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Development of synthetic membranes for gas and vapor separation

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Abstract - The development of a synthetic membrane and a suitable module for the separation of organic vapors from waste air streams is described. Parameters determining the selectivity and permeability of a membrane in gas separation are discussed and criteria for the selection of a suitable polymer for manufacturing these membranes are described. Composite-membranes produced as flat sheets and in hollow fiber form using polydimethylsiloxane as the selective barrier are tested with various solvent vapors. The permeabilities of these solvents are determined to be more than 1000 times higher than that of nitrogen. Finally, a process for the continuous removal and recovery of toluene from a painting procedure waste air stream is described and the costs for the process are estimated.

INTRODUCTION

The traditional use of synthetic membranes in recent years has been in the separation of aqueous mixtures. The desalination of sea and brackish water by reverse osmosis or electrodialysis and the production of ultra-pure water by ultra- or microfiltration are today industrial processes with substantial technical and commercial significance. More recently synthetic membranes have also been utilized for the separation of various gas mixtures. The recovery of hydrogen from petrochemical purge gas streams and the production of ammonia are two areas where membranes have established themselves as a very useful tool. The enrichment of oxygen or nitrogen from air and the removal of carbon dioxide from natural gas are other examples of the successful industrial use of synthetic membranes. Since membranes can be tailored to fit a certain mass separation task, the separation problems which are difficult to handel by conventional procedures, may be treatable by a membrane process. One of these problems, the removal of organic solvents from waste air streams, is discussed in this paper. In industrial processes such as painting, printing, dry cleaning and metal processing large amounts of solvents such as toluene, xylene, dichloroethane, trichloroethane, and acetone are emitted into the atmosphere. These solvents are not only a severe environmental hazard but also a significant economical loss. Most traditional methods to recover these solvents, such as carbon adsorption, have so far proved to be unsatisfactory. For membrane processes to be useful, membranes are required that have a much higher permeability to organic solvents than to air. These membranes have to be installed into suitable units, i. e., a module, and the separation process itself has to be adjusted to the special requirements of the problem. In this paper the development of a membrane, a membrane module, and a process suited for the recovery of organic solvents from industrial waste air streams is described.

MEMBRANE DEVELOPMENT

The key component in any membrane-based gas separation system is the polymer from which the membrane is made. This polymer should have a high permeability and good selectivity for the solvents to be recovered. Also, it should be easily formed into a suitable membrane structure and an economical membrane module.

Fundamentals of membrane gas separation

For a better understanding of the problem of selecting the proper polymer for the preparation a membrane capable of removing organic solvents efficiently from air, a brief discussion of the basics of the mass transport through membranes is very helpful.

The permeation of a gaseous component through a homogeneous membrane can to a first approximation be described by the solution diffusion membrane model and is determined mainly by three parameters: (1) The permeability, (2) the concentration of the component in the membrane phase and (3) the driving force or driving forces acting on this component. The driving force for the mass transport in membrane processes are differences in the electrochemical potential between the outer phases separated by the membrane. Thus the transport of a component i through a membrane can be described to a first approximation which neglects all kinetic coupling between permeating components by (ref.1):

$$J_i = L_i \operatorname{grad} \mu_i \tag{1}$$

Here is J_i the permeation rate of the component i through the membrane, L_i is the permeability, and grad μ_i is the gradient of the chemical potential of the component i across the membrane.

Gradients in the chemical potential of a component in a membrane can be caused by differences in concentration, pressure, or temperature between the two phases separated by the membrane. For simple gases, which do not chemically interact with the polymer matrix or other permeating components the gradient in the chemical potential can be expressed by (ref. 2):

$$\operatorname{grad} \mu_i = \frac{RT}{C_i} \frac{\Delta C_i}{\Delta x} \tag{2}$$

Introducing equation (2) into equation (1) leads to:

$$J_i = L_i \frac{RT}{C_i} \frac{\Delta C_i}{\Delta x} \tag{3}$$

Here is J_i the mass flux of the component i through the membrane L_i is a phenomenological permeability coefficient, C_i the concentration and ΔC_i the concentration gradient in the membrane of the component i, R is the gas constant and T the absolute temperature. Since, furthermore,

$$L_i \frac{RT}{C_i} = - D_i \tag{4}$$

the flux of an ideal gas through a homogeneous polymer membrane can be described by Fick's law of diffusion:

$$J_i = -D_i \frac{\Delta C_i}{\Delta x_i} \tag{5}$$

The assumption that the concentration of the gas in the polymer is proportional to the partial pressure of the gas in the adjacent phases leads to:

$$C_i = k_i \, p_i \tag{6}$$

Here C_i is the concentration of the component i in the polymer, and k_i its distribution coefficient between the gas and the polymer phase, and p_i its partial pressure in the gas phase.

Introducing equation (6) into (5) leads to a very simple relation for the transport of gases through a polymer barrier:

$$J_i = -D_i \, k_i \frac{\Delta p_i}{\Delta x} \tag{7}$$

Here is J_i the gas flux, D_i is the diffusion coefficient of the component i in the polymer matrix, k_i is its distribution coefficient between the gas and the polymer phase, Δp_i the difference in its partial pressure in the two phases separated by the membrane, and Δx is the thickness of the polymer barrier.

For reasons of convenience the product of D_i and k_i is in the literature often referred to as permeability:

$$P_i = D_i \, k_i \tag{8}$$

It has, however, to be kept in mind, that the very simple relation expressed in equation (7) holds true only for ideal gases. For organic vapors the diffusion coefficient D_i as well as the distribution coefficient are both a function of the composition of the gas phase. Usually the diffusion and the distribution coefficient of an organic vapor increases drastically with an increase in its initial pressure in the gas phase.

For a first evaluation of polymer to be used for the preparation of gas and vapor separating membranes equation (7) is quite useful, however (ref. 3).

Polymer selection criteria

A polymer to be used for the preparation of gas and vapor separating membranes should have the following intrinsic properties: (1) high selectivity for the components to be separated, (2) high permeability for the permeating components, and (3) high life expectance under operating condition, i. e., good thermal, chemical and mechanical stability.

There is a great deal of data in the literature describing the permeation of gases and vapors through polymers. In general the diffusion coefficient decreases with increasing permeant diameter. On the other hand, the distribution coefficient which is determined by the solubility of the gas in the polymer matrix, generally increases with the permeant diameter. With simple gases these two effects are comparable, as indicated in Figure 1 which shows the diffusion coefficient and solubility or distribution coefficient of various gases in polydimethylsiloxane as a function of the Lenard-Jones molecular diameter of the permeant. If the permeability, i. e., the product of D_i k_i, is plotted versus the permeant molecular diameter relatively high permeabilities are found in almost all polymers for very small molecules such as hydrogen and helium because of high diffusion coefficient. Rather large molecules such as CO_2 also have a high permeability because of a high solubility. Gases such as N_2, O_2 and CO have a relatively low permeability. But in any case the differences in permeabilities are rather moderate for these gases. This is true for a whole series of polymers (4). There are, however, two classes of polymers which show significant differences in their gas permeabilities: (1) elastomers such as silicon rubber show relatively high permeabilities for all gases but low selectivities for different components, (2) glassy and crystalline polymers such as polystyrene show lower permeabilities but higher selectivities than the elastomers. This is indicated in Figure 2 which shows the permeability of various gases in different polymers as a function of the permeant diameter.

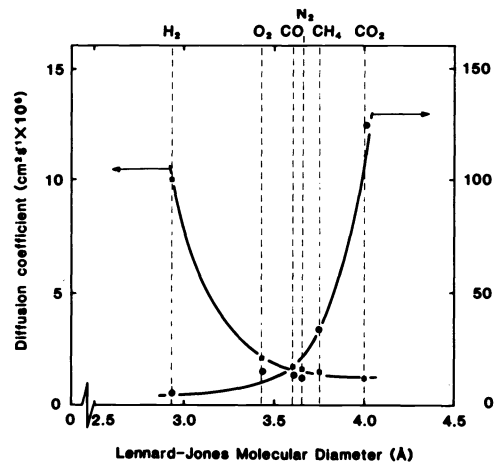

Fig. 1. Diffusion coefficient and solubility of various gases in polydimethylsiloxane as a function of the Lennard-Jones molecule diameter of the gases.

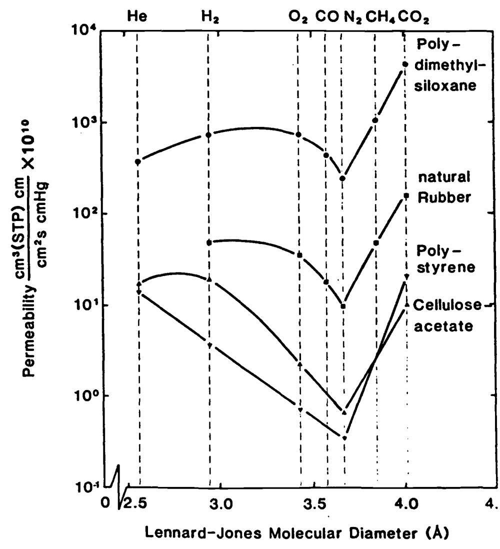

Fig. 2. Permeability of various gases in different polymers as a function of the Lennard-Jones molecule diameter of the gases.

The permeabilities of different simple gases in most polymers may vary by a factor of 2 to 50. Separation factors obtained in gas separation tests are, therefore, accordingly low. Vapors show a significantly higher permeability than simple gases in most polymers. This is shown by the data in Figure 3, which shows a plot of gas and vapor permeability versus vapor critical point termperature. The vapor critical point temperature is a measure of the condensability and hence the polymer sorption of vapor. This data shows the dramatic increase in permeability with increased vapor critical point of the permeant. The data also indicate that permeabilities of organic solvent vapors such as octane, toluene, trichloroethane, etc., are 1000 to 10000 times higher than that of nitrogen or oxygen. It should, therefore, be relatively easy to separate organic solvent vapors from air.

It can further be noticed that the permeabilities of simple gases such as oxygen, nitrogen, etc., are in almost all polymers independent of concentration, i. e., independent of their partial pressure in the gas phase. The permeabilities of organic solvent vapors on the other hand increase drastically with increasing solvent vapor pressure in the gas phase. This is indicated in Figure 4, where the permeability of various solvent vapors and of nitrogen in polydimethylsiloxane and Fluorel®, a fluor elastomer produced by the 3M Corporation, are plotted against the solvent vapor or gas pressure.

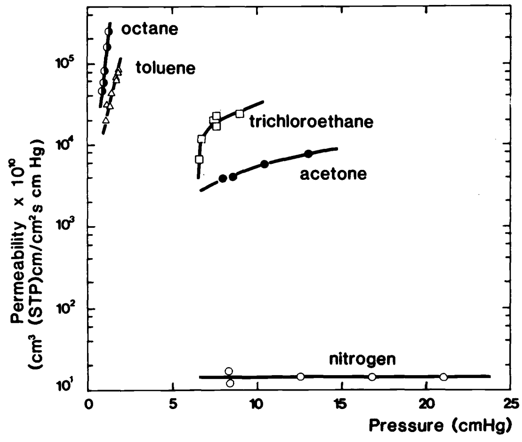

Fig. 3. Permeability of various gases or vapors in polydimethylsiloxane as a function of the critical point temperature.

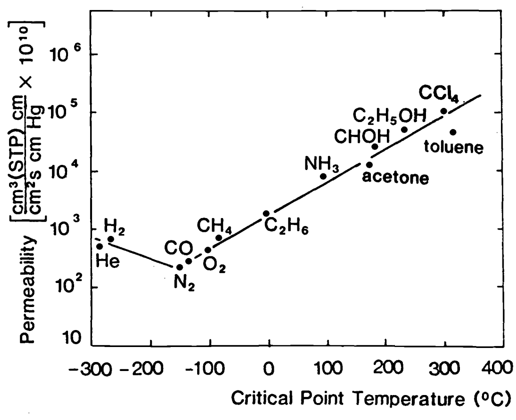

Fig. 4. Permeability of various solvents as a function of their vapor pressure.

By studying organic vapor permeability data in the literature it is clear that with many polymers selectivities of 1000 to 10000 for some organic solvents, such as toluene or octane, over nitrogen may be obtained(5). Furthermore, it can be concluded that elastomers such as dimethyl siloxane have in general significantly higher permeabilities than glassy polymers.

Membrane preparation and module design

There are a variety of polymers available which show excellent organic vapor to nitgrogen selectivities. To be used in practical applications these polymers have to be fabricated first into a membrane and then into a membrane module. For economical reasons the actual selective barrier should always be as thin as possible to obtain maximum transmembrane fluxes for a given set of experimental conditions. Very thin selective membranes are usually prepared as asymmetric structures consisting of a thin homogeneous polymer layer supported on a microporous substructure. The microporous substructure provides the mechanical strength, while the homogeneous polymer acts as the selective barrier. Many polymers such as polyamides, polysulfones, cellulose acetates, etc., are fabricated as an asymmetric structure in a one-step precipitation procedure. Other polymers such as most elastomers, however, are not suited for this manufacturing method. In these cases membranes can be prepared as so-called thin-film-composite structures, where the actual selective barrier is produced in a different process and of a different polymer than the microporous substructure. Two different techniques are used today for preparing thin-film-composite membranes on an industrial scale (ref. 6):

1. Interfacial polymerization of monomers from two non-miscible solutions
2. Coating a microporous substructure with a dilute polymer solution and evaporation of the solvent.

For the preparation of elastomeric gas separating membranes the second technique works particularly well and was used to prepare the membranes for the work described in this paper.

The microporous support has a significant effect on the performance of the thin-film-composite membrane. First of all it should provide the necessary strength to support the selective barrier under the operating conditions. Gas separation membranes may be operated at hydrostatic pressure driving forces up to 10000 kPa. The microporous support, secondly, should have a high surface porosity to prevent blocking the gases which have permeated the selective layer.

On the other hand, however, these surface pores should be small enough to prevent penetration of the polymer into the substructure. Finally, the substructure should be insoluble in the solvent from which the barrier polymer is applied. For the work discussed in this paper polysulfone was used as the substructure which supported a thin film of polydimethylsiloxane. Polysulfone can be easily manufactured into an asymmetric microporous membrane with the desired high surface porosity and surface pore sizes of less than 20 nm to retain the polydimethylsiloxane. Polydimethylsiloxane is available as a prepolymer with a molecular weight of about 6×10^6 and is soluble in toluene. Polysulfone can also be easily fabricated into microporous hollow fiber membranes. For gas separations, hollow fiber membranes and membrane modules are particularly suited, because they provide a maximum surface area per unit volume. Hollow fiber membranes are able to withstand the high operating pressures, and the cost to manufacture this type of membrane is low. Concentration polarization effects which are a problem when liquids are processed in hollow fiber systems, are of no importance in separation of gas mixtures because of the high diffusivity in the gaseous phase. For the preparation of membranes and membrane modules to be used for the removal of organic vapors from waste air streams a microporous asymmetric polysulfone hollow fiber membrane with the skin on the inside was prepared by a wet spinning process. The cross-section of this type of fiber is shown in the scanning electron micrograph in Figure 5. The fiber has an inner diameter of about 200 µm. The pores on the inside fiber wall are about 20 nm in diameter. The surface porosity is about 25 %. The fibers are installed into a shell tubing which is sealed on both ends by an epoxide resin to build the hollow fiber module, shown schematically in Figure 6.

A module 0.5 m long and 0.1 m in diameter provides an active membrane surface area of about 5 m^2. To form the selective polydimethylsiloxane layer on the hollow fiber support the entire module is rinsed with a 1 - 2 % solution of linear polydimethylsiloxane prepolymer which is commercially available in an average molecular weight of $1 - 6 \times 10^6$. The solvent is then evaporated leaving a 0.2 to 2 µm thick polymer film on the surface. In a subsequent heat treatment procedure and in the presence of an appropriate cross-linking agent, the polydimethylsiloxane is three-dimensionally cross-linked, as indicated in the reaction scheme of Figure 7. Since the molecular diameter of the prepolymer is larger than the average pore diameter of the surface pores of the support hollow fiber no penetration into the microporous support occurs, except for pinholes which are then automatically plugged, thus preventing any gas leakage. This in indicated in the schematic drawing of Figure 8. The actual composite membrane is shown in the scanning electron micrograph in Figure 9.

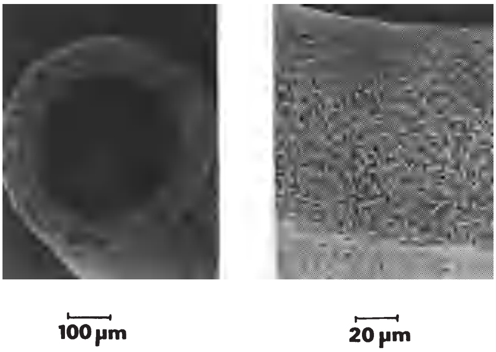

Fig. 5. Scanning electron micrograph of the cross-section of an asymmetric polysulfone hollow fiber membrane.

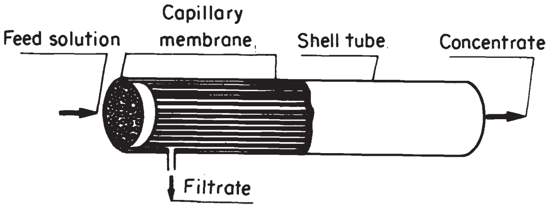

Fig. 6. Schematic diagram of a hollow fiber membrane module.

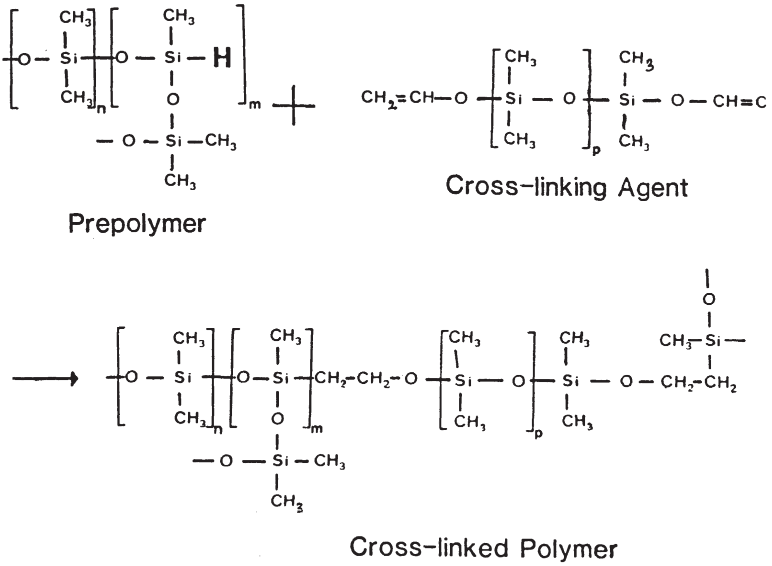

Fig. 7.
Reaction scheme for the formation of the cross-linked polydimethylsiloxane selective barrier.

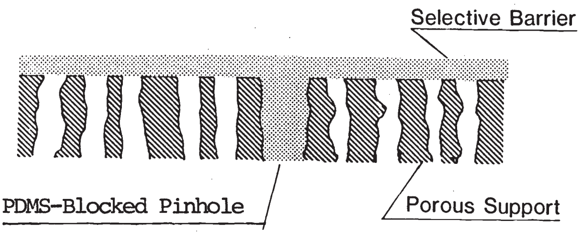

Fig. 8. Schematic diagram of a composite membrane prepared by casting of a prepolymer solution on a microporous support.

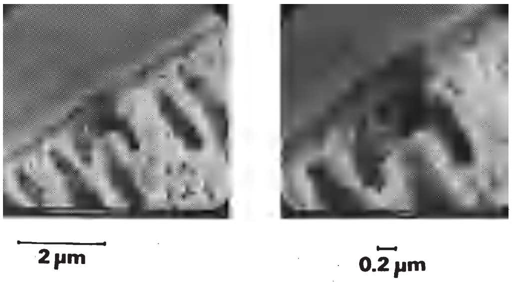

Fig. 9. Scanning electron micrograph of a composite membrane consisting of cross-linked polydimethylsiloxane on a microporous polysulfone substructure.

PRACTICAL APPLICATIONS OF GAS AND VAPOR SEPARATING MEMBRANES

In recent years industries producing solvent-containing air exhaust streams have come under increasing regulatory and economical pressure to clean these air streams and to recover the solvents for reuse. Commercially available conventional processes such as carbon adsorption are unsatisfactory in many applications. Membrane processes may, in some applications, be a suitable alternative to the conventional waste air cleaning procedures. In the work reported in this paper hollow fiber thin-film-composite membranes are used to recover organic solvents such as toluene, acetone, and xylene from painting operations.

Process design and best procedure

The process used to recover organic solvents from waste air streams from a metal painting process is shown in the flow diagram in Figure 10.

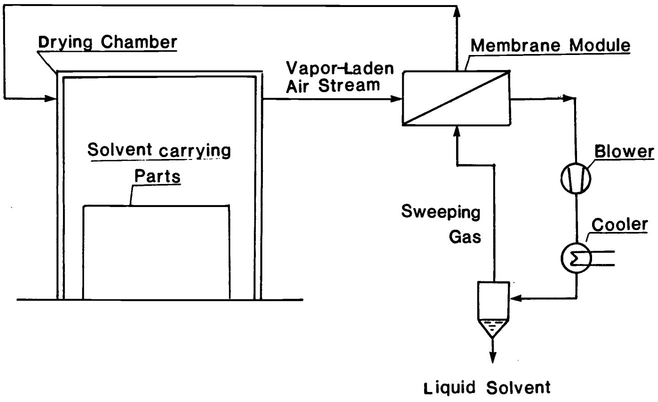

Fig. 10.
Flow diagram of a membrane solvent recovery system.

The solvent laden exhaust air stream exits a solvent drying oven and is passed through the hollow fiber membrane module which contains polydimethylsiloxane as the active barrier. The organic vapors pass through the membrane. The solvent depleted air is recycled to the oven where it is again loaded with organic solvent vapors providing a more or less closed system with the membrane functioning as a "kidney" for the continuous removal of solvent vapors. A vacuum pump on the downstream side of the membrane, operating at about 1000 Pa, provides the necessary driving force for the solvent transmembrane flux. The solvent vapors are condensed in a heat exchanger and recovered as liquid. A bleed stream of air which has passed the membrane is fed back into the downstream side of the membrane module acting as "sweeping" gas.

Test results

The test results obtained with the polydimethylsiloxane composite hollow fiber membrane system described above are summarized in Figures 11 and 12. The organic solvents tested, i. e., octane, toluene, trichloroethane, and acetone, gave solvent fluxes up to 18 l/m^2 d. The actual flux obtained

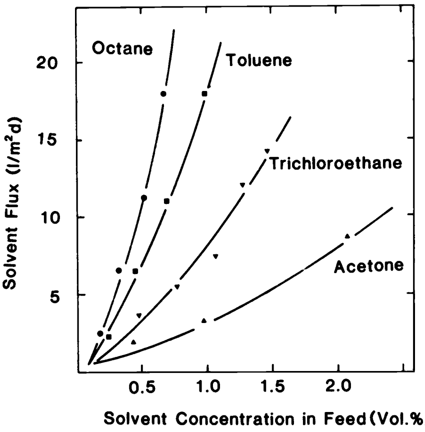

Fig. 11. Fluxes of different solvent vapors through a polydimethylsiloxane composite hollow fiber membrane as a function of the vapor pressure.

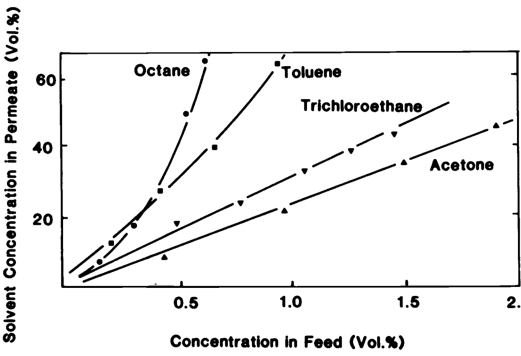

Fig. 12. Solvent vapor concentration in the permeate of the hollow fiber membrane system as a function of the vapor pressure in the feed.

depends on the solvent vapor concentration in the exhaust air stream, as indicated in Figure 11. Octane and toluene show the highest fluxes. The increase in solvent concentration on the downstream side of the module also depends on the feed gas concentration. This is indicated in Figure 12 which shows the permeate solvent concentration as a function of the feed gas concentration for various solvents.

Cost estimate and practical feasibility

While the separation of organic solvent vapors from waste air streams seems to be technically feasible, there is still the question of economics. Based on the data obtained in the experimental part of this study, a preliminary cost estimate provides some information about the economies of the process. As an example for a practical application the cost for the removal of an organic solvent from the waste air stream of a painting process drying chamber is given. The cost calculation is based on the following process parameters:

Volume of the drying chamber	50 m^3	
Waste air stream	500 m^3/h	
Solvent in waste air stream	0,5 Vol%	20 g/m^3
Solvent carried out by waste air	10 kg/h	240 kg/d
Membrane solvent flux	3 kg/m^2 d	
Membranelife	2 years	
Required membrane area	80 m^2	
Required pumps (1000 Pa vacuum)	10 kW	

For these process parameters the costs are calculated as follows:

Capital costs	
Membrane modules (DM 300.-/m^2)	DM 24000.-
System (piping, controls, etc.)	DM 30000.-
Pumps	DM 30000.-
	DM 84000.-
Operating costs	
Annual fixed costs (20 % investment not including membranes)	DM 12000.-
Membrane replacement (2 years membrane life)	DM 12000.-
Maintenance (0,2 ma)	DM 8000.-
Energy (12 kW, 1 kWh = 0.1 DM, 300 d/a)	DM 8640.-
	DM 40640.-
Recovered solvent (240 kg/d, 300 d/a)	72000 kg
Process cost/kg recovered solvent	DM 0.56

The costs calculated for the practical studies application are estimated to be DM 0.56 per kg recovered solvent. In this case the recovered solvent by itself makes the process economically feasible. It has, however, to be kept in mind that (1) a complete removal of the solvent is not possible or requires extremely large membrane areas and (2) that the amount of solvent recovered by a certain size membrane unit depends very much on the solvent vapor concentration in the exhaust air stream. The most favorable case is achieved when the exhaust air has a high solvent vapor concentration and is recycled to the drying chamber only partially depleted of solvent.

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