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MEMBRANE VAPOR RECOVERY SYSTEMS

Phase II ^{Progress} ~~Final~~ Report

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prepared by

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ABSTRACT

This report describes Phase II of a project to design, construct, and demonstrate in the field a condensation/membrane separation system able to recover volatile organic compounds from effluent air streams. In the first phase of the program, a number of the high-pressure membrane modules to be installed in the system were constructed and evaluated, and the Field Demonstration Unit was designed. In the second phase, the Field Demonstration System was constructed and operated at MTR's laboratories with perchloroethylene, trichlorotrifluoroethane, and hexane, representative of chlorinated hydrocarbons, chlorofluorocarbons and fuel hydrocarbons, respectively. VOC removal from the feed stream was between 80% and 99.8%. Removal increased with increasing VOC content and with decreasing VOC volatility.

A Module Field Evaluation Unit was also constructed for testing at the El Dorado plant of Great Lakes Chemical Corporation. The system, consisting of one membrane module housing containing one module insert, is installed on the pressurized vent from a condenser. No reliable performance data have been obtained thus far, because the vent stream flow rate is much smaller than initially expected. Monitoring the one-module system will continue in Phase III.

The next step is to demonstrate the system in the field. Contacts were made with over ten companies in the chemical, petro-chemical and pharmaceutical industries. Several promising host sites were identified, but no definite site has yet been arranged.

1. SUMMARY

This report describes the work performed at Membrane Technology and Research, Inc. (MTR), under DOE Grant DE-FC02-90GE40903. The period covered is from October 1, 1990 to September 29, 1992, representing Phase II of the project.

The overall objective of the project is to design, construct; and demonstrate in the field a condensation/membrane separation system able to recover volatile organic compounds from effluent air streams. In the first phase of the program, a number of the high-pressure membrane modules to be installed in the system were constructed and evaluated, and the Field Demonstration Unit was designed. In the second phase, reported here, the Field Demonstration System was constructed and operated at MTR's laboratories with three different volatile organic compounds (VOCs): perchloroethylene, trichlorotrifluoroethane, and hexane. These VOCs represent three classes of compounds: chlorinated hydrocarbons, chlorofluorocarbons (CFCs, often referred to as Freons, a trademark of Du Pont), and alkanes or fuel hydrocarbons, respectively. A total of 93 sets of experimental data were obtained. The Field Demonstration System performed satisfactorily and removed between 80% and 99.8% of the VOC from the air stream fed into the system. Removal increased with increasing VOC concentration in the system inlet stream and with decreasing volatility of the VOC.

A single module Field Evaluation Unit was constructed and installed at the El Dorado plant of Great Lakes Chemical Corporation. The system consisted of one membrane module housing containing one module insert. The stream treated by the one-module system is a pressurized vent from a condenser. No reliable performance data have been obtained thus far, because the vent stream flow rate is much smaller than initially expected. Both Great Lakes and MTR are working on a solution to this problem. Monitoring the one-module system will continue in Phase III.

One objective of the Phase II effort that was not met is to find one, or preferably more, industrial host sites for the Field Demonstration System. Contacts were made with over ten companies in the chemical, petro-chemical and pharmaceutical industries. Several promising host sites were identified, but no definite site has been arranged. The search for host sites will have highest priority as Phase III of the project starts.

2. BACKGROUND

A. Condensation/Membrane Separation Hybrid Systems

Gas streams containing volatile organic compounds (VOCs) are produced by numerous industrial and commercial processes. Venting such gases to the atmosphere wastes resources and causes pollution problems. Industries throughout the world are, therefore, under increasing pressure to clean up waste gas emissions. A widely used treatment method is condensation, in which the gas is cooled and/or compressed beyond the dew point of the condensable constituent.

A portion of this component condenses and can be drawn off as a liquid for reuse or disposal. Problems encountered in such processes are (1) a low concentration of the condensable component in the stream, or a condensable component with a low boiling point, so that the dew point is difficult to reach, and (2) a need for regular defrosting of the condenser, if condensation is below the freezing point of water. These problems place limits on the practical operating range of a condensation system. Compressing the gas stream above about 10-15 atmospheres consumes large amounts of energy and costs increase rapidly in proportion to compressor capacity. If the gas must be cooled below 0°C, ice formation in the condenser from water vapor entrained in the feed vapor may occur. Even under favorable operating conditions, 20% or more of the condensable component may be left in the non-condensed bleed gas from the condenser.

Although condensation has proved to be a valuable method of waste treatment and pollution control, there remains a long-standing need to improve condensation technology. Recent evidence concerning the adverse environmental effects of halogenated hydrocarbons and, specifically, chlorofluorocarbons (CFCs), as common volatile organic emissions, has dramatically intensified that need.

The present project involves a combined, or hybrid, process of condensation and membrane separation that can reduce the concentration of a condensable component in a gas stream to 5% or less of its original level. Because of the inherent complementary features of the two methods, the hybrid process can do this in a highly efficient, economic manner.

The process involves two main steps: condensation and membrane concentration. The condensation step is conventional, and involves compressing the feed gas stream, then chilling it to condense a portion of the VOC content. The membrane step is innovative, and involves the use of high performance membranes selectively permeable to organic vapors over nitrogen, air or other gases. The hybrid process is designed to yield only two product streams: the condensed liquid, ready for recovery and reuse, and a gas stream containing as little as 1% or less of the original condensable content, which, in most cases, will be clean enough for direct discharge. This result is achieved by recycling streams within the process.

The process is illustrated schematically in Figure 1. A VOC-contaminated air stream is compressed and then cooled in a condenser, to remove a portion of the VOC content. The compressed condenser bleed air, still containing a substantial amount of VOC, is then passed to a membrane unit, which removes the remaining VOC, producing a VOC-depleted air stream suitable for venting.

003-15

Figure 1. Flow schematic of condensation/membrane separation hybrid process.

The enriched permeate stream from the membrane step is returned and fed back into the condensation process. Thus, no secondary wastes or pollution problems are created by the process, and the organic content of the stream is reduced to 5% or less of its original level. The technical feasibility of condensation as a treatment and recovery method has long been established. The technical feasibility of membrane systems for treatment of streams containing organic vapors has been demonstrated at pilot-plant level by MTR, using membranes, modules, and systems under development exclusively by MTR since 1983. Some of this technology is now commercial. All of our expertise in designing and optimizing membrane systems for particular applications is available for the design, economic assessment, and demonstration of the new hybrid systems. The technical feasibility of the new hybrid systems, therefore, appears to be solidly supported.

B. Membranes and Modules

This new process requires membranes that are highly selective to the volatile organic components in the waste stream. The membranes we produce are composites having the multilayer structure illustrated in Figure 2. A tough, open microporous polymer layer provides mechanical strength, and an ultrathin, dense polymer coating provides the separation properties. These membranes have high fluxes and are much more permeable to organic vapors than to air.

Figure 2. Schematic of an MTR composite membrane. MTR produces these membranes in rolls 100-200 yards long and 40 inches wide.

Some typical data obtained when membranes are used to treat airstreams containing various halocarbons are given in Figure 3. Similar data have been generated for a wide variety of organic vapors, including hydrocarbons, chlorinated hydrocarbons, and chlorofluorocarbons.

Figure 3. Performance of MTR composite membranes with various halocarbon airstreams.

From data of this type, the membrane selectivity $\alpha_{(\text{VOC}/\text{air})}$ can be obtained. This parameter is defined as the ratio of the VOC permeability through the membrane (P_{VOC}) to the air permeability through the membrane (P_{air}):

$$\alpha_{(\text{VOC}/\text{air})} = \frac{P_{\text{VOC}}}{P_{\text{air}}} \quad (1)$$

The membrane selectivity is a measure of the efficiency with which a membrane is able to separate a particular VOC from an air stream. Our experience has shown that, generally, a membrane selectivity of 10 and preferably greater than 20 is required if a membrane process is to be economical. However, under certain conditions, such as the gas stream being available at high pressure or at reduced temperature, a membrane selectivity of 5-10 is sufficient. Some typical selectivity data obtained with a variety of organic compounds at room temperature are listed in Table 1. The selectivity for Halon 1301 at -20°C is included as an example of the general rule that selectivity improves at lower temperatures.

Table 1. Selectivities of MTR Membranes to a Representative Series of Common Industrial Solvent Vapors. Temperature is 20°C unless otherwise indicated.

Vapor	Membrane Selectivity
Octane	90 - 100
1,1,2-Trichloroethane	60
Isopentane	30 - 60
Methylene chloride	50
CFC-11 (CCl ₃ F)	45
1,1,1-Trichloroethane	30 - 40
Isobutane	20 - 40
Tetrahydrofuran	20 - 30
CFC-113 (C ₂ Cl ₃ F ₃)	25
Acetone	15 - 25
CFC-114 (C ₂ Cl ₂ F ₄)	10
Halon-1301 (CF ₃ Br) - at 20°C	3
at -20°C	10

As shown, our existing membranes have adequate selectivity for handling most common organic compounds. Very little additional membrane development work was needed for this program and the full-scale, 40-inch-wide casting and coating machinery required to produce high-quality, organic vapor selective membranes on a commercial scale was already available.

At MTR, the composite membranes are fabricated into spiral-wound modules of the type shown schematically in Figure 4. In these modules, the membrane is supported on the feed and permeate sides by plastic mesh spacers. The membrane and spacers are wound spirally around a central collection pipe. During operation, feed liquid enters the module and flows between the membrane leaves. The permeate fraction spirals inward to a central collection pipe. The remainder of the feed flows across the membrane surface and exits as the residue. The pressure difference across the membrane is provided by drawing a partial vacuum on the permeate side.

Membrane systems used with compression-condensation equipment must operate at pressures as high as 10-20 atmospheres on the feed side of the membrane. Industrial vapor separation modules produced at MTR prior to this program were designed for operation at feed-side pressures of 1-2 atmospheres. Under high pressure conditions, the membrane layer could be forced into the interstices of the spacer, damaging the membrane, and collapsing the permeate channel. Therefore, in this program, the first task was to develop modules suitable for operation at high feed pressures.

Figure 4. A spiral-wound membrane module.

The overall project consists of the design, construction and evaluation in the field of a proof-of-concept system. The system is a multi-module system, with a very flexible design, so that a number of possible hybrid condensation/membrane separation systems can be evaluated. Although we had not previously constructed such a high-pressure membrane system, we had built a number of low-pressure pilot systems, operating at pressures of 1-2 atmospheres absolute. A photograph of our first low-pressure pilot system, designed to operate on a concentrated fluorinated solvent stream, is shown in Figure 5.

Figure 5. A 30- to 60-scfm, low-pressure pilot unit used in the first field test of our vapor separation technology.

3. OVERALL PROJECT OBJECTIVES

The overall objective of this project is full-scale engineering development and demonstration of condensation/membrane separation systems for improved treatment of waste streams containing volatile organic compounds (VOCs).

If successfully demonstrated, such a system would have a major impact on VOC emissions in many situations. The present program involves the construction of a pilot-scale, proof-of-principle system to be evaluated on industrial sites with actual vent streams containing VOCs. Great Lakes Chemical Corporation is interested in this novel technology to treat vent streams that contain Halons, CFCs and other halocarbons. The company is contributing financial support to the project and has made a test site available. Other industrial collaborators are being sought to obtain access to additional test sites and gain financial support for the program.

The project is divided into three separate phases, as shown in Table 2. In Phase I, module development work was performed, and a proof-of-concept system was designed. In Phase II, the system was built and subjected to a series of laboratory-scale parametric tests at MTR. In Phase III, the unit will be installed at the facilities of one or more industrial collaborators and will be operated on selected target streams for long-term continuous performance tests of up to three months each. The objective of these tests is to demonstrate the overall reliability and efficiency of the process.

Table 2. Program Tasks

PHASE I

- Task 1. Develop High-Pressure Modules
- Task 2. Design Demonstration System
- Task 3. Project Management and Reporting

PHASE II

- Task 4. Construct Membrane Modules
- Task 5. Construct Demonstration System
- Task 6. Seek Industrial Support
- Task 7. System Testing at MTR
- Task 8. Project Management and Reporting

PHASE III

- Task 9. Install and Evaluate the Demonstration System in the Field
- Task 10. Perform Laboratory Support Studies
- Task 11. Perform Economic Analysis
- Task 12. Technology Dissemination
- Task 13. Project Management and Reporting

This report describes the work accomplished in Phase II, in which the Field Demonstration System was constructed and operated at MTR's facilities.

4. TASK 1. PREPARATION OF MODULES

The Field Demonstration System contains ten spiral-wound membrane modules. These modules operate at feed gas pressures between 100 and 150 psig. The spacer configuration of the modules was developed in the first phase of this program.

A total of twenty modules (two full sets) were prepared. Ten modules were prepared with the MTR-1135 membrane, which is MTR's standard vapor separation membrane. Ten more modules were prepared with the MTR-4135 membrane, which has the same selective layer as the MTR-1135 membrane but has an improved, more chemically resistant support membrane. The properties of the two types of module are given in Table 3. The nitrogen flux of the modules is normalized with respect to the design value. Variations from the design value are due to either or both of the following two factors: (1) the normalized nitrogen flux of the membrane used differs from the design value, and (2) the membrane area differs from the design value. Table 3 shows that the nitrogen permeation flow rate is very close to the design value for all modules. The oxygen/nitrogen selectivity of all the modules is within 10% of 2.2, the intrinsic selectivity of the membrane material, showing that the modules are free of defects.

The support membrane used in the MTR-1135 membrane is stable in the presence of most organic vapors, but is not stable in the presence of liquid-phase chlorinated hydrocarbons and aromatic hydrocarbons. The novel support membrane used in the MTR-4135 membrane is stable with virtually all liquid-phase organic solvents. Liquid-phase organics are normally not present in the gas stream fed into the membrane modules. However, upsets in the process upstream from the modules could result in small amounts of liquid being transferred to the modules. Employing the MTR-4135 membrane thus eliminates the risk of membrane failure due to presence of liquid-phase organics in the feed stream.

Table 3. Properties of the Modules Prepared for the Field Demonstration System

Nitrogen permeation flow determined at 5 psig feed pressure.
Maximum O₂/N₂ selectivity of selective material is 2.2

Module #	N ₂ permeation flow rate Design value = 1.00	O ₂ /N ₂ selectivity (-)
MTR-1135		
316	1.05	2.01
317	1.00	2.10
320	1.02	2.14
321	1.05	2.14
322	1.11	2.15
324	1.08	2.04
325	1.02	2.08
327	1.00	2.09
328	1.00	2.11
329	0.98	2.08
Mean Value	1.03 ± 0.04	2.09 ± 0.04
MTR-4135		
411	1.00	2.16
412	1.03	2.15
413	1.00	2.08
414	1.00	2.11
415	1.03	2.10
416	1.03	2.10
417	1.04	2.10
430	1.04	2.08
431	1.04	2.09
432	0.99	2.16
Mean Value	1.02 ± 0.02	2.11 ± 0.03

5. TASK 2. CONSTRUCTION OF FIELD DEMONSTRATION SYSTEM

The Field Demonstration System is identical to the system designed in Phase I of this project, except for one feature. The actual system contains two compressors in a parallel configuration, whereas the original Phase I design had a single compressor. The advantage of the two-compressor configuration is increased flexibility in handling different streams. In particular, the system can handle an increased range of feed gas flow rates; the minimum flow rate is 20 scfm and the maximum is 70 scfm.

A. Description of the Field Demonstration System

A simplified flow diagram of the field demonstration system in base-case configuration is shown in Figure 6. The system contains two liquid-ring compressors, two condensers, ten pressure housings that can each contain one membrane module insert, and a liquid-ring vacuum pump. The VOC-laden vent stream is compressed to about 100 psig. The condensers, operating at temperatures between 5°C and 15°C, remove part of the VOC by condensation. The gas stream leaving the condensers, which is saturated with VOCs at the condenser temperature and pressure conditions, is fed into the membrane modules. The membrane is more permeable to the VOCs than to the noncondensable gases. The VOC-enriched permeate stream exits the modules at a pressure of about 2 psia (26 inHg vacuum). After recompression in the vacuum pump, the permeate stream is recirculated to the inlet of the compressors. Thus, the VOCs removed by the membrane system are eventually condensed. The residue gas stream exiting the membrane modules is depleted in VOC content and can safely be vented into the atmosphere.

The membrane part of the system is divided into two separate sections. The sections are indicated in Figure 6 as step 1 and step 2 and are connected in series. This arrangement allows operation of the system in two different configurations: (1) the one-step configuration, in which the permeate streams from both membrane steps are fed into the vacuum pump and the permeate pressures of both steps are equal and less than ambient pressure, and (2) the two-step configuration, in which the permeate stream from step 1 is directly recirculated to the compressors and only the permeate from step 2 is fed into the vacuum pump. In the two-step configuration, the permeate pressure in step 1 is ambient, whereas the permeate pressure in step 2 is less than ambient and less than the permeate pressure obtained in the one-step configuration. As will be discussed in Section 5B of this report, the two-step configuration is advantageous if the VOC concentration fed into step 1 is relatively high.

Figure 6. Simplified flow diagram of the field demonstration system in its base case configuration.

Figure 7 gives a more detailed flow diagram of the Field Demonstration System. The diagram shows the locations of pressure gauges (P), temperature gauge (T), flow meters (V), and sample ports for composition analysis (GC). Figure 8 is a photograph of the Field Demonstration System.

Figure 7. Detailed flow diagram of the Field Demonstration System.

Figure 8. Photograph of the Field Demonstration System.

The design of the system allows operation in six different configurations, as shown in Figure 9. The main difference between configurations A through C and configurations D through F is that, in the latter group, the permeate stream is recompressed and fed into the condenser without being mixed with the feed gas. This improves the performance of the system when the feed gas itself does not contain enough condensable material for condensation to occur. The flexible design of the demonstration unit will allow selection of the optimum process configuration for the particular applications that might be encountered at field sites.

During the parametric testing at MTR, the system was operated in configurations A and B. Configuration A is referred to as the one-step configuration and configuration B is referred to as the two-step configuration.

Figure 9. Six configurations possible with the VaporSep field demonstration system.

B. Initial Shake-Down Experiments

After the Field Demonstration System was constructed, the system was started up with ambient air as the inlet stream. The modules installed in the system contained the MTR-1135 membrane. All connections were checked for leaks and adjustments were made where necessary. The system operated satisfactorily. By measuring the oxygen concentration in the gas stream entering the membrane modules and the oxygen concentration of the permeate gas leaving the modules, we were able to calculate the effective oxygen/nitrogen selectivity of the modules in the system. The value obtained of 2.00 is very close to the mean value obtained for the modules during the quality assurance test (see Table 3).

6. TASK 3. PARAMETRIC TESTING WITH FIELD DEMONSTRATION SYSTEM

The Field Demonstration System was operated in MTR's laboratories with three different volatile organic contaminants: perchloroethylene, trichlorotrifluoroethane and hexane. These VOCs represent three classes of compounds: chlorinated hydrocarbons, chlorofluorocarbons (CFCs, often referred to as Freons, a trademark of Du Pont), and alkanes or fuel hydrocarbons, respectively. A total of 93 sets of experimental data were obtained. Table 4 gives a summary of the experiments performed. The Field Demonstration System in the one-step configuration removed between 80% and 99.8% of the VOC from the air stream fed into the system. Removal increased with increasing VOC concentration in the system inlet stream and with decreasing volatility of the VOC.

Table 4. Summary of experiments performed at MTR with the Field Demonstration System.

Experiment No.	VOC	VOC Inlet Concentration	System configuration
1.1 - 1.4	Perchloroethylene	1,700 - 1,900 ppmv	One-step Inlet: 32 scfm
1.5 - 1.7	Perchloroethylene	700 - 800 ppmv	One-step Inlet: 32 scfm
2.1 - 2.5	Perchloroethylene	750 - 850 ppmv	Two-step Inlet: 33 scfm
3.1 - 3.4	Trichlorotrifluoroethane	1,400 - 1,600 ppmv	Two-step Inlet: 31 scfm
4.1 - 4.3	Trichlorotrifluoroethane	1,500 - 1,600 ppmv	One-step Inlet: 30 scfm
5.1 - 5.3	Trichlorotrifluoroethane	630 - 650 ppmv	One-step Inlet: 73 scfm
6.1 - 6.3	Trichlorotrifluoroethane	1,500 - 1,600 ppmv	One-step Inlet: 30 scfm
7.1 - 7.6	Trichlorotrifluoroethane	1,100 - 1,300 ppmv	One-step Inlet: 39 scfm
8.1 - 8.4	Trichlorotrifluoroethane	1,400 - 1,500 ppmv	One-step Inlet: 33 scfm
9.1 - 9.3	Trichlorotrifluoroethane	1,400 - 1,500 ppmv	Two-step Inlet: 31 scfm
10.1 - 10.10	Trichlorotrifluoroethane	1,100 - 1,200 ppmv	Two-step Inlet: 41 scfm
11.1 - 11.5	Trichlorotrifluoroethane	1,600 - 1,700 ppmv	One-step Inlet: 29 scfm
12.1 - 12.2	Trichlorotrifluoroethane	600 - 700 ppmv	One-step Inlet: 70 scfm
13.1 - 13.7	Hexane isomers	1,600 - 1,700 ppmv	One-step Inlet: 59 scfm
14.1 - 14.15	Hexane isomers	3,900 - 4,700 ppmv	One-step Inlet: 25 scfm
15.1 - 15.8	Hexane isomers	3,400 - 5,200 ppmv	One-step Inlet: 20-29 scfm
16.1 - 16.4	Hexane isomers	4,400 - 5,300 ppmv	Two-step Inlet: 22 scfm

A. Definition of Performance Parameters

The performance of the system in removing VOC from the inlet stream is expressed by a reduction factor, RF_{system} , which is defined as

System VOC Reduction Factor =

$$RF_{\text{system}} = \frac{\text{VOC concentration in system inlet stream}}{\text{VOC concentration in system discharge stream}} \quad (1)$$

A related parameter is the VOC removal achieved by the system, R_{system} , which is defined as

$$\text{System VOC Removal} = R_{\text{system}} = (1 - 1/RF_{\text{system}}) \cdot 100\% \quad (2)$$

Thus, VOC removal is 90% if the reduction factor is equal to ten.

The stream entering the membrane modules contains VOC at a concentration determined by the condenser temperature and pressure. This concentration normally is different from the VOC concentration in the system inlet stream and we can define a membrane reduction factor, RF_{membrane} , as follows

Membrane VOC Reduction Factor =

$$RF_{\text{membrane}} = \frac{\text{VOC concentration in membrane modules inlet stream}}{\text{VOC concentration in system discharge stream}} \quad (3)$$

The corresponding VOC removal obtained by the membrane modules is given by

$$\text{Membrane VOC Removal} = R_{\text{membrane}} = (1 - 1/RF_{\text{membrane}}) \cdot 100\% \quad (4)$$

In the following sections we will discuss the influence of various parameters on system performance as expressed in reduction factors and removals.

B. Analysis of System Performance

The parameters kept constant during the experiments were (1) the condenser pressure, at 100 to 110 psia; (2) the condenser temperature, at 8°C to 12 °C; (3) the membrane modules used in the system; and (4) the inlet air temperature and pressure, at 20°C to 22°C and 14.7

psia. The variable parameters were (1) the VOC concentration in the system inlet stream; (2) the system configuration, one-step and two-step; (3) the type of VOC present in the air stream, perchloroethylene, CFC-113 (trichlorotrifluoroethane), and hexane isomers; (4) the system inlet stream flow rate; (5) the stage-cut; and (6) the permeate pressure for both first and second steps.

(1) Effect of VOC Concentration in Inlet Stream on System Performance

The combined compression-condensation/membrane system is expected to remove VOCs more efficiently if the VOC is present at higher concentrations. The condenser will reduce the VOC concentration to the equilibrium concentration determined by the condenser temperature and pressure. This means that the VOC concentration fed to the membrane system is independent of the actual VOC concentration in the overall system inlet stream. Thus, as the VOC concentration in the inlet stream increases, the condenser becomes more efficient, and the membrane system efficiency is not changed. Thus, the overall VOC system reduction factor (or VOC removal) increases.

Figures 10 through 12 show the system VOC reduction factors (and the corresponding system VOC removals) measured for perchloroethylene, CFC-113, and hexane, respectively, as a function of the VOC concentration in the system inlet stream. The inlet flow rate was 29 to 33 scfm in all cases. Figure 10 shows that the system VOC reduction factor does indeed increase with increasing perchloroethylene concentration with the system in its one-step configuration. The solid lines drawn in Figures 9 through 11 are calculated with the aid of a computer model that predicts performance of the combined compression-condensation/membrane system. The computer program uses as input parameters the vapor pressure data of the VOC, the effective membrane permeation rates of both air and VOC, and the system operating conditions (pressures, temperatures and flow rates). This program allows us to predict system performance as a function of the VOC inlet concentration as well as other operating conditions. The predictions are especially reliable when the effective membrane permeation data used have been determined under conditions that are close to the conditions for which the calculations are performed.

The data shown in Figures 10 through 12 show that the system VOC reduction factor is proportional to the VOC inlet concentration for both system configurations. This is easily understood by realizing that, because the condenser fixes the VOC concentration fed into the membrane system, the VOC concentration in the system discharge stream is independent of the VOC concentration in the system inlet stream. In that case the reduction factor as defined in equation (1) is proportional to the inlet concentration in that case.

Figure 10. System VOC reduction factors (and the corresponding system VOC removals) as a function of the perchloroethylene concentration in the system inlet stream. The inlet flow rate is 29 to 33 scfm in all experiments. The solid lines represent the calculated performance of the system based on the intrinsic selectivity of the membrane modules.

Figure 11. System VOC reduction factors (and the corresponding system removals) as a function of the CFC-113 concentration in the system inlet stream. The inlet flow rate is 29 to 33 scfm in all experiments. Solid lines are calculated data.

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Figure 12. System VOC reduction factors (and the corresponding system VOC removals) as a function of the hexane concentration in the system inlet stream. The inlet flow rate is 29 to 33 scfm in all experiments. Solid lines are calculated data.

(2) Effect of System Configuration on System Performance

Figure 10 through 12 contain experimental data obtained for the system operating in the one-step configuration as well as the two-step configuration. As has been discussed earlier in Section 5A, the system can be operated in two different configurations: (1) the one-step configuration [see Figure 9(A)], in which the permeate streams from both membrane steps are fed into the vacuum pump and the permeate pressures of both steps are equal and less than ambient pressure, and (2) the two-step configuration [see Figure 9(B)], in which the permeate stream from step 1 is directly recirculated to the compressors and only the permeate from step 2 is fed into the vacuum pump. In the two-step configuration, the permeate pressure in step 1 is ambient, whereas the permeate pressure in step 2 is less than ambient pressure and typically half of the permeate pressure obtained in the one step configuration.

It can be seen from Figures 10 through 12 that VOC removal is more efficient in the one-step configuration than in the two-step configuration. An analysis of membrane system performance shows that in the one-step configuration the VOC removal achieved by the membrane is determined mainly by the membrane selectivity and is not influenced very much by the pressure ratio (pressure ratio is defined as feed-side pressure divided by permeate-side pressure). Switching to the two step configuration means (a) that the pressure ratio in membrane

step 2 is roughly doubled, which does not improve VOC removal, and (b) that the pressure ratio in membrane step 1 is reduced by a factor of about 5, which means that the VOC removal is reduced because removal is now determined by the pressure ratio. The overall effect is a decrease in VOC removal by the membrane system, and thus in VOC removal by the combined system, if the system operates in the two-step configuration

The VOC removal by the two-step configuration is more efficient, however, if the VOC concentration fed into the membrane step 1 is relatively high. We calculated system performance for both one-step and two-step configurations as a function of the VOC concentration in the membrane step 1 inlet stream. In these calculations, the VOC concentration in the system inlet stream was kept constant, whereas the VOC concentration in the membrane inlet stream was varied by varying the condenser temperature. The results given in Figure 13 show that, at high VOC concentrations, the two-step configuration does yield higher reduction factors. This is because the limitation by the pressure ratio in the first step is removed at high VOC inlet concentrations.

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Figure 13. System VOC reduction factor as a function of VOC concentration in membrane step 1 inlet stream calculated for both one-step and two-step configurations. In these calculations, the VOC concentration in the system inlet stream was kept constant, whereas the VOC concentration in the membrane inlet stream was varied by varying the condenser temperature. Lines calculated with the following parameter values:

Membrane VOC/air selectivity: 20
 Pressure ratio: 30 (step 1 and step 2 in one-step)
 10 (step 1 in two-step)
 60 (step 2 in two-step)

(3) Effect of VOC Type on System Performance

The three VOCs used in the experiments can be ranked in order of increasing reduction factor and removal as

perchloroethylene > hexane > CFC-113,

when reduction factors are compared at the same inlet concentration.

As shown in Table 5, this ranking is in order of decreasing condensability. It is obvious that the compression-condensation step removes more condensable VOCs with increased efficiency, but the effect of condensability on the membrane separation efficiency is less clear. In addition to condensability, the membrane permeation rate of VOC is determined by the affinity between the VOC and the membrane material. However, for a homologous series of chemicals, where affinity is relatively the same for each member of the series, condensability correlates well with permeability. Figure 14 gives the halocarbon over nitrogen selectivity of MTR's standard vapor separation membrane as a function of the boiling point of the halocarbon. The increase in membrane selectivity with increasing boiling point (or increasing condensability) is clear. Thus, for a homologous series of chemicals we can safely predict that compounds with higher boiling points will be removed with higher efficiency if the inlet concentrations are comparable. It should be noted, however, that the feed concentration of compounds with higher boiling points is likely to be lower.

Table 5. Comparison of System Reduction Factors at 1,000 ppmv Inlet Concentration for Chloroethylene, CFC-113 and Hexane.

VOC	Boiling point (°C)	Vapor pressure at 20°C (torr)	System reduction factor at 1,000 ppmv inlet concentration (-)
Perchloroethylene	121	14	350
Hexanes	69	126	32
CFC-113	46	304	3.5

Figure 14. Halocarbon/nitrogen selectivity as a function of the boiling point of the halocarbon. Data obtained with MTR's standard vapor separation membrane at room temperature.

(4) Effect of Inlet Flow Rate on System Performance

For a system with a fixed membrane area, we expect the VOC removal to decrease if the inlet flow rate is increased. The experimental data obtained with isomeric hexanes given in Figure 15 confirms this. The hexane removal obtained by the system decreases with increasing flow rate because the hexane removal obtained by the membrane system decreases. A membrane system with fixed membrane area produces a permeate stream of fixed flow rate (at constant operating conditions) which means that, as the membrane feed flow rate increases, the ratio of permeate flow rate to feed flow rate decreases. As will be shown in the next section on the effect of stage cut, this reduces the VOC removal by the membrane system.

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Figure 15. System VOC reduction factors (and the corresponding system VOC removals) as a function of the hexane concentration in the system inlet stream for three different inlet flow rates. Solid lines are calculated data.

(5) Effect of Stage Cut on Membrane Performance

Figures 16 through 18 give the membrane VOC reduction factors (and the corresponding membrane VOC removals) as a function of stage cut for two different permeate pressures. Stage cut is defined as permeate flow rate divided by feed flow rate and, in addition to membrane selectivity and pressure ratio, is an important parameter that determines the performance of a membrane system. The experimental data given in Figures 16 through 18 show that VOC removal increases as stage cut increases. For a system of fixed membrane area, this means that VOC removal increases as the feed flow rate decreases. The solid lines in Figures 16 through 18 represent calculated data obtained with the computer program described earlier.

Figures 16 through 18 each contain five different sets of data which are discussed below.

- (1) System operating in one-step configuration, data for the two membrane steps combined: Both membrane steps are operated at a permeate pressure of about 2 psia.
- (2) System operating in two-step configuration, data for second membrane step only: Second membrane step is operated at a permeate pressure of about 1 psia. Figures 16 through 18 show that data sets (1) and (2) fall on the same calculated line.

- (3) System operating in two-step configuration, data for first membrane step only: First membrane step is operated at a permeate pressure of about 15 psia. Figures 16 through 18 show that the data set (3) falls on a different calculated line than data sets (1) and (2) and that, as expected, the VOC removal obtained by the membrane system is lower at higher permeate pressures.
- (4) System operating in two-step configuration, data for the two membrane steps combined: First membrane step operates at a permeate pressure of 15 psia, whereas the second step operates at a permeate pressure of about 1 psia. As expected, data set (4) falls in between sets (1) and (2) on the one hand and set (3) on the other hand.
- (5) System operating in one-step configuration without the vacuum pump, data for the two membrane steps combined: Both membrane steps are operated at a permeate pressure of 15 psia. This data set is only present in Figure 18, which contains data obtained with hexane. Figure 18 shows that data set (5) falls on the same calculated line as data set (3). This is expected as both data sets were obtained at permeate pressures of 15 psia.

Figure 16. Membrane VOC reduction factors (and the corresponding membrane VOC removals) as a function of stage cut for two different permeate pressures. Stage cut is defined as permeate flow rate divided by feed flow rate. Data obtained with perchloroethylene. Solid lines are calculated data.

Figure 17. Membrane VOC reduction factors (and the corresponding membrane VOC removals) as a function of stage cut for two different permeate pressures. Stage cut is defined as permeate flow rate divided by feed flow rate. Data obtained with CFC-113. Solid lines are calculated data.

Figure 18. Membrane VOC reduction factors (and the corresponding membrane VOC removals) as a function of stage cut for two different permeate pressures. Stage cut is defined as permeate flow rate divided by feed flow rate. Data obtained with hexane. Solid lines are calculated data.

(6) Effect of Permeate Pressure on Normalized Membrane Permeation Fluxes

The data presented in Figures 10 through 12 and in Figures 16 through 18 show that VOC removal is improved by reducing the permeate pressure. The effect of permeate pressure on the normalized membrane permeation flux is shown in Figures 19 through 21. The normalized permeation flux for a permeating vapor or gas is defined as the amount of vapor or gas in $\text{cm}^3(\text{STP})$ that permeates the membrane per unit membrane area in cm^2 , per unit time in seconds, and per partial pressure driving force across the membrane expressed in cmHg . The dimension of normalized permeation flux is thus $\text{cm}^3(\text{STP})/\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$.

In ideal cases, a normalized permeation flux is expected to be independent of operating conditions such as the permeate pressure because it is normalized with respect to the driving force for permeation. In practice, however, the normalized permeation flux can be influenced by the permeate pressure if permeate-side pressure drops occur in the membrane module. These pressure drops will reduce the driving force for permeation. The normalized permeation rate calculated from experimental separation data will decrease with decreasing permeate pressure as the pressure drop becomes more severe at the lower pressures. This phenomenon usually only affects the compound that is being enriched in the permeate, that is, the compound with the highest normalized flux.

Figures 19 through 21 show that the air normalized flux is independent of the permeate pressure and independent of the type of VOC present in the feed gas. The perchloroethylene, CFC-113 and hexane normalized fluxes, however, decrease with decreasing permeate pressure. This is a clear indication of the existence of permeate-side pressure drops in the membrane modules used in the system. During Phase I of this project, a simple test was performed with the same type of module to check for permeate-side pressure drops. In this test, the effect of permeate pressure variation on the nitrogen permeation rate was determined. The conclusion from the test was that no pressure drops were present; thus, we have to conclude that the simple nitrogen test is inadequate.

The performance of the Field Demonstration System could be improved by reducing the permeate-side pressure drops in the membrane modules. In the follow-on Phase III of this project, we will further investigate module modifications that may alleviate the pressure drops. However, the modules work satisfactorily even with the occurrence of pressure drops, as is evidenced by the high VOC removals obtained by the Field Demonstration System and by the high VOC normalized permeation fluxes shown in Figures 19 through 21.

Figure 19. Normalized permeation fluxes of perchloroethylene and air as a function of permeate pressure. Normalized permeation fluxes calculated from experimental separation data obtained with Field Demonstration System.

Figure 20. Normalized permeation fluxes of CFC-113 and air as a function of permeate pressure. Normalized permeation fluxes calculated from experimental separation data obtained with Field Demonstration System.

Figure 21. Normalized permeation fluxes of hexane and air as a function of permeate pressure. Normalized permeation fluxes calculated from experimental separation data obtained with Field Demonstration System.

7. TASK 4. MONITOR MODULE TEST SYSTEM AT GREAT LAKES

A single Module Field Evaluation Unit was constructed and installed at the El Dorado plant of Great Lakes Chemical Corporation. The system essentially consists of one membrane module housing containing one module insert. A schematic diagram of the membrane module housing is shown in Figure 22. The housing is jacketed to allow operation at reduced temperatures. The goal of the module test was to obtain information on membrane and module life at low temperatures. As described in the original proposal, our laboratory results show that gas streams containing very volatile VOCs such as Halon 1301, CFC-12, CFC-13, and CFC-23, must be cooled substantially to obtain the selectivity required for efficient separation. The GLC plant uses many low-temperature processes and has an abundance of cooling brines available in the temperature range from -20° to -30°C .

Before the unit was shipped to Great Lakes Chemical Corporation, a Halon 1311/nitrogen separation experiment was performed with the module at temperatures ranging from room temperature to -18°C . Figure 23 gives the Halon 1301/nitrogen selectivity calculated from the experiments as a function of temperature. These data confirm earlier data obtained with membrane stamps: selectivity increases with decreasing temperature and the selectivity equals about 10 at -20°C .

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Figure 22. Schematic diagram of a jacketed membrane module housing, for operation at reduced temperatures.

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Figure 23. Halon 1301/nitrogen selectivity calculated from separation experiments as a function of temperature.

At the Great Lakes plant, the unit is connected to the vent port of an existing heat exchanger/condenser. This heat exchanger/condenser, E301, vents a pressurized gas stream, containing mostly CFC-22, to the atmosphere. The Module Field Evaluation Unit was designed to separate this stream into a high-pressure, VOC-depleted stream to be vented and a low-pressure, VOC-enriched stream to be recirculated to the process. Figure 24 gives the flow diagram of the system installed at Great Lakes.

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Figure 24. Flow diagram of the Module Field Evaluation Unit installed at Great Lakes.

The system was installed at the Great Lakes plant in February 1992. After installation it became apparent that the vent stream was very intermittent. The pressure in the condenser is allowed to increase to a certain set point, after which a valve opens and the pressure decreases until the valve closes at a second set point. Replacing the existing off/on valve with a backpressure valve, which maintains a constant pressure in the condenser, improved the situation but did not result in a constant flow rate. An additional problem encountered was that the average vent flow rate is small, usually less than 2 L/min, whereas the system was designed for a vent flow rate of at least 2 scfm. After several months of inactivity, the system was restarted in October 1992. The condenser set point pressure was reduced to increase the vent flow rate. On several occasions, the vent flow rate was at least 4.5 L/min at a condenser pressure of 58 psig. The best separation data obtained show that the module reduced the halocarbon content of the vent stream from 67.5% to 26.1%. Based on computer simulations, we expect the separation to be substantially better. The probable explanation is that poor flow distribution in the module, caused by the very low flow rates, reduces the separation efficiency of the membrane.

We will continue to work with Great Lakes Chemical to further improve the test conditions for the module unit. MTR will likely replace the existing module insert with a new insert with a reduced membrane area to compensate for the small vent flow rate. Testing will continue for the duration of Phase III of the project.

8. TASK 5. SEEK INDUSTRIAL SUPPORT

The ultimate goal of the project is to install and operate the Field Demonstration Unit at one, and preferably more, industrial site(s) to demonstrate MTR's vapor separation technology. The host companies are asked to contribute the following to the project:

- (1) Financial support: start-up costs and a nominal monthly rent for the system. Typical payment would be \$15,000 for a four-month test, which will be added to the project budget as a cost share.
- (2) Operating support: internal labor and miscellaneous expenses for installation and operation of the system and for monitoring the performance of the system.

In return, MTR will provide extensive support to the host company during the field test. MTR engineers will train host site personnel, will assist during start-up, and will visit the site whenever necessary.

During Phase I of the project (August 1991 through February 1992), a total of twelve companies expressed an initial interest in participating in the project. No firm commitments were given since the earliest date at which the Field Demonstration System would be available was June 1992. Later in Phase II, more serious discussions were held. Discussions were taken the furthest with the three companies listed in Table 6.

Table 6. Three Host Sites Under Consideration During Phase II

Type of Company	Stream components	Concentration	Flow rate (scfm)
1. Chemical	Ethylacetate Nitrogen	0.2 to 3 % balance	50
2. Chemical	Benzene Nitrogen	5% balance	100
3. Chemical	C ₂ through C ₁₀ olefins Oxygen Nitrogen	3% 4% balance	1,500

Out of the three potential host sites, two are still being actively pursued. The first site listed in Table 6 has been dropped. The vent stream at that site was to be produced by a pilot plant in which a novel process was to be developed to full-scale operation. However, the company decided as part of cost-cutting measures to postpone this project.

The most promising opportunity at this moment seems to be the benzene in nitrogen vent stream. According to information provided by the company involved, the vent stream is currently incinerated at a fuel cost of \$175,000/yr. The incinerated benzene would be worth about \$50,000, if recovered. Preliminary calculations show that a membrane vapor recovery system that recovers 99%+ of the benzene would have an annual operating cost of about \$60,000. This makes the membrane system a very attractive alternative. The configuration of the proposed system is identical to the configuration of the Field Demonstration System, which makes this site an excellent opportunity. The Field Demonstration System operating on a 40-scfm slip stream would demonstrate 99%+ benzene recovery. We hope that the company involved will decide to join the demonstration effort within two months.

9. COMMERCIAL ACTIVITIES AT MTR

To date, MTR has constructed and installed the thirteen commercial vapor separation systems listed in Table 7. Most of the systems are small and all operate on feed streams containing nonflammable VOCs. One of the purposes of the Field Demonstration Unit is to demonstrate the process with flammable vapors, thereby extending the range of applications for the technology.

Table 7. VaporSep™ Commercial Installations

Company	Flow rate (scfm)	Months in operation	VOC recovered
Nestle	10	26	CFC-12
Du Pont	15	26	CFC-11; CFC-113
Du Pont	25	24	CFC-11; CFC-113
Goodyear	50	22	Vinyl chloride
"Fortune 100"	50	14	HCFC-123
Great Lakes Chemicals	5	9	Halon 1301
Westinghouse	35	4	Perchloroethylene; chloroform
Dow	2	2	CFC-12
B.F. Goodrich	10	4	Vinyl chloride
Donaldson	4	3	CFC-12; ethylene oxide
Donaldson	4	1	CFC-12; ethylene oxide
Dow	2	2	CFC-12
Vista Chemical	10	*	Vinyl chloride

* Under construction.

One of the two larger systems was built and installed during the early stages of the present DOE program, in response to an urgent customer need for VOC recovery technology. The membrane vapor separation system is installed at a facility of a U.S. "Fortune 100" company. The system treats 50 scfm of air containing between 6 and 7% by volume of HCFC-123, a nonflammable halogenated hydrocarbon with a boiling point in the range 40-60 °C. The membrane modules operate at a feed pressure of 140 psig and a permeate pressure of 3 psia. The membrane system reduces the VOC content to less than 100 ppm by volume and recovers 70-80 pounds of VOC per hour. The operating costs of the system are more than off-set by the value of the recovered VOC. The system is operated an average of 6 hours/day for

3 days/week. After installation of the system, a compatibility problem between the hydrocarbon and a module component was discovered. The problem has been solved by installing a new set of modules. The system currently operates satisfactorily and has logged about 900 hours of operation.

10. CONCLUSIONS

The Field Demonstration System constructed in this phase of the project, performed well during parametric testing at MTR's facilities. In experiments with perchloroethylene, trichlorotrifluoroethane, and hexane as model VOCs, the system achieved VOC removal between 80 and 99.8%. These results demonstrate that the compression-condensation/membrane-hybrid configuration of the Field Demonstration System is highly efficient.

The search for industrial host sites for the Field Demonstration System has not yet been successful. Several promising sites have been identified, but no definite site has been arranged. The search for host sites will have the highest priority as Phase III of the project starts.

APPENDIX A

Presentations on Membrane Vapor Separation Systems given at national meetings with plant engineers in attendance.

J.G. Wijmans, J. Kaschemekat and R.W. Baker (Membrane Technology and Research, Inc.), "A Membrane Process for the Recovery of Volatile Organic Compounds from Process and Vent Streams," Proceedings of the 84th Annual Meeting of the Air and Waste Management Association, Vancouver, British Columbia, June 16-21, (1991).

B. Rose (Goodyear Tire and Rubber Company), "Recovery of Vinyl Chloride Monomer by Membranes," Proceedings of the Annual Meeting of the Vinyl Chloride Safety Association, Denver, Colorado, September 23-27, (1991).

R.W. Baker, V.L. Simmons, J.G. Wijmans and J. Kaschemekat (Membrane Technology and Research, Inc.), "Membrane Vapor Separation System Applications and Case Histories," AIChE Spring Meeting, New Orleans, Louisiana, March 29 - April 2 (1992).

R.W. Baker, J. Kaschemekat, J.G. Wijmans and V.L. Simmons (Membrane Technology and Research, Inc.), "Membrane Vapor Separation Systems for the Recovery of VOCs," Proceedings of the 85th Annual Meeting of the Air and Waste Management Association, Kansas, Missouri, June 21-26, (1992).

R.J. Lahiere and M.W. Hellums (Vista Chemical Company), J.G. Wijmans and J. Kaschemekat (Membrane Technology and Research, Inc.), "Membrane Vapor Separation: Recovery of Vinyl Chloride Monomer from PVC Reactor Vents," AIChE 1992 Annual Meeting, Miami Beach, Florida, November 1 - 6 (1992)

APPENDIX B

MEMBRANE VAPOR RECOVERY SYSTEMS

DESCRIPTION OF DEMONSTRATION UNIT

Treatment of effluent airstreams containing organic vapors by condensation of the organic components has proven a valuable method of waste treatment and pollution control. There remains, however, a long-standing need for improved condensation technology. Recent evidence concerning the adverse environmental effects of halogenated hydrocarbons and specifically chlorofluorocarbons (CFCs) has dramatically intensified that need.

For the past six years, Membrane Technology and Research, Inc. (MTR) has been developing membrane separation systems able to remove organic vapors from air. The Department of Energy, Office of Industrial Programs, was an early sponsor of this work. The technology is currently in the early stage of commercialization. Six units are in operation at industrial facilities. Data from these installations indicate that the process is reliable and effective.

Currently, the Department of Energy, through its Industrial Waste Reduction Program, is sponsoring development work to extend this technology to a combined condensation/membrane separation system for improved recovery of volatile organic compounds (VOCs) from waste streams. As part of this program, MTR is constructing a 25-90 scfm demonstration system to be evaluated on industrial streams.

The system will be completed in April 1992. It will be fully tested at MTR's facilities and available for demonstration at industrial sites by June 1992.

PROCESS PRINCIPLES

The VOC vapor recovery process described here is based on the use of composite membranes that are more permeable to organic compounds than they are to air. The hybrid process, combining these membranes with condensation, is very efficient in recovering organic compounds because of the inherent complimentary features of the two processes.

The process involves two main steps, a condensation step and a membrane concentration step. The condensation step is conventional, and typically involves compressing the gas stream to be treated, then chilling it to condense a portion of the VOC content. The membrane step is new, and involves the use of high performance composite membranes that are permeable to organic compounds and relatively impermeable to air. The hybrid process is designed to yield only two product streams: the condensed liquid, ready for recovery and reuse, and a gas stream sufficiently depleted of VOCs to be vented.

The process is illustrated in Figure 1. A VOC-contaminated air stream is compressed and then cooled in a condenser to remove a portion of the VOC content. The compressed condenser bleed air, still containing a substantial amount of VOC, is then passed to a membrane unit, which removes the remaining VOC, producing a VOC-depleted air stream suitable for venting. Because the membrane is 10-100 times more permeable to organic vapor than air, a significant enrichment of organic vapor on the permeate side of the membrane is achieved. The enriched permeate stream from the membrane step is recycled to the condenser. Thus, no secondary waste streams are created by this process. The VOC content of the original stream can be reduced by at least 95%. Because the VOC is recycled to the condenser, the process is able to produce condensation even in very dilute feed streams that do not initially condense after compression. In this case, VOCs build up in the recirculating gas until the concentration of the vapor passing through the condenser reaches the condensation point.

MTR-003-1S

Figure 1. Hybrid compression-condensation/VaporSep membrane process flow diagram.

APPLICATIONS FOR THE TECHNOLOGY

Systems incorporating the hybrid compression-condenser VaporSep membrane process have been installed in several industrial processes. Two of these systems are described below to illustrate some of the possible applications for the technology.

Vinyl Chloride Recovery from PVC Manufacturing

The complementary aspects of membrane recovery and condensation can be utilized in retrofitting an existing vent condenser with a membrane unit. A VaporSep system has been installed in this way to recover vinyl chloride monomer from the polyvinyl chloride (PVC) manufacturing process. PVC manufacture, and many other polymerization reactions, produce an off-gas stream that contains a significant amount of unreacted monomer. Most PVC processes compress and cool this off-gas to recover a portion of the unreacted vinyl chloride monomer. However, vinyl chloride is extremely volatile (boiling point, -13°C) and the condenser vent still contains up to 50% vinyl chloride. Because of the toxicity of vinyl chloride, most U.S. PVC manufacturers incinerate this condenser vent stream.

The vinyl chloride lost by incineration is up to 1% of the total vinyl chloride used in the process. An average PVC manufacturer loses 500,000 pounds of valuable vinyl chloride feedstock per year by incinerating this waste stream. Recent legislation aimed at eliminating acid rain has targeted incineration of vinyl chloride as a source of hydrochloric acid emissions. The legislation will require the addition of a costly scrubber to most incinerators.

The installation of an MTR membrane vapor recovery system allows 90-99% recovery and direct recycle of the vinyl chloride from the condenser vent, eliminating the need for an HCl scrubber. The process is illustrated in Figure 2. The vent gas from the process is compressed to 65 psig and liquid vinyl chloride is condensed from this stream at -10°C . The vent from this existing condenser, containing up to 50% vinyl chloride monomer, is sent to the membrane unit. The membrane unit recovers the vinyl chloride monomer contained in the stream as a concentrated permeate which is recycled to the process. The vent from the membrane unit may be discharged directly or sent to an incinerator without the need for a scrubber.

A VaporSep unit installed at the Goodyear Tire and Rubber Company in Niagara Falls, NY is recovering 100-200 pounds of vinyl chloride per hour and has reduced the emissions from their incinerator sufficiently to meet stringent New York State requirements. Based on the value of the recovered vinyl chloride, this unit will have a payback time of 6-12 months.

Figure 2. Flow diagram of a membrane system for the recovery of vinyl chloride monomer (VCM) from the PVC manufacturing process.

HCFC-123 Recovery from a Film-Drying Process

The second example of how VaporSep membrane technology has been applied in combination with condensation is in the recovery of HCFC-123 from a film-drying process. Industrial coating and cleaning operations rely heavily on the use of volatile organic solvents, such as CFCs and 1,1,1-trichloroethane. The production of these solvents will be phased out during this decade. The available replacement solvents, such as HCFC-123, are very expensive and subject to stringent environmental emission limits. Viable conversion of an existing process to the new materials requires the availability of efficient recovery technology. The MTR membrane vapor recovery process has been demonstrated to be effective for recovery of HCFCs, HFCs (hydrofluorocarbons) and perfluorinated compounds.

A VaporSep system was recently installed to recover HCFC-123 vapors from the drying chamber of a film-coating operation. A flow diagram and photograph of the system are shown in Figure 4. HCFC-123 vapors exit the drying chamber at a concentration of 7.2% in air. The vapor stream is compressed to 125 psig and cooled to -15°C. A dryer removes water vapor from the stream to prevent ice formation in the condenser. The condenser vent is routed to the membrane modules. The concentration of HCFC-123 in the resulting vent stream never exceeds 100 ppm. The unit recovers 70 pounds of HCFC-123 per hour. Based on a price of \$5/lb for this material, the membrane system will pay for itself after 3,000 hours of operation.

Figure 4. Flow diagram and photograph of a VaporSep membrane system to recover 99.8% of the HCFC-123 lost in a film drying operation.

Gasoline Vapor Recovery

A third example of how VaporSep technology can be applied to emission control is the recovery of gasoline vapors from tank vent streams. The performance obtained with a 30-scfm pilot system is illustrated in Figure 5. The initial feed contains as much as 40% gasoline vapors, primarily butane and pentane. After compression to 90 psig by a liquid-ring compressor using gasoline as the sealant fluid, the gas passes to a condenser at 10°C. The condenser lowers the gasoline concentration to approximately 10%, and this stream passes to the membrane unit which produces a vent stream containing approximately 1% gasoline and a permeate recycle stream containing 50% gasoline vapors. Thus, the overall VOC removal is more than 98%.

MTR-048-1S

Figure 5. Flow diagram of a VaporSep system to recover gasoline vapors from tank vents.

DESCRIPTION OF THE DEMONSTRATION SYSTEM

The hybrid condensation VaporSep membrane system has been demonstrated in a limited number of applications. To gain widespread industrial acceptance, it will be necessary to provide potential users with a pilot system for demonstration at the host facility. Under a contract with the Department of Energy, MTR is constructing a pilot unit for this purpose. The demonstration system has a capacity of 25-90 scfm, and is designed to be appropriate for a wide range of applications, including flammable VOC/air mixtures.

A flow diagram of the field demonstration system is shown in Figure 6. The system contains two liquid-ring compressors, a liquid-ring vacuum pump, a condenser and ten membrane modules. The components of the system are described in more detail in the Component Specification (Attachment 1). The design of the system allows operation in six different configurations, as shown in Figure 7. The main difference between configurations A through C and configurations D through F is that, in the latter group, the permeate stream is recompressed and fed into the condenser without being mixed with the feed gas. This improves the performance of the system when the feed gas itself does not contain enough condensable material to make condensation feasible. The flexible design of the demonstration unit will allow selection of the optimum process configuration for a particular application.

077-25

Figure 6. Flow diagram of the field demonstration system.

079-25

Figure 7. Six configurations possible with the VaporSep field demonstration system.

HOST SITE REQUIREMENTS

The demonstration VaporSep system will be available for field installation in June 1992. MTR is actively seeking host sites. The objective of the demonstrations is to prove the economic and environmental benefits of the technology and to make the results of these demonstrations available to other industrial users. The host site will be responsible for preparing the site for installation, day-to-day operation of the system, and analysis of appropriate stream samples. MTR will be responsible for start-up, engineering support during the entire demonstration period, and analysis of the performance data. MTR will provide a written report at the end of the demonstration, containing a summary of the data, a proposed full-scale VaporSep system design, and a recommended course of action. Specific details of participation as a host site are discussed below.

Costs

The host site will be expected to contribute to the costs of the demonstration, as follows:

Shipping, crating	\$ 4,000 (estimated)
Start-up and first month's engineering support	5,000 per month
Subsequent months' engineering support	2,000 per month

The host site will also be responsible for the miscellaneous expenses associated with installation, operation, and analysis.

Timing

The demonstration unit will be available by June 1992. The duration of the field test will be agreed by the host site and MTR. The expected length for each demonstration is between three and six months.

Public Awareness

The technical results of the demonstrations will be reported to the Department of Energy, and are eventually released to the public in the form of a final report on this project. Information considered to be proprietary to the host company need not be disclosed in these reports. MTR is willing to sign a non-disclosure agreement with the host company, assuring that only those technical details specifically pertaining to the VaporSep demonstration system will be disclosed.

Who To Contact

Additional details concerning participation as a host site can be obtained by calling Vicki Simmons at MTR (415-328-2228).

COMPONENT SPECIFICATIONS

Compressor: 2 Siemens liquid-ring compressors, Model 2BG2084-7BY2
 Motor: 460V/60Hz/3-phase, 30 hp
 Stainless steel/carbon steel/cast iron construction
 Class I, Division 2, Groups C and D

Vacuum pump: Siemens liquid-ring vacuum pump, Model 2BE1102-0BY4
 Motor: 460V/60Hz/3-phase, 15 hp
 Stainless steel/carbon steel/cast iron construction

Frames: 2-in and 1½-in square tube
 Powder-coated, dark green

The complete VaporSep unit will consist of four skids:

Modules:	approx. 72 x 90 x 60 in (w x l x h)
Compressors:	approx. 64 x 90 x 84 in (w x l x h)
Vacuum pump:	approx. 30 x 80 x 60 in (w x l x h)
Controls:	approx. 30 x 45 x 60 in (w x l x h)

When connected, the overall dimensions of the unit will be approximately 146 x 150 x 84 in (w x l x h).

Condenser: Shell and tube (ITT 03014)
 316 stainless steel

Modules: 10 MTR-1435 membrane modules
 Stainless steel housings
 4-in diameter, 40-in length

Solvent station: Stainless steel, Teflon construction
 Stainless steel tank
 Level switch
 Solenoid valve

Energy requirements: 460V/60Hz/3-phase

Other utilities: Cooling water for the compressors and vacuum pump, 15-25°C
 Coolant for the condenser, 5-25°C

**DATE
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8 / 17 / 93

END