Recovery of VOCs from High-Volume, Low-VOC-Concentration Air Streams

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High-volume, low-VOC-concentration air streams are produced by a broad range of industries. The most widely used treatment technology is carbon adsorption, which produces dilute aqueous waste streams as a secondary waste, is difficult to adapt to particulate-containing streams, and is too expensive to be applied by some industries. Scrubbing the air with an absorbent liquid is economical, but limited to scrubbing with water due to the expense and difficulty of regenerating nonaqueous scrubbing liquids. A low-volatility organic scrubbing liquid regenerated by a stripper/membrane vapor-separation unit was used to remove VOCs from the dilute air stream. The technical and economic feasibility of the scrubbing/stripping/membrane separation hybrid process was evaluated in laboratory tests with a pilot-scale system. The unit, operated with model-contaminated gas streams containing 100 to 2,000 ppm methylene/chloride, removed 95% of the methylene chloride in the feed air as a condensed liquid. The experimental data show that the process offers significant cost and operating benefits over other technologies for streams in the 500 to 2,000 ppm VOC concentration range. It can be applied to treating effluent air streams from painting, degreasing, and printing operations.

Introduction

Volatile organic compound (VOC) emissions are one of the major sources of air pollution. Such emissions are a particular problem where low concentrations of VOC are present in large gas flows, particularly if the gas also contains submicron-size particulate matter. VOC concentrations in the streams are often in the 50–2,000-ppm range; flow rates in the 1,000–10,000-scfm range are common. Although these high-volume effluent streams are dilute, in aggregate they represent a significant fraction of the total VOC emissions from U.S. industrial processes.

A number of treatment techniques are available for handling VOC-laden air streams. [See review by Hagler Bailery & Company for the U.S. Department of Energy (1986).] Carbon adsorption can be used, provided the air stream is clean and free of particulates. However, over 50% of VOC-laden streams also contain aerosols and submicron particles, which foul carbon beds. Steam regeneration of carbon adsorption beds also produces hazardous aqueous waste streams contaminated with dissolved VOCs. Catalytic incineration can be used to treat air streams containing both VOCs and particulates, but is subject to catalyst deactivation, is not suitable for chlorinated VOCs, and can be difficult to permit.

Scrubbing with an absorbent liquid is an economical and efficient technique for treating low-concentration, high-volume air streams containing water-soluble VOCs, and can be used on streams containing particulates. In a scrubbing unit, the VOC-laden air is contacted with a liquid, generally water, in which the VOCs dissolve. A number of different scrubber configurations are in use, including packed towers, atomized mist scrubbers, and venturi scrubbers. Atomized mist scrubbers are most efficient at treating dilute VOC streams in applications such as odor control. Venturi scrubbers are used to remove aerosols and airborne particulates. However, the wet scrubbing process is limited in scope.

In most applications, the scrubbing liquid is not regenerated and recycled and must, therefore, be low cost—water is generally used. This means that the process is limited to water-soluble VOCs, such as acetone, ethanol, methanol, or acidic or basic compounds, such as acetic acid or amines (Zenz, 1979; Hicht, 1988; Armand et al., 1990; Geisthardt et

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al., 1989). The solubilities of hydrophobic VOCs, such as chlorinated solvents, aromatics, and naphthas, in water are low, and impossibly large scrubbing units and huge volumes of water would be required to strip them from the air. Consequently, although the air stream could be scrubbed free of VOCs, the process would produce a large-volume aqueous stream containing very low levels of VOC for disposal by a secondary process, such as biological water treatment. Development of absorbent scrubbing technology that removes hydrophobic VOCs from air streams in an efficient and economical operation that produces no secondary wastes would be a valuable step in reducing airborne pollution and energy usage.

The system described here combines absorbent scrubbing with stripping/membrane vapor separation to regenerate the scrubbing liquid. This approach solves the problems limiting the application of absorbent scrubbing processes and allow VOCs of all types, including chlorinated solvents, aromatics, and naphthas, to be removed efficiently from waste air streams. The process operates as a closed loop, with only clean air and condensed liquid VOC exiting the system.

A conceptual design of the system is shown in Figure 1. A scrubbing unit is used to contact the incoming air with an organic scrubbing liquid in which the VOC contaminant is soluble. The airborne VOC dissolves in the absorbent liquid and is removed with the liquid from the bottom of the unit. The resulting clean air stream is vented to the atmosphere. The VOC-laden absorbent liquid is heated and passed to a vacuum stripping column, where it is purged under vacuum with a nitrogen strip gas. The small volume of off-gas from the stripper is sent to a membrane vapor recovery system that separates the gas into two streams: a small-volume VOC liquid stream, which is sent to an offsite reclaimer, and a clean, VOC-free nitrogen stream, which is recycled to the stripping column. For good performance of the stripper in regenerating the absorbent fluid, good removal of VOCs from the recirculating strip gas is essential; this is the purpose of the membrane vapor separation step. In this process the absorber/stripper unit acts as a preconcentrator, concentrating the VOCs 20- to 30-fold to 1–5% VOC. Gas streams containing VOCs in this concentration range are efficiently and economically treated by membrane vapor separation systems (Baker and Wijmans, 1994).

Background

A key part of the proposed process is a membrane system that removes organic vapors from air streams efficiently and economically. Membrane separation is an efficient, cost-competitive process for recovering VOCs from gas streams provided the gas contains more than about 0.5% VOC. The scrubber/stripper portion of the process shown in Figure 1 concentrates the VOC-containing gas 20- to 30-fold. This brings many low-concentration streams into the concentration range in which membrane systems are most competitive. Provided the cost of the preconcentration operation is low, the total process could be very competitive with other technologies.

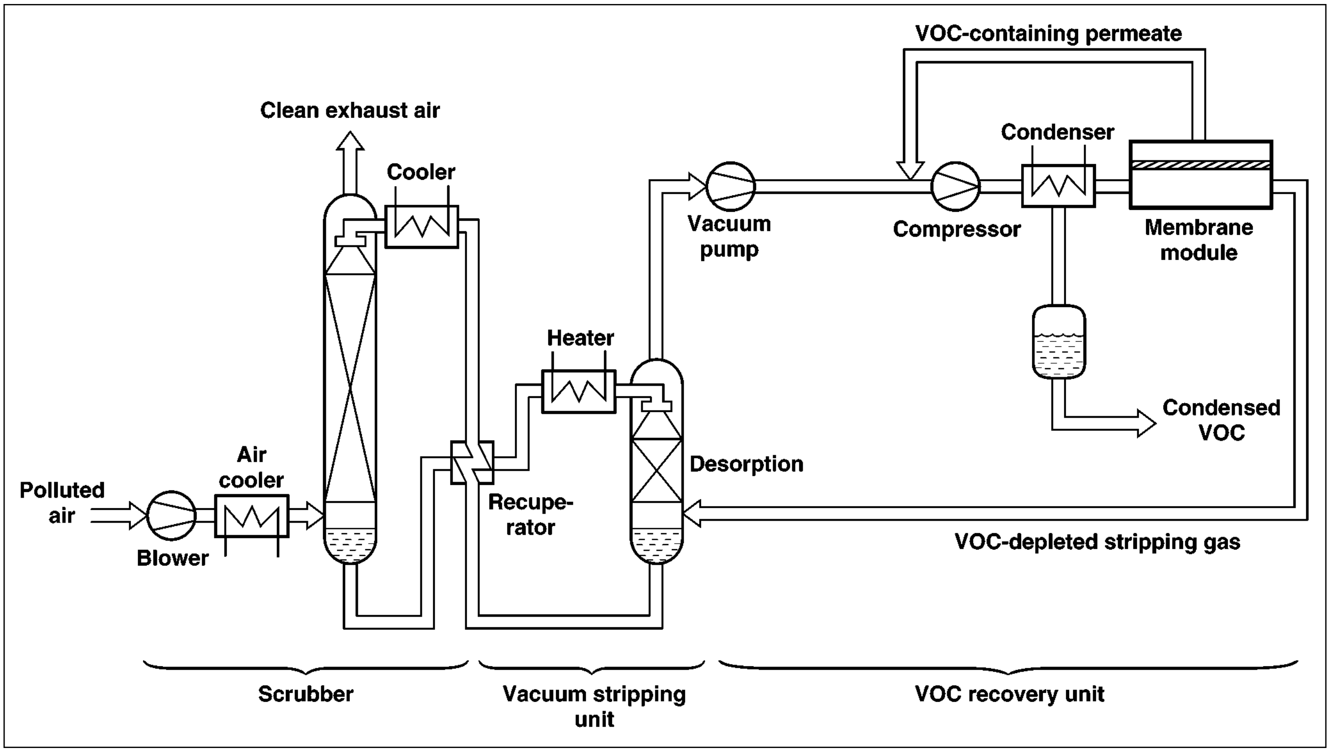

Figure 1. Scrubber/stripper/membrane vapor separation system.

The scrubber/stripper system effectively acts as a preconcentrator to the membrane unit, increasing the VOC concentration from the 100–1,000 ppm range to the 0.5–5% range, at which the membrane is extremely efficient.

The membrane VOC recovery unit concentrates the vapor components in the overhead gas from the stripper column into a condensed liquid stream. The VOC-containing gas from the stripper column, containing 0.5–5 vol % vapor, is compressed and cooled, condensing a portion of the vapors as a liquid that is removed for reuse. The remaining gas, which still contains a significant amount of vapor, is fed to the membrane module. The membrane separates the gas into two streams: a residue stream stripped of the vapor, and a permeate gas enriched in the vapor. The permeate gas is recycled to the front of the compressor to be treated a second time. The membranes employed in this system separate the feed-gas components on the basis of relative solubility in the membrane material. Because of their higher solubility in the membrane, organic vapors preferentially permeate over air even though their molecules are larger. One feature of the membrane vapor system design is that the concentration of VOC in the treated gas is independent of the concentration in the feed gas to the system. This is because the VOC concentration in the gas stream entering the membrane unit is constant and fixed by the temperature and pressure of the condenser even though the feed gas concentration may vary. Because the gas concentration entering the membrane unit is constant, the gas concentration leaving is also constant (Baker et al., 1998).

Choice of the scrubbing liquid

Absorbent scrubbing combined with the proposed membrane-based regeneration/VOC recovery system will have significant technical and economic advantages over other processes for cleaning gas streams, provided a suitable low-cost scrubbing liquid is available. A suitable scrubbing liquid has the following properties:

- Good solubility and high selectivity for VOCs
- Low vapor pressure to minimize losses with the clean gas
- Low viscosity
- Good hydrolytic and oxidative stability at stripping temperature
- High ignition and flash point to minimize fire hazards
- Easy regeneration
- Modest to low water solubility to minimize water sorption from humid air
- Low toxicity

A number of liquids meet these criteria, including triethylene glycol dibutyl ether, low-viscosity silicone oil, and Paratherm NF, a commercially available heat-transfer fluid. In this work we selected triethylene glycol dibutyl ether, which is commercially available as Genosorb 1843 from Hoechst-Celanese, Charlotte, North Carolina (see paper on Genosorb, 1994, and Geisthardt et al., 1989). Solubility of the VOC in the scrubbing liquid is a key requirement, and Genosorb has high sorption coefficients for most of the common VOCs.

Experimental Results

To evaluate the utility of the process, a pilot-scale absorber/stripper unit designed to treat 50 to 150 std. ft^3/min (24 to 71 L/s) of contaminated air was built. For these experiments, the unit was built as a closed-loop, full-recirculation system. The treated clean air discharged from the top of the scrubber was mixed with methylene chloride delivered by a metering pump, then recirculated to the bottom of the scrubber. The scrubber column was 12 in. (305 mm) in internal diameter and 16 ft (4.9 m) tall. Plastic packing, 1 in. (25 mm) diameter was used; four plastic flow distributors were placed in the column to minimize liquid channeling. The effective length of the column was 12 ft (3.7 m). The air blower flow could be regulated from 50 to 150 std. ft^3/min (24 to 71 L/s), and the liquid flow rate could be varied from 1 to 3 gal/min (3.8 to 11.4 L/min).

Methylene chloride added to the incoming gas stream was absorbed into the counterflowing Genosorb 1843 liquid and pumped through a shell-and-tube economizer and then through a 12-kW water immersion heater to increase the liquid temperature to between 60 and 90°C. This hot liquid was then stripped by passing it countercurrent to a small flow of nitrogen gas in the vacuum stripping column. Like the scrubbing column, the stripping column was constructed of fiberglass and packed with 1-in.-diameter (25.4-mm-dia.) plastic packing. The off-gas from the stripper, consisting of about 4–5 std. ft^3/min (1.9 to 2.4 L/s) of a nitrogen/methylene chloride mixture, was passed to the membrane vapor separation system, which separated the mixture into condensed liquid methylene chloride and a nitrogen stream containing only a few ppm methylene chloride. The liquid methylene chloride was collected for reuse, and the pure nitrogen was recycled to the stripping column.

Because the pilot system was a completely closed loop, once charged with nitrogen gas and 1–2 L of methylene chloride, it could be operated continuously for several hours. The unit was built on three connected skids carrying, respectively, the membrane vapor separation unit; the scrubber/stripper unit, including liquid recirculation pumps, heat exchangers, and a heater; and the vacuum pump unit required for the stripper column. The system was controlled by two panels: a programmable logic panel to control the membrane recovery system and a second panel using relays to control the scrubber/stripper unit. After a few preliminary range-finding experiments, a parametric study was performed with this system following the protocol outlined in Table 1.

The results of a typical base-case run are illustrated in Figure 2. The concentrations of methylene chloride in the gas and liquid stream were measured at six points around the system as shown. An FID gas chromatograph fitted with a 20% SP2100 + 0.1% CW1500 on Chromosorb WHP column was used for the measurements. In the run shown, the methylene chloride concentration in the 75-std. ft^3/min (35-L/s) feed air stream was reduced from 855 to 47 ppm, representing 94.7% removal by the scrubber. The methylene chloride was concentrated 30-fold to 2.69 vol % in the stripper unit. This gas stream was sent to the membrane vapor separation system, which recovered the methylene chloride as a condensed liquid. The treated gas stream, now containing 77 ppm methylene chloride, was recycled to the stripper.

Our parametric study showed that the performance of the system was limited primarily by the scrubbing unit rather than by the stripper. Better performance would have been obtained by using larger liquid pumps to decrease the gas-to-liquid ratio in the scrubber. This would have increased demand on the stripper but, based on our results, the stripper unit could have handled the extra flow. Details of the parametric test are given below.

Table 1. Parameters Varied in Experimental Study

Parameter	Base Case	Range
Feed-gas flow rate to scrubber (std. ft^3/min)	75	50–150
Scrubbing liquid flow rate (gal/min)	3	2–3
Scrubber temp. (°C)	30	20–30
Stripper temp. (°C)	80	50–80
Feed-gas methylene chloride conc. (ppm)	1,000	100–2,000

SI conversion: L/s = ft^3/min × 0.472; L = gal × 3.79

Effect of feed-gas flow rate

The gas-to-liquid ratio could be increased by either increasing the gas flow rate to the scrubber or by decreasing the liquid (Genosorb) flow rate. The effect of changing the gas flow rate is shown in Figure 3. At a feed-gas flow rate of 50 std. ft^3/min (24 L/s) and a liquid flow of 3 gal/min, the system removes 93% of the methylene chloride, but at a gas flow rate of 155 std. ft^3/min (7/L/s), the removal drops to 73%.

Effect of absorbent liquid flow rate

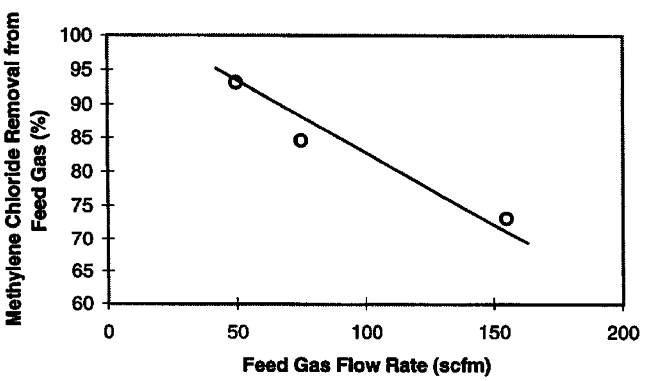

Figure 3. Effect of scrubber feed-gas flow rate on methylene chloride removal.

Liquid flow rate: 3 gal/min; stripper temperature: 80°C; feed methylene chloride concentration: ≈ 1,000 ppm).

The gas-to-liquid ratio can also be varied by changing the Genosorb liquid flow rate, but the available pump limited the liquid flow rate to a maximum of 3 gal/min (6.8 L/min). At a gas flow rate of 50 std. ft^3/min (24 L/s), however, lowering the liquid flow rate from 3 to 2 gal/min (6.8 to 7.6 L/min) decreased methylene chloride removal from 93% to 87%. The data obtained at 2 gal/min and 3 gal/min flow rates are shown in Figure 4, in which all the data obtained at different gas and liquid flow rates are normalized to a single line. Based on this figure, a gas-to-liquid ratio of less than 100 is required to achieve better than 90% removal of methylene chloride from the feed gas stream.

Effect of scrubber and stripper temperatures

The effect of stripper temperature on methylene chloride removal is shown in Figure 5. Removal of methylene chloride from the Genosorb liquid is strongly affected by the stripper temperature increasing from 62% at 50°C to 93% at 80°C. However, in the same experiments, the fractional removal from the feed gas was almost independent of stripper temperature. Our experiments showed that the overall performance of the scrubber/stripper/membrane system was con-

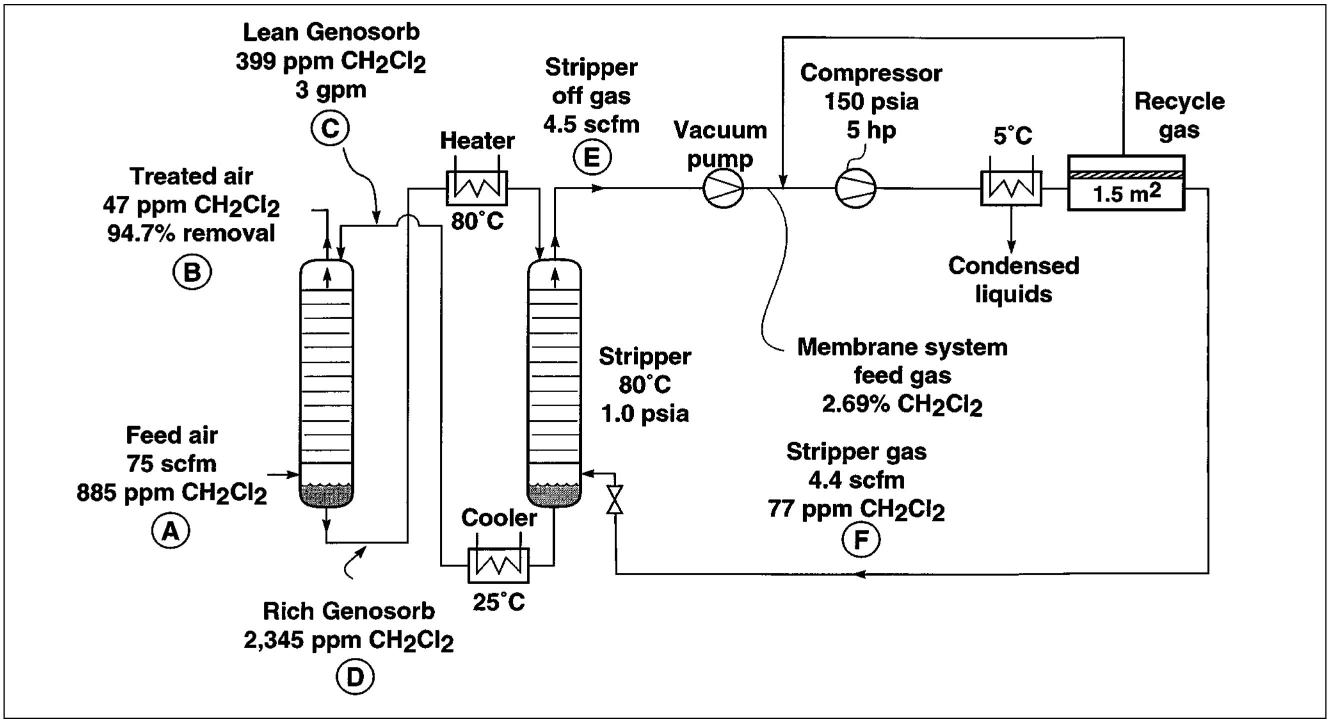

Figure 2. Methylene chloride concentrations in the gas and liquid streams in a typical test run with the pilot system.

In this example the system achieves 94.7% methylene chloride removal from the feed gas.

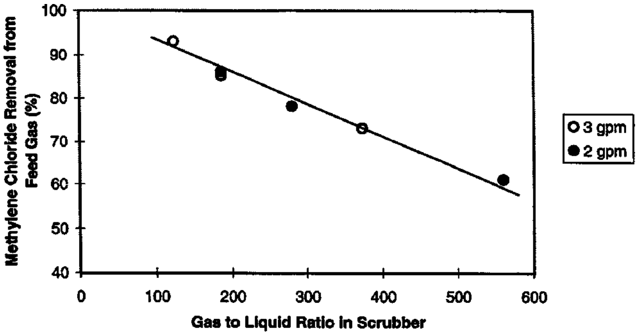

Figure 4. Methylene chloride removal from the feed-gas stream as a function of the gas to scrubber liquid volume ratio.

Stripper temperature: 80°C; concentration of feed gas: 1,000 ppm.

trolled primarily by the scrubbing unit and was relatively independent of the stripper and membrane systems.

Effect of methylene chloride concentration

The concentration of methylene chloride in the stripper overhead gas depended on the operating conditions of the unit and varied over a wide range, from 1% to 3% methylene chloride. However, the treated air from the membrane unit returned to the stripper consistently contained only 40 to 50 ppm methylene chloride, representing 99.9 to 99.99% removal. The experimental data are shown in Figure 6.

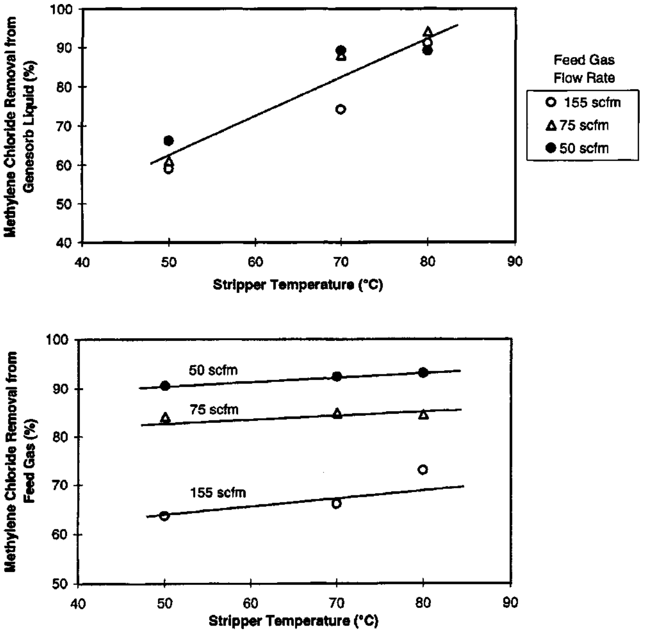

Figure 5. Effect of stripper temperature on methylene chloride removal from the stripper liquid and feed-gas streams.

Liquid flow rate: 3 gal/min (1.4 L/s) methylene chloride feed gas concentration: 1,000 ppm.

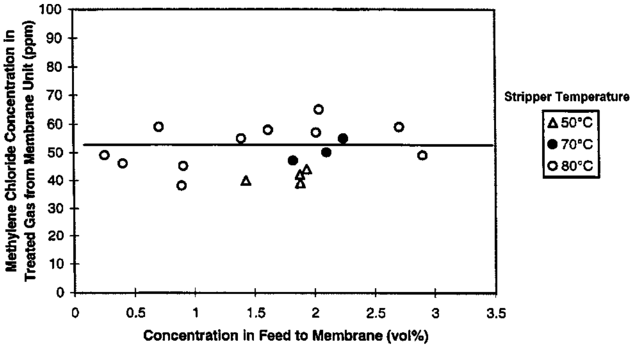

Figure 6. Methylene chloride concentration in the treated gas from the membrane unit as a function of methylene chloride gas concentration in the feed to the membrane unit.

The treated gas concentration is essentially independent of the feed concentration.

Technical and Economic Analysis

To perform a technical analysis of the process, a computer simulation was prepared using a commercial simulation package, ChemCad III (ChemStation, Inc., Houston, TX), modified with our own code for the membrane separation step. The computer simulation of the process was modified to obtain agreement between calculation and experiment. The principal variable turned out to be the efficiency of the scrubber and stripper towers. The best agreement between the calculated data and the experimental data was obtained when the towers were assumed to consist of three to five theoretical stages. The selectivity of the membrane used in the membrane unit was determined by independent measurements. The agreement between the experimental data and the computer simulation is illustrated in Table 2; the system operating conditions and measurement points are as shown in Figure 2. The simulation package contains no data for Genosorb 1843 (triethylene glycol dibutyl ether), but does not have physical data for the related glycol ether, tetraethylene glycol dimethyl ether. This ether was used as the model scrubbing liquid for these calculations. The ChemCad design program calculates the flow composition, temperature, and pressure of every stream in the process.

Economic analysis

Having verified the reliability of the computer model, an economic analysis was performed for a system designed to

Table 2. Measured vs. Calculated Performance of the Pilot-Scale System

Stream*	Meas. Sys. Perform. (CH_2Cl_2 Conc.) (ppm)	Calc. Sys. Perform. (CH_2Cl_2 Conc.) (ppm)
(A) Feed air	885	885
(B) Treated air	47	45
(C) Scrubber feed liquid	400	310
(D) Scrubber loaded liquid	2,340	1,830
(E) Stripper off-gas	26,900	20,700
(F) Stripper feed gas	77	28

*Streams are illustrated in Figure 2.

Table 3. Performance of an Absorption/Stripper/Membrane System Designed to Treat 10,000 std. ft^3/min of Methylene Chloride Contaminated Air

Parameter	Feed Air	Treated Air	Lean Absorbent Liquid	Rich Absorbent Liquid	Memb. System Feed Gas	Memb. System Discharge	Recov. VOC Liquids
Temp. (°C)	25	25	25	25	90	25	5
Pres. (psia)	15	15	10	15	1	1	200
Gas flow (ft^3/min)	10,000	997	—	—	476	453	—
Liquid flow (lb/h)	—	—	304,000	304,000	—	—	167
Component (vol %)							
Genosorb	0	0	99.9	99.6	0.4	0	0.02
Nitrogen	97.9	98.1	0.01	0.13	95.2	99.8	0.90
Water	2.0	1.9	0	0.13	2.2	0	52.5
Methylene chloride	0.1	0.04	0.02	0.15	2.2	0.15	46.6

SI conversion: L/s = ft^{3}min × 0.472; kPa = psi × 6.89; kg = lb × 0.454.

recover more than 95% of the methylene chloride from a 1,000-ppm feed air stream. Based on the analysis of the parametric study results, we concluded that the pilot membrane system was oversized for the towers used. Also, lower air-to-liquid ratios could be obtained in these towers by increasing the liquid recirculation rate without leading to channeling. Finally, to increase the efficiency of the stripper the temperature of this column was increased from 10°C to 90°C. A process flow scheme for a full-sized (10,000 std. ft^3/min, 4,720 L/s) system able to achieve 95–98% methylene chloride removal was prepared. The expected performance of this system is shown in Table 3. By using the scrubber/stripper concentration system, the gas flow to the membrane unit is reduced 20-fold and the methylene chloride concentration proportionately increased, considerably reducing the cost of the system. The estimated capital and operating costs of this system are shown in Table 4.

These capital and operating costs are competitive with carbon adsorption, the only available technology in this flow/VOC concentration range. In this range, the cost of carbon adsorption systems scales in proportion to the VOC concentration. A typical unit would cost approximately $100/std. ft^3/min ($212/L/s) capacity for very dilute streams in the 100-ppm VOC range, increasing to $300/std. ft^3/min ($636/L/s) capacity for streams in the 1,000-ppm VOC range. The absorption/membrane system appears to be competitive simply on a capital cost basis aross the whole range. The other features of the new process—no secondary waste streams, continuous operation, ability to treat particulate-containing gas streams—are additional technical advantages. The operating cost for a 1,000-ppm VOC stream is approximately $1.70/lb ($3.74/kg) of VOC recovered. With a recovered volume of VOC of more than 300,000 lb/yr (661 Mg/yr), some form of recovery for credit is likely to be practiced.

Table 4. Costs for 10,000-std. ft^3/min Scrubber/Stripper/Membrane Vapor Separation System Designed for 95–98% VOC Recovery from Air Streams in the 100–5,000 ppm Concentration Range

Capital Cost	
Major capital equipment	
Compressor (300 hp at $400/hp)	$120,000
Vacuum pump (134 hp at $570/hp)	$76,000
Scrubbing column	$20,000
Stripping column	$25,000
Membrane modules and housings (100 m^2 at $500/ m^2)	$50,000
Condensers, heat exchanger	$60,000
Heaters, chiller	$40,000
Valves, controls, PLC	$80,000
Frame	$30,000
	$501,000
Engineering, fabrication, and contingencies at 100% of major capital equipment	$501,000
Total Capital Cost	$1,002,000
or	$100/std. ft^3/min
Annual Operating Costs	
Capital and interest costs at 20% of total capital cost/year	$200,000
Energy at $0.05/kWh at 600 kW	$216,000
Maintenance/labor at 10% of capital	$100,000
Module replacement—3-yr life at $400/m^2	$17,000
Chemicals 2,500 lb/yr at $0.07/lb of Genosorb	$18,000
	$551,000
Recovered VOC at 45 lb/h or 324,000 lb/yr	
Operating cost/lb of VOC recovered	$1.70

SI conversion: kg = lb × 0.454; kW = hp × 9.81; L/s = ft^3/min × 0.472.

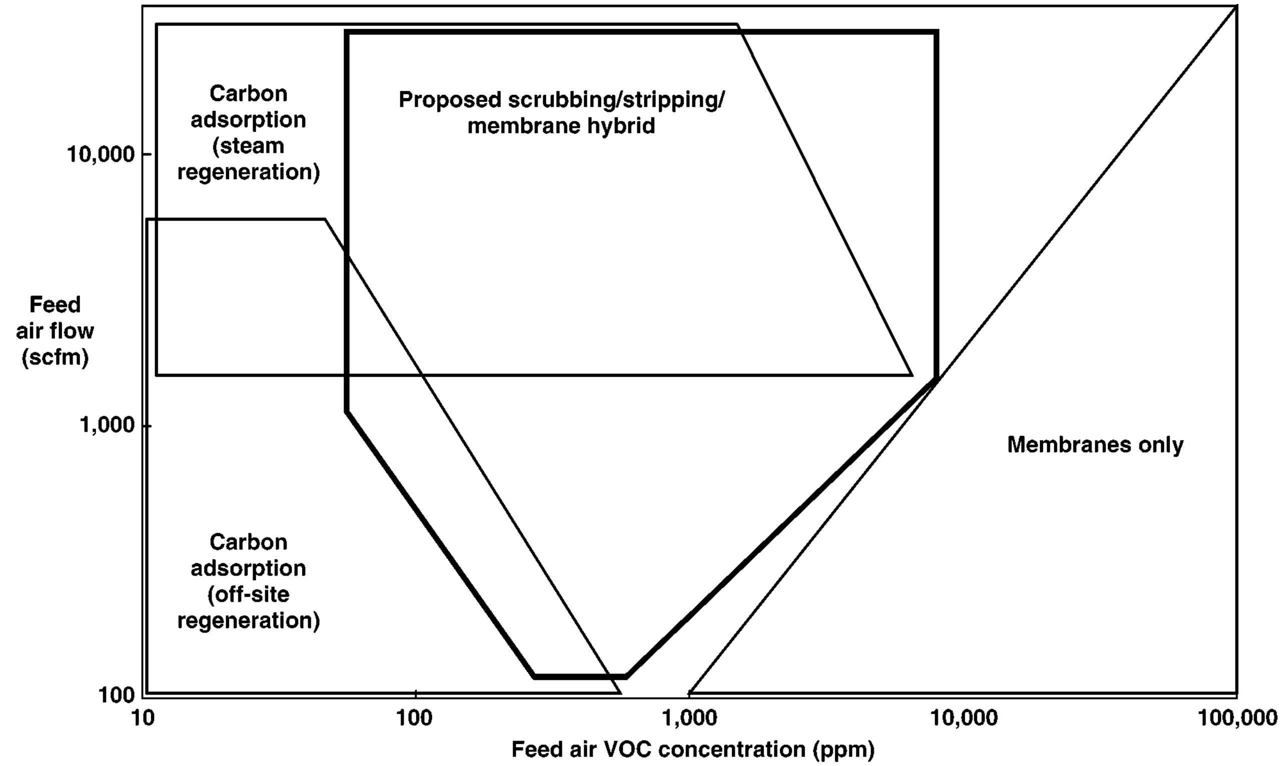

Figure 7. Competitive range of membrane-only and carbon adsorption VOC-recovery technologies with the proposed scrubbing/stripping/membrane separation hybrid technology.

Based on these cost calculations we believe the expected application range of the technology will be for gas streams containing 500–2,000 ppm VOC with total flows of more than 1,000 std. ft^3/min (472 L/s). Flows below 1,000 st. ft^3/min, if dilute, would be treated by carbon adsorption with off-site regeneration of the carbon or, if concentrated, would be treated by incineration, membrane separation, or perhaps condensation. Figure 7 provides an overview of the expected competitive range of the technology compared with that for carbon adsorption, the principal competing technology.

Conclusions

This work demonstrated the technical and economic feasibility of the scrubbing/stripping membrane vapor separation process. A pilot-scale scrubber/stripper/membrane hybrid system was constructed and operated successfully. Parametric tests demonstrated both the ability of the scrubbing unit to remove VOC from the air feed and the stripping/membrane process to regenerate the scrubbing liquid by removing the VOC. The capital and operating costs of the complete process were calculated and compared to the alternative technology of carbon adsorption. The process seems best suited to streams containing 500–2,000 ppm of VOC and having flow rates above 1,000 std. ft^3/min. Such streams are too concentrated for carbon adsorption units to be economical, but too dilute to be economically treated by membrane-only units.

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