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Removal/Recovery of VOCs Using a Rubbery Polymeric Membrane

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Rubbery 고분자 막을 이용한 휘발성 유기화합물의 제거 및 회수

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Abstract: Common volatile organic compounds(VOCs) such as toluene and methanol were removed successfully from N_2 using a novel silicone-coated hollow fiber membrane module. This novel membrane is a thin film composite(TFC) and was highly efficient in removing VOCs selectively from a N_2 stream. This membrane had some innate advantages over other silicone-based membrane in that the selective barrier was ultrathin(~1㎛) and the porosity of the polypropylene substrate was high which leads to a low permeation resistance. The substrate was very strongly bonded to the coating layer by plasma polymerization and can withstand a very high pressure. A small hollow fiber module having a length of 25cm and 50 fibers could remove 96~99% of toluene as well as methanol vapors when the feed flow rate was up to 60cc/min. The percent removal of VOCs were even higher when the feed inlet concentration was higher. This process is especially suitable for treating streams having a low flow rate and high VOCs concentration. The permeances of VOCs through this membrane was in the range of $4\sim30\times10^{-9}$ gmol/sec · cm^2 · cmHg for both toluene and methanol, and nitrogen permeance was between $3\sim9\times10^{-10}$gmol/sec · cm^2 · cmHg. High separation factor between 10~55 for toluene/N_2 and 15~125 for methanol/N_2 were obtained depending on the feed flow rate ranges and feed VOCs concentration levels.

요 약: 실리콘 코팅한 복합막을 이용하여 톨루엔이나 메탄올같은 휘발성 유기화합물의 제거 및 회수에 관한 연구를 수행하였다. 사용된 막은 코팅층의 두께가 얇고(~1㎛), 지지층의 기공율이 커서 투과저항은 적었으며 코팅층과 지지층은 플라즈마 중합에 의해 결합되어 있어서 높은 압력에도 견딜 수 있었다. Feed의 유속이 60cc/min. 이하일 때 사용된 모듈에 의해 휘발성 유기화합물의 제거율은 96~99%이었으며, feed의 농도가 높을수록 제거율은 더 증가하였다. 이 공정은 휘발성 유기화합물의 농도가 높고 유속이 낮은 흐름을 처리하는데 아주 적합함을 알 수 있었다. 사용된 막을 통한 휘발성 유기화합물들의 투과도는 $4\sim30\times10^{-9}$gmol/sec · cm^2 · cmHg이었고, 질소의 투과도는 $3\sim9\times10^{-10}$gmol/sec · cm^2 · cmHg의 범위에 있었다. 휘발성 유기화합물과 질소의 선택도는 유속과 휘발성 유기화합물의 농도에 따라 톨루엔/질소의 경우 10~55, 메탄올/질소의 경우 15~125의 값을 얻었다.

1. Introduction

Although research on membrane gas separation processes has been going on for more than 20 years, the research on vapor permeation/separation using membranes has a relatively short history. Membrane vapor permeation is quite similar to pervaporation[1]. In pervaporation, the feed mixture is a liquid and the component to be separated from a feed permeates through the membrane and evaporated as a vapor. In membrane vapor permeation, the feed mixture is in a gas/vapor state and the component to be separated from the feed is just permeating through the permselective, nonporous membrane. The separation of organic vapors by membranes is generally a low-pressure membrane process[2].

The permeation of gases/vapors through a nonporous membrane is generally analyzed by the solution diffusion model. The effects of diffusivity and solubility on the permeability are comparable in the case of simple gases. The permeabilities of simple gases such as He, H_2, O_2, N_2 through a nonporous polymeric membrane are generally not a function of their concentration or partial pressure in the gas phase. For rubbery membranes, the permeabilities of the simple gases are taken as constant[3]. For glassy membranes, the permeabilities, although generally constant, are considerably lower. For vapors, however, the permeabilities are significantly higher than simple gases in most polymers[4-7]. Transport of a vapor through a rubbery polymeric membrane is determined more by its solubility than by its diffusivity. Higher permeability of the vapors is first attributed to the higher solubility of the vapors in the membrane. Further higher sorption at high organic vapor pressures also leads to plasticization of the membrane ; this will increase the diffusivity of organic vapor through the plasticized polymer matrix. Permeabilities of organic vapors are therefore a strong function of their partial vapor pressure in the gas phase ; it increases drastically with increasing vapor concentrations.

It is well known that the nonporous silicone rubbery membranes have an extremely high permeabilities for VOCs and comparatively lower permeabilities for nitrogen or oxygen. It is therefore one of the widely used membrane polymers as far as the organic vapor separation is concerned[8, 9].

The general objective of this study was to develop selective permeation-recovery of VOCs from N_2 via a novel highly VOC-selective silicone coated hollow fiber membrane. This study explored experimentally the extent of selective removal of VOCs from N_2 and provided a basis for modeling the separation performance of the hollow fiber permeator.

2. Experimental

2.1 Membrane form, Structure and Operational Mode

The membrane form, structure and operational mode chosen for this study are likely to be optimal. Hollow fibers provided high membrane surface packing density. Celgard X-20 substrate is cheap, strong, chemically resistant and has a high porosity. The actual silicone membrane is ultrathin, has a low permeation resistance but is strongly bonded to the highly porous substrate to handle high pressure drops. Feed gas flows through the fiber bore to provide high separation, no feed bypassing and high partial pressure driving force.

A schematic of VOC permeation at atmospheric pressure using vacuum mode of operation and a hollow fiber membrane module is illustrated in Fig. 1.

2.2. Hollow Fiber Module Preparation

Three layer potting was carried out to prepare a leak-free module. Fig. 2 shows the cross-section of one fiber and one module end containing

Table 1. Specifications of the Module Prepared

#	# of Fibers	Effective Fiber Length(cm)	Surface Area of Module(cm^2)	I.D./O.D. of the Fibers (μm)	Coated Layer Thickness (μm)	Average Support Porosity	Average Support Pore Size(μm)
1	30	10	24.9	240/290	~1	0.4	0.03
2	50	25	103.8	240/290	~1	0.4	0.03
3	50	12.7	52.7	240/290	~1	0.4	0.03

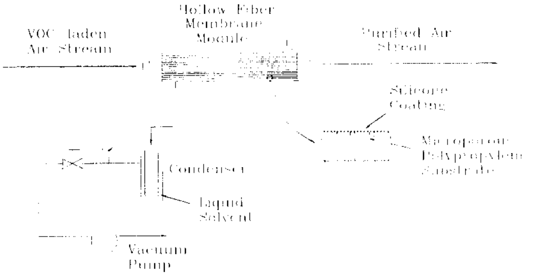

Fig. 1. Schematic of VOC separation from N_2 at atmospheric pressure by permeation through a hollow fiber module.

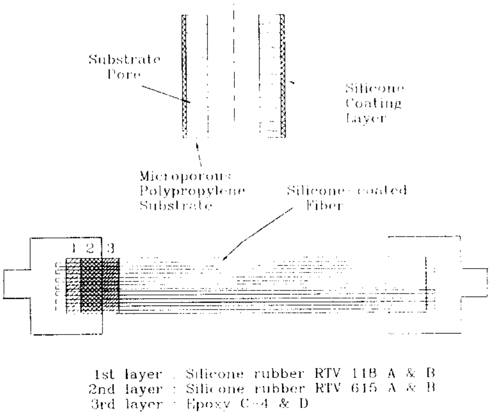

Fig. 2. Schematics of silicone-coated fiber and potting.

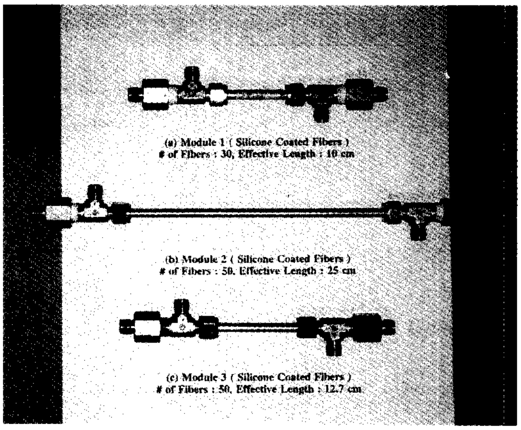

Fig. 3. Photograph of three membrane modules used.

three layers of potting. A two component RTV 118 translucent silicone rubber adhesive sealant was applied as the first layer. After 1 day cure, another two-component silicone rubber, RTV 615 mixed throughly using 10% by weight of the B curing agent with the A silicone compound was applied as a second layer. This compound develops crosslinking via an addition hydrosililation reaction. After a 4-day cure, epoxy(C-4 : resin, D : deactivator, weight ratio : 4/1) was applied as a third layer. This epoxy has also a good resistance to the VOCs used in the experiments. The specifications of the modules are given in Table 1 and Fig. 3 shows the photograph of the three membrane modules used in this study. Module 2 was used throughout the experiments. The smaller module 1 was used for the measurement of permeability of VOCs as well as nitrogen. Module 3 was used to determine the feasibility of the process.

2.3. Experimental Apparatus

The nitrogen stream from a N_2 cylinder was divided into two lines ; one was sent into the VOC containing bubbler and the other line was blended with the first VOC containing nitrogen

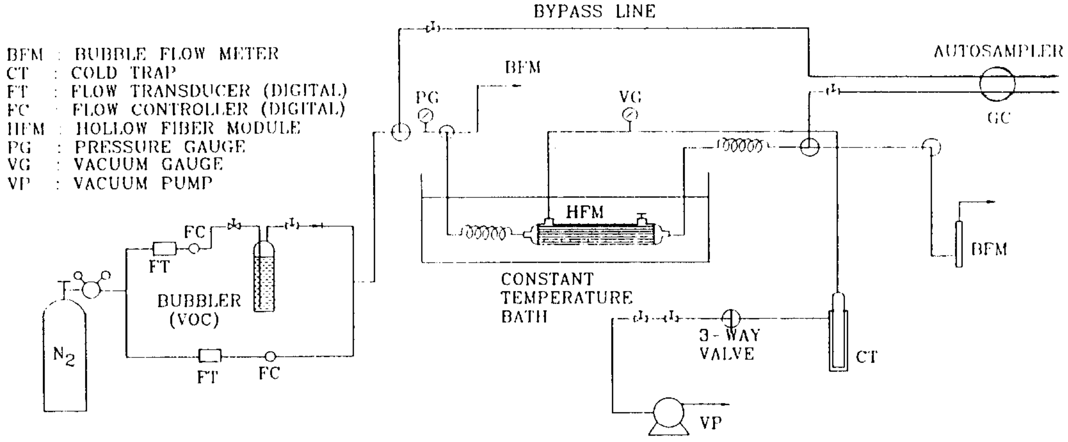

Fig. 4. Schematic diagram of experimental setup for VOC permeation from N_2 using a rubbery membrane.

line to form the feed gas/vapor mixture. This feed gas/vapor mixture was also divided into two lines using two different valves. One line which had a very small flow rate(1cc) of feed gas sample was directly connected to sample loop 1 of the automatic gas sampler and the rest of the feed mixture was sent through the membrane module. The feed outlet flow line was connected to the sample loop 2 of the automatic gas sampler. Using two different valves, only 1cc of feed outlet sample was injected to the GC and the rest of the flow was vented. In this way, both samples(feed inlet and feed outlet) were analyzed simultaneously during the experimental runs.

The membrane module was immersed in a constant temperature water bath and the water temperature was controlled by an attached heater. For these experiments, the temperature of the water bath was maintained at 30℃. The flow direction in the shell side was countercurrent to that of the feed side. In the cold trap, a mixture of dry ice and acetone was used to condense the VOCs inside the trap. A schematic diagram of the experimental setup is shown in Fig. 4.

2. 4. Experimental Procedure

Module 1 having a smaller area was used to measure the specific permeability(or permeance) of VOCs through the rubbery polymeric membrane. In the case of toluene, the feed inlet concentration was varied from 650ppmv to 26,000 ppmv. It was important to maintain the feed toluene concentration as constant as possible throughout the module because the purpose of these experiments was to obtain the relationship of permeance of toluene at given toluene concentration levels.

The feed flow rate was varied from 10 to 600cc/min. At each flow rate, 4~5 different concentrations of organic vapors were used(2,000~14,000ppmv for toluene and 400~50,000ppmv for methanol). Feed gas/vapor mixture was introduced to the tube side of the membrane permeator and most experiments were performed at a very high shell side vacuum level close to −29.9 inHg.

3. Results and Discussion

When nitrogen is present with an organic vapor as a feed, nitrogen permeation will greatly affect the selectivity. Pure nitrogen permeance value through this membrane is an important quantity. Different feed pressures were used on the tube side of each module and the permeation rate was measured from the shell side. The

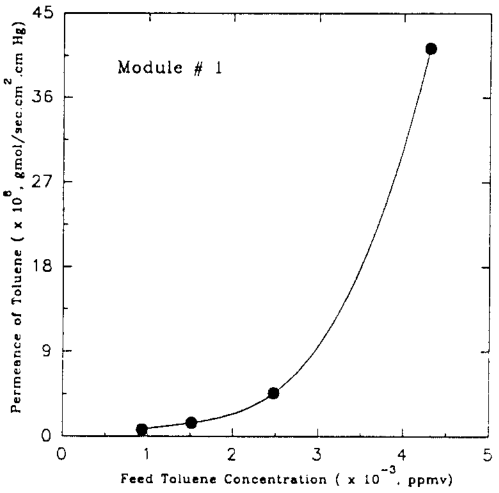

Fig. 5. Permeance of toluene vapor as a function of feed toluene concentration.

steady state permeation rate obtained from module 2 had a value of 4~5cc/min. Based on these experimental data, nitrogen permeance was calculated to be 3.9×10^{-10}gmol/sec · cm^2 · cmHg.

The calculated permeance of toluene vapor plotted as a function of the average feed side concentration is shown in Fig. 5. The relation between Q_t and partial pressure of toluene vapor could be best described by an exponential equation, $Q_t = a\times\exp(b\times P\cdot x)$. Here P is a total pressure and x is a mole fraction of toluene vapor. Accordingly, $P\cdot x$ represents a partial pressure of toluene vapor. The regression results for a and b were 2.33×10^{-9}gmol/sec · cm^2 · cmHg and 12.1cmHg^{-1}, respectively. Such a behavior may provide the framework needed for future modeling of VOC separation in such membrane module. However, the higher partial pressure of toluene in the permeate side suggests that Q_t should be a function of permeate side partial pressure as well ; or conditions must be such that permeate side partial pressure should be very small compared to feed side partial pressure. Further attention has to be paid to any possible boundary layer effects on the observed toluene permeance since it is so high.

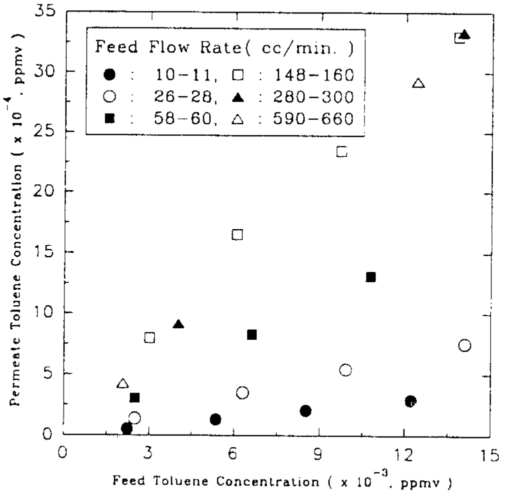

Fig. 6. Permeate toluene concentration vs. feed toluene concentration at variable feed flow rates.

In the low feed flow rate range up to 60cc/min., there was no pressure drop in the tube side. Toluene vapor mole fraction change between feed inlet and outlet increased as the feed inlet toluene vapor concentration increased since the permeation of toluene vapor increases strongly with an increase in the partial vapor pressure difference across the membrane. Calculated values of permeate side mole fraction of toluene vapor were found to increase with the increase of the feed inlet toluene vapor concentration(Fig. 6).

Fig. 7 shows the effect of feed toluene vapor concentration on the permeate toluene vapor flux. Toluene vapor permeation flux increased with an increase in the feed toluene vapor concentrations at a given feed flow rate. The toluene vapor flux for a given driving force is expected to be quite high due to the ultrathin nature of the silicone coating layer since species flux through such a membrane is inversely proportional to the thickness of the coating layer. The microporous polypropylene hollow fiber substrate has a high porosity(~0.4) ; therefore this substrate will not reduce the intrinsically high permeation rate through the silicone rubber skin. Experimental

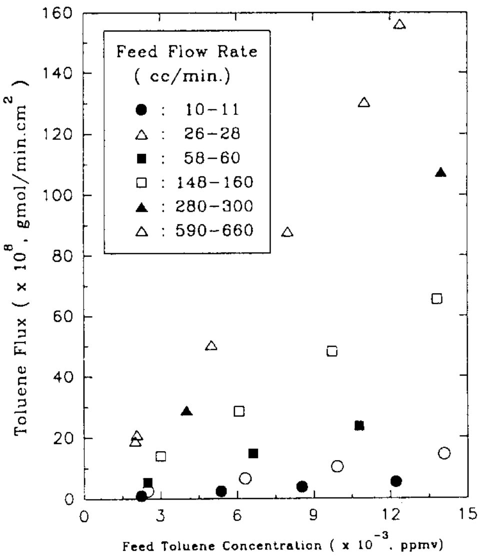

Fig. 7. Toluene vapor flux vs. feed toluene concentration at variable feed flow rates.

toluene vapor flux data using a dry asymmetric poly(ether imide) membrane was found to be 1.8 $\sim 3.0 \times 10^{-7}$gmol/cm^2 · min.(Feng et al., 1991) which was similar obtained with a silicone coated membrane. In higher feed toluene concentration ranges at relatively higher feed flow rate, the permeated toluene flux was higher in the silicone coated membrane compared to the poly(ether imide) membrane.

The permeance of nitrogen was found to be 3.8 $\times 10^{-10}$gmol/sec · cm^2 · cmHg and it was almost independent of the concentration(or partial pressure) of toluene vapor in the low feed flow rate ranges below 60cc/min.

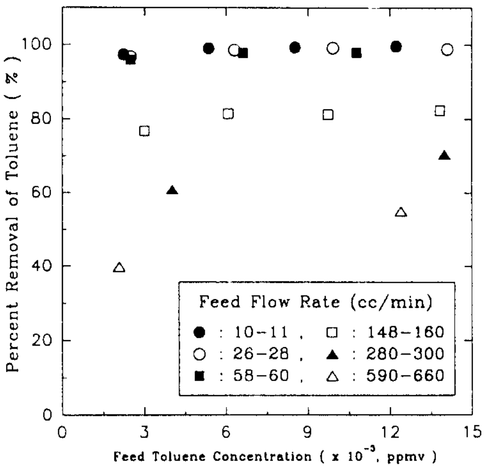

Fig. 8. Percent removal of toluene vapor vs. feed toluene concentration at variable feed flow rates.

Percent removal of toluene is plotted in Fig. 8 for changing feed toluene concentrations. For feed flow rates below 60cc/min., 96~99% removal of toluene vapor was achieved over the whole feed concentration range ; this corresponds to 1.2cc/min. per fiber feed flow rate for a fiber length of 25cm. For feed toluene concentration above 5,000ppmv and a flow rate of 30cc /min., more than 98% removal of toluene vapor was achieved. The percent removal of toluene vapor was reduced at higher feed flow rates, however, it was still considerable. For example, around 80% of toluene in the feed stream was removed at 150cc/min. of feed flow rate. The percent removal at a given feed flow rate increases with increasing feed inlet toluene vapor concentration.

The separation factor, which is defined as the ratio of permeances of toluene vapor and nitrogen, has been plotted in Fig. 9 as a function of feed toluene concentration. Separation factor increases slightly with increasing feed toluene concentration at a given feed flow rate. The calculated permeances of toluene vapor and nitrogen used was based on the whole permeator(module-averaged). Since toluene vapor concentration change along the permeator is very large, the calculated permeance of toluene vapor does not have a specific meaning. The nitrogen flux was similar in the low feed flow rate range ; the toluene vapor flux was increasing with increasing feed flow rate. The calculated permeance of toluene vapor was accordingly increased as the feed flow rate increased which resulted in a higher separation factor at higher feed flow rates.

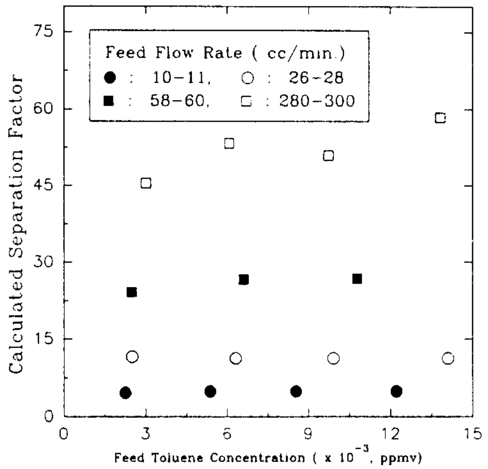

Fig. 9. Separation factor vs. feed toluene concentration at variable feed flow rates.

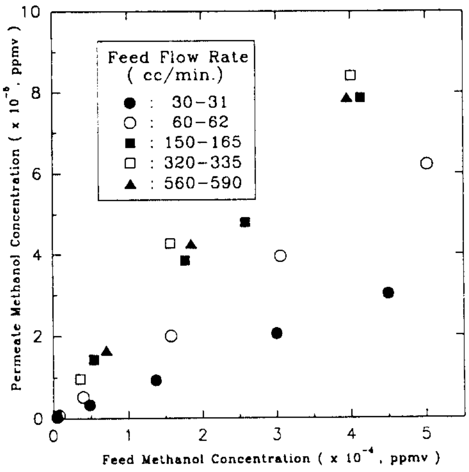

Fig. 10. Permeate methanol concentration vs. feed methanol concentration at variable feed flow rates.

In Fig. 10, permeate methanol vapor concentration is plotted as a function of feed methanol concentration. At feed methanol vapor concentrations below 1%(10,000ppmv), the enriched methanol vapor concentration in the permeate was less than 20% ; in the case of high feed methanol vapor concentration(around 5%) at a

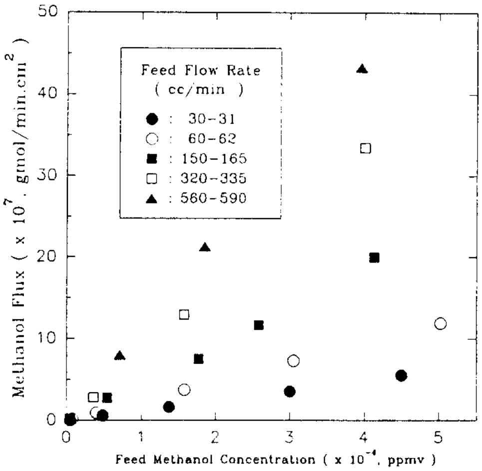

Fig. 11. Methanol vapor flux vs. feed methanol concentration at variable feed flow rates.

relatively high feed flow rate, methanol vapor concentration in the permeate side was as high as 80%.

Permeation fluxes of methanol vapor is shown in Fig. 11. Methanol vapor flux through the membrane increased with the increasing feed methanol vapor concentration as was observed for toluene vapor. The interaction of the vapor species with the silicone membrane causes the swelling of the polymer which strongly influences the sorption and diffusion behavior of the permeating species. The increase of vapor species flux with increasing feed vapor concentration becomes even higher for the more selective membrane.

Percent removal of methanol vapor as a function of feed methanol concentration is illustrated in Fig. 12. More than 96% of methanol vapor was removed for feed flow rates below 60cc/min. (1.2cc/min/fiber). When methanol vapor concentration was above 1,000ppmv for a feed flow rate of 30cc/min., more than 98% of methanol vapor removal was achieved. Generally the percent removal of methanol vapor was increased with increasing feed methanol concentration ; but at very high flow rates(above 300cc/min.) it remained almost constant. As feed flow rate was

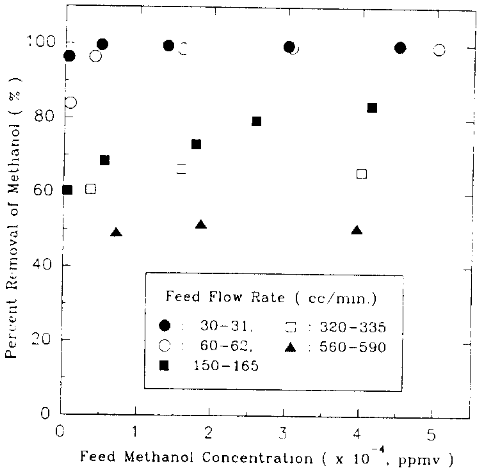

Fig. 12. Percent removal of methanol vs. feed methanol concentration at variable feed flow rates.

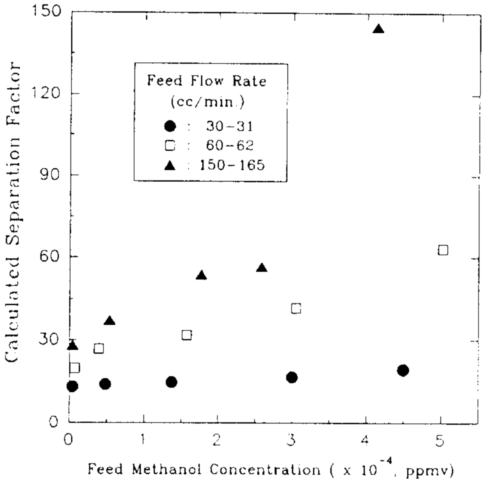

Fig. 13. Separation factor vs. feed methanol concentration at variable feed flow rates.

increased, percent removal of methanol vapor decreased.

Separation factor of methanol over nitrogen is plotted in Fig. 13 for changing feed methanol vapor concentration. Separation factor was generally higher at higher feed flow rates. In the low ranges of methanol vapor concentration where the nitrogen flux does not change much with the methanol concentration, separation factor remained similar at a given feed flow rate. In the higher methanol vapor concentrations at high feed flow rate, increasing methanol vapor flux combined with decreasing nitrogen flux was yielding a separation factor as high as 150.

4. Conclusions

The novel silicone-coated hollow fiber module was very efficient in removing VOCs such as toluene or methanol from N_2 stream. More than 96 % of VOCs were removed from a feed stream of 60cc/min. using a small module having a length of 25cm and 50 fibers when the permeate side was subjected to a high vacuum. These membranes were especially suitable for higher feed VOCs concentrations since the permeance of VOCs appears to increase very rapidly with increasing VOCs concentration.

The permeances of VOCs were at least an order of magnitude higher compared to nitrogen permeance yielding a high separation factor in the range of 10~125 depending on the feed flow rate, VOCs and VOCs concentration levels. Higher VOC-enriched permeate stream up to 80% could be obtained from a N_2 feed containing a relatively high concentration (5%) of methanol vapor.

The innate advantages of this membrane compared to other membranes used in VOCs removal and its optimal operating modes have resulted in a highly efficient performance for removing VOCs selectively from N_2 stream.

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