Membrane Techniques in Air Cleaning

M. Bodzek

Silesian Technical University, Faculty of Environmental and Energy Engineering,
ul. Konarskiego 18, 44-100 Gliwice, Poland

Abstract

The state of the art of application of membrane techniques for air cleaning is presented. The most characteristic parameters of membrane separation of gases and vapours are described. Separation of gases and vapours has been applied practically in the industry for the following areas: removal of volatile organics from the air and from industrial waste flows, oxygen enrichment of air and vice versa and the membrane absorption process.

Keywords: gas separation, membranes, air pollution, membrane absorption

Introduction

Air pollution is most often affected by the emission of pollution generated by industry, power plants, car transport, and agricultural and municipal waste [1].

Pollution is exceptionally hazardous when it involves the emission of so-called acid gases (SO_2, NO_X) and volatile organic compounds, mainly halogen-derived hydrocarbons and aromatic compounds which destroy the ozone layer and contribute to the creation of the greenhouse effect. Different methods are used to eliminate these substances, and they are presented in Fig. 1 [1]. Particular techniques have been classified according to optimum range of concentration at which they are working. Appropriate combining of these processes (hybrid processes) can be advantageous from the economic and technical viewpoints. The removal of volatile organic compounds can be carried out with the recovery of solvent or without it, although from environmental and economic viewpoints, the second solution is favored.

Another problem connected with pollution of the atmosphere is the generation of vast volumes of gases, which contributes to the creation of the greenhouse effect - carbon dioxide while burning carbon-derived fuels and simultaneous emission of methane and carbon dioxide from solid waste dumps. With respect to the latter case, it seems to be beneficial to recover methane since it is a valuable source of energy [2, 3] and is characterized by higher global greenhouse factor than carbon dioxide (Table 1) [4].

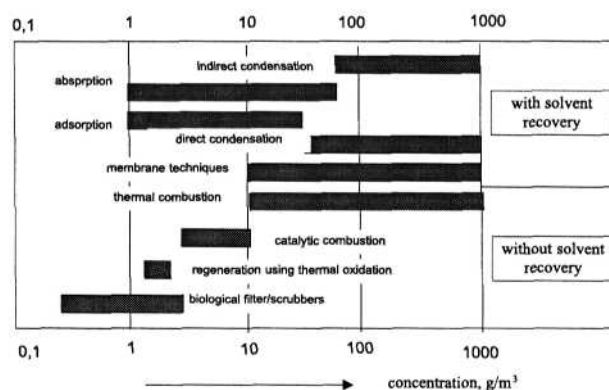In the 1980s the application of the membrane technique was initiated on an industrial scale for the

Fig.l. Separation processes in air purification from volatile organic compounds.

Table 1, Influence of particular gases on the greenhouse effect.

Component	Comparative index inducing greenhouse effect	Concentration*
CO_2	1	56
CH_4	32	25
halogen derived hydrocarbons	ca. 15,000	8
O_3	2000	9
NO	150	2

* relative concentration without taking nitrogen and oxygen into consideration.

treatment of gases. It was possible due to the development of polymeric membranes of respective selectivity. Table 2 presents the potentials involving the application of various membrane processes for the removal of pollution from the air [1-3].

Table 2. Membrane processes in air purification.

Pollution	Membrane process
vapours of organic compounds (halogen-derived hydrocarbons, aromatic compounds)	permeation of vapours, membrane contactors
SO_2, NO_x, CO_2 (combustion products)	liquid membranes, membrane contactors
NH_3	liquid membranes, membrane contactors
H_2S (natural gas)	gas separation, liquid membranes, membrane contactors, membrane reactors
CH_4, CO_2 (biogas)	gas separation

Separation (Permeation) of Gases and Vapours

Separation of gases and pervaporation are membrane techniques where the driving force is made up by the difference of concentrations (activity) on both sides of the membrane [5]. These processes have one common characteristic, i.e. they are applied for the realization of non-porous polymeric membranes. Some authors single out a so-called vapour permeation, which is closely connected with the separation (permeation) of gas [6]. In the separation process of vapours, the mixture subjected to separation contains substances which undergo condensation in normal conditions (101.3kPa and 273K), whereas in the separation process of gases the components do not undergo condensation [6]. The difference between vapour permeation and pervaporation consists in the difference of phase composition of feeding flux; in the first case it is made up by a mixture of vapours and in the second case by a mixture of liquids [6, 7]. The similarities and differences of the three membrane techniques mentioned above are presented in Fig. 2 [6].

Permeation of various gases (vapours) through non-porous glassy and flexible materials is very different, which is connected with the mobility of polymeric segments or chains. This mobility increases considerably in the presence of liquid or gaseous substances penetrating the structure of polymer, effecting the increase of permeability (diffusivity) of membranes. The concentration of substances penetrating the inside part of the membrane depends principally on its affinity to material from which membranes are made. The solubility of gases in polymers is small, but with respect to liquids it is considerable, principally due to polymer swelling, due to which even large particles of chemical compounds can permeate (dialysis).
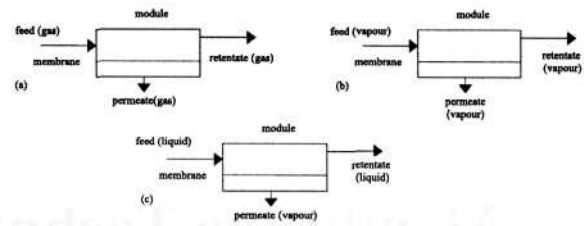

Fig. 2. Diagrams presenting processes of gas permeation (a), vapour permeation (b) and pervaporation (c).

Fig. 3 presents the dependence of diffusion coefficient of low-molecular substances on the rate of membrane swelling (weight ratio between the substance penetrating the membrane and the weight of dry membrane material). Diffusion coefficient increases with the increase of swelling rate from 10^{-9} to 10^{-9} m^2/s [5]. This means that by the mobility of polymeric chain the diffusion coefficient increases to the value characteristic for diffusion in liquids (ca. 10^{-9} m^2/s). Therefore, swelling of membrane material is a very important factor in the transport of substances through non-porous membranes.
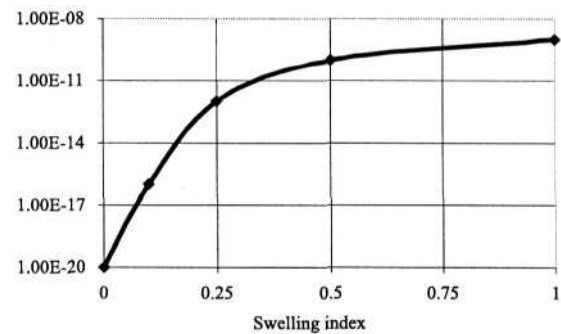
Diffusion coefficient, m^2/s

Fig. 3. Dependence of diffusion index on the swelling rate of non-porous polymers.

Separation of gases and vapours can be carried out both by porous membranes and by the non-porous ones, but the second solution has better application potentials in practice.

Separation of gases by non-porous membranes depends on the difference in permeability of the membrane with respect to different gases. The transport of gases through the membrane can be described in the simplest way by the first Fick's law [5]:

$$J = -D \cdot dC/dx \qquad (1)$$

where:

J   - gas flux passing through the membrane,
x   - membrane thickness
dC/dx - concentration gradient on both sides of the membrane,
D   - gas diffusion coefficient in the membrane.

In equilibrium conditions, after integration, the equation (1) assumes the following form:

$$J = D \cdot (C_o - C_p)/x \qquad (2)$$

where:
C_o - gas concentration in feeding solution,
C_p - gas concentration in permeate.

According to Henry's law, there is linear dependency between gas concentration inside the membrane (C) and its partial pressure outside (p):

$$C = S \cdot p \qquad (3)$$

where S is the solubility index.

Joining the equations (2) and (3) we obtain a dependence which is commonly used to describe the transport of gas and vapour through the membrane [5]:

$$J = D \cdot S \cdot (p_o - p_p)/x \qquad (4)$$

where:
p_o p_p - partial pressure of gas respectively on the side of feeding solution and permeate.

The product of diffusion coefficient and solubility indexes is referred to as permeability index (P)[8]:

$$P = D \cdot S \qquad (5)$$

Then, the equation (4), which describes the volume of gas (vapour) flux passing through the membrane assumes the following form:

$$J = P \cdot (p_o - p_p)/x \qquad (6)$$

This results from the equation (6) that gas flux passing through the membrane is directly proportional to the difference of partial pressures of gas, and adversely proportional to the membrane's thickness. The membrane's selectivity (a) can then be expressed by the following dependence:

$$\alpha = P_i / P_j$$

P_i - permeability of gas "i";
P_j - permeability of gas "j".

Selectivity of the membrane depends therefore both on diffusion coefficient of gas and on its solubility in the membrane. Real selectivity depends on the relation of partial pressures of gas on both sides of the membrane. When the difference value is high, separation efficiency is maximum, and it is decreasing along with the decreases of the difference value.

In practice, the process of gas separation is carried out using high pressure on the side of feeding solution, or reduced pressure on the side of permeate, or both solutions simultaneously (Fig. 4) [5].
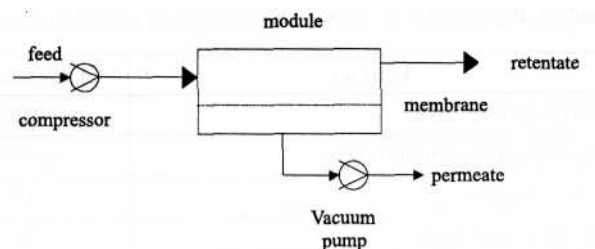

Fig. 4. Diagram of gas separation process.

Permeability is an important parameter allowing to compare separation properties of different membranes with respect to a given gas mixture, and makes it possible to compare distribution properties of different gases by membranes from a given polymer. Furthermore, while selecting polymer material for the production of membrane, two parameters connected with its structure should be taken into consideration: glassy temperature and crystallinity ratio of polymer [5].

Permeability of gas through flexible polymers is much higher than through glassy polymers, due to higher mobility of segments of polymeric chain in the first case. Table 3 presents permeability of carbon dioxide and selectivity with respect to methane for membranes from different polymers, whereas Table 4 presents permeability indexes of oxygen and nitrogen as well as $\alpha_{O2/N2}$ for membranes from glassy polymers [5].

Table 3. Permeability of carbon dioxide and methane through membranes from different polymers.

Polymer	P_{CO_2} (Barrer)	P_{CO_2}/P_{CH_4}
polytrimethylosiliolopropyne	33100	2.0
silicone rubber	3200	3.4
natural rubber	130	4.6
polystyrene	11	8.5
polyamide (nylon 6)	0.16	11.2
poly(vinyl) chloride	0.16	15.1
polycarbonate (Lexan)	10.0	26.8
polysulfone	4.4	28.0
poly(ether sulfone) (Victrex)	7.4	32.0
cellulose acetate	6.0	31.0
poly(ether imide) (Ultem)	1.5	45.0
polyimide (Kapton)	0.2	64.0

1 Barrer = 10^{-10} cm^3 (of normal conditions)$\cdot$cm$\cdot$cm$^{-2}\cdot$s$^{-1}\cdot$ (cmHg)$^{-1}$.

As mentioned before, gas permeability depends distinctively on the type of polymer used for the preparation of membranes. However, with respect to the same membrane material, considerable differences in permeability of different gases can be observed (Table 5) [5]. This is particularly characteristic for vapours of organic compounds.

Table 4. Permeability of oxygen and nitrogen of some flexible and glassy polymers.

Polymer	Glassy temp. °C	P_{O2} (Barrer)	P_{N2} (Barrer)	P_{O2}/P_{N2}
polypropylene oxide	210	16.8	3.8	4.4
polytrimethylosiliolopropyne	ca.200	10040	6745	1.5
ethyl cellulose	43	11.2	3.3	3.4
polymethylopentene	29	37.2	8.9	4.2
polypropylene	-10	1.6	0.3	5.4
polychloroprene	-73	4.0	1.2	3.3
polyethylene LD	-73	2.9	1.0	2.9
polyethylene HD	-23	0.4	0.14	2.9

Table 5. Permeability of gases and vapours through membranes from polydimethylooxosilanes.

Gas	Permeability (Barrer)	Gas	Permeability (Barrer)
nitrogen	280	chloroform	284,000
oxygen	600	carbon tetrachloride	200,000
methane	940	1,2-chloroethane	248,000
carbon dioxide	3200	1,1,1-trichloroethane	247,000
ethanol	45,000	trichloroethylene	614,000
methylene chloride	168,000	toluene	1,460,000

The concept of gas separation through membranes is based on the mechanism of dissolution and diffusion. As compared to liquids, gases are characterized by low affinity to polymers and therefore their solubility in such materials is also low (usually <0.2%). Solubility of a given gas in polymer increases along with the increase of affinity to polymer; for example, the solubility of carbon dioxide is higher in hydrophilic polymers than in hydrophobic polymers.

Another factor which affects gas permeability through polymers is the diffusion coefficient, which depends principally on the size of gas particle and polymer type. Particles of longer diameters are characterized by lower diffusion coefficients and vice versa.

In practice, membranes from flexible polymers are used for the separation of gases and vapours. The most important are polyethers such as oxosilane resins and natural rubber [5]. However, with respect to certain specific applications it is necessary to use membranes from glassy polymers. Permeability of gas through the membrane considerably depends on its thickness, and therefore optimization of this parameter is very important. Asymmetric membranes from one polymer are used as well as composite membranes. The former ones are prepared using the wet method of phase inversion, whereas with respect to composite membranes, a very thin active layer is introduced on the support surface by means of [5]:

- dip plating
- surface polymerization
- polymerization in plasma

It is very important that the thin active layer in asymmetric or composite membranes should have no mechanical defects whatsoever, which could drastically change its selectivity without noticeable change of gas flux passing through the membrane.

Separation of gases and vapours has been applied practically in the industry for splitting the following systems [5]:

- CO_2/CH_4 - biogas, natural gas,
- H_2 or He from other gases,
- H_2S/CH_4 - natural gas,
- O_2/N_2 - oxygen enrichment of air and vice versa,
- H_2O - drying of gases,
- SO_2 - desulphurization of gases,
- vapours of organic compounds - removal from the air and from industrial waste flows.

The list presented below presents the most characteristic parameters of membrane separation of gases and vapours:

- membrane: composite or asymmetric containing active layer from flexible or glassy polymer,
- membrane thickness: active layer from 0.1 to several urn,
- pore size - nonporous membrane (or porous one <0.1 μm),
- driving force: pressure up to 10 MPa or vacuum on the side of permeate,
- separation mechanism: dissolution and diffusion,
- membrane material: flexible polymers, polydimethylooxosilane, polymethylopentene, glassy polymers, polyimide, polysulfone.

Application of Membranes for the Removal of Volatile Organic Compounds from the Air

Industrial processes where volatile organic solvents are applied contribute to the generation of waste gas flows polluted by the vapours of these compounds. They are not only hazardous for the environment but they have some kind of economic value connected with the recovery of chemical substances and energy. Table 6 [1] presents the emission of volatile organic compounds to the air recorded in the year 1987 in Holland. By the application of currently applied conventional techniques for the removal of volatile organic compounds from the air we cannot nowadays fully recover and reuse these compounds.

Table 6. Emission of solvents to the air in Holland.

Solvent	Emission ratio Mg/year
Aliphatic saturated hydrocarbons	50,099
Aliphatic unsaturated hydrocarbons	7,309
Aromatic hydrocarbons	20,110
Chlorocarbons	9,445
Fluorcarbons	3,790
Hydroxile aliphatic compounds	12,369
Esters	6,779
Ketones	7,147
Aldehydes	731
Ethers	1,049
Aromatic oxygen compounds	646
Aromatic nitrogen compounds	1,709
Multi-functional organic compounds	8,982
Total	130,165

In modern solutions solvents are recovered from waste gases by means of membranes for gas separation. The process was initiated by the application of composite membranes, which are characterized by high permeability with respect to vapours of organic compounds, but they are practically unpermeable for the air and other gases which do not undergo condensation [9]. A general diagram for the recovery of solvents with the application of membranes is presented in Fig. 5 [9].

The polluted air flux passes over the membrane surface, which is permeable for the vapours of organic compounds. The vacuum pump maintains low partial pressure of solvent vapours on the permeate side, which facilitates its flow through the membrane. Then, the vapours of organic compound are subjected to cooling and
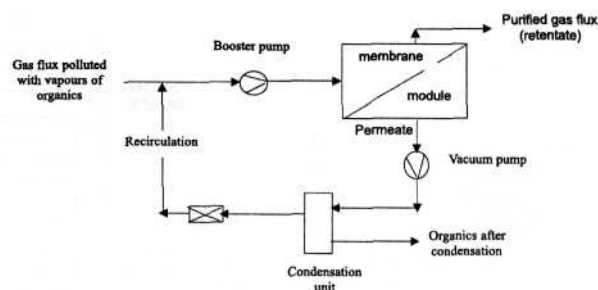

Fig. 5. Diagram of a membrane system for the recovery of solvents from the air.

condensation, and the gas flux, after the liquid has been separated, is returned to the feed. Purified air (retentate) is returned to the atmosphere or is subjected to further purification, for example by catalytic combustion or pressure adsorption in moving bed, depending on what purity level of air is required [9].

Examples for the Industrial Application of Membrane Systems for the Recovery of Vapours of Organic Substances from the Air

In 1989 the first installation for the recovery of vapours of organic substances based on the membrane technique was put to use in the warehouse of liquid fuels. At present, there are 20 such installations, either under construction or already working, of output ranging from 100 to 2000 m^3/h, either as single membrane systems or hybrid ones combined with catalytic exhaust reheat, gas engine or pressure adsorption in moving bed. Smaller membrane installations for the removal of volatile organic compounds polluting the air are gaining popularity with the chemical industry and pharmaceutical industry where they are often applied. In the following section we present flow charts and operating data of some industrial installations. The installations are frequently furnished with flat membranes and modules produced by GKSS (Germany) so-called "GS-modules". They are modernized plate-frame modules 500 mm long, of diameter 320 mm and membrane surface from 8-10 m^2 [9].

Recovery of Fuel Vapours

In 1989 the first installation of output 300 m^3/h based on membrane technique was put into operation for the recovery of vapours of organic compounds from waste gases generated by storage and distribution of petrol in the VTG fuel warehouse in Munich (Fig. 6) [9]. The introduction of this technology was enforced by new legal regulations in Germany involving air pollution (so called TA-Luft). The regulations are very strict as to the content of volatile organic compounds in the air - the content of petrol vapours (propane, butane, benzene) must not exceed 150 mg/m^3, and aromatic hydrocarbons, e.g. benzene 5 mg/m^3.
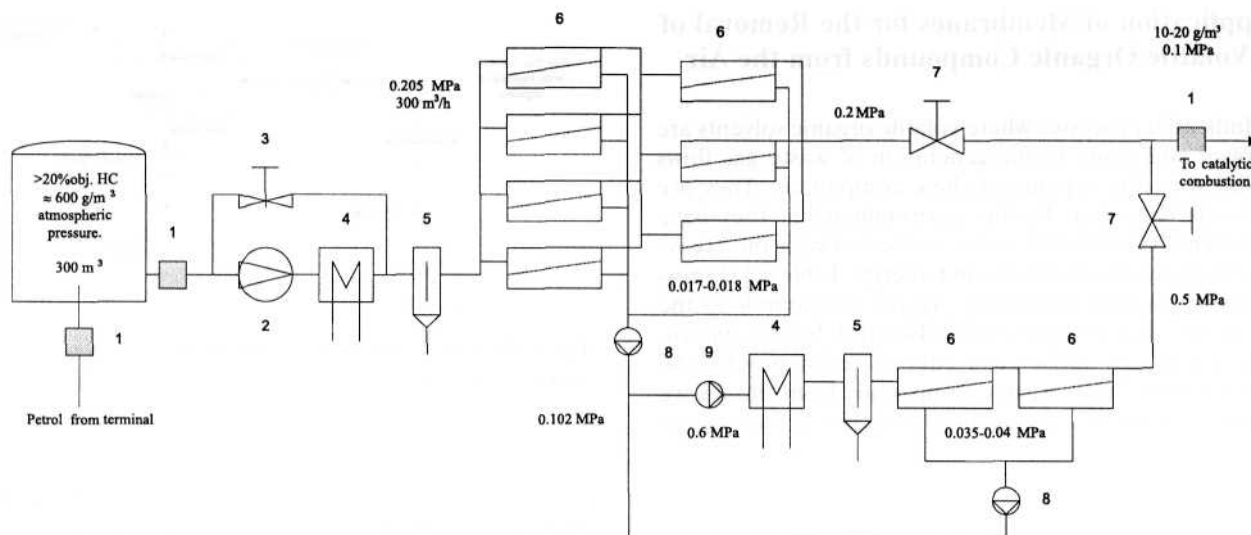
Fig. 6. Diagram of tne installation tor tne recovery ot organic compounds vapours in Munich.
(1 - fire protection, 2 - compressor, 3 - by-pass valve, 4 - heat exchanger, 5 - cartridge filter, 6 - membrane system, 7 - pressure control valve, 8 - vacuum pump, 9 - screw compressor).

The installation presented in Fig. 6 has the following characteristic properties:
- two-stage membrane process,
- gas pump replaced by a blower,
- recovery of hydrocarbons by means of pressure compressor,
- compression of enriched vapour using a screw compressor,
- rotary-worm vacuum pump for permeate,
- final purification using catalytic combustion.

The installation has been working since 1989 with the original membrane unit still in use, which proves that process conditions were selected correctly. It is the only installation working as combined with catalytic combustion.

A similar installation was also built at the VTG fuel station in Duisburg (Germany), but instead of catalytic combustion a gas engine was applied, which eliminated residual content of hydrocarbons from retentate [9].

In the years 1991-1992 an installation for the recovery of organic compounds' vapours was put into operation at BP fuel warehouse in Hamburg-Finkenwerder, in order to reduce emission of pollution to the air [9]. That installation was a hybrid system of the output 1500 m^3/h combining the membrane process and gas engine. Gas engines combined with the generator are working continually, supplying electric energy consumed during the operation. They were designed in such a way that energy supply is switched over from natural gas to the retentate of membrane installation when it is working. The concentration of hydrocarbons in retentate is approximately 50 g/m^3, membrane surface 70 m^2, with the flow 1500 m^3/h, pressure 0.35 MPa and permeate pressure 0.02 MPa.

A big commercial success involving the removal of organic compounds' vapours was achieved by a hybrid process combining the membrane process and pressure adsorption in moving bed (Fig. 7) [10]. At present two installations of that type are working and a further six are being designed or built.

Waste gas from the fuel warehouse is collected in a gas tank from which the compressor sucks in the air polluted with hydrocarbons, and after it has been compressed it is passed onto the scrubber where the petrol from warehouse is the absorbent. The concentration of hydrocarbons in the gas leaving the scrubber depends on pressure and temperature. Then, the flux is passed to the system of membrane modules whose membrane surface and permeate pressure depend on the permissible concentration of hydrocarbons introduced to adsorption. Two adsorbers are installed, they work alternately, one in the adsorption cycle and the second in the regeneration cycle. A flux of purified gas was used as purifying gas in regeneration. To maintain low vacuum, a vacuum pump was applied on the permeate side. Another aim of this pump was to support desorption of adsorption column. Active carbon or made from carbon or inorganic molecular sieves were used as adsorption material. Typical installation based on the presented principles is operating in the Shell fuel warehouse in Ludwigshafen (Germany).
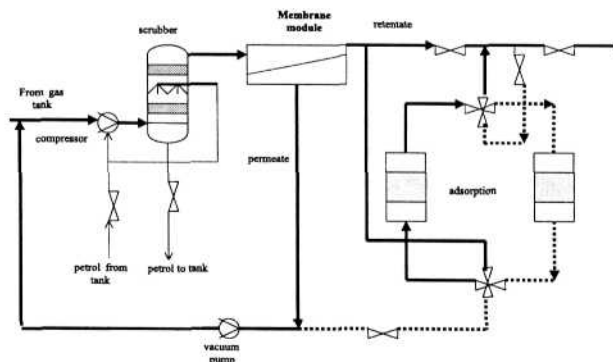

Fig. 7. Integrated system for the recovery of volatile organic compounds from the air using the membrane separation method and pressure adsorption in moving bed.

Legal acts regulating the purity of air in the USA and Germany forced the installation of systems removing petrol vapours at filling stands of petrol stations. In conventional solutions open-vacuum systems are used, which consist of a nozzle which sucks out petrol vapour using an internal channel. Mean recovery of petrol vapours in such systems is from 68 to 74% depending on the kind of vehicle. In order to prevent the emission from the tank of the vehicle being filled to the tank from which the petrol is taken, it must be ensured that the ratio between the volumes of petrol vapours and air be equal to the volume of pumped liquid petrol. With the application of membrane module the volume of flow is divided into the flux upgraded with hydrocarbons, corresponding with the volume of pumped petrol, and weakened flux which is transferred to the atmosphere. In order to obtain invariable ratio of pressure values on both sides of the membrane, which in practice ensures constant concentration of retentate, vacuum pump should be installed both on the side of retentate and permeate (Fig. 8) [9].

Pilot installation of that type was installed in January 1993 at the petrol station in Luebeck (Germany), and it was working 24 h a day over six months [9]. Depending on the type of vehicle, the recovery of petrol vapours ranged from 90-95%. Basing on the obtained results, an industrial prototype unit was designed. The standard for the recovery of petrol vapours is set at the value over 90%, whereas vacuum systems, which do not have membranes, offer only 75%. However, the investment costs are higher due to the cost of membrane module and the second vacuum pump.

Installation for Air Treatment Used in the Chemical and Pharmaceutical Industries

In the chemical or pharmaceutical industry, small units are applied (output: 1-20 m^3/h) for the recovery from air of such solvents as hexane, toluene, 1,2-dichloroethane and methyloethylketone. In design projects
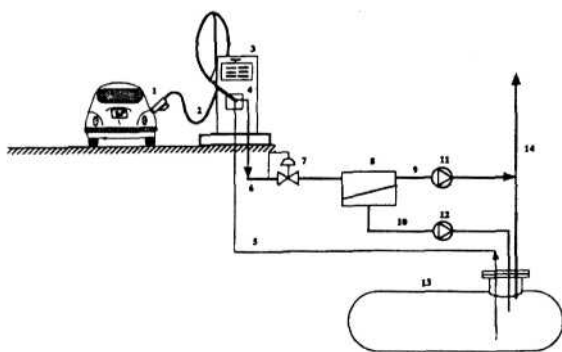

Fig. 8. Diagram of the system for the recovery of petrol vapours containing a membrane module.
(1 - filling nozzle with internal channel for vapour, 2 - coaxial hose, 3 - metering pump, 4 - solenoid valve, 5 - petrol conduit, 6 - return conduit of petrol vapours, 7 - pressure control valve, 8 - membrane module, 9 - retentate conduit, 10 - permeate conduit, 11 - vacuum pump of retentate, 12 - vacuum pump of permeate, 13 - tank, 14 - air-escape conduit.

there is either feed compressor and vacuum pump on the permeate side or an integrated system containing only one pump which is pumping the feed and creates vacuum. The right selection of an appropriate system depends on the maximum output of the installation.

The second solution is typically applied for the separation of 1,2-dichloroethane present in the air, passed for neutralization by catalytic after-burning. The flux of that type contains 80 g/m^3 of 1,2-dichloroethane, and after it has been mixed with the flux of recycling permeate (concentration 128 g/m^3) it is passed to the membrane module which lowers the concentration of vapours to the level 330-350 mg/m^3. The vacuum on the permeate side equaling 0.01 MPa is generated with the help of vacuum ring pump where 1,2-dichloroethane is used as working agent, cooled to the temperature 10°C. 1,2-dichloroethane is separated in a separator cooled with water. Fig. 9 presents technical data of such a process [9].
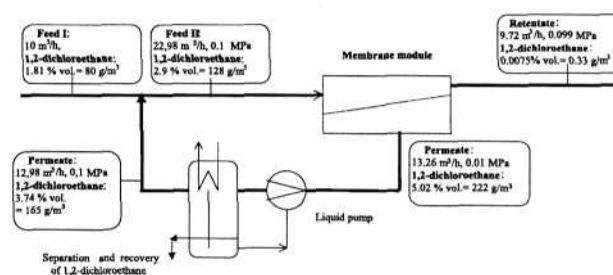

Fig. 9. Technical data involving the recovery process of 1,2-dichloroethane from the air.

Separation of vapours of organic compounds from the air or from other gas fluxes can be regarded as a dynamically developing process. First pieces of information on that subject were provided by literature 10 years ago [9], and at present the said technique has already been incorporated into industrial applications. It principally involves installations set up in places posing some hazard, mainly for the elimination of petrol or solvent vapours. There are great application potentials of the solutions containing selective membranes, with respect to solvents, in process fluxes of the chemical or petrochemical industries.

Application of Membrane Absorption Process for Air Treatment

Polymeric membranes have also found a new application possibility - as a separation (contact) surface of two phases. For example two flowing liquids, or flowing gas and liquid can be separated by means of a porous hydrophobic membrane. Since the membrane is porous, the contact between two liquids is possible in spite of the fact that it forms a separating barrier between both phases. In order to separate water phase from gas phase or from another water phase the membrane must have hydrophobic character. Due to the above it is possible to carry out a process similar to extraction, and the absorption of gases with the use of membrane units. By the application

of capillary membranes for that purpose (e.g. from polyp-ropylene) we can obtain high phase contact surfaces (over 1000 m^2/m^3). Such compact installations are cheaper than classical absorbers having a contact surface of about 100 m^2/m^3.

A membrane can form a permeable barrier between the liquid and gas phase. When the membrane is porous, gas impurities diffuse through the pores and are absorbed by the liquid passing on its other side, and in the case of nonporous membrane the impurities dissolve in the material of the membrane and then diffuse through it. The contact surface between gas phase and liquid phase depends solely on the type of membrane, and not on the flux volume of flowing media. Absorption in the liquid phase can be effected by physical separation or chemical reaction, and the separation selectivity only depends on the type of absorbent. Fig. 10 presents the functioning of the porous membrane in the process of gas absorption **[11].**
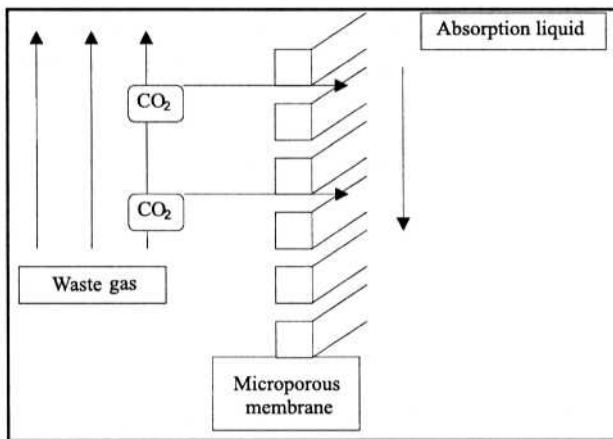

Fig. 10. Process of membrane absorption of gas using porous membranes.

With the application of capillary modules [11], very efficient contactors of the gas-liquid type can be const-ructed. Most of the absorbents applied in the conven-tional absorption process can be also used in membrane absorbers. During the utilization of membrane gas ab-sorbers it must be ensured that the liquid phase is not mixed with the gas phase. This means that with respect to porous membranes, the absorption liquid should not be allowed to penetrate inside the pores. It depends on the size of pores, pressure difference on both sides of mem-brane and the affinity of absorption liquid with the mem-brane material, and it is connected with the wettability in the system solid body (membrane) - liquid. Membrane pores do not get wet when the wetting angle is higher than 90 and pressure difference on both sides of the membrane is limited by the size of pores. For water ab-sorption liquids there are suitable membrane materials such as polypropylene and teflon. Since surface tension is decreasing along with temperature, the breakthrough pressure (opening of pores) decreases along with the in-crease of temperature. For nonporous membranes, the permeation of liquid depends on pressure difference and

affinity between polymer and absorption liquid since the liquid must first of all penetrate the inside of the matrix. When there are fast chemical reactions taking place in the presence of membranes, the transport of matter is limited by diffusion stage in gas phase and therefore it depends on hydrodynamic conditions over the membrane surface, its properties (porosity, thickness, morphology) and transport properties (diffusion index). The values of mass transfer coefficient in such conditions range from 0.001 to 0.1 m/s [11].

The application of membranes for gas absorption has a lot of advantages over the conventional solutions where columns with filling are used:
- operation of contact unit does not depend on the vol ume of gas flux or liquid flux,
- such phenomena as snatching up of liquid drops by gas, column flooding, formation of channels or foam ing do not occur,
- the units are compact due to the application of memb ranes from capillary fibers.

The last advantage contributes to the reduction of in-vestment costs and energy consumed by the working pumps.

Application of Membrane Gas Absorption

Membrane gas absorbers can be applied for the re-moval of various gas impurities present in the air. The following gases are most often referred to [11]:

SO_2, NO_X, HCl, CO_2 - from exhaust gases;
H_2O, H_2S, CO_2, Hg   - from natural gases, biogas, gas
                                  from   waste   dumps;
NH_3, H_2S, CO_2,   - volatile substances from waste
                                  gases.

Since the membrane facilities are of modular charac-ter, the application of membrane gas absorbers is also economic on a small scale. It is particularly significant with respect to applications connected with environmental protection, since they can effectively and economically purify gas from sources emitting it in small volume. Since the regeneration of absorbent cannot be carried out in the same facility as absorption, a central regeneration station is necessary.

Removal of SO$_2$ from Exhaust Gases

Various absorption processes are used for the removal of SO_2 from exhaust gases. One of the most commonly used is the so called "double alkaline process" which can also be applied to membrane absorbers. The process is based on the following two chemical reactions:

absorption stage:
   $SO_2 + Na_2SO_4 + H_2O \rightarrow 2NaHSO_3$
regeneration stage:
   $Na_2CO_3 + 2NaHSO_3 \rightarrow 2Na_2SO_3 + H_2O + CO_2$
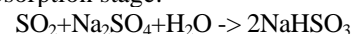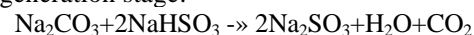
The designing process of the facility for membrane absorption of sulfur dioxide present in exhaust gases

should be started with the calculation, based on respective models of matter transport, of the length of capillary fibres necessary to remove the element to the required degree. Based on such calculations, laboratory tests of absorption of SO_2 present in nitrogen were carried out with the application of a small laboratory capillary module of the fiber diameter 0.6 mm [11]. Experimental results confirmed the calculations - fiber of 25 cm length resulted in the removal of over 99% of SO_2. The laboratory model was also tested using real exhaust gas coming from coal combustion. The 500 h long operation yielded an equally high removal level of SO_2 as from the model gas. Laboratory tests facilitated the construction of pilot installation of the output 100 m^3/h by TNO (Holland) [11]. They applied gas coming from the installation for biogas combustion, which contained SO_2. Sulfur dioxide, which was being recovered by membrane absorption in the form of sodium sulfate(IV), may be again used in the production process. Over the 6 months of testing, over 95% of SO_2 was recovered with the output 120 m^3/h. There were no disturbances observed in the operation caused by fluctuations in the volume of gas flux or content of SO_2. Also, the fouling of membrane was not observed since in the process of gas separation only the diffusive transport of substances takes place, and convection transport (which is principally responsible for this process) is not observed.

Purification of Air from Cigarette Smoke in Closed Rooms

Cigarette smoke contains a few hundred chemical compounds, in both the solid and gas phases. The existing systems of mechanical ventilation in houses and in offices do not guarantee good air quality with many heavy smokers around. The quality of the air indoors could be improved by the application of a portable facility for air purification, which enforces air circulation through a system of filters. Classical facilities for air purification make use of electrostatic or cloth filters and sometimes of filters from wood coal. However, most filters are not effective with respect to most gas substances generated during cigarette smoking. The problem can be solved by membrane filters.

Looking for the possibility to apply membrane gas absorbers for the removal of cigarette smoke components, six laboratory membrane modules produced by different manufactures were subjected to tests [11]. With the velocity of gas flow between 2 and 30 dm^3/min, pressure drop in the module was from 1 to 30 hPa and was changing linearly with the change of flow velocity. The experiments were carried out with tap water used as absorption medium, which was flowing outside the fibre (whereas gas was inside the fibre). The first experiment series was carried out using four chemical compounds - formaldehyde, nitrogen dioxide, acetone and ammonia. The observed removal level of chemicals was high, but the removal effectiveness was becoming lower with the increase of air flow velocity. The results served as a background for the selection of the best module for the second experiment series, where the compounds present in cigarette smoke were generated in a specific facility, in compliance with

ISO standard 7210 [11]. Table 7 shows the removal effectiveness of compounds used in the tests. As had been anticipated, the level of hydrocarbon removal was low since they do not dissolve in water. It means that for their absorption another absorption liquid should be applied. Compounds soluble in water were characterized by high removal effectiveness. The tests have proven that the tested membrane facilities for air purification are useful filtration systems which are characterized by high removal effectiveness of compounds soluble in water and small values of pressure drop. The facilities are compact due to the application of capillary modules.

Table 7. Effectiveness of membrane facility for purification of air containing cigarette smoke.

Component	Removal effectiveness [%]
Acetone	96.6
Styrene	15
Formaldehyde	98.4
Nicotine	99.1
Ammonia	95
Aroma	49-54

Removal of CO_2 with the Use of Membranes

Conventional techniques for the removal of carbon dioxide from the air are based principally on the process of chemical and/or physical absorption. It is absorbed by solvents in low temperature and/or under low pressure. The following solvents are the most typical [11]: monoethanoloamine (MEA), diethanoloamine (DEA), triethanoloamine (TEA), potassium carbonate (Benfield), methylodiethanoloamine (MDEA), methanol (Rectisol), N-methylo-2-pyrolidon (Purisol), polyethylene glycol (Selexol), propylene carbonate (Fluor solvent) and the system sulfolane/diisopropanoloamine//water (Sulfinol)

Chemical solvents are used when the concentration of carbon dioxide in the air is low and when carbon dioxide obtained in the product should have high purity. But with the high concentration of carbon dioxide in the inlet gas and with smaller requirements involving its purity in the product, physical solvents are favored. Due to low partial pressure of carbon dioxide in exhaust gases, in practice the absorption/desorption process is applied with the use of monoethanoloamine. Absorption is carried out in the temperature only slightly higher than ambient temperature and desorption in the temperature of about 110ºC. A diagram of the process is presented in Fig. 11 [11].

The required membrane surface in the absorption stage can be calculated from respective equations. Assuming that the transport index of matter is limited solely by the diffusion stage in gas filling membrane pores, we can accept that it equals 0.02 m/s for typical capillary membranes (1mm of external diameter). For the flow of exhaust gases at the rate 600 m^3/s and carbon dioxide recovery at the level 70%, the required membrane surface will be 35,500 m^2. Introductory economic analyses

indicate that the costs of the absorber alone could be reduced by 30%, assuming the cost of membrane at about 40 DEM/m^2, and the total cost of the installation absorption/desorption can be reduced by 10% [11].

Apart from the absorption stage, the desorption stage also can be carried out with the application of membrane modules. However, the effects of such a solution on the consumption of energy requires further research and analyses.
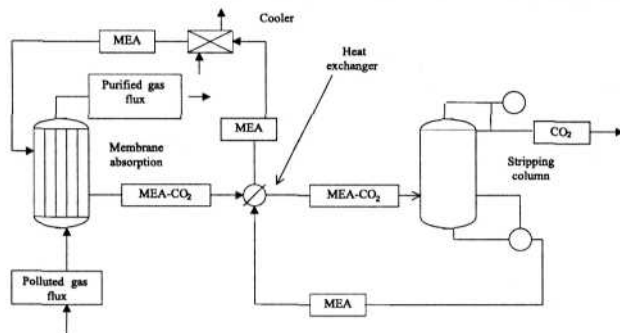

Fig.ll. Diagram of the installation for absorption/desorption with the use of monoethanoloamine (MEA).

Removal of Volatile Organic Compounds from the Air Using Membrane Absorption

For the absorption of volatile organic compounds, non-aqueous liquids are applied (mainly nonpolar hydrocarbons, mineral oils and silicone oil), which can pass through hydrophobic membranes. In order to prevent this phenomenon, composite membranes coated with reticulated polydimethylosiloxane (PDMS) are applied in the removal processes of organic compounds from the air, since it is permeable for volatile organic compounds. Separation technology with the use of that technique is being tested at present in ten pilot installations in Europe.

Selective membrane absorption used for the removal of volatile organic compounds integrates the advantages of absorption and membrane gas separation. There are the following properties of such solutions:
- compact capillary membranes are characterized by short diffusion path,
- the surface of phase separation is taken up by the membrane,
- the recovery of volatile organic compounds is taking place even at low concentrations,
- energy consumption is low,
- the technique is not destructive,
- flexibility of process system.

Gas flux containing volatile organic compounds is flowing on one side of the membrane, and the absorption liquid of high affinity to these compounds on the other side. As a result the driving force of the process increases as compared to a typical membrane separation of gas.

The system combining membrane process and absorption makes it possible to recover volatile organic com-

pounds at very low concentrations (0.6 mg/m^3 was documented) by concentrating them in absorption liquid. Then, gas recycling is possible (e.g. air), and the obtained organic compounds can be used again, by the regeneration of absorption medium.

In the process of selective membrane absorption, modules from capillary fibers are used, where the flow, carried out inside or outside the fibers, effects high velocities of matter exchange, which in consequence ensures that the designed facilities have high compactness. Due to a module system the output of the installation can be changed flexibly. Therefore even installations of very small output can be designed. The process can be potentially applied in chemical industry, paint and varnish industry, metal processing, petrochemical, papermaking, food, rubber and plastics industries.

The process of selective membrane absorption is currently subjected to very intensive research studies aiming to determine optimal processing systems and possible types of feed that can be applied. Special attention is focused on the optimization of matter transport with respect to gas phase, membrane, membrane matrix and liquid phase. The testing also involves available capillary membranes for the recovery of volatile organic compounds, with the application of a wide range of absorption liquids, such for example as silicone oil, kerosene, decaline or mixtures of various components showing optimum affinity to volatile organic compounds. It is also very important to select the best regeneration method of absorption liquid. Such processes are taken into consideration as: distillation, pervaporation or striping with heated air, as it has been presented in Fig. 12 [11].
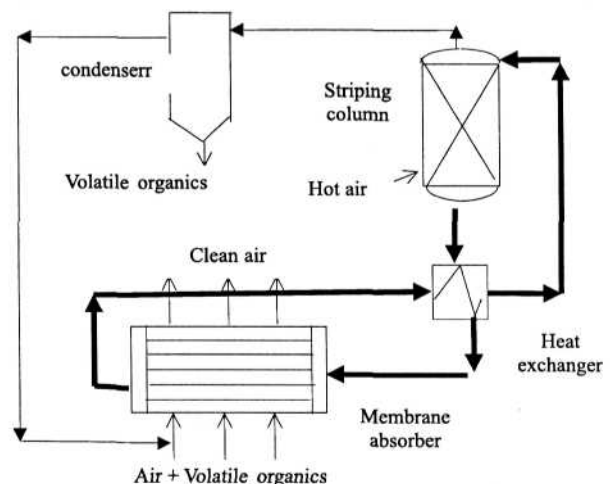

Fig. 12. Diagram of selective membrane absorption with the application of heated air striping.

Separation of Air

A totally new domain of potentials involving the possibility to control combustion processes in power engineering has been created by the introduction of separation membrane technologies. Even now, in the process of single-stage separation of gases, it is possible to upgrade

the air with oxygen to the content of about 45% [12]. This means that the content of nitrogen in the air passed to the furnace is reduced by 25%. The same reduction rate refers to nitrogen oxides present in products emitted to the atmosphere [13]. It is, however, not possible to obtain such a concentration of oxygen at which the necessity to maintain low combustion temperature would definitely disappear, due to the limitation involving the formation of nitrogen oxides. The increase of oxygen concentration in the furnace also entails higher effectiveness of fuel combustion itself.

Fig. 13. presents schematically the separation process of air components using the gas separation method into nitrogen and oxygen by means of membrane separation of gas [12].
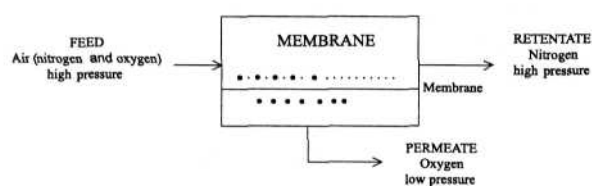

Fig. 13. Diagram of membrane separation of air.

Feeding flux (air) is passed under pressure over the membrane surface in the "flow-cross" system. Since the membrane is better permeable for oxygen than for nitrogen, the permeate is upgraded with oxygen. And the flux of retentate is upgraded with nitrogen, but total separation is not achieved. The separation degree depends on the selectivity of membrane and process conditions (pressure, temperature, flow velocity, membrane surface etc.) **[12].**

Using the membranes currently available on the market we cannot obtain high separation levels of O_2/N_2. Oxygen purity of 30-40% can be obtained in the system of single-stage separation [12].

Fig. 14 presents the permeability of oxygen through various membrane materials as well as separation coefficients in the system O_2/N_2 [13]. The most suitable membranes are those which are characterized by both high permeability and high separation coefficients, but most of them have high permeability but low selectivity. In general, membranes of high permeability are made from rubber-type polymers whereas the membranes characterized by high selectivity are of the glassy type.

Fig. 15 presents the diagram of installation for the acquisition of air upgraded with oxygen [14]. The air is passed to the module with the help of a fan, under the pressure $1.03 \cdot 10^5$ Pa, and the permeate, which is the product of the process, is sucked out from the system with a vacuum pump under the pressure $0.2 - 0.3 \cdot 10^5$ Pa. Usually, permeate (upgraded air) contains 27-35% of oxygen. The facilities for industrial application are designed with membrane surface 86 m^2 [14], equipped with the membranes having the output 3.4 N m^3/m^2-hbar and selectivity involving the relation O_2/N_2 equaling only 2.1.
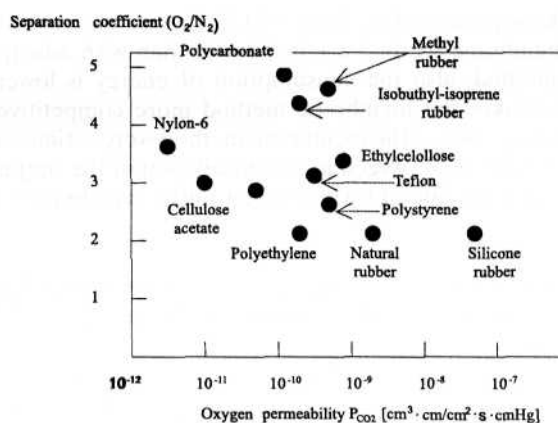

Fig. 14. Selectivity of system O_2/N_2 and permeability for oxygen for membranes made from various polymers.
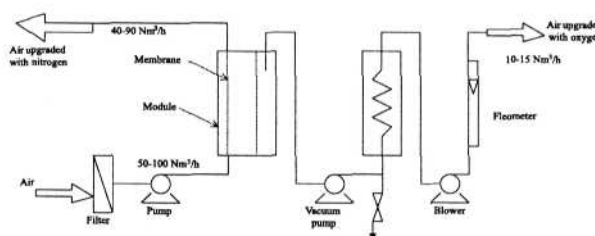

Fig. 15. Membrane process of air upgrading with oxygen.

However, membranes for medical purposes are characterized by lower output, but higher selectivity equaling 4.0 [14]. Predominantly plate-frame modules are applied based on silicone composite membranes. By the application of plate-frame modules the costs of air compression can be reduced. With respect to pilot projects, membranes in the form of capillary fibres are also used.

Apart from other applications, air upgraded with oxygen can potentially be used in medicine [12, 13]. The superiority of air obtained by means of membrane method as compared with conventional systems consists in the elimination of mixing air with pure oxygen and of wetting stage, as well as its quality after filtration, with respect to solid impurities, is perfect. The air used in medicine is 40% oxygen [13].

Another application of air upgraded with oxygen can be found in combustion processes, and in particular in power engineering in combustion process [12, **13**]. Combustion in air containing 30% oxygen increases its efficiency and eliminates the pollution of flux after combustion. A typical single-stage membrane system which is producing nitrogen of purity 97% is simultaneously yielding permeate of oxygen concentration 30%. Higher concentrations of oxygen can be obtained by increasing the flow velocity of feed, reduction of membrane surface or increasing pressure difference, which is unfortunately connected with an increase of costs.

A comparison involving the production costs of oxygen-upgraded air using membrane methods with adsorption in moving bed made by the firm A/G Technology

(USA) is presented in Table 8 [12]. Investment costs of the membrane method are half lower than with adsorption method, also the consumption of energy is lower, which makes the membrane method more competitive. Operating costs of the membrane method were estimated at 28 USD/ton of oxygen in the installation of the output up to 20 tons/24h and with oxygen purity equaling 35% [12].

Table 8. Comparison of production costs of oxygen upgraded air of the concentration 35% (output of the installation 10 tons/24h).

	Membrane installation of A/G Technology	Installation based on adsorption in moving bed
Investment costs (thousands US dollars)	288	552
Operating costs (US dollars/24h):		
Replacement of membranes	38	–
Energy	86	131
Credit costs	105	202
Depreciation	33	63
Others	18	27
Total (US dollars/24h)	280	423
Total (US dollars/ton)	28	42

Oxygen-upgraded air is also applied in the chemical, metallurgical, and metals producing industries, as well as for aeration in biological treatment plants and in fish ponds [13, 14].

References

1. MULDER M., The use of membrane processes in environmental problems. An introduction, in: "Membrane Processes in Separation and Purification" (Crepso J.G., Boddeker K.W., Eds.), Kluwer Academic Publishers, Dordrecht-Boston-London, pp.229-262, **1994.**
2. RAUTENBACH R., EHRESMAN H., Upgrading of landfill gas by membranes - process design and cost evaluation, AIChE.Symp.Ser., **85** (272), 48, **1989.**
3. RAUTENBACH R., WELSCH K., Treatment of landfill gas by gas permeation - pilot plant results and comparison to alternatives., Desalination, **90,** 193, **1993.**
4. DICKINSON R.E., CICERONE R.J., Future global warn ing from atmospheric trace gases, Nature, pp.109-115, **1986.**
5. MULDER M., Basic Principles of Membrane Technology, Kluwer Academic Publishers, Dordrecht-Boston-London **1991.**
6. CEN Y, LICHTENTHALER R.N., Vapour permeation, in: "Membrane Separation Technology. Principles and Applications" (Noble R.D., Stern S.A., Eds.), Elsevier Science, Amsterdam - Lausanne - New York - Oxford - Shannon - Tokyo, pp. 85-109, **1995.**
7. NEEL J., Pervaporation, in "Membrane Separation Techno logy. Principles and Applications" (Noble R.D., Stern S.A., Eds.), Elsevier, Amsterdam, pp.143-211, **1995.**
8. GROBER H., ERK S., GRIGULL U., Fundamentals of Heat Transfer, Me Graw-Hill, New York **1961.**
9. PEINEMANN K.V., OHLROGGE K, Separation of or ganic vapours from air with membranes, in: "Membrane Pro cesses in Separation and Purification" (Crepso J.G., BOddeker K.W., Eds.), Kluwer Academic Publishers, Dor drecht-Boston-London, , pp.357-372, **1994.**
10. OHLROGGE K., KYBURZ E., SCHLICHT B., Membran-ferfahren mit integrierter Druckwechseladsorption - Eine neue Generation der Kohlenwasserstoff-Ruckgcwinnun-gsanlagen, DGMK - Tagungsbericht, 9303 pp. 31-40, **1993.**
11. JANSEN A.E., KLAASSEN R, FERON P.H.M., HANE-MAAIJER J.H., MEULEN B., Membrane gas adsorption processes in environmental applications, in: "Membrane Processes in Separation and Purification" (Crepso J.G., Bod deker K.W., Eds.), Kluwer Academic Publishers, Dor drecht-Boston-London, pp. 343-356, **1994.**
12. SPILLMAN R., Economics of gas separation membrane processes, in: "Membrane Separation Technology. Principles and Applications" (Noble R.D., Stern S.A., Eds.), Elsevier Science, Amsterdam-Lausanne-New York-Oxford-Shan non-Tokyo, pp. 589-663, **1995.**
13. TURLEY J., GAINULLIN F.G., IRKLEY A.A., Nitrogen production by means of membrane technology for safety en hancement in marine and on-shore petroleum and natural gas facilities, in: Effective Industrial Membrane Processes - Benefits and Opportunities (Turner M.K. Ed.), Elsevier Applied Science, London-New York, pp.345-380, **1991.**
14. SCOTT K., Handbook of Industrial Membranes, Elsevier Advanced Technology, Oxford **1995.**