ABSTRACT

REMOVAL OF VOCs FROM WASTE GAS STREAMS
BY
CYCLIC MEMBRANE SEPARATION TECHNIQUES

by
Gordana Obuskovic

In this study, new separation techniques called Flow Swing Membrane Absorption Permeation (FSMABP) and Flow Swing Membrane Permeation (FSMP) were used for the removal of the volatile organic compounds (VOCs). In both cases, processes are cyclic in terms of feed flow while desorption of the VOCs is constantly taking place. The transport mechanism in the FSMABP process is selective permeation followed by absorption of the VOCs into the stagnant nonvolatile absorbent liquid on the shell side of the membrane module and then desorption through a similar polymeric membrane. In the FSMP process, VOCs selectively permeate through the membrane into the shell side due to the partial pressure difference across the membrane. Hollow Fiber Modules (HFM) which were used for this experimental work were effective in removing various VOCs from gas streams. High percent removal of VOCs in case of FSMABP and FSMP was achieved at lower feed flow rates and shorter cycle times. Organic contamination in the feed gas stream could be almost totally removed to obtain highly purified treated gas. The advantage of the FSMABP process is that the enrichment of the permeate is much higher compared to the FSMP. Low nitrogen

solubility in mineral oil ensures that the permeate is much more concentrated in VOCs, thus facilitating not only removal of organics but also recovery of these commercially valuable solvents. For the same process inlet conditions, lower concentrations of the treated stream were achieved in FSMP. Silicone coated membrane used in this experimental work showed reasonable high selectivity for VOCs over nitrogen.

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by
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APPROVAL PAGE

REMOVAL OF VOCs FROM WASTE GAS STREAMS
BY
CYCLIC MEMBRANE SEPARATION TECHNIQUES

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This thesis is dedicated to my mother Vera, father Stevan
and my sister Nina

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INTRODUCTION

Stringent emission standards are making control of the emission of volatile organic compounds (VOCs) from chemical process facilities more difficult. As VOC emissions represent not only an environmental concern but also an economic loss, it becomes necessary to recover VOCs from the waste streams in the most economical way. Techniques available at present for regeneration of VOCs from gaseous streams are:

- carbon adsorption
- absorption
- condensation
- membrane technology

Most of the existing techniques for VOC-emission control and recovery have proved to be unsatisfactory in terms of safety, performance, operating costs and facility space (Theodore and Buonicore, 1988).

Carbon adsorption is suitable for low concentrations and gases with humidity less than 50%. Also, regeneration energy demand is high and there is a risk of self-ignition because adsorption process is exothermic. Further carbon beds are bulky and construction materials are expensive.

Absorption is suitable for high gas flow rates but changes in gas flow rates can cause problems. This system is also bulky and flooding and loading can be a problem.

Condensation is a process with very high energy demand because oversaturation of the VOCs is achieved by chilling of the large volume of waste gas stream.

Recently, interest in membrane separation processes has increased. These processes are not sensitive to sudden changes in concentration or introduction of new compounds; they are simple with low energy demands, easy start-up and low maintenance. Membrane technology is a relatively new technique for recovery of the organic solvents from the air. For the separation of the VOCs using membranes, important parameters are selectivity, permeability and membrane material (has to be resistant to organic vapors). The shortcoming of these process is that high degree of gas purification is not practical; thus the VOC level cannot be easily reduced to below 100 ppmv.

Membrane modules have two types of configurations:

- Planar membranes in spiral wound modules
- Hollow fiber modules

Inside (i.d.) and outside (o.d.) diameters of typical hollow fibers ranges from 80-300 and 150-1000 μm respectively. Small dimension of these fibers gives rise to the high specific surface area per unit volume (>1000 m^2/m^3).

Gas separation using microporous hollow fiber-based gas-liquid contactors has been studied recently. Separation of CO_2-N_2 and SO_2-N_2 was carried out in a microporous hollow fiber device in a parallel flow configuration (Karoor and Sirkar, 1993). It was shown that in countercurrent gas-liquid contacting in such devices the separation can be reduced considerably because of shell-side liquid flow bypassing (Karoor, 1992; Karoor and Sirkar, 1993; Yang and Cussler, 1986).

To avoid shell-side liquid flow bypassing and to reduce the number of devices needed for the separation, another system with stagnant absorbent liquid was employed for CO_2-N_2 separation. This process, called Rapid Pressure Swing Absorption (RAPSAB), (Bhaumik, 1993; Bhaumik et al., 1995) incorporated the best features of gas-liquid absorption, pressure swing adsorption (PSA) and membrane gas contacting processes.

Selective membrane absorption (SMA) is a continuous absorption process which utilizes microporous VOC-selective hollow fiber membranes having a thin polydimethylsiloxane coating (Jansen et al., 1993) for VOC separation. The absorbent liquid flows on one side of the membrane and the gas stream containing VOCs flows on the other side creating a driving force for absorption. They however did not suggest the criteria for nondispersive operation. Nondispersive absorption of VOCs from a gas mixture has been carried out successfully in a microporous hydrophobic hollow fiber device with ultrathin nonporous silicone coating (Poddar, 1995). Such a process requires two vessels, one for stripping and the other for absorption (Poddar et al., 1995). The stripping was carried out in a membrane module built of hydrophobic microporous hollow fibers having a thin nonporous highly VOC-selective silicone skin. The organic absorbent employed was inert, high boiling and viscous.

In this study, an effort has been initiated to incorporate the best features of PSA, gas-liquid absorption, hollow fiber-based membrane gas-liquid contacting and membrane gas permeation in a new separation technique. Depending on the membrane used, it will be identified as Flow Swing Membrane Absorption-Permeation (FSMABP) or Flow Swing Membrane Permeation (FSMP).

The two techniques are briefly described below. Flow Swing Membrane Absorption Permeation (FSMABP) was experimentally investigated in a hollow fiber module shown in Figure 1.1 using N_2-VOC mixtures. This module, later referred to as Module 2, utilizes two sets of commingled microporous hollow fibers having a thin nonporous silicone coating on the outside surface. The VOC impurity is to be removed from the nitrogen stream using a nonvolatile, inert organic solvent as the absorbent liquid. Hollow fibers provide the gas-membrane-liquid contact area for the mass transfer. While the N_2-VOC gas stream is passing through the tube side of the feed hollow fibers, the VOC is absorbed in the stagnant absorbent liquid. Stripping is carried out by continuously applying a vacuum through the tube side of another set of silicone-coated hollow fibers well-mixed with the first fiber set. The feed flow into the system is periodically shut down without decreasing the feed side pressure. This brief shutdown allows VOCs to be recovered and absorbent liquid to be regenerated. The gas left in the feed fibers bore is also purified of VOCs during this feed flow shutdown.

This VOC absorption-permeation technique employed microporous hydrophobic hollow fibers with an ultrathin (~1μm) plasma polymerized nonporous silicone layer on the outer side of the hollow fibers which is highly permeable for VOCs. Since the thin silicone skin substantially retards the absorbent molecule from permeation, the gas stream is essentially free of any absorbent vapors. Also, the presence of plasma polymerized silicone coating on

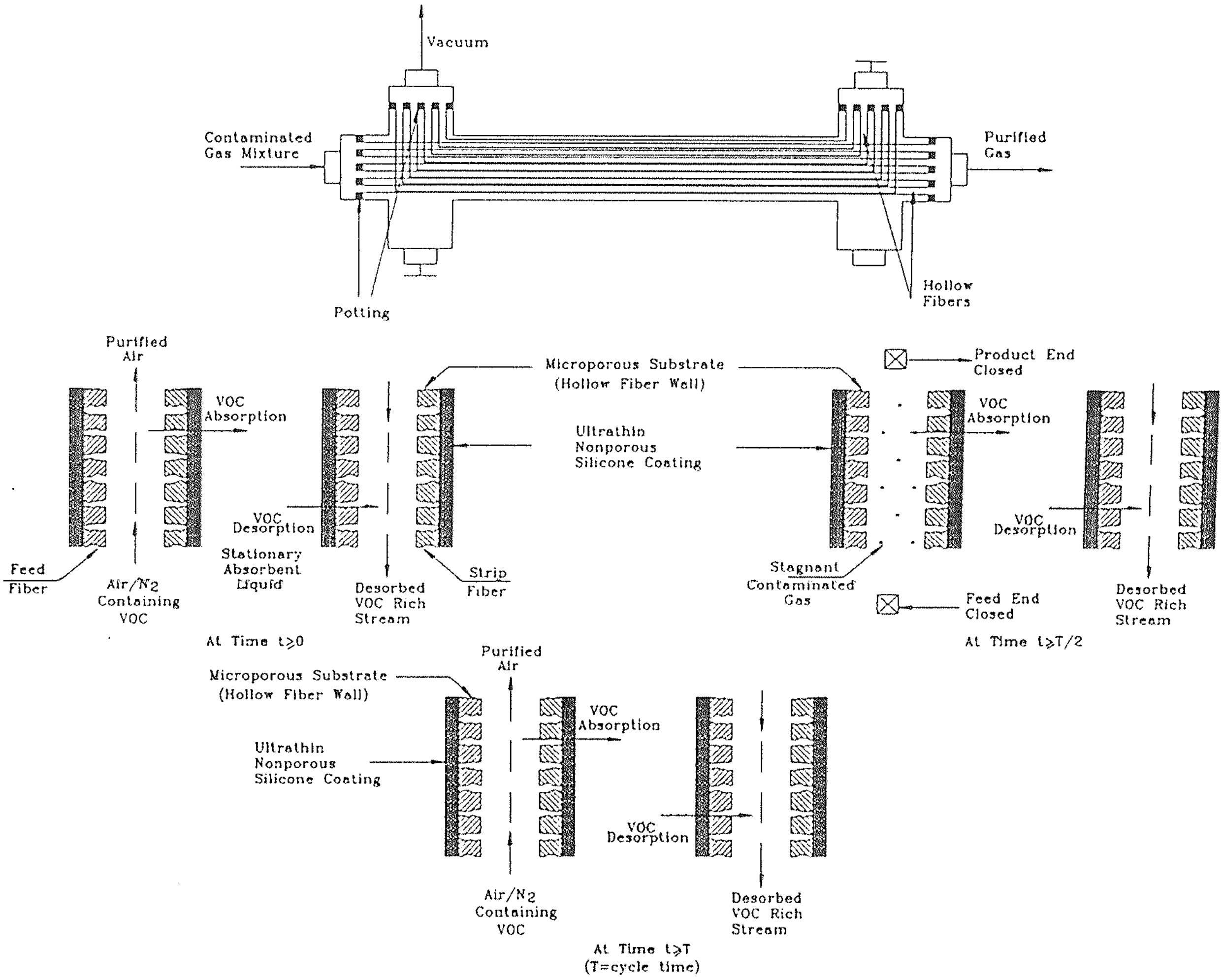


Figure 1.1 Schematic of a Hollow Fiber Module with Two Sets of Fibers and the Nature of Operation in FSMABP

the microporous hollow fiber substrate provides better resistance to swelling in the presence of organic solvents than conventional silicone rubber coatings.

The pressure of the liquid phase on the shell-side was maintained slightly higher than that of the tube-side gas phase (Poddar, 1995). This prevented the bubbling of the nitrogen, which can easily permeate through the silicone skin into the absorbent liquid. However, nitrogen has extremely low solubility in the shell-side nonvolatile absorbent oil. As a result, the permeated gas stream consisted essentially of VOCs but very little N_2.

The feasibility of the FSMABP process was studied using Silicone oil 50cs as an absorbent media and four different VOCs: acetone, methylene chloride, toluene and methanol. Also the FSMABP cycle times and feed flow rates are important variables. Since the FSMABP process should be used as a polishing technique (to replace, say, carbon beds) for VOC removal, the inlet concentration levels are low (<1000 ppmv).

The system proposed above has many advantages:

(1) High surface area can be packed in this device.

(2) No hydrodynamical problems of flooding, loading, weeping.

(3) One vessel replaces an absorber and a stripper used in conventional processes.

(4) Low energy consumption.

(5) Flexibility.

(6) Volumetric mass transfer coefficient is higher than in a conventional contacting unit.

(7) Short cycle time improves the rate of absorption.

(8) Pumping of the high molecular weight inert absorbent oil (Poddar, 1995) is avoided.

The Flow Swing Membrane Permeation (FSMP) process employs a hollow fiber module (Module 1) containing only one set of fibers without any absorbent on the shell side. The hollow fibers are similar to those in FSMABP, in that they have a thin nonporous silicone coating on the outside surface. It is also operated exactly as in FSMABP-feed gas is introduced for a specific period while the permeate side vacuum is on. After some time, the feed gas flow is stopped without reducing the feed pressure. This allows purification of the gas left inside the fiber.

Experiments were also carried out in the RAPSAB mode using a single-fiber (Module 1) set hollow fiber module (Figure 2.2) and an absorbent on the shell side. The process is cyclic since both absorption and desorption occur in a cyclic fashion. Separation takes place by absorption of VOCs into the stagnant absorbent liquid on the shell side, while the feed gas mixture is flowing through the tube side of the membrane module. Absorption is followed by desorption part of the cycle, which is made possible by maintaining a vacuum on the feed end of the tube side. Removal of VOCs from N_2 gas stream in RAPSAB mode is studied using two different absorbent media: Silicone oil and Paratherm® oil and four different VOCs mentioned earlier.

CHAPTER 2

EXPERIMENTAL

2.1 Rapid Pressure Swing Absorption (RAPSAB)

Before studying the Flow Swing Membrane Absorption-Permeation (FSMABP) process, preliminary RAPSAB experiments were carried out with the setup shown in Figure 2.1 for the separation of the volatile organic compounds (VOCs) from a nitrogen stream. The RAPSAB process is cyclic and it consists of short periods of absorption of the VOCs into the stagnant absorbent liquid on the shell side of the membrane module followed by desorption in a given cycle.

During the absorption part of the cycle, the contaminated gas stream was allowed to enter the tube side of the membrane module for a short time. During that time, the purified gas was taken out at the exit of the module. After the absorption part of the cycle, feed flow was stopped and VOCs absorbed in the absorbent liquid on the shell-side of the module was desorbed by vacuum applied to the feed end of the tube side of the membrane module. To achieve this type of operation, two solenoid valves, one at the inlet and the other at the outlet of the module, were used.

Duration of the feed flow coming in to the module corresponds to the absorption part of the cycle. This is done by synchronizing the actions of the two solenoid valves at the inlet and outlet of the module, both being open.

Module 1 (Figure 2.2) used for these experiments, had one set of 300 microporous hydrophobic polypropylene hollow fibers with thin nonporous

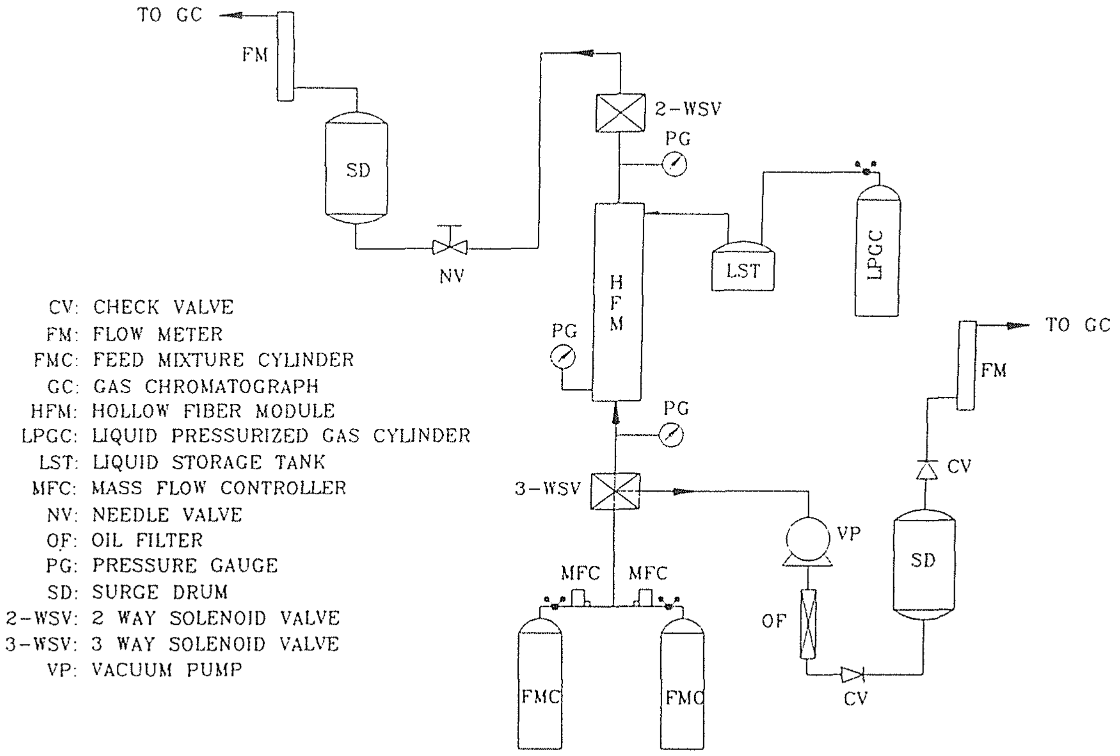


Figure 2.1 Experimental Setup for RAPSAB

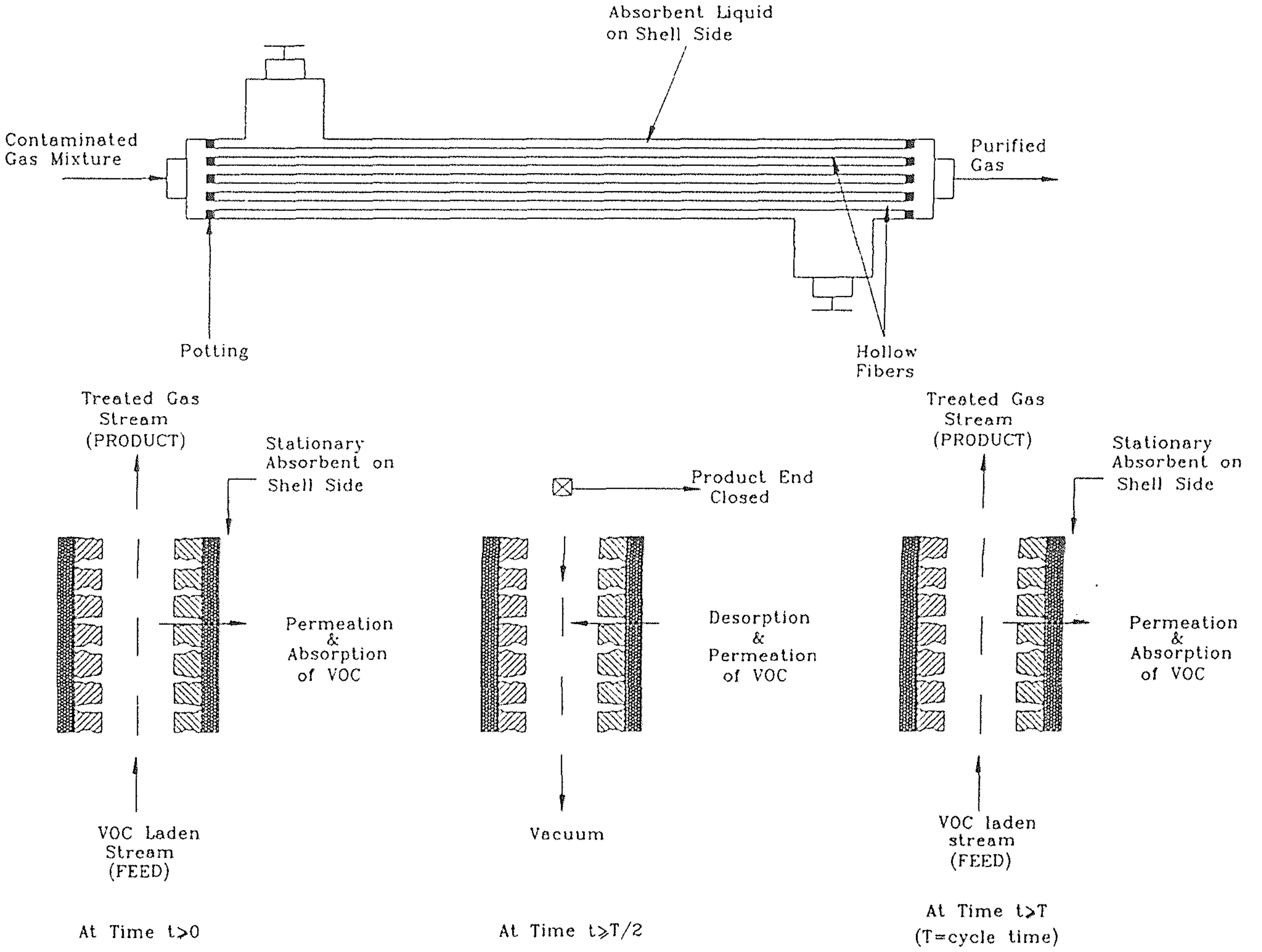


Figure 2.2 Schematic of the Hollow Fiber Module with One Set of Fibers and the Nature of Operation in RAPSAB

silicone coating on the outside surface of the hollow fibers (Celgard®, ID/OD: 240μm/300μm). Detailed characteristics of the module are given in Table 2.1.

These experiments were carried out to develop a better understanding of the RAPSAB technique and thereby facilitate the construction of another module using two sets of fibers for FSMABP studies.

2.1.1 Experimental Setup for RAPSAB

The setup used to carry out the initial experimental work is described below. As mentioned earlier, RAPSAB process consists of short periods of absorption followed by desorption in a given cycle. Durations of the absorption and desorption parts of the cycle were controlled with two solenoid valves. Both solenoid valves, at the inlet and outlet of the membrane module, were controlled with a single timer. During the absorption part of the cycle, the contaminated gas mixture was sent through the tube side of the hollow fiber module. Desired concentration of the feed gas mixture was achieved by mixing pure nitrogen with the VOC/nitrogen mixture. The flow rate of each gas stream was controlled by an electronic mass control flow meter (Matheson, E.Rutherford, NJ). The purified feed gas was collected into the surge drums and was then sent to a gas chromatograph (GC) (Star 3400, Varian, Sugarland, TX) for analysis. The same connection existed for the permeate side analyses. The composition of the permeate could not be estimated exactly using the above GC since it was suspected that the oil used as the lubricant for the vacuum pump (HyVac® Products, Inc., Norristown, PA) could absorb VOCs from the permeate stream.

Table 2.1 Geometrical Characteristics of Different Hollow Fiber Modules

Module No.	Type of fiber	Fiber ID (cm)	Fiber OD (cm)	Effective length (cm)	Shell ID (cm)	No. of fibers	Void fraction (%)	Mass transfer area (cm^2)*	Mass transfer area/ volume (cm^2)/(cm^3)*
1	Celgard** with a silicone skin	0.024	0.030	20.5	0.80	300	57.81	579.62	56.25
2	Celgard** with a silicone skin	0.024	0.029	42.5	0.92	150!	70.19	580.80	29.29

* Calculation based on outer diameter of the fiber

** AMT Inc., Minnetonka, MN

! Number of fibers in each set

Initially the shell side was filled with the selected absorbent liquid. For these experiments two kinds of inert, essentially nonvolatile oil were used: Silicone oil (Cramer Chemicals, Clifton, NJ) and Paratherm® oil (heat transfer fluid) (Paratherm Corporation, Conshohocken, PA). The shell-side liquid pressure was maintained 5-10 psig higher than the feed-gas pressure to prevent the bubbling of the nitrogen into the shell-side absorbent liquid. The pressure of the absorbent liquid was monitored through a pressure gauge.

At the inlet of the membrane module, a three-way solenoid valve (3-WSV) (Component and Control, Carlstad, NJ) served to control the feed gas mixture entering the module and the vacuum being applied in the next part of the cycle. At the other end of the module, a two-way solenoid valve (2-WSV) (Component and Control, Carlstad, NJ) controlled the collection of the purified gas at the outlet of the module and functioned as a sealed end while vacuum was applied to the feed end to regenerate the absorbent. During the first part of the cycle, when absorption occurred, one port of the 3-WSV valve at the inlet and one port of the 2-WSV valve at the outlet of the module remained open for the feed gas to enter and the purified gas to exit the module. VOCs from the feed stream which enter the tube side would permeate through the silicone coating and get absorbed into the stagnant absorbent liquid on the shell side of the module.

After the absorption part of the cycle, the 3-WSV valve ports were switched so that feed gas flow was stopped and vacuum line was opened. Simultaneously, the 2-WSV at the other end was closed. The vacuum applied to the tube side created the driving force for the removal of the VOCs from the shell-side absorbent liquid. VOCs which were desorbed from the absorbent liquid permeated back through the silicone coating into the tube side of the hollow fiber module. In such a way the absorbent oil was purified and prepared for the next absorption cycle. The RAPSAB process is schematically explained in Figure 2.2.

All pressure and vacuum gauges used for these experiments along with the gases were obtained from Matheson Gas Products (Matheson, E.Rutherford, NJ). Connection lines were of 1/8-inch soft copper tubing (McMaster Carr, New Brunswick, NJ). Only the vacuum line was 1/4 inch soft copper tubing.

2.2 Flow Swing Membrane Absorption-Permeation (FSMABP)

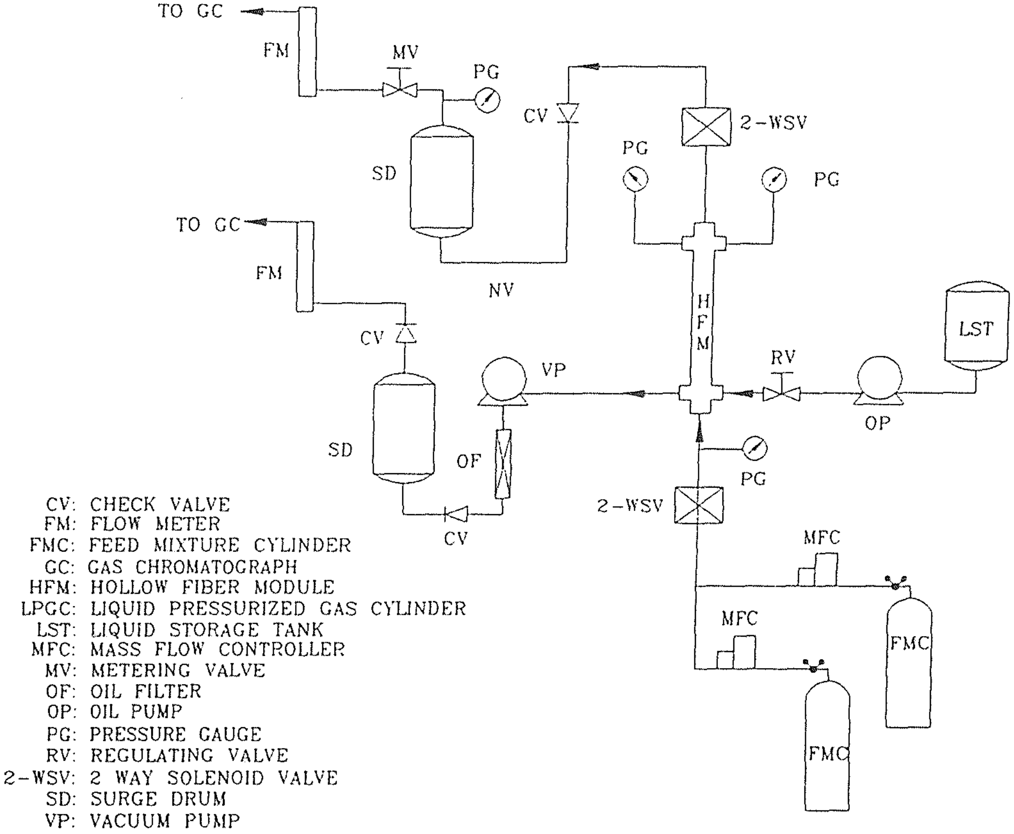
Flow Swing Membrane Absorption-Permeation (FSMABP) separation technique was used to separate different VOCs from VOC-nitrogen gas mixtures. Module 2 used for these experiments previously shown in Figure 1.1 contained two sets of hollow fibers, each set having 150 fibers. Characteristics of the Module 2 are given in Table 2.1. Each hollow fiber had a microporous polypropylene substrate with a thin nonporous silicone coating on the outer surface of the fiber (AMT, Minnetonka, MN). Thin (~1 μm) silicone membrane skin has a high permeance for VOCs and the VOC-air selectivity is high. This technology uses one set of hollow fibers to absorb VOCs from the gas feed into the inert absorbent oil on the shell side of the cylindrical module. Absorbed VOCs permeate through the stagnant absorbent liquid and are desorbed by continuously applying vacuum through the tube side of the second set of hollow fibers, called strip fibers, in the same module. The process is cyclic in terms of absorption of VOCs only. Feed is sent into the module for a short period of time (first part) and then, it is totally stopped till the end of the cycle (second part). On the other hand, desorption of the VOCs is a continuous process as the vacuum is being continuously applied. The FSMABP process is illustrated in Figure 1.1.

2.2.1 Experimental Setup for FSMABP

The experimental setup used for this study is shown in Figure 2.3. A mixture of VOC and nitrogen from a cylinder was mixed with pure nitrogen to prepare a VOC-nitrogen feed mixture having the desired concentration. This gas mixture was fed through the tube side of one set of fibers for a short time and then the feed gas flow was stopped; a two-way solenoid valve (2-WSV) (Components and Control, Carlstadt, NJ) was used for this purpose. The feed flow rate was controlled with an electronic mass flow metering valve (Matheson, E.Rutherford, 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 shell side of the module had been previously filled with silicone oil through a check valve using a pump. Once the shell side was filled with silicone oil, both ends of the shell side were kept closed. The pressure of the silicone oil, was maintained at 10 psi which was always higher than the pressure of the incoming feed gas (~5 psi).

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



CV: CHECK VALVE
FM: FLOW METER
FMC: FEED MIXTURE CYLINDER
GC: GAS CHROMATOGRAPH
HFM: HOLLOW FIBER MODULE
LPGC: LIQUID PRESSURIZED GAS CYLINDER
LST: LIQUID STORAGE TANK
MFC: MASS FLOW CONTROLLER
MV: METERING VALVE
OF: OIL FILTER
OP: OIL PUMP
PG: PRESSURE GAUGE
RV: REGULATING VALVE
2-WSV: 2 WAY SOLENOID VALVE
SD: SURGE DRUM
VP: VACUUM PUMP

Figure 2.3 Experimental Setup for FSMABP hollow fibers selectively over N_2/air and were 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 the hollow fibers, strip fibers, created a continuous driving force for the desorption of 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 with a possibility of permeate gas analysis. In this case also, determining the permeate concentration was tedious because of the use of an oil lubricated vacuum pump (HyVac® Products, Inc., Norristown, PA) and the lack of an analytical means to calculate the amount of nitrogen in permeate. 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 feed outlet end was open), and it was sent to the gas chromatograph (GC) (Star 3400, Varian, Sugarland, TX) for the feed outlet gas analysis.

All connecting lines used for this experiment were 1/8-inch 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).

2.3 Flow Swing Membrane Permeation (FSMP)

Flow Swing Membrane Permeation (FSMP) process was used for removal of VOC from VOC- N_2 gas streams. In the case of FSMP only the feed flow was in cyclic mode of operation while vacuum was constantly applied on the shell side. Feed gas mixture was passed through the tube side of the membrane module for a certain period of time, followed by a cutoff of the feed flow for the same time duration. This allowed purification of the contaminated gas left inside the fibers. The VOC impurity to be removed permeated through the silicone skin into the shell side along with N_2. Simple description of the FSMP process along with a diagram of the module is presented in Figure 2.4. Feed flow swing was done by synchronizing the actions of two solenoid valves placed at the inlet and the outlet of the membrane module. Module employed for these experiments is same as Module 1 used for RAPSAB study (Table 2.1), and the mode of operation is shown in Figure 2.5.

2.3.1 Experimental Setup for FSMP

The experimental setup for Flow Swing Membrane Permeation shown in Figure 2.5 is similar to the RAPSAB setup. A 3-WSV valve (Component and Control, Carlstad, NJ) at the inlet of the cylindrical module, which was used in the RAPSAB case, was replaced by a 2-WSV valve (Component and Control, Carlstad, NJ). During the short time both 2-WSVs 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 applied. Pressure difference between the feed and the vacuum side created the partial

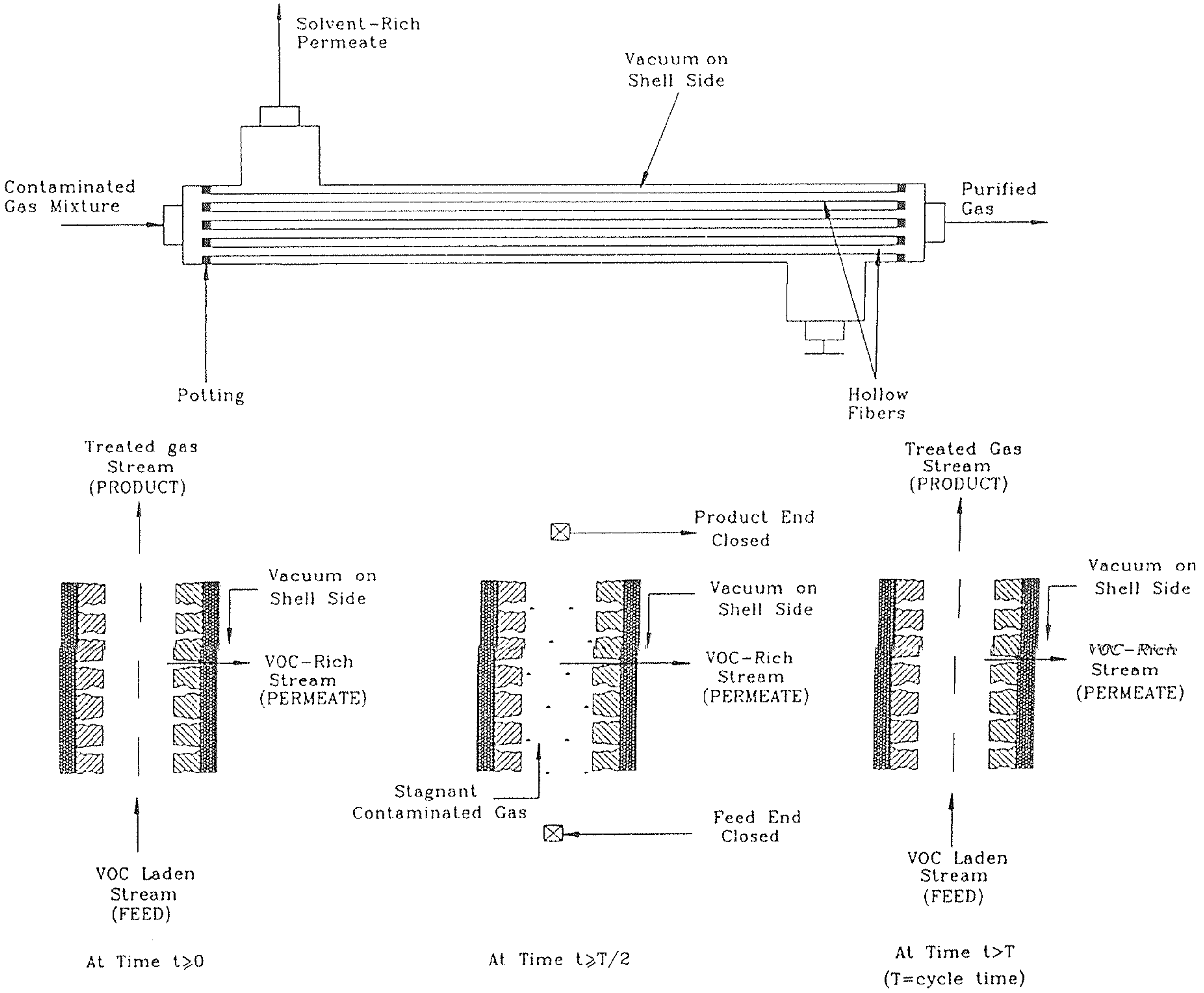


Figure 2.4 Schematic of the Hollow Fiber Module with One Set of Fibers and the Nature of Operation in FSMP

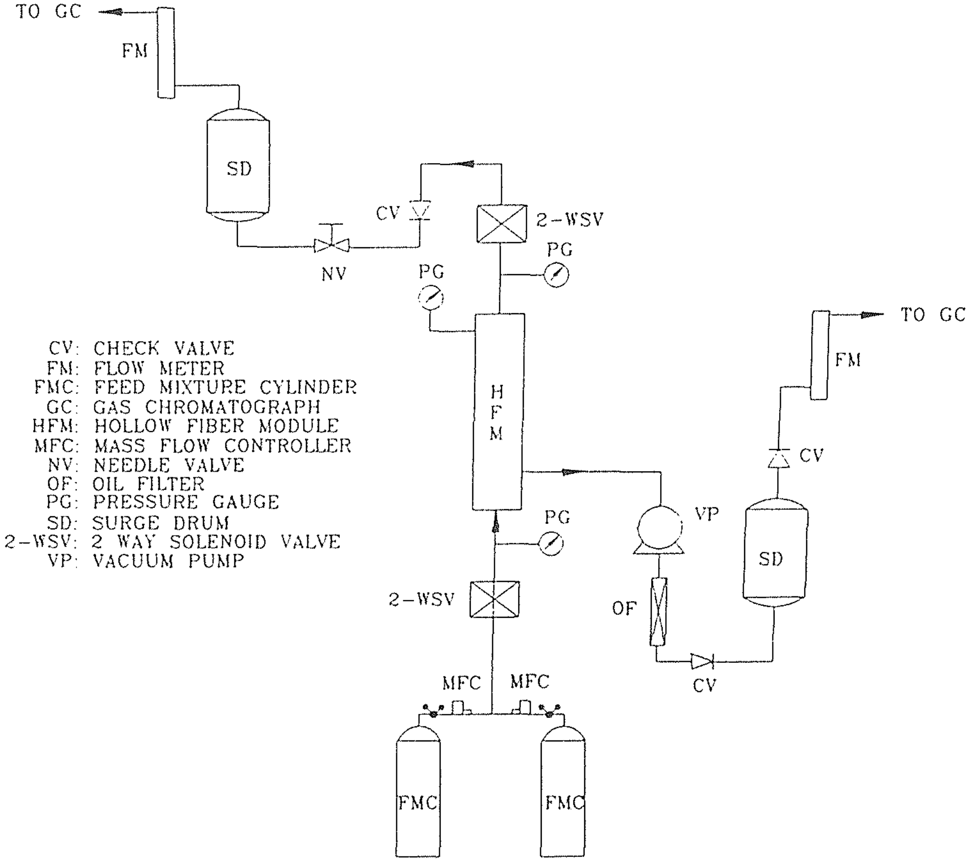


Figure 2.5 Experimental Setup for FSMP

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 permeate stream and purified feed gas were sent for analysis to the gas chromatograph (Star 3400, Varian, Sugarland, TX).

Gas connection lines were 1/8 inch soft copper tubing and vacuum line was 1/4 inch soft copper tubing (McMaster Carr, New Brunswick, NJ). All pressure gauges and all the gases used for these experiments were obtained from Matheson Gas Products (Matheson, E.Rutherford, NJ).

2.4 Fabrication of the Hollow Fiber Module

To carry out the Flow Swing Membrane Absorption-Permeation (FSMABP) experimental work, a module (Module 2) containing two sets of hollow fibers with 150 fibers in each set, was made (Figure 1.1). Based on the preliminary experiments done with Module 1, some decisions were taken regarding the dimensions of Module 2. The membrane area for the absorption of the VOCs into the stagnant absorbent liquid should remain approximately the same, but providing the same membrane surface area for the continuous removal of VOCs should result in better separation.

The first step in module making was matting the fibers. Each fiber (ID: 240µm; OD: 290µm) was taken from the bobbin and cut to the desired length. Each end of the fiber was attached to a vinyl sheet using scotch tape. When all 300 fibers were placed, the middle portion of all the fibers was mixed, while the ends of each set of 150 fibers were separated. Distilled water was sprayed over the fibers for easy handling. The ends and the middle portion of the fibers were tied with cotton threads which were removed slowly as the fibers were inserted inside the bore of a stainless steel pipe (OD:1/4 inch schedule 40, length:16 inch). The ends of the pipe were fitted with 1/4 inch cross connections (R.S.Crum, Mountainside, NJ). Two ends of the cross connections fitted with 1/4 inch nipples (R.S.Crum, Mountainside, NJ) were used for placing the fibers and one end as absorbent liquid entering/exiting port.

Once the ends of the fibers were placed through the nipples, they were potted first with silicone rubber adhesive (RTV11, General Electric, Waterford, NY). After curing for one day, a layer of two-component silicone rubber, RTV 615 (GE Silicones, General Electric Co., Waterford, NY) with 10% by weight of the B curing agent with A silicone compound was applied through the shell side openings. Before applying the second layer of potting the mixture of two component silicone rubber was exposed to the vacuum for 5-6 minutes for degasification. This layer of potting was necessary because epoxy (which is used as a third layer) does not make good bonding with silicone coating of the fibers. Epoxy resin mixture with 4:1 ratio of C-4 resin to activator D (Beacon Chemical Co., Mt. Vernon, NY) was used to seal with the module metal parts. As in the previous case, the epoxy mixture was exposed to vacuum for a short time to remove any gases from the mixture. This layer was also poured through the shell side of the hollow fiber module until the nipple fitting was full. The epoxy was allowed to cure for 10 hours. All four ends were potted in the same manner.

After potting was finished and epoxy layer was completely cured, the module was tested for leakage. The permeator shell side was filled with deionized water and then pressurized with nitrogen while the other ends were closed. The pressure was increased slowly up to 20 psig. No water came through the tube side; the module was deemed leak-free.

CHAPTER 3

RESULTS AND DISCUSSION

The results for removal of volatile organic compounds (VOCs) via Rapid Pressure Swing Absorption (RAPSAB), Flow Swing Membrane Absorption-Permeation (FSMABP) and Flow Swing Membrane Permeation (FSMP) are presented and discussed here. Module 1 was used for the first and third type of experiments, and Module 2, with two sets of fibers, was specifically made for the FSMABP experiments.

The results obtained from the preliminary experiments using Module 1 for the absorption of VOCs via the RAPSAB technique are presented in Tables 3.1 and 3.2, in terms of different absorption times, feed gas/treated gas compositions and flow rates. For these experiments, two different types of absorbent liquids were used: Silicone oil and Paratherm® oil.

As the Tables 3.1 and 3.2 show, the best results were obtained for toluene, which showed nearly perfect removal from N_2 when Paratherm® mineral oil was used. For toluene, separation was not influenced much by variation of absorption/desorption cycle durations and feed flow rates; this was not true for methanol and methylene chloride. This is due to lower solubilities of these VOCs in the mineral oil. Comparing the results of methanol and methylene chloride from Tables 3.1 and 3.2, better separation was achieved if Silicone oil was used. Hence, Silicone oil has been used in further experimental work. Figure 3.1 compares percent removal of methylene chloride for the case of these two

Table 3.1 Experimental Results for RAPSAB Using Module 1 and Paratherm Oil as an Absorbent

VOC in N_2	Absorption time (s)	Desorption time (s)	Feed flow rate during absorption (cc/min)	Continuous product flow rate from surge drum (cc/min)	VOC concentration in feed N_2 (ppmv)	VOC concentration in treated gas stream (ppmv)
Methylene Chloride	40	40	40	~15	284	102
	10	100	40	~9	1000	336
	20	100	30	~5	1000	299
	40	40	30	~10	214	75
Methanol	10	100	30	~2	500	20
	10	60	30	~2	500	20
	40	40	30	~8	168	75
	20	40	30	~6	500	27

Table 3.1 (continued)

VOC in N_2	Absorption time (s)	Desorption time (s)	Feed flow rate during absorption (cc/min)	Continuous product flow rate from surge drum (cc/min)	VOC concentration in feed N_2 (ppmv)	VOC concentration in treated gas stream (ppmv)
Toluene	40	40	150	~70	253	0
	40	20	150	~70	253	~0.15
	40	40	80	~35	253	0
	40	40	44	~20	253	0
	20	60	30	~8	253	0
	10	100	20	~2	253	0

Table 3.2 Experimental Results for RAPSAB Using Module 1 and Silicone Oil as an Absorbent

VOC in N_2	Absorption time (s)	Desorption time (s)	Feed flow rate during absorption (cc/min)	Continuous product flow rate from surge drum (cc/min)	VOC concentration in feed N_2 (ppmv)	VOC concentration in treated gas stream (ppmv)
Methylene Chloride	40	40	30	~5	335	62
	40	40	30	~5	330	57
Methanol	40	40	30	~5	500	148
	40	40	30	~5	155	39

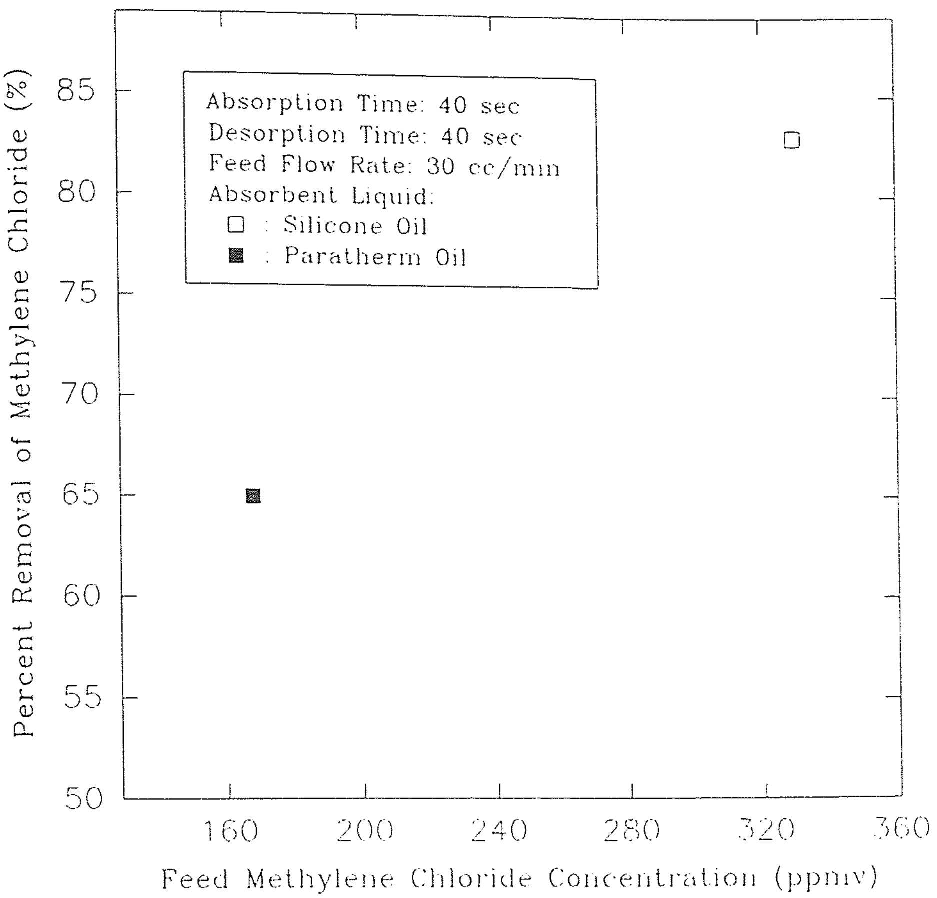


Figure 3.1 Variation of Percent Removal of Methylene Chloride with Feed Concentration for Two Different Absorbent Liquids for RAPSAB

absorbents, where better separation results were obtained with Silicone oil although the feed inlet concentration was doubled.

From these experimental results, it can be concluded that toluene gets absorbed with the greatest ease because the solubility of toluene is the highest. Due to unsteady-state operation, a large section of the absorbent liquid (the downstream end) does not get saturated by the time absorption cycle is complete, and hence, this makes desorption of the VOC easier. In the case of methanol and methylene chloride, perfect separation could not be obtained because their solubilities are lesser compared to that of toluene; this requires particular combinations of flow rates (lower) and cycle time for absorption/desorption which was difficult to achieve due to the small membrane module being employed and experimental difficulties in maintaining the appropriate flow rates.

RAPSAB process has been used effectively to study separation of VOCs like methanol, toluene and methylene chloride from their mixtures in nitrogen gas. The results depend on duration of absorption/desorption periods, feed flow rates, type of VOC and absorbent media. Variations in desorption times do not influence separation to a considerable extent unlike changes in the other three variables viz. absorption cycle length, feed flow rates and types of VOCs. Percent removal of methylene chloride and toluene versus feed flow rate, when Paratherm® oil is used as an absorbent, is plotted on Figure 3.2 where in case of methylene chloride better removal was achieved if the flow rate was lower. That was not the case with toluene which showed nearly perfect separation regardless of the changes in flow rates. Absorption time highly influenced the separation of

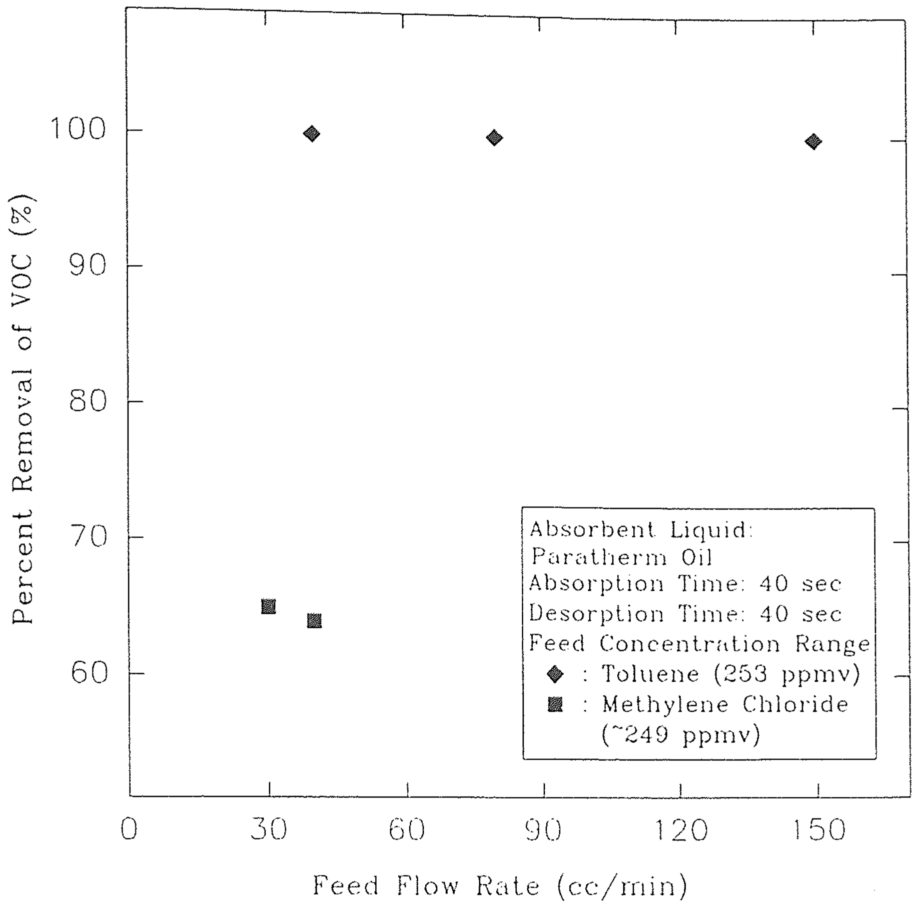


Figure 3.2 Variation of Percent Removal of Methylene Chloride and Toluene with Feed Flow Rate for RAPSAB

methanol. Table 3.1 shows that better removal of methanol was achieved when the absorption time was reduced to 20 seconds irrespective of the increase in feed inlet concentration for same feed gas flow rates. Percent removal also depends on type of VOC. Of the three VOCs being studied toluene showed the best results followed by methylene chloride and methanol.

The subsequent experiments employed FSMABP; they were oriented towards resolving these RAPSAB shortcomings, namely, making a bigger module with two sets of fibers where desorption is a continuous process and a better absorbent media (Silicone oil) is used for VOC separation.

In the case of Flow Swing Membrane Absorption-Permeation experiments, lower outlet concentrations were obtained using Module 2 (with two sets of fiber) since low feed flow rates could be maintained for a fixed inlet concentration. For RAPSAB process, low feed flow rates could not be used because it was difficult to maintain a constant product flow rate from the surge drum and therefore lower outlet concentrations were not achievable. Minimal operating feed gas flow rate for RAPSAB experiments was ~30 cc/min and for FSMABP ~3 cc/min. This resulted in a better separation for FSMABP case. FSMABP experiments were carried out by varying feed flow rates and absorption times as illustrated in Table 3.3.

A plot of percent removal against absorption times for methanol and methylene chloride is shown in Figures 3.3. It can be observed that lowering absorption time improves separation of VOCs while keeping the feed flow rate constant. It can be concluded from the same graph that under same conditions

Table 3.3 Experimental Results for FSMABP Using Module 2 and Silicone Oil as an Absorbent

VOC in N_2	Absorption time (s)	Total cycle time (s)	Feed flow rate during absorption (cc/min)	Continuous product flow rate from surge drum (cc/min)	VOC concentration in feed N_2 (ppmv)	VOC concentration in treated gas stream (ppmv)
Toluene	20	40	30	~15	253	0
	20	40	25	~12	253	0
Methylene Chloride	10	110	30	~3	207	104
	40	80	30	~16	206	96
	20	40	10	~5	292	43
	40	80	10	~5	285	38
	40	80	6	~3	284	21

Table 3.3 (continued)

VOC in N_2	Absorption time (s)	Total cycle time (s)	Feed flow rate during absorption (cc/min)	Continuous product flow rate from surge drum (cc/min)	VOC concentration in feed N_2 (ppmv)	VOC concentration in treated gas stream (ppmv)
Methylene Chloride	20	40	6	~3	285	15
	10	20	6	~2.5	290	15
	20	40	6	~3	321	5
Acetone	20	40	6	~2.5	284	21
	20	40	15	~6	331	169

Table 3.3 (continued)

VOC in N_2	Absorption time (s)	Total cycle time (s)	Feed flow rate during absorption (cc/min)	Continuous product flow rate from surge drum (cc/min)	VOC concentration in feed N_2 (ppmv)	VOC concentration in treated gas stream (ppmv)
Methanol	10	10	26	~12	191	91
	40	40	6	~3.5	225	22
	10	10	6	~3	207	19
	20	20	6	~3	204	16
	10	10	3.3	~1.5	261	5

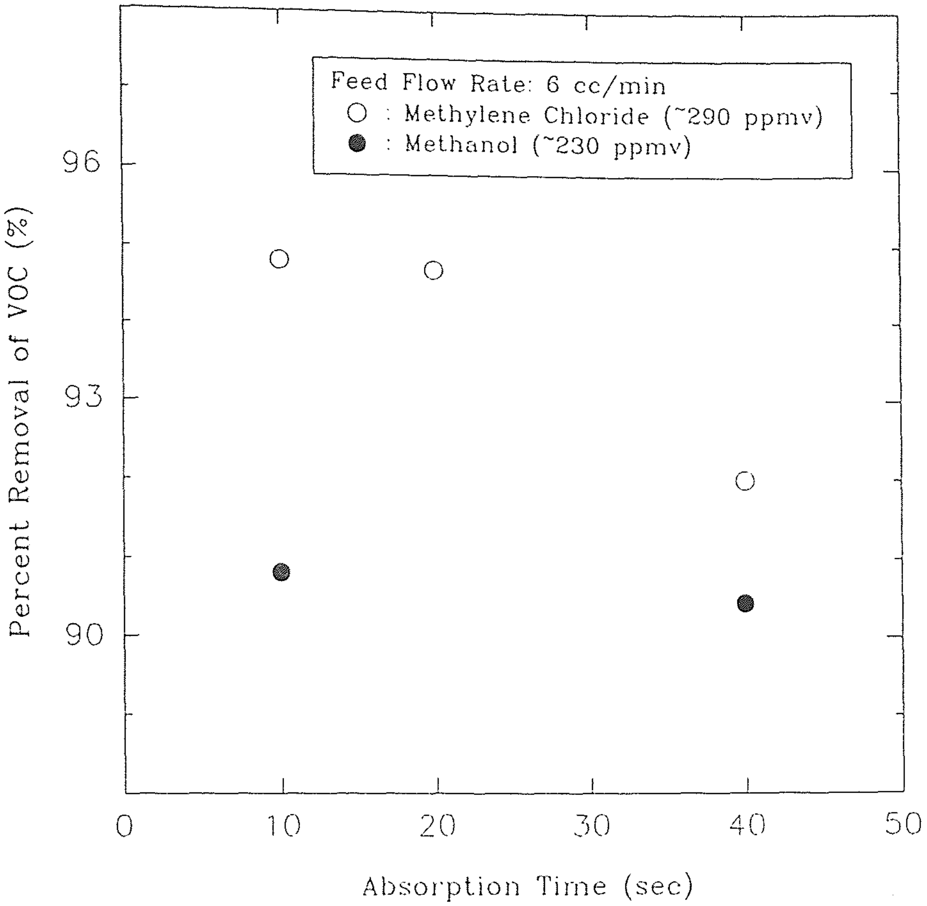


Figure 3.3 Variation of Percent Removal of Methylene Chloride and Methanol with Absorption Time for FSMABP

methylene chloride showed better separation than methanol. Changes in feed flow rates influenced percent removal of methanol as shown on Figure 3.4; better separation is achieved if the feed flow rates are lower.

The experimental results for the selective-membrane-based FSMP process are presented in Tables 3.4 through 3.8. These experiments were carried out by changing only the feed flow rate values. To avoid simple permeation, the absorption time was kept short. FSMP separation results are presented in Figure 3.5; percent removal is plotted versus feed flow rate. As observed during the experimental work separation of VOCs decreased significantly with an increase in feed flow rates. Best separation results were obtained in case of toluene for all feed flow rates followed by methylene chloride, methanol and acetone.

Permeate side VOC concentration was not as high as expected, which can be due to higher nitrogen permeation and vacuum pump leakage. This is primarily due to not-a-very-high VOC-N_2 selectivity of the silicone membrane. If a very high selectivity polymeric membrane were employed, it would have yielded as rich a permeate as in FSMABP process. The most concentrated permeate stream was obtained in the case of methylene chloride, where permeate composition was approximately five times higher than the feed.

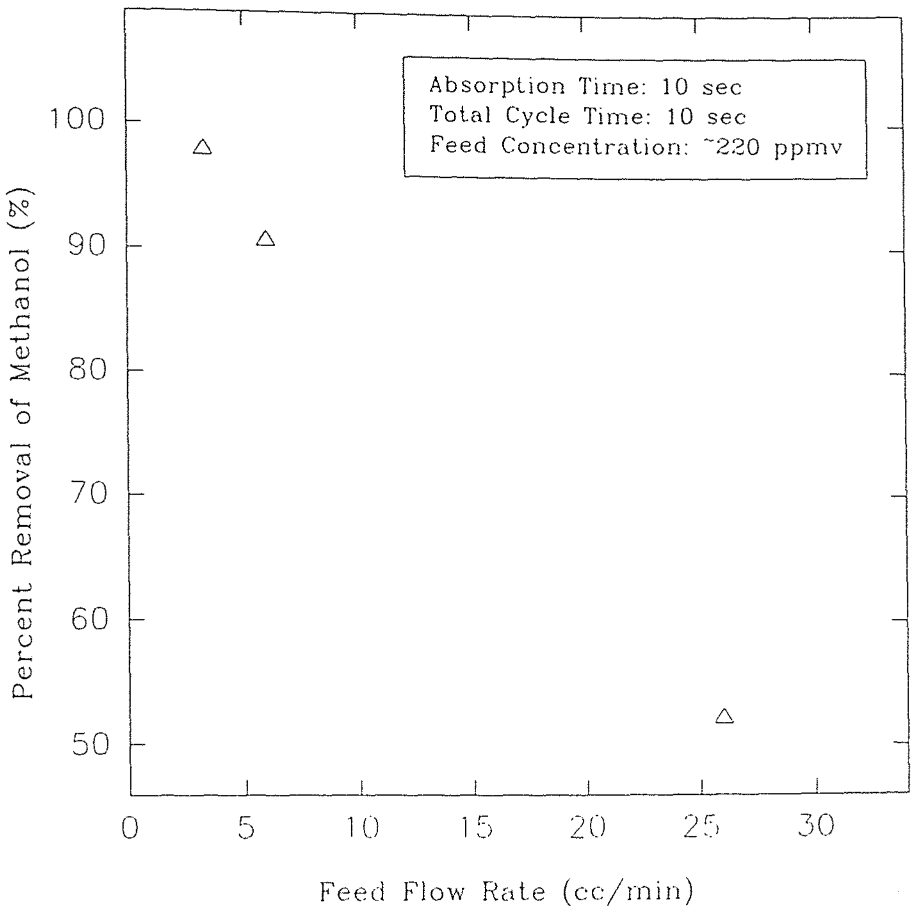


Figure 3.4 Variation of Percent Removal of Methanol with Feed Flow Rate for FSMABP

Table 3.4 Experimental Results for FSMP of Acetone Using Module 1

Feed flow duration time (s)	Total cycle time (s)	Feed flow rate (cc/min)	Continuous product flow rate from the surge drum (cc/min)	Permeate flow rate (cc/min)	VOC conc. in feed N_2 (ppmv)	VOC conc. in treated gas stream	Permeate VOC conc.
10	20	30	~12.5	~5	359	11	344
10	20	60	~18	~24	303	39	387
10	20	80	~24	~32	308	54	780
10	20	100	~28	~44.5	310	74	303

Table 3.5 Experimental Results for FSMP of Methylene Chloride Using Module 1

Feed flow duration time (s)	Total cycle time (s)	Feed flow rate (cc/min)	Continuous product flow rate from surge drum (cc/min)	Permeate flow rate (cc/min)	VOC conc. in feed N_2 (ppmv)	VOC conc. in treated gas stream (ppmv)	Permeate VOC conc.
10	20	30	~10	~11	360	0	273
10	20	60	~18	~23	329	10	762
10	20	80	~24	~31.5	334	23	1452
10	20	100	~27	~45	331	33	1663

Table 3.6 Experimental Results for FSMP of Methanol Using Module 1

Feed flow duration time (s)	Total cycle time (s)	Feed flow rate (cc/min)	Continuous flow rate from surge drum (cc/min)	Permeate flow rate (cc/min)	VOC conc. in feed N_2 (ppmv)	VOC conc. in treated gas stream (ppmv)	Permeate VOC conc. (ppmv)
10	20	30	~11	~12	270	5	424
10	20	60	~18	~24	280	28	835
10	20	80	~25	~32	262	25	836
10	20	100	~30	~40	270	61	823

Table 3.7 Experimental Results for FSMP of Toluene Using Module 1

Feed flow duration time (s)	Total cycle time (s)	Feed flow rate (cc/min)	Continuous flow rate from surge drum (cc/min)	Permeate flow rate (cc/min)	VOC conc. in feed N_2 (ppmv)	VOC conc. in treated gas stream (ppmv)	Permeate VOC conc. (ppmv)
10	20	30	~8.5	~13	216	0	48
10	20	60	~19	~21	216	0	98
10	20	80	~23.5	~33	216	0	187
10	20	100	~28.5	~43	210	4	370

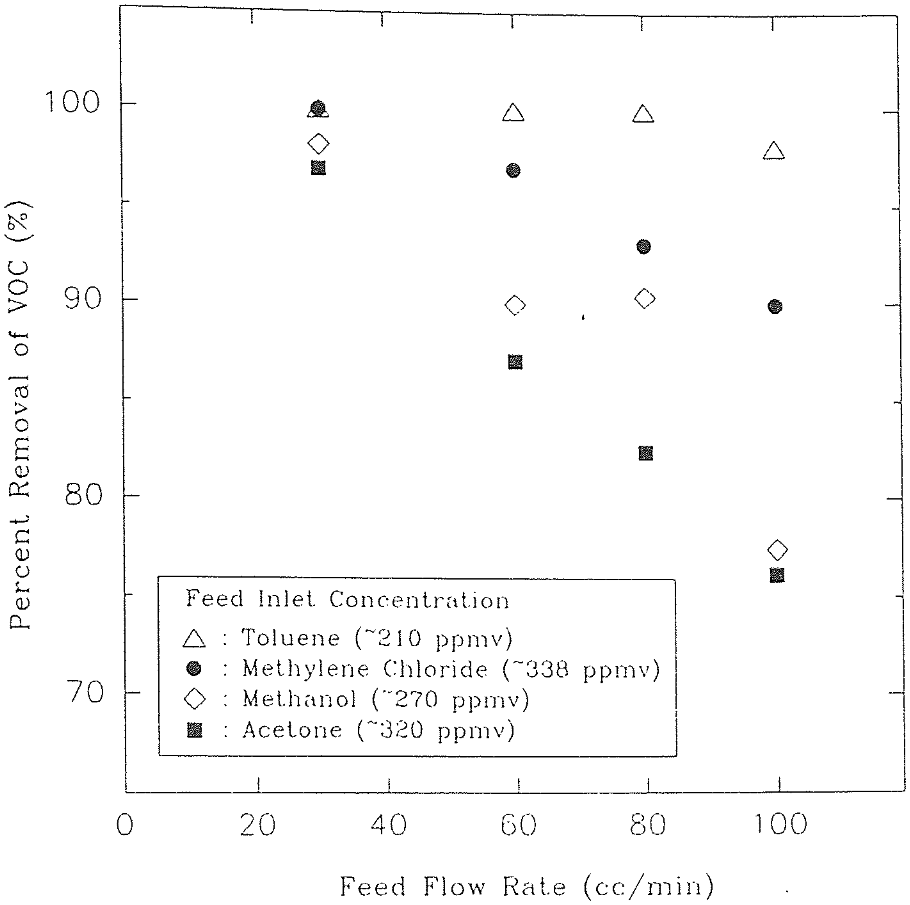


Figure 3.5 Variation of Percent Removal of Different VOCs with Feed Flow Rate for FSMP

CHAPTER 4

CONCLUSIONS

Flow Swing Membrane Absorption-Permeation (FSMABP) and Flow Swing Membrane Permeation (FSMP) processes were successful in removal of volatile organic compounds (VOCs) from the nitrogen gas streams using hollow fiber membrane modules. Polypropylene microporous membrane with plasma polymerized nonporous silicone coating was found to perform efficiently during the experimental work. The presence of a highly organic selective silicone coating, their commercial availability and relatively low costs of these membranes makes them the most appropriate kind, suitable for these studies.

The performance of the above mentioned processes strongly depends on the duration of absorption and desorption in a given cycle and feed gas flow rates. Efficiency of the FSMABP process increases with decreasing flow rates and absorption time. A balance has to be achieved between these two operating parameters to optimize the system efficiency. To obtain high efficiency (~95-100%) with FSMP process feed flow rates should be moderate (~30 cc/min) and flow duration time short. The effect of flow swing which results in higher feed pressure leads to higher nitrogen permeation compared to the case of simple permeation with no flow swing and where the feed pressure does not go up. High percent removal (~98-100%) of all four VOCs studied could be obtained using both separation techniques. Methanol and acetone removal efficiency was reasonably good, while toluene and methylene chloride in some cases showed almost perfect cleanup.

Obtaining a more concentrated permeate stream is important in the context of reducing the economical loss. Permeate stream in FSMABP process is much more concentrated than in FSMP due to lower nitrogen permeation, and hence recovery of the organics is easier in the former case.

Novel separation techniques mentioned above are expected to provide the alternate solution to the conventional methods for removal of VOCs due to compactness of the device, ease of organic recovery and reduction of separation costs. These processes are recommended for the treatment of gas streams with lower level of contaminants (<500 ppmv) and lower feed flow rates.

Further studies on VOC removal using FSMABP and FSMP techniques should focus on:

(1) developing mathematical models for both processes;

(2) carrying experiments with N_2 containing multiple VOCs;

(3) recovery of the VOCs.

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