submerged in a temperature-regulated bath with a Lauda® circulation bath heater (Brinkmann Instruments, Inc., Westbury, NY). The hydrocarbon liquid is introduced on one side of the filter holder and stored in a stainless steel reservoir. This side of the filter holder is equilibrated at the total pressure of the feed gas stream of the system. On the other side of the filter holder, the high-pressure gas stream contacts the silicone rubber "membrane" through the opening of the inner bore of double-bore tubing. The now hydrocarbon-containing gas stream
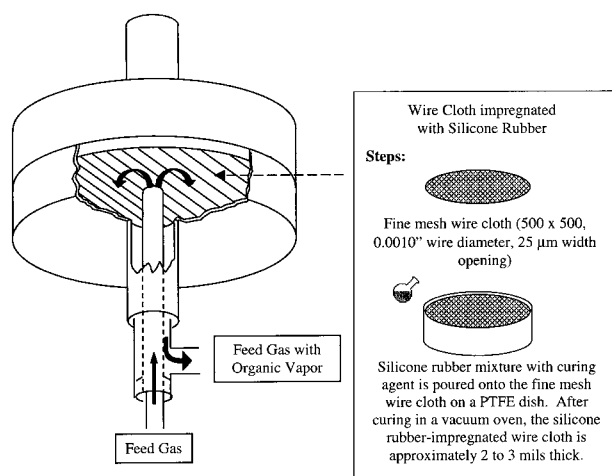

Figure 2   Cross-section of filter holder used to introduce gas streams with organic hydrocarbon using pervaporative method.

exits through the outer bore (annular region) and can be used as the mixed feed gas to the membrane module, as shown in Figure 2. This stream, the hydrocarbon-containing side of the filter holder, is attached to a digital Heise® high-pressure gauge (0 to 2000 psia). The original mixed feed gas, the hydrocarbon-containing feed gas, the permeate stream, and the retentive stream are attached to a four-port valve that connects to the gas chromatograph for analysis (Fig. 1).

Convenient variables for controlling the extent of saturation of the feed gas stream include the silicone rubber (membrane) surface area, the silicone rubber thickness, the feed gas flow rate, the ratio of feed gas bypass, and saturation temperature. Using one or more of these variables, it is possible to develop a calibration for the extent of saturation of the gas stream.

RESULTS

An experiment was performed to determine the permeability of a typical organic liquid in the silicone rubber using the laboratory pervaporation system. Nitrogen gas from a cylinder (Praxair, Austin, TX) was used as a typical feed gas stream. A cryogenic trap (liquid nitrogen) was placed on the end of the line after the pervaporation step to collect entrained organic vapor in the feed stream. With constant nitrogen gas flow rate and pressure, the rate of organic liquid accumulation was used to calculate the permeability of the organic vapor through the silicone rubber. After steady-state conditions were reached, the permeability of the organic vapor through the silicone rubber membrane could be calculated with the following equation:

$$\mathscr{P}_i = \frac{22{,}400 \cdot m}{(\text{MW}) \cdot A \cdot \Delta t} \frac{\ell}{[\Delta p_i]}$$

where $\mathscr{P}_i$ is the permeability of component i at 0°C, 1 atm (STP), m is the weight of the component i in the cold trap, MW is the molecular weight of component i, A is the active membrane area, Δt is the time during which component i of mass m was collected, ℓ is the effective thickness of the silicone rubber membrane, and Δp_i is the partial-pressure driving force between the saturated vapor on the organic liquid side of the membrane and the "dry" feed gas. The dimensions of the fine wire cloth are taken into account in calculating the effective area and thickness of the silicone rubber.

To demonstrate the concept of the system, an experiment was performed to introduce toluene vapor into a "dry" nitrogen gas stream. For this experiment, the silicone rubber membrane had an effective area of 0.18 cm^2 (the 25.0% open area in the wire cloth mesh is taken into account) with a thickness of 38 μm. At a constant temperature of 24°C with 100 psia N_2 gas feed, a permeability of 1.07×10^6 Barrers [1 Barrer = 1×10^{-10} cm^3 (STP) · cm/(cm^2 · s · cm Hg)] was obtained. This value closely matches the reported toluene permeability of 1.46×10^6 Barrers at 40°C through silicone rubber.[9] So, this system is an effective pervaporation method. Furthermore, by controlling the process and membrane variables (mentioned earlier), it is possible to control the amount of vapor introduced into the feed stream.

CONCLUSION

Presented is a method for making single-fiber and multi-fiber minimodules and an introduction to a permeation testing apparatus with the capability to saturate feed gas streams with organic vapor. The minimodule construction permits both bore- and shell-side feeding. In addition, for shell-side feeding, permeate can be withdrawn from both ends of the module, reducing the pressure drop in the bore. This configuration is unique and advantageous because most laboratory-scale minimodules are one-ended modules with permeate withdrawn at only one end.

The permeation testing system described in this note offers the ability to introduce feed gas streams with organic hydrocarbon components through a pervaporation technique. The concentration of the organic vapor can also be controlled through several process variables. Laboratory experiments have verified the feasibility of this apparatus.

This approach is straightforward and can be easily adapted because it relies on the principle of gas-liquid equilibria. The system can be modified to use for other membrane materials and configurations. For example, other polymeric materials (i.e., cellulose acetate or Teflon®) insoluble to the desired organic hydrocarbon component can be used. Furthermore, other membrane configurations, such as hollow fiber membranes, can be substituted in place of the flat-sheet membranes discussed in this report. For instance, this approach provides an alternative to commercially available permeation tubes that are placed inline with gas streams to generate calibrated concentrations of various compounds into a carrier stream.[10,11] These small permeation tubes contain the desired permeant gas in equilibrium with its liquid phase. Permeant vapor is released from the sealed cylinder through permeable walls at a constant rate at a constant temperature. However, these permeation tubes are expensive, have limited life, and are designed for small-scale applications, such as calibrating gas analyzer systems. The approach in this report offers significant advantages to these deficiencies and can be easily scalable.

APPENDIX

Hollow-Fiber Module Construction

This section describes the construction of a double-ended hollow-fiber module for laboratory-scale experiments. This design has been used in a number of previous studies by our group,[12,13] but has not yet been reported in the open literature. The simple, reliable fabrication procedure has been optimized over several generations and is described herein to document recommended procedures we find minimize artifacts in the results. The module consists of brass and 316 stainless steel (316 SS) Swagelok® and NPT fittings: two Swagelok 1/4″ union tees (316 SS), one 1/4″ port connector (316 SS), two adapters for 1/4″ NPT female to 1/4″ tubing (brass), two adapters for 1/4″ NPT male to 1/4″ tubing (brass), four 1/4″ nuts with ferrules (brass), and two 1/4″ nuts with ferrules (316 SS). The material selection is based on the reusability and cost of the parts. Both the port connector and the two union tees are reusable for future module housings; hence, 316 stainless steel is chosen for its durability. However, the NPT fittings at the ends are not reusable; so, inexpensive brass fittings are used.

The module housing is first constructed with the two Swagelok® 1/4″ union tees (316 SS), 1/4″ port connector (316 SS), two adapters for 1/4″ NPT female to 1/4″ tubing (brass), two 1/4″ nuts with ferrules (brass), and two 1/4″ nuts with ferrules (316 SS), as shown in Figure 3. Modules can be formed in either a multi-fiber bundle or a single-fiber form. In either case, the recommended potting compound is a general purpose epoxy encapsulant (Stycast® 2651 from Emerson & Cuming, Billerica, MA) that has excellent adhesion to a wide range of substrates and adequately low viscosity to flow between fibers for potting. In addition, the epoxy material after application has high tensile strength (>6500 psi) for high-pressure applications and a relatively high upper temperature tolerance (130°C).[14]

Polymeric Fiber Bundle Preparation

Several polymeric fibers (approximately 10 to 25) are first cut into 50-cm segments, and bundled. Monofilament fishing line (15-lb. test) is used to form a knot in
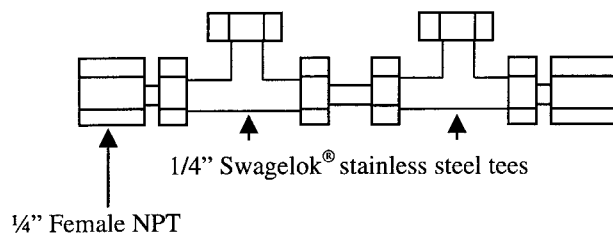
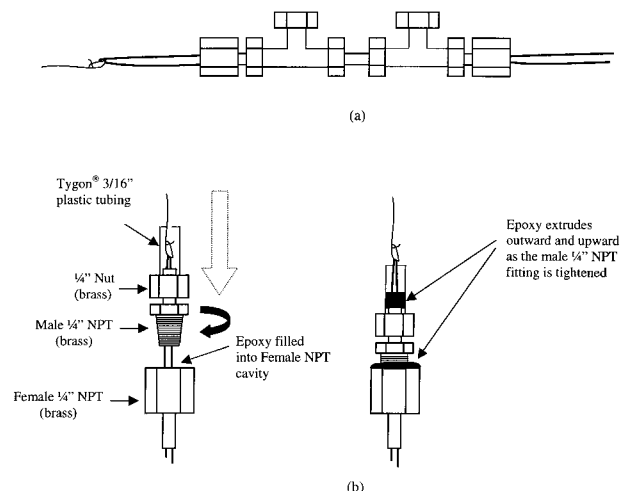**Figure 3** Construction of module housing.

Figure 4 Module construction for multi-fiber bundle. (a) Fiber bundle through module housing; (b) module ends potted with epoxy.

the middle part of the bundle to pull the fiber bundle into the module housing [Fig. 4(a)]. Before the epoxy mix is poured into the female NPT, PTFE (Teflon) tape is gently "stuffed" between the female NPT around the bundled fibers to secure them in place and to prevent flow of epoxy mix down into the module housing. With the fibers thereby secured in the module housing, the epoxy can be applied.

The Stycast® 2651 epoxy encapsulant (resin) is mixed with Catalyst 9 (Emerson & Cuming) [7 parts Catalyst 9 per 100 parts Stycast® 2651 (by weight)]. After mixing for approximately 3–5 min, the epoxy is poured into the cavity of the 1/4″ NPT female fitting at one end of the module. Next, the 1/4″ NPT male to 1/4″ tubing (brass) adapter is used. A 1/4″ brass nut and a 3-cm piece of 3/16″ inner diameter Tygon® tubing is attached to the brass tubing end of the NPT adapter. The NPT adapter is threaded through the fibers and tightened into the 1/4″ NPT female fitting. The adapter is tightened to the desired level with the epoxy extruding upward but contained by the Tygon® tubing [Fig. 4(b)]. A period of one day is necessary for the mix to cure at room temperature. The other end is potted in the same manner. The Tygon® tubings at the ends are snapped off by hand by applying a small transverse force, resulting in a level epoxy surface.

Single Carbon Fiber Preparation

The module preparation for a single carbon fiber is similar to the procedure in the previous section. The hollow fiber carbon membrane (approximately 30 cm in length) is threaded through the module housing, so that a length (approximately 7 to 8 cm) of carbon fiber extends on each end. Before the addition of the epoxy,

the fiber is secured into the module by the use of plastic holders. The plastic holders are obtained from cutting small hemispherical sections from the spherocylindrical bulbs of standard 6″ polyethylene, disposable transfer pipets (Fisherbrand, Pittsburgh, PA). Next, a needle is used to pierce a small hole in the center of each hemispherical plastic section. The carbon fiber is threaded through the small aperture of the plastic section. The aperture should be small enough so that it can shrink (i.e., "heal") to conform to the diameter of the fiber after threading. The plastic holder should prevent the epoxy from dripping down the fiber. PTFE (Teflon®) tape is not used.

The carbon fiber with the plastic section attached at one end is slipped through the module housing until the hemispherical plastic section (concave up) rests outside on top of the 1/4″ NPT female fitting. Forceps are used to gently push the plastic section down so that it rests firmly and conforms tightly to the bottom curvature of the 1/4″ NPT female fitting. Care is taken to avoid breaking the carbon fiber as the plastic section is pushed down the NPT female fitting. The end of the fiber with the plastic section should extend approximately 7 to 8 cm beyond the fitting. On the other end of the module housing, the carbon fiber is threaded through another hemispherical plastic section. Forceps are used again to secure the plastic section to the bottom curvature of the 1/4″ NPT female fitting.

Stycast® epoxy and 1/4″ male NPT fittings are applied in the same manner as the previous description. To hasten the curing process, the epoxy is dried in an oven at 65°C for 2 h after applying epoxy to each end. Finally, the epoxy is cured more extensively at 65°C under vacuum overnight. The Tygon® tubing and the ends of the carbon fiber membrane are snapped off after the epoxy hardens. The potting procedure is shown in Figure 5. An advantage of this module con-
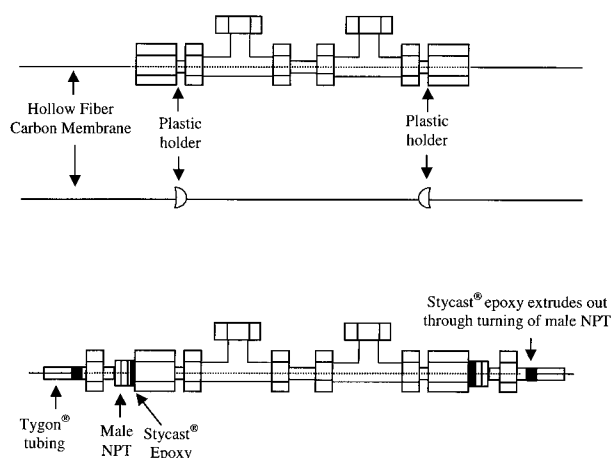

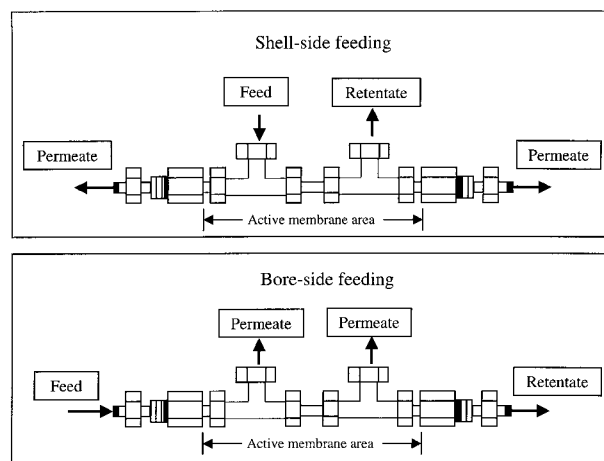**Figure 5** Module construction for single carbon fiber.

Figure 6 Shell- and bore-side feeding with the module construction.

struction permits both bore-side and shell-side feeding, as shown in Figure 6.

REFERENCES

1. Mazur, W. H.; Chan, M. C. Chem Eng Prog 1982, 78, 37.
2. Funk, E. W.; Kulkarni, S. S.; Swamikannu, A. X. AIChE Symp Ser 1986, 82, 27.
3. Schell, W. J.; Wensley, C. G.; Chen, M. S. K.; Venugopal, K. G.; Miller, B. D.; Stuart, J. A. Gas Sep Purif 1989, 3, 162.
4. Lee, S. Y.; Minhas, B. S.; Donohue, M. D. AIChE Symp Ser 1988, 84, 93.
5. White, L. S.; Blinka, T. A.; Kloczewski, H. A.; Wang, I.-f. J Membr Sci 1995, 103, 73.
6. Jones, C. W.; Koros, W. J. Carbon 1994, 32, 1427.
7. Tanihara, N.; Shimazaki, H.; Hirayama, Y.; Nakanishi, S.; Yoshinaga, T.; Kusuki, Y. J Membr Sci 1999, 160, 179.
8. Kamaruddin, H. D. Ph.D. Thesis, The University of Texas at Austin, 1997.
9. Blume, I.; Schwering, P. J. F.; Mulder, M. H. V.; Smolders, C. A. J Membr Sci 1991, 61, 85.
10. Yi-yan, N.; Felder, R. M.; Koros, W. J. J Appl Polym Sci 1983, 25, 1775.
11. Valco Instruments Company, Inc. technical literature, Dynacal® permeation devices; Houston, TX, 1999.
12. McKelvey, S. A. Ph.D. Thesis, The University of Texas at Austin, 1994.
13. Clausi, D. T. Ph.D. Thesis, The University of Texas at Austin, 1998.
14. Emerson & Cuming Specialty Polymers technical literature, STYCAST® 2651 General Purpose, Epoxy Encapsulant; Billerica, MA, 1998.