

Flow Swing Membrane Absorption–Permeation

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A cyclically-operated membrane permeation technique, flow swing membrane permeation (FSMP), has been studied for effective removal of volatile organic compounds (VOCs) from a gas stream to obtain a highly purified gas stream. Feed gas mixture is supplied to the lumen of hollow fiber membranes for a short period of time; then the feed flow is stopped for a brief period after which the feed gas flow into the fiber lumen is resumed. A vacuum is maintained continuously on the shell side for selective permeation and removal of VOCs from the feed gas mixture. Silicone-coated hollow fibers were employed to bring down the VOC concentration in feed N₂ to as low as 1–5 ppmv from feed concentration levels around 200–300 ppmv. The VOCs investigated were methanol, methylene chloride, acetone, and toluene. The purification capacity of the FSMP process has been shown to be considerably higher than that of the conventional steady-state operation of the membrane. To improve the membrane selectivity drastically, a contained liquid membrane concept was employed also using two sets of silicone-coated hollow fibers and silicone oil on the shell side. The permeate in this flow swing membrane absorption–permeation (FSMABP) process was almost pure VOC. Results of performances for such novel cyclic processes are presented. The potential of such techniques for various gas separations problems has been pointed out.

Introduction

High purification of a gas mixture is generally achieved in industry by means of pressure swing adsorption (PSA) processes (Yang, 1987). A gas mixture flows along a bed of adsorbents for a short period of time; the front end of the gas mixture is highly purified and is taken out as the product. After a short period of time, the flow of the fresh gaseous feed into the bed is stopped to prevent a breakthrough of the feed gas through the product end. The exhausted bed is either evacuated and/or cleaned by a purge gas to regenerate the bed of adsorbents for another cycle of adsorption-based purification of the feed gas mixture. The multistep process of bed regeneration is generally complex; PSA beds are bulky. It would be useful if a membrane device could be economically used to purify the feed gas mixture to the same extent. Membrane devices are compact and modular; further membrane capital costs are generally lower. However, membrane separation processes operated conventionally in a steady-state fashion are known to be efficient for bulk gas separation only (Beaver et al., 1988).

Existing cyclically-operated membrane-based separation processes are of two types. *In the first type of processes*, polymeric gas separation membrane-based devices are operated with a cyclic pulsing of the gas pressure on the upstream side of the membrane between a high value of P , the feed gas pressure, and p , the permeate side pressure ($<P$). The total permeate side pressure p is always maintained at a low value (Paul, 1971). For a gas mixture, such an operation allows an improved selectivity between a rapidly-diffusing species

1 and slower-diffusing species 2. The first fraction of the permeate collected is more enriched in species 1 than is possible in steady-state gas permeation processes.

A recent minor variation of such a process may introduce an inert purge gas or inert liquid into the feed gas side during the interval when the high-pressure feed gas flow on the feed side is stopped (LaPack and Dupuis, 1994). Another variation of Paul (1971) suggested by LaPack and Dupuis (1994) involves collecting a second permeate fraction more enriched in species 2 during a brief period of time after the first period used to collect a permeate fraction enriched in species 1. There is another variation suggested for the first type of processes. Ueda et al. (1990) implemented alternate introduction of feed gas under pressure to the feed side and evacuation of the permeating gas under vacuum to maximize the driving pressure difference between the feed and the permeate side.

It is useful to point out here about a class of steady-state processes with special provisions for start-up time-dependency. In air dehydration processes by a membrane unit, at steady state, the membrane unit delivers adequately dehumidified air. However, during start-up with a compressor, there are problems due to low pressure and residual moisture in the permeator from an earlier period. A purge gas stream is introduced at atmospheric pressure from the high-pressure dried product gas end during the interrupted period when no high-pressure feed gas is being supplied. Usually the purge gas is obtained from the purified high-pressure product gas obtained from the earlier operation (Rice and Brown, 1991). The utility of the high-pressure purge stream has also been demonstrated in the production of N₂. To avoid using a purge stream in air dehydration processes of Rice and Brown (1991), Brockmen and Rice (1992) have suggested a delay at the

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beginning of the process as well as additional condensation of moisture beyond the compressor prior to introduction of the high-pressure feed air into the membrane dehumidifier.

In the second type of processes, microporous hollow fiber membranes have been employed along with adsorbent particles (Gilleskie et al., 1995) or an aqueous absorbent liquid that does not wet the pores of the membrane (Bhaumik et al., 1996) on the shell side. The feed gas mixture flows through the bores of the hollow fine fibers. The adsorbent particle adsorbs specific species from the feed gas mixture; alternately the aqueous absorbent liquid absorbs the selected species. The high-pressure feed gas leaving the exit end of the feed fibers is highly purified; the feed gas flow is stopped after sometime to prevent breakthrough of the species at the exit end. The bed of adsorbents or the shell-side liquid absorbent is then regenerated by a variety of demanding multistep procedures borrowed from PSA processes. While such processes are inherently capable of producing a highly purified gas stream from the incoming high-pressure feed gas, the bed regeneration process leaves much to be desired especially when the rapid cyclic processes are implemented for high levels of feed gas purification (Bhaumik et al., 1996). The membrane in such a process does not perform any chemical separation as such.

We present here a rapid and simple cyclic process for the separation of a binary gas mixture by a contained liquid membrane. The process is called "flow swing membrane absorption-permeation" (FSMABP) and is illustrated here for the separation of volatile organic compounds (VOCs) from nitrogen at essentially atmospheric pressure. The process may also be termed as "flow swing liquid membrane permeation" (FSLMP). For the system of VOC-N₂ chosen, this process *very simply* provides two almost pure streams, a N₂ stream containing very little VOC and a VOC stream containing almost no N₂. We illustrate here the process also for the situation where only a polymeric VOC-selective layer on the hollow fiber is used as the selective membrane. This membrane has a much lower VOC-N₂ selectivity and the permeate stream in this case has limited enrichment in the VOCs. "Flow swing membrane permeation" (FSMP) would be an appropriate name to characterize such a process. The VOCs selected for the study were methanol, methylene chloride, acetone, and toluene. The concentration of such VOCs used in the N₂ feed gas at essentially atmospheric pressure was around 200–300 ppmv. For a particular set of experiments, 900 ppmv of VOC in N₂ was employed. The permeate side vacuum was 28.4 in. of Hg or upward.

Cyclic Flow Swing Membrane Permeation Process

We now describe the processes of FSMP and FSMABP in that order. In the FSMP process, the feed gas mixture is cyclically introduced into the feed channel inlet and flows on one side of the membrane and exits at the end of the membrane feed channel. On the other (permeate) side of the membrane, the permeate channel conditions are maintained for permeation of the feed gas species from the feed side to the permeate side. The condition may be created by having the permeate side total pressure less or very much less than the feed side total pressure; alternately there may be a sweep fluid (gas or liquid) flowing on the permeate side to ensure

the $p_i \ll P_i$. This mode of gas permeation when carried out in a steady-state manner results in conventional membrane gas permeation processes. The process of this study is operated such that the feed gas flow into the membrane device feed channel is *intermittent or cyclic*.

For a short period of time, say 10 or 20 s or 1 min, etc., the feed gas flows into the membrane channel which has the feed gas pressure (Figure 1). This time may be called the adsorption time or adsorption time t_{ads} . The front end of the feed gas stream will be highly purified because the membrane acts as an adsorber for species A. During this time, the permeate side pressure will be lower than the feed side pressure or the permeate side is maintained under vacuum or a sweep fluid is passed over the permeate side so that the feed gas species permeate through the membrane to the permeate side. Figure 1 illustrates the case where a volatile organic compound (VOC) present as a vapor is being removed by selective permeation through a silicone-coated hollow fiber membrane from a nitrogen or air feed gas stream. After this *adsorption time* or *adsorption time* is over, the feed gas flow into the membrane feed channel is stopped for an amount of time, t_{reg} , called the *stripping time* or *regeneration time*. The membrane feed channel exit is also closed; no retentate stream is withdrawn. However, during this time, species A (e.g., the VOC) present in the remaining feed gas, the retentate, in the feed channel (especially near the back end, namely the feed entry location) will be preferentially removed by permeation through the membrane. Thus the gas remaining in the feed channel will be highly purified in species B (e.g., N₂ or air). The gas pressure in the feed channel will be marginally reduced from the feed gas pressure due to permeation through the membrane during the short period (t_{reg} in seconds). After adequate purification of the remaining gas, the feed gas flow into the membrane feed channel is initiated again and a new cycle begins. The total cycle time T_{cycle} ($=t_{ads} + t_{reg}$) is the sum of the adsorption time and the regeneration time.

When the feed gas is reintroduced into the membrane feed channel after the *regeneration time* is over, the gas that is pushed out first as the retentate stream at the exit end is very highly purified in species B. Also the gas leaving the feed side exit location as the retentate during the short adsorption/adsorption time t_{ads} is highly purified in B. The reason is as follows: the membrane facing the feed gas mixture acts as an adsorber/adsorber for species A in preference to species B. Thus during the short period of t_{ads} , the *adsorption time* or *adsorption time*, the feed gas flowing into the feed membrane channel is purified due to removal of species A in the membrane acting as an adsorber/adsorber. The retentate gas that leaves the membrane unit at the other exit end during this period is highly purified in B. Thus, the gas stream withdrawn as the retentate from the feed channel exit during the adsorption/adsorption time after one cycle is highly purified in species B due to two reasons: *first*, the gas left after regeneration time is highly purified in B; *second*, the front end of the fresh feed gas introduced at the beginning of the adsorption time gets highly purified by adsorption/adsorption in the membrane acting as an adsorber/adsorber.

The process illustrated may be utilized for a variety of processes: using an O₂-selective membrane, N₂-enriched air with very little O₂ may be produced; using

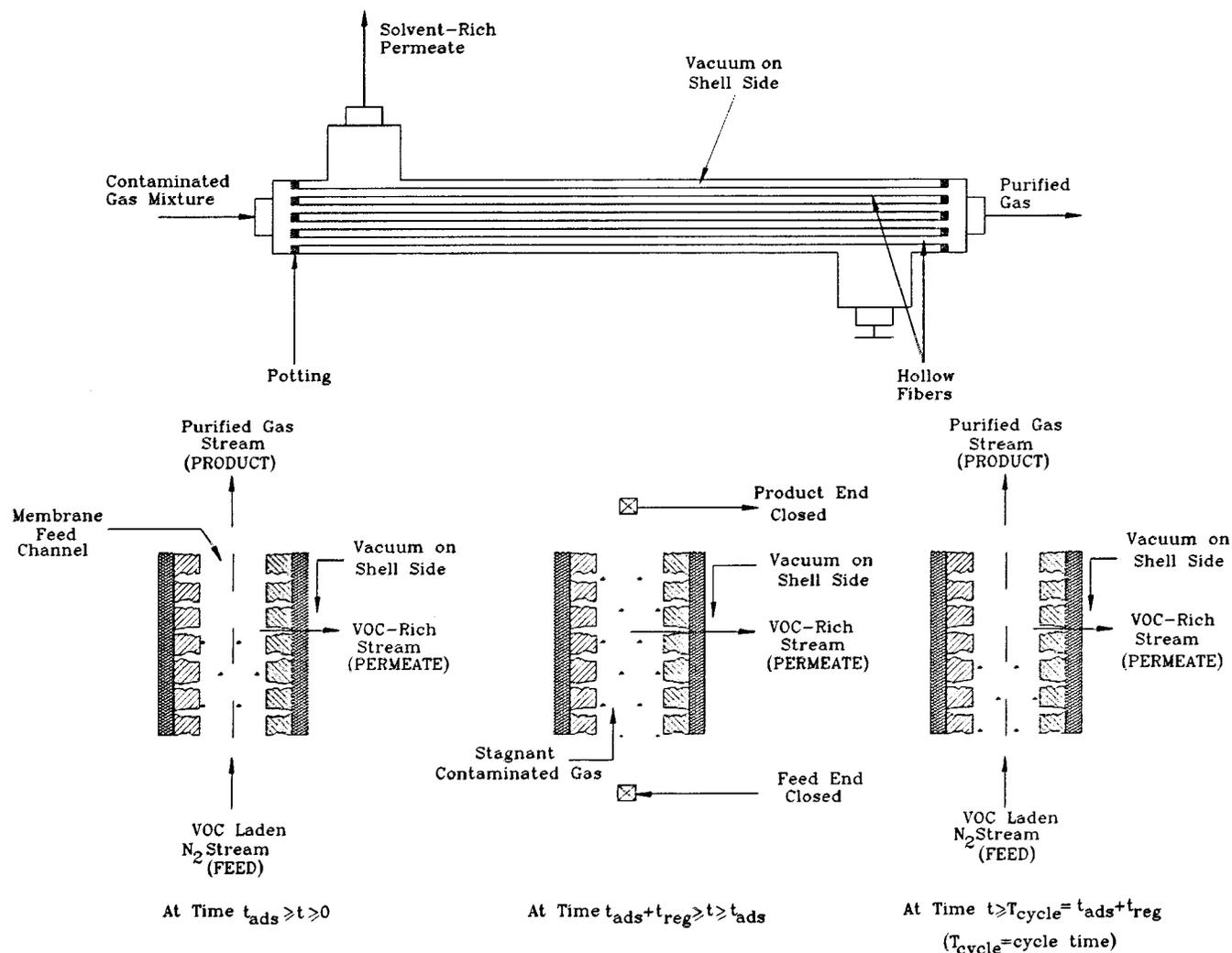


Figure 1. Schematic of a hollow fiber module with one set of fibers and the nature of operation in flow swing membrane permeation (FSMP).

a CO_2 -selective membrane, methane from natural gas can be highly purified; using a membrane that is highly selective for olefins over paraffins, a paraffinic feed gas may be purified of olefins to a very high degree just as a highly olefin-rich permeate will be produced.

The membrane illustrated in Figure 1 is a polymeric hollow fiber; specifically, it is a thin film composite membrane having a selective nonporous polymeric membrane coating on the outside diameter over a microporous substrate. The feed gas was allowed to flow into the fiber bore at close to atmospheric pressure and vacuum was maintained on the shell side of the hollow fiber device. The process may be operated with the feed gas stream on the shell side and the permeate stream on the fiber bore side as well.

Figure 1 illustrates a polymeric hollow fiber membrane. Liquid membranes are known to be efficient for gas separation as well. Figure 2 illustrates a flow swing membrane absorption-permeation (FSMABP) process employing a coated hollow fiber contained liquid membrane configuration (Papadopoulos and Sirkar, 1994). The feed gas mixture flows through the bores of one set of fibers used in the FSMP process, the feed fibers, while the permeate gas stream flows through the bores of a second (usually identical) set of fibers, the strip or regeneration fibers. In between these fibers, the shell side is filled with a liquid highly selective for species A

to be removed from the feed gas stream. In this case, a VOC-containing N_2 stream was fed into the bores of the feed fibers and a vacuum was pulled in the bores of the second set of fibers. A highly VOC-selective essentially nonvolatile oil like Paratherm (a mineral oil) or silicone oil was used as the liquid membrane. Since N_2 has an extremely low solubility in this liquid membrane, the permeate gas stream flowing through the second set of fibers was virtually pure VOC. Thus, two essentially pure streams are produced in the process: an essentially VOC-free N_2 stream from the exit end of the feed fibers and an essentially VOC-containing vapor stream from the strip fibers. As the VOC-containing N_2 stream enters the feed fibers, the VOCs are absorbed in the oil; the bed of oil acts as an adsorber bed producing a very pure N_2 at the exit of the feed fibers. However, after a short adsorption/absorption time, t_{ads} , the feed gas flow is stopped and both ends of the feed fibers are shut off. Meanwhile, a vacuum is always maintained in the strip fibers. During the next part of the cycle lasting for t_{reg} seconds, this oil as well as the feed gas left in the feed fiber are purified by selective permeation-based removal of the VOC. (Note that this purification also takes place during t_{ads} .) Such a process may also be implemented with a single set of fibers as in Figure 1: if a nonvolatile species A-selective liquid is immobilized in the pores of the porous substrate of the thin film composite hollow

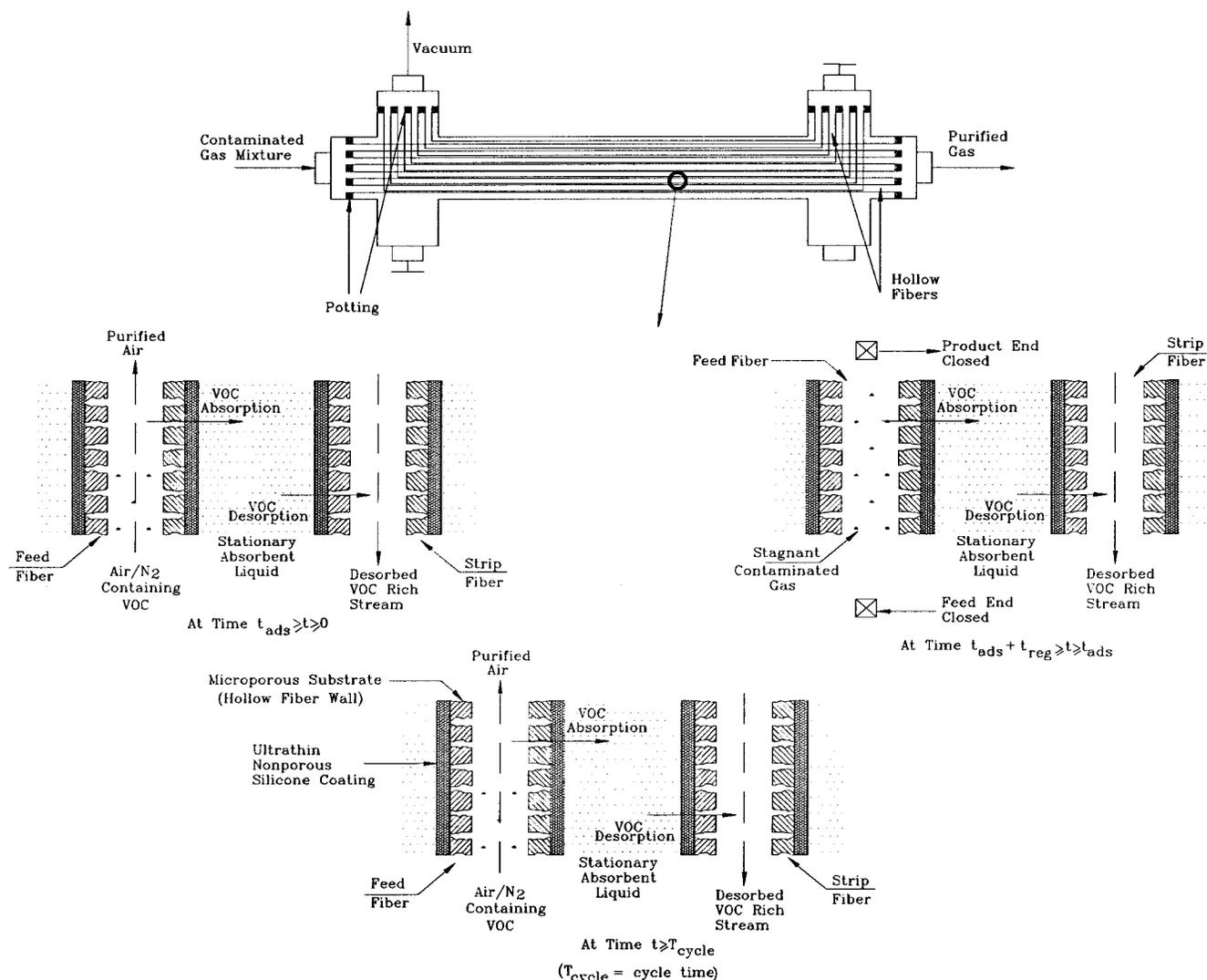


Figure 2. Schematic of a hollow fiber module with two sets of fibers and the nature of operation in flow swing membrane absorption-permeation (FSMABP).

Table 1. Geometrical Characteristics of Different Hollow Fiber Modules

module no.	type of fiber	fiber i.d. (cm)	fiber o.d. (cm)	effective length (cm)	shell i.d. (cm)	no. of fibers	void fraction (%)	mass-transfer area (cm ²) ^a	mass-transfer area/volume (cm ²)/(cm ³) ^a
1	Celgard ^b with a silicone skin	0.024	0.030	20.5	0.80	300	57.81	579.62	56.25
2	Celgard ^b with a silicone skin	0.024	0.029	42.5	0.92	150 ^c	70.19	580.80	29.29
3	Celgard ^b with a silicone skin	0.024	0.029	25.4	0.46	50	80.09	115.7	27.75

^a Calculation based on outer diameter of the fiber. ^b AMT Inc., Minnetonka, MN. ^c Number of fibers in each set.

fiber membrane shown in Figure 1, then the FSMABP process can also be implemented successfully.

This cyclic process of flow swing membrane permeation (FSMP) or flow swing liquid membrane-permeation (FSLMP) or flow swing membrane absorption-permeation (FSMABP) produces a time-dependent highly purified species B containing stream at the exit end of the membrane feed channel. To obtain a steady output, one may use a surge drum to collect this unsteady output and withdraw a smaller steady stream (see Experimental Section). Alternately, one can use two or three or more membrane devices in parallel with the programmed feed side inlet gas valve control such that the sum of t_{ads} 's for the different membrane devices is equal to the cycle time T_{cycle} for the process. Similarly,

the sum of $t_{ads} + t_{reg}$ for each of the different membrane devices should equal the cycle time T_{cycle} for the process.

It is useful to point out here that the process studied by Poddar et al. (1996a, 1996b), namely, a steady and continuous process of VOC absorption in a countercurrent membrane absorber (employing silicone oil or Paratherm oil as an absorbent) and subsequent stripping of VOCs from the absorbent in a separate membrane stripper by vacuum as the absorbent is recirculating between the absorber and the stripper effectively achieves the same goal as the FSMABP process here. The present process does not have to pump the viscous oil. It further avoids saturation or near-saturation of the absorbent at the front end since it is being continu-

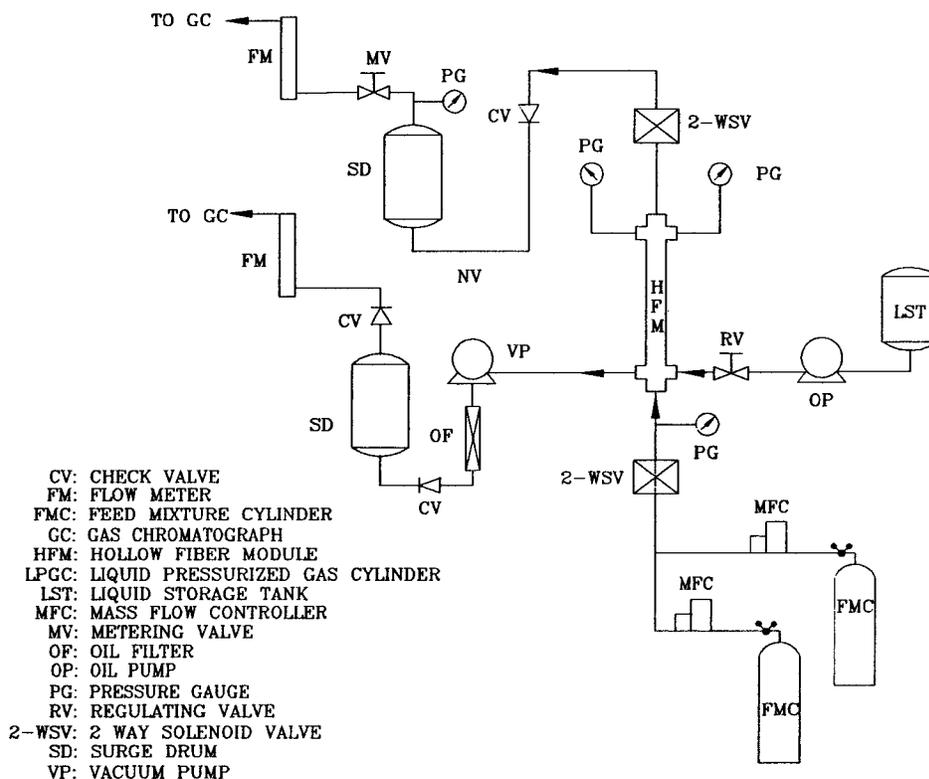


Figure 3. Experimental setup for FSMABP.

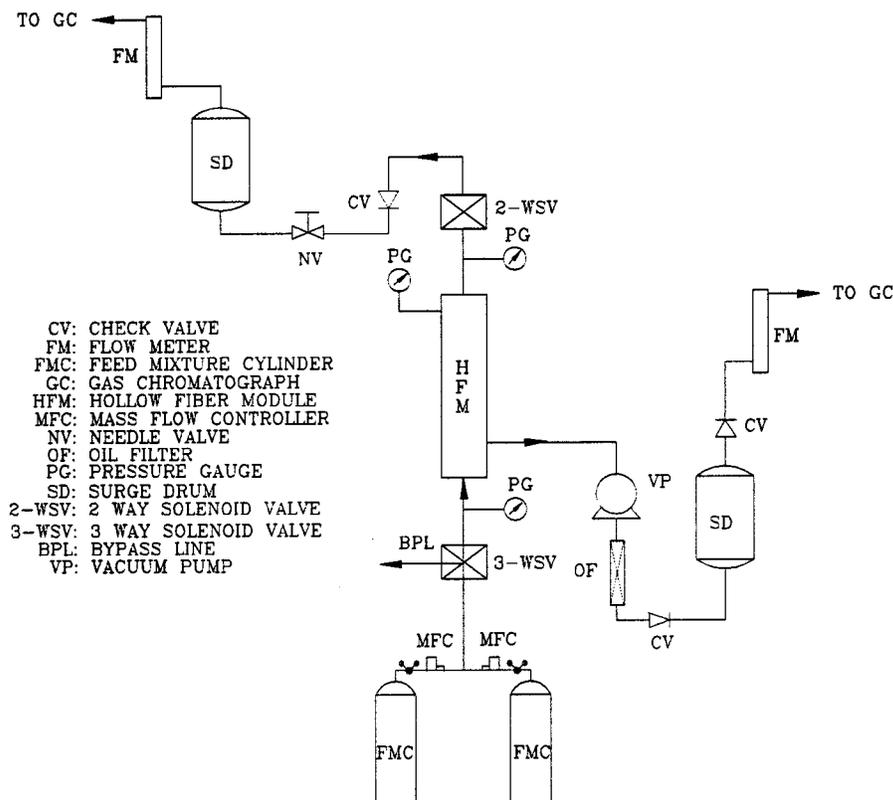


Figure 4. Experimental setup for FSMP.

ously regenerated by vacuum. As a result, this device is a more efficient purifier than those of Poddar et al. (1996a,b). The present device functions just like a carbon bed except vacuum is being employed to continuously regenerate it. Further, the regeneration process is simple and there is no evacuation of the bed.

Experimental Section

Three membrane modules were employed. As shown in Table 1, module no. 1 has a single set of 300 fibers; these fibers are microporous polypropylene hollow fibers (Hoechst Celanese, SPD, Charlotte, NC) X-10 (0.03 μm

Table 2. Experimental Results for FSMABP for Methanol Separation from N₂ in Module No. 2

VOC	total cycle time (s)	absorption time (s)	gas flow rate (cm ³ /min)		VOC concentration (ppmv)	
			feed	product	feed	product
methanol	20	10	26	12	191	91
	20	10	6	3	207	19
	20	10	3.3	1.5	261	5
	40	20	6	3	204	16
	80	40	6	3.5	225	22

Table 3. Experimental Results for FSMABP for Methylene Chloride Separation from N₂ in Module No. 2

VOC	total cycle time (s)	absorption time (s)	gas flow rate (cm ³ /min)		VOC concentration (ppmv)	
			feed	product	feed	product
methylene chloride	110	10	30	3	207	104
	20	10	6	2.5	290	15
	40	20	10	5	292	43
	40	20	6	3	285	15
	80	40	30	16	206	96
	80	40	10	5	285	38
	80	40	6	3	284	21

Table 4. Experimental Results for FSMABP for Toluene and Acetone Separation from N₂ in Module No. 2

VOC	total cycle time (s)	absorption time (s)	gas flow rate (cm ³ /min)		VOC concentration (ppmv)	
			feed	product	feed	product
toluene	40	20	30	15	253	~0
	40	20	25	12	253	~0
acetone	40	20	15	6	331	169
	40	40	6	2.5	284	21

pore size) with a thin plasma-polymerized nonporous coating of silicone on the outside diameter (prepared by AMT Inc., Minnetonka, MN). Module no. 2 has two sets of 150 identical fibers, each fiber set having a separate inlet and outlet. Module no. 3 has only 50 fibers with a more selective and permeable membrane. The method of preparation of these modules has been detailed in Papadopoulos (1992).

The experimental setup for FSMABP is shown in Figure 3. A mixture of the VOC and nitrogen from a cylinder was mixed with pure nitrogen to prepare a feed mixture having the desired composition. This gas mixture was fed through the bores of one set of fibers for a short time; then the feed gas flow was stopped by a two-way solenoid valve (2-WSV) (Components and Control, Carlstadt, NJ). The outlet end of the feed mixture also had a similar solenoid valve which worked in perfect synchronization with the one at the feed inlet end. Both two-way solenoid valves were controlled by a single timer. The feed flow rate was controlled by an electronic mass-flow metering valve (Matheson, E. Rutherford, NJ).

The shell side of the module had been previously filled with silicone oil (Silicone 200, Dow Corning, Midland, MI) through a check valve using a pump. Once it was filled with the oil, both ends of the shell side were kept closed. The pressure of the silicone oil was maintained at 10 psig which was always higher than the incoming feed gas pressure (~5 psig) to prevent bubbling (Poddar et al., 1996a).

During the part of the cycle meant for direct absorption of the VOC from the flowing feed stream, the VOC permeated through the silicone coating of the hollow

fibers selectively over N₂/air and was absorbed in the stationary absorbent liquid (silicone oil) on the shell side of the cylindrical module. Continuous vacuum applied through the tube side of the second set of fibers, the strip fibers, provided a continuous driving force for the desorption of the VOCs from the absorbent liquid. Thus, the VOCs in the silicone oil were desorbed and then permeated through the silicone coating of the second set of hollow fibers. This concentrated stream was collected in a surge vessel. The purified gas was collected in another surge vessel at the feed outlet end during the first part of the absorption cycle (when the solenoid valve at the feed outlet end was open). It was sent to a gas chromatograph (GC) (Star 3400, Varian, Sugarland, TX) for analysis.

All connecting lines used for these experiments were 1/8 in. soft copper tubing (McMaster Carr, New Brunswick, NJ). Inlet feed pressure and the vacuum level were measured with pressure gauges (Matheson, E. Rutherford, NJ). All gas mixtures used for these experiments were obtained from Matheson Gas Products (Matheson, E. Rutherford, NJ).

The experimental setup for flow swing membrane permeation (FSMP) is shown in Figure 4. A 3-WSV valve (Components and Control, Carlstadt, NJ) was used at the inlet of the cylindrical module. At the treated gas exit, a 2-WSV valve was used. For a short period of time, both valves were open for the feed to enter and the purified gas to exit the tube side of the module. VOCs from the feed stream permeated through the silicone coating of the hollow fibers into the shell side where desorption was constantly taking place as the vacuum was constantly applied. Pressure difference between the feed and the vacuum side created the partial pressure driving force for the removal of the VOCs. Opening and closing of these two solenoid valves were simultaneously controlled with a single timer. Concentrated permeated stream and purified feed gas were analyzed in the GC (Star 3400, Varian, Sugarland, TX). For steady-state operation, the solenoid valves were turned off so that the feed gas mixture could flow continuously into the membrane module and the product gas was removed continuously from the fiber bore at the exit.

Results and Discussion

The experimental results for the removal of VOCs from N₂ by two processes, FSMABP and FSMP, are presented here. Module 2 containing two sets of fibers was employed for FSMABP studies with silicone oil on the shell side. Module 1 was primarily used to study the FSMP-based separation. Module 3 was used to compare steady-state separation with unsteady-state cyclic separation studied here. The cycle time T_{cycle} was varied initially over a wide range. Afterwards, T_{cycle} was varied at the most up to 120 s; more often it was limited to 20–40 s. Usually a run was carried out for a period of 4–8 h. Results obtained after a considerable number of cycles (after 2–3 h) are reported here. Sometimes these runs were continued for over 24–36 h. Essentially no differences were observed in the performance over these extended periods.

Table 2 illustrates the results obtained for FSMABP separation of methanol from the feed N₂ stream. As the feed gas flow rate was decreased from 26 to 3.3 cm³/min, the methanol concentration in the treated gas from the surge drum was reduced from 91 to 5 ppmv for

Table 5. FSMP Experiments^a for Methanol Separation from N₂

total ^c cycle time (s)	gas flow rate (cm ³ /min)			VOC concentration (ppmv)			surge ^b drum pressure (psig)	feed pressure (psig)	vacuum (in Hg)
	feed	product	permeate	feed	product	permeate			
20	100	23.4	26.6	259	19	1428	5	6	28.4
20	80	18.3	21.7	265	13	1452	4	5	29.2
20	60	13.0	17.0	279	7	1299	3	4	29.2
20	30	5.5	9.5	298	2	831	1	2	29.2

^a All runs were for ~20 h. ^b Product surge drum volume: 150 cm³. ^c t_{ads} , $t_{\text{reg}} = 10$ s.

Table 6. FSMP Experiments^a for Methylene Chloride Separation from N₂

total ^c cycle time (s)	gas flow rate (cm ³ /min)			VOC concentration (ppmv)			surge ^b drum pressure (psig)	feed pressure (psig)	vacuum (in Hg)
	feed	product	permeate	feed	product	permeate			
20	100	23.4	26.6	330	13	1639	5	6	29
20	80	20.0	20.0	339	12	1578	4	5	29
20	60	12.6	17.4	321	12	1090	3	4	29
20	60	12.4	17.6	319	2	995	3	4	29.6
20	30	4.8	10.2	335	1.5	994	1	2	29

^a All runs were for ~20 h. ^b Product surge drum volume: 150 cm³. ^c t_{ads} , $t_{\text{reg}} = 10$ s.

Table 7. FSMP Experiments^a for Acetone Separation from N₂

total ^c cycle time (s)	gas flow rate (cm ³ /min)			VOC concentration (ppmv)			surge ^b drum pressure (psig)	feed pressure (psig)	vacuum (in Hg)
	feed	product	permeate	feed	product	permeate			
20	100	23.2	26.8	348	36	1085	5	6	29.1
20	80	17.9	22.1	331	26	1270	4	5	28.4
20	60	12.6	17.4	338	22	1195	3	4	29.2
20	30	5.6	9.4	330	3.1	862	1	2	28.4

^a All runs were for ~20 h. ^b Product surge drum volume: 150 cm³. ^c t_{ads} , $t_{\text{reg}} = 10$ s.

processes with $T_{\text{cycle}} = 20$ s and $t_{\text{ads}} = 10$ s. Obviously, at higher flow rates, the absorption capacity of the system is limited and the extent of gas purification is less than desired. As the gas flow rate is decreased, the absorption capacity of the system can handle the VOC load and delivers the purified gas at 5 ppmv or lower. This table further shows that an increase in t_{ads} (and therefore of T_{cycle}) from 10 to 40 s (T_{cycle} values are correspondingly 20 and 80 s) marginally increases the VOC concentration in the treated gas.

Table 3 illustrates a somewhat similar behavior for the removal of methylene chloride. As the feed flow rate is reduced from 30 to 6 cm³/min for $t_{\text{ads}} = 40$ s ($T_{\text{cycle}} = 80$ s), the VOC concentration in the treated gas is reduced to 21 ppmv. For 6 cm³/min feed flow rate, at two smaller t_{ads} values, e.g., 20 and 10 s, the treated gas compositions are somewhat lower (~15 ppmv). At lower feed gas flow rates and lower values of t_{ads} , the extent of gas purification will be increased considerably. We have not provided any information in either Table 2 or 3 about the permeate stream. Silicone oil has an extremely low solubility for N₂. The permeate stream was essentially pure VOC with very small amounts of nitrogen.

Table 4 provides a limited amount of data obtained by purification of nitrogen streams containing either toluene or acetone. The purification of N₂ was very high for the case of toluene; toluene was not detectible in the treated gas. Silicone oil is a very good absorbent for toluene. Poddar et al. (1996a) had also observed that toluene absorption in silicone oil was always much better than those of methylene chloride, acetone, and methanol.

We now focus on the results of the FSMP process for purification of similar VOC-containing N₂ streams employing module no. 1 containing a single set of silicone rubber-coated hollow fibers. These coatings have much lower selectivities for VOC over N₂, especially at these low VOC concentrations. As a result, the

permeate stream VOC concentrations are not expected to be high. Table 5 provides the results for methanol separation from N₂. As the feed gas flow rate was reduced from 100 to 30 cm³/min, the methanol concentration in the treated gas was reduced from 19 to 2 ppmv. Correspondingly, the permeate methanol concentration was reduced from 1428 to 831 ppmv. Obviously, the permeate side enrichment was low since the feed inlet concentration was around 259–298 ppmv and the membrane selectivity was not high.

The separation performances of the FSMP process for N₂ containing methylene chloride are given in Table 6. As before, we observe that as the feed gas flow rate is reduced for a cycle time of 20 s ($t_{\text{ads}} = 10$ s), the extent of the gas purification increases; the purified N₂ stream had only 1.5 ppmv of the VOC. Focusing on a feed flow rate of 60 cm³/min, we find that a higher level of purification is achieved by a higher vacuum level (29.6 in. of Hg compared to 29 in. of Hg). This explains why the purified gas composition is around 2 ppmv compared to 12 ppmv with the lower level of vacuum. Table 7 shows the results for purification of N₂ by membrane removal of acetone. Again, the purification behavior is similar; only acetone is somewhat more difficult to remove. Hence, the treated N₂ gas has somewhat higher concentrations.

Figure 5 illustrates how concentration of the treated gas varies with time over an extended period for the system methanol/nitrogen for a feed flow rate of 60 cm³/min and a feed concentration of 279 ppmv and t_{ads} , $t_{\text{reg}} = 10$ s. The initial low value is due to pure N₂ in the surge drum tank. Within 2–3 h, it achieves a steady state. Any fluctuation in the output values is due to fluctuations in temperature and vacuum. The steady-state response of the cyclic process is provided in every one of the tables considered so far.

The inherent superiority of the FSMABP and FSMP process for gas purification may be appreciated by

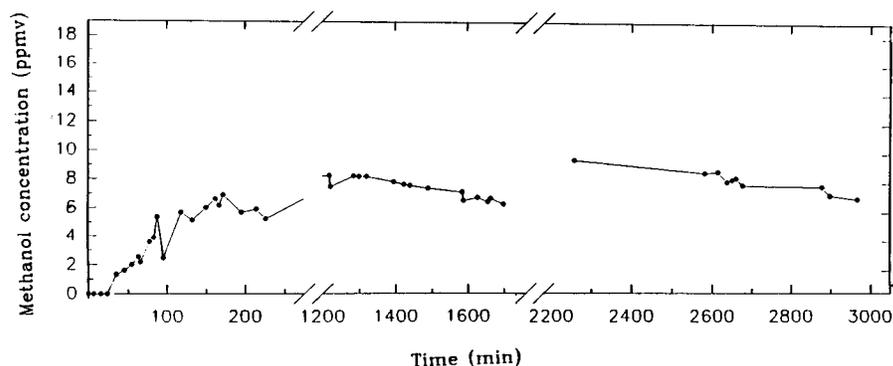


Figure 5. Methanol concentration in the treated N_2 stream over an extended period of time.

Table 8. Comparison of FSMP Process and the Conventional Steady-State Gas Permeation Process for Separation of Methanol or Acetone from N_2 Using Module No. 3

component (mode of operation)	total ^b cycle time (s)	feed comp. (ppmv)	product comp. (ppmv)	permeate comp. (ppmv)	feed flow rate (cm^3/min)	product flow rate (cm^3/min)	surge ^a drum press. (psig)	feed press. (psig)	vacuum (in Hg)
methanol (cyclic)	20	900	~0	4652	100	18.9	5	6	29.3
methanol (steady state)		900	35	21 542	100	95	5	6	28.9
methanol (cyclic)	20	900	~0	7450	150	35.1	7	8	29.6
methanol (steady state)		900	83	26 466	150	139	7	8	28.9
acetone (cyclic)	20	990	67	3144	100	17.7	5	6	29.5
acetone (steady state)		990	330	10 806	100	94	5	6	29.2
acetone (cyclic)	20	990	16	1969	80	8.2	5	6	29.5
acetone (steady state)		990	242	8998	80	95	5	6	29.3

^a Product surge drum volume: 150 cm^3 . ^b t_{ads} , $t_{reg} = 10\text{ s}$.

comparing methanol removal results in Poddar et al. (1996b) with those obtained here. Both Tables 2 and 5 show that methanol concentration may be reduced to very low levels (1.5 and ~ 2 ppmv, respectively) at low gas flow rates. Poddar et al. (1996b) had difficulty in reducing the concentration to a level lower than 25 ppmv at low gas flow rates. Stripping is quite demanding in Poddar et al. (1996b) since all of the absorbent has to be stripped to a low level. This is not a requirement in the present process. The level of contamination of the front end of the absorbent can be easily maintained at a low level, ensuring very high levels of gas purification.

An experimental validation of the inherent superiority of the new processes of this study for high purification of gaseous mixtures will be provided now. The process of FSMP will be compared with the conventional steady-state mode of gas separation using module no. 3. A vacuum was used on the permeate side in both cases. A few results are presented in Table 8. First, we observe for methanol that steady-state operation leads to a purified product level of 35 ppmv whereas under the same flow rate of $100\text{ cm}^3/min$, the treated feed gas VOC concentration is essentially zero when the FSMP process is employed. As the feed flow rate is raised to $150\text{ cm}^3/min$, the permeate composition in both processes are increased; the purified product gas has a higher composition of 83 ppmv in the steady-state process as it should be due to higher flow rate. The performance of this particular module no. 3 is better than that of module no. 1 since the hollow fiber membranes in module no. 3 are better.

The behavior for acetone is generally similar except that at the high gas flow rate employed (100 and $80\text{ cm}^3/min$), the system has limited purification capacity for the polar VOC, acetone. The cyclic process produced a purified gas composition of 67 or 16 ppmv (depending

on the flow rate) whereas the steady-state process yielded much higher values of 330 and 242 ppmv, respectively.

Concluding Remarks

A cyclically-operated membrane permeation process has been proposed for gas purification. There are no drastic changes of pressure on either side of the membrane in such a process unlike pressure swing adsorption processes or their corresponding membrane process analogs. The process proposed is relatively simple and is demonstrably capable of a very high degree of feed gas purification. If the membrane is highly selective, the permeate stream can be highly purified too. Such a system can replace activated carbon beds effectively for gas purification. The ability to employ suitable nonvolatile liquid absorbents to increase the membrane selectivity drastically is an added advantage.

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Notation

- P = feed side total pressure (psig)
- P_i = feed side partial pressure of species i (psig)
- p = permeate side total pressure (psig)
- p_i = permeate side partial pressure of species i (psig)

t_{ads} = adsorption/absorption time (s)

t_{reg} = stripping/regeneration time (s)

T_{cycle} = total cycle time (s)

Literature Cited

- Beaver, E. R.; Bhat P. V.; Sarcia D. S. Integration of Membranes with Other Air Separation Technologies. *AIChE Symp. Ser.* **1988**, 84 (261), 118.
- Bhaumik, S.; Majumdar, S.; Sirkar, K. K. Hollow-Fiber Membrane Based Rapid Pressure Swing Absorption. *AIChE J.* **1996**, 42, 409.
- Brockman, T. J.; Rice, A. W. Pressure Control for Improved Gas Dehydration in Systems which Employ Membrane Dryers in Intermittent Service. U.S. Patent 5,131,929, 1992.
- Gilleskie, G. L.; Parker, J. L.; Cussler, E. L. Gas Separations in Hollow-Fiber Adsorbers. *AIChE J.* **1995**, 41, 1413.
- LaPack, M. A.; Dupuis, P. F. Dynamic Membrane Separation Process for Improved Selectivity. U.S. Patent 5,354,474, 1994.
- Papadopoulos, T. H. Further Studies on Hollow Fiber Contained Liquid Membrane Separation of Gas and Liquid Mixtures. Ph.D. Dissertation, Stevens Institute of Technology, Hoboken, NJ, 1992.

- Papadopoulos, T. H.; Sirkar K. K. A Modified Hollow Fiber Contained Liquid Membrane Technique for Gas Separation at High Pressure. *J. Membr. Sci.* **1994**, 94, 163.
- Paul, D. R. Membrane Separation of Gases Using Steady Cyclic Operation. *Ind. Eng. Chem. Process Des. Dev.* **1971**, 10, 375.
- Poddar, T. K.; Majumdar, S.; Sirkar, K. K. Membrane-Based Absorption of VOCs from a Gas Stream. *AIChE J.* **1996a**, 42, 3267.
- Poddar, T. K.; Majumdar, S.; Sirkar, K. K. Removal of VOCs from Air by Membrane-Based Absorption and Stripping. *J. Membr. Sci.* **1996b**, 120, 221.
- Rice, A. W.; Brown, J. G., Jr. System and Method for Separating a Portion of a Gas from a Mixture of Gases. U.S. Patent 5,030, 251, 1991.
- Ueda, K.; Haruna, K.; Inoue, M. Process for Separating Gas. U.S. Patent 4,955,998, 1990.
- Yang, R. T. *Gas Separation by Adsorption Processes*; Butterworths: Boston, 1987.

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