Ind. Eng. Chem. Res. 1995, 34, 1769-1778
SEPARATIONS

High-Efficiency Separation of an Ethylene/Ethane Mixture by a Large-Scale Liquid-Membrane Contactor Containing Flat-Sheet Nonporous Polymeric Gas-Separation Membranes and a Selective Flowing-Liquid Absorbent

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Ethylene and ethane were effectively separated from a mixture comprising these two gases by means of a large-scale liquid-membrane contactor (membrane permabsorber). The contactor comprised composite flat-sheet membranes with a nonporous diffusional layer made from polyblock copolymer poly(dimethylsiloxane)/poly(phenylsilsesquioxane) and an aqueous solution of silver nitrate flowing along turbulence-promoter spacers between the membranes. The membrane permabsorber permitted ethylene and ethane to be separated effectively from a binary mixture. The problem with the selection of suitable membranes is discussed. It was shown that the efficiency of the separation process could be varied by changing the liquid-flow rate, the membrane area, the concentration of the selective carrier in the liquid, the temperature of the liquid absorbent, and the gas-separation properties of the membranes.

Introduction

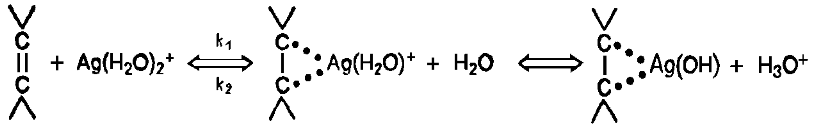
With the development of synthetic polymeric nonporous membranes, the membrane gas-separation technique has become important, and for many years, investigations have been undertaken to develop a convenient and reliable technique for separating gases from mixtures. An area of membrane technology of continuing interest is the improvement of the productivities and selectivities of these gas-separation systems.

However, the number of commercial membranes suitable for gas separation that have come onto the market in the last five to six years is not large (Yampol'skii, 1993). Despite many improvements in the membrane gas-separation technique, in the resistance of membranes to high temperatures and chemicals, and in the development of reliable processes and the control of fouling, a few problems remain to be solved. One of the problems which arises with passive gas separation by means of nonporous polymeric membranes is that of separating gases that have the same or nearly the same permeabilities, although their diffusivities and solubilities differ considerably.

The separation of unsaturated hydrocarbons, such as ethylene and propylene, is one of the most important processes in the petrochemical industry. Since the boiling points of paraffin/olefin counterparts lie within very narrow temperature ranges, conventional distillation is difficult and expensive. A review of traditional and nontraditional technologies for the separation of light olefina and paraffins was presented by Eldridge (1993). Lee and Hwang (1992) have reported on the separation of propylene and propane by means of polyimide membranes with a selectivity of 15 and a productivity of $5.81*10^{-8}$ cm^{3} (STP)/cm^{2}*s*cmHg for propylene. Stern et al. (1987, 1990) have reported some data on permeabilities of ethylene and ethane in different poly(dimethylsiloxane)- (PDMS) contained membranes. These data show that the application of nonporous polymeric membranes in the separation of olefin/paraffin gas mixtures, in particular of propylene/propane and ethylene/ethane mixtures, is not attractive for industrial purposes because of the low separation, factors obtained. To produce 99.95-99.96 (vol %) pure ethylene from an 80/20 (vol %) ethylene/ethane feed stream, membrane selectivities of 100-1000 are required (Sluys et al., 1994).

One possible way of increasing the selectivity of passive gas separation is to generate unsteady-state, boundary conditions at the membrane inlet. It has been, predicted that the selectivity of the membrane separation process will rise if a concentration pulse is passed, through the membrane (Paul, 1971; Higuchi and Nakagava, 1989; Beckman et al., 1991). Other approaches include the use of immobilized liquid membrane (ILM) with carriers that can selectively and reversibly bind certain permeate species. ILM membranes show very high selectivity values (Scholander et nl., 1960; Ward, 1970; Cussler, 1971; Schultz et al., 1974). The facilitated transport mechanism in different membrane systems has been studied by Niiya and Noble (1985), c Way and Noble (1989), and Noble (1992).

Selectivities considerably higher than those of passive diffusional membrane separation can be achieved in olefin/paraffin separation if the ILM or other variations of the contained liquid membranes (CLM) are used wan Raay et al., 1959; Baker et al., 1961; Steigelmann et al., 1977; Kraus et al., 1986, Tsou et al., 1992). The process is based on the ability of silver ions (as well as of copper and some other metals) to reversibly coordinate unsaturated hydrocarbons (Brandt, 1959; Baker, 19G4). Bevenvijk et al. (1970) have comprehensively reviewed organosilver chemistry, and Hughes et al. (1986) have presented an excellent review of the subject. Schematically, the reversible complcxation of the silver ions and olefins is as follows (Brandt, 1959):



(1)

Brandt (1959) also showed that the equilibrium of the reaction is strongly dependent on temperatures so that the use of hot solutions of the selective carriers in the desorption process is attractive; in this case, the membrane must be suitably stable.

Data in the literature on the separation of olefin/paraffin gas mixtures are very diverse. The use of different membranes under various pressure differences over membranes with permeabilities of up to 2.2 x 10^{-6} cm^3 (STP) cm/cm^2 s cmHg has been reported to give an ethylene/ethane selectivity of 470 (Kimura et al., 1979). Teramoto ct al. (1986) have reported successful separation of ethylene and ethane by means of supported liquid membranes (SLM) comprising silver nitrate ns a carrier. The immobilized liquid-membrane technique and other variations, however, have major shortcomings. Renewal or replacement of poisoned or otherwise polluted liquid membranes presents severe problems (Kimura and Walmet, 1980; Matson el al., 1983). Also, these systems cannot be operated under high pressure differences since when pressure differences are high, the liquid is blown out of the pores. The maximum obtainable pressure difference depends on, among other variables, the diameter of the pores and the type of solvent used. The service life of a great number of polymers, at certain pressure differences, is shorted because of swelling of the polymer membrane by the solvent. In general, the main problem in the particular case of olefin/paraffin gas-mixture separation associated with ILM is the narrow range of the transmembrane pressure at which the process can be operated.

The need to reduce processing costs in industry demands new separation processes with greater selectivity. Certain improvements can be obtained by combining a second separation technology with membrane technology to create, for instance, an integrated membrane hybrid process (IMHP). IMHP is a collective term for various process configurations, such as when high selectivity of affinity interactions and high throughput of membrane separations are integrated into a hybrid separation technology. There arc numerous variations of these systems (Qi and Cussler, 1985; Yang and Cussler, 1986; Majumdar et al., 1988). Davis et al. (1993) have reported on the use of facilitated transport membrane hybrid systems coupled with a distillation process for the separation and purification of olefins.

Recently, flowing-liquid membranes, in which a liquid-membrane solution flows over the surface of a microporous membrane, have been proposed (Teramoto et al., 1989). In this particular case, the ethylene/ethane gas mixture was separated by means of the flowing-liquid membrane containing silver nitrate as a carrier. This process also includes the use of porous membranes to form channels for the flowing selective-liquid absorbent.

The use of nonporous gas-separation membranes and flowing-liquid absorbent in the IMHP for CO2 removal and purification has been reported by Shelekhin and Beckman (1992). This approach led to the creation of the terms "membrane permabsorber" and "selective membrane valve" (Beckman et al., 1993; Bessarabov and Beckman, 1993 a,b). Bessarabov et al. (1994 a,b), who investigated the separation of ethylene and methane by means of a membrane permabsorber containing asymmetric nonporous PVTMS gas-separation membranes and flowing solutions of silver nitrate, reported that the productivity of such a system was more than $4.5*10^{-5}$ cm/cm^2 s cmHg for ethylene. The separation factor for the ethylene/methane mixture was greater than 3000. The advantages of such a system are the reduction of the diffusional resistance of the liquid film by circulation of liquid along turbulence-promoter spacers between membranes, the possibility of simultaneously obtaining two high-purity gas streams, and the stability of the liquid membrane for a certain period of time due to locking of liquid solution inside the membrane system. The nonporous polymeric membranes function as gas-permeable barriers, and selectivity is determined by the liquid phase containing the silver ions. Nonporous membranes can be subjected to high pressure, and the use of high gas pressure increases the mass transfer. Bessarabov and Beckman (1993b) derived a simple model of mass transfer for the quasicirculation mode in the membrane permabsorber.

This paper focused on a process for separating ethylene/ethane mixtures by means of a large-scale membrane permabsorber (liquid-membrane contactor) comprising hydrocarbon-stable composite asymmetric nonporous gas-separation flat-sheet membranes made from the copolymer polj(dimethylsiloxane)/poly(phenylsilsesquioxane) (PDMS/PPSQ) with a high permeability for hydrocarbons with a flowing-aqueous solution of silver nitrate used as a selective absorbent for ethylene. Studies on the dependence of the membrane permabsorber productivity and selectivity on the liquid-flow rate, the concentration of silver nitrate in water and the temperature of the flowing liquid, and the total surface area of the membrane in the desorber module were carried out.

Membrane Permabsorber

The membrane permabsorber consists of at least one membrane absorption module (absorber) and one membrane desorption module (stripper) (Figure 1). The absorber and stripper contain nonporous polymer» membranes. The liquid absorbents flow between the absorber and the stripper at various rates and temperatures.

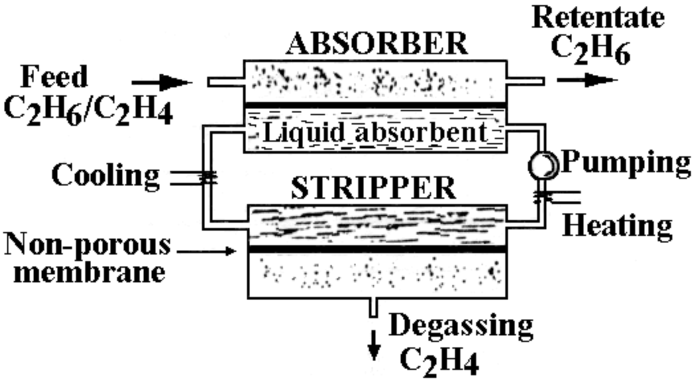


Figure 1. Schematic diagram of the membrane permabsorber.

The membrane permabsorber has one inlet for the feed and two outlets for the products (retentate and desorbate). The first component of the feed (retentat is insoluble in a liquid; the other, which is soluble in liquid, diffuses through the nonporous polymeric membrane and is absorbed and pumped away to be degassed in a stripper.

In the absorption module, the feed-gas mixture passed over a membrane consisting of a thin polymer film and a thin layer of flowing liquid. The gases that permeate the polymeric membrane, and which are soluble in the liquid layer, pass into the desorption module to be degassed through the other polymeric membrane. These membranes can be similar or different in composition. As a rule, the membrane permabsorber consists of absorption and desorption membrane modules operating in a circulation mode.

The liquid absorbent can be nonspecific in relation to the components of the gas mixture; the solubilities of the gaseous components in a liquid can differ considerably and, also, a liquid can react with one or several of the gas components. The productivity and selectivity of the membrane permabsorber depend on the gas-transport properties of the polymeric membranes, on the temperature of the liquid absorbent in the absorber find in the stripper, on the flow rate of liquid absorbents, on the concentration of a selective carrier in a liquid, on the salting-out factor, and on the physical variables of the process.

Experimental Section

Choice of the Membrane. Data in the literature indicate that the liquid-film resistance is normally larger than the membrane resistance in liquid-membrane contactor systems (Yasuda, 1972). Yang and Cussler (1986) showed that the liquid-film resistance controls the mass transfer in gas-separation liquid-membrane systems if the gas component does not react chemically with the liquid phase. However, the rapid reaction of the gas component with a liquid phase accelerates mass transfer in the liquid bulk so that the membrane can limit the mass transfer (Yang and Cussler, 1986; Kreulen et al., 1993). When the reaction is rapid, the liquid-membrane film resistance is almost certainly not important for the membrane permabsorber and the permeabilities of the nonporous membranes limit the mass transfer. The choice of a suitable membrane and membrane material to be used when the reaction in the liquid phase will be rapid, therefore, becomes very important. The configuration of the liquid-membrane module is also very important. The minimum requirements for a membrane to be used in such a system are (1) high permeability to hydrocarbons, (2) stability in hydrocarbons, (3) low permeability to vapors of the liquid absorbent, (4) stability in the selective liquid absorbent, and (5) good mechanical properties.

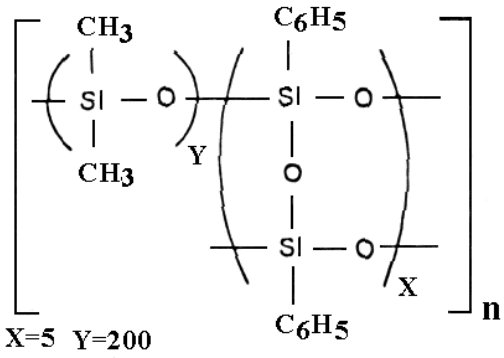


Figure 2. Chemical structure of the PDMS/PPSQ [poli(dimetylsiloxane)/poly(phenylsilsesquioxane)] copolymer.

Recently, composite membranes for gas and vapor separation, coated with different silica-based copolymers and with a thin dense diffusion layer, have been developed (Kaluzhni et al., 1991). We investigated the separation of ethylene and ethane by means of one of these membranes, in which the dense layer was mat from the copolymer PDMS/PPSQ (a polyblock copolymer with a ladder structure, Figure 2). The composite go separation membrane (Figure 3, SEM picture of the cross section of the membrane) coated with this copolymer has a three-layer structure. A porous support made, for instance, from polypropylene provides excellent mechanical properties for the membrane (the thickness of this support layer is about 60 μm). The middle layer is made from fluoroplastic material, for instance, poly(tetrafluoroethylene)/PVDF. This lay has an ultraporous structure 20-30 μm thick. The surface of this layer is coated with a 2-5 μm thick layer of PDMS/PPSQ copolymer. The choice of the membrane material was determined by its excellent mechanical properties, high gas permeability, and solubility in different organic substances, which made the membrane potentially very attractive for the separate of hydrocarbons. Sidorenko (1991) has reported standard productivity (cm^3 (STP)/cm^2 s cmHg) of the membrane for different paraffin's: 4.0*10^{-4} for CH_4, 1.0*10^{-3} for C_2H_6, 2.1*10^{-3} for C_3H_8, and 3.8*10^{-3} for C_4H_{10}.

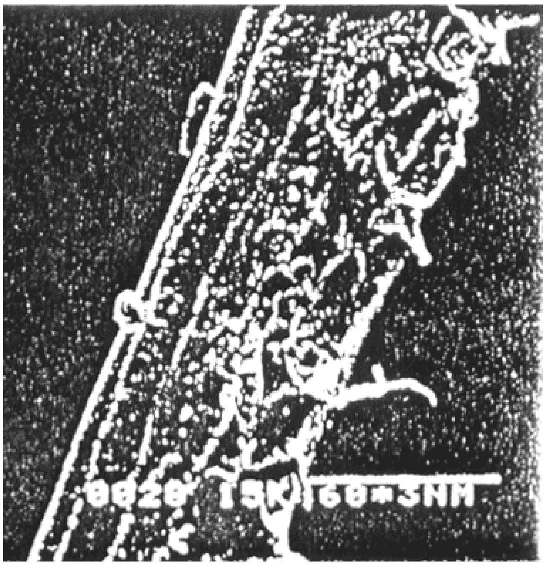


Figure 3. Scanning electron micrograph picture of the cross-section of the membrane.

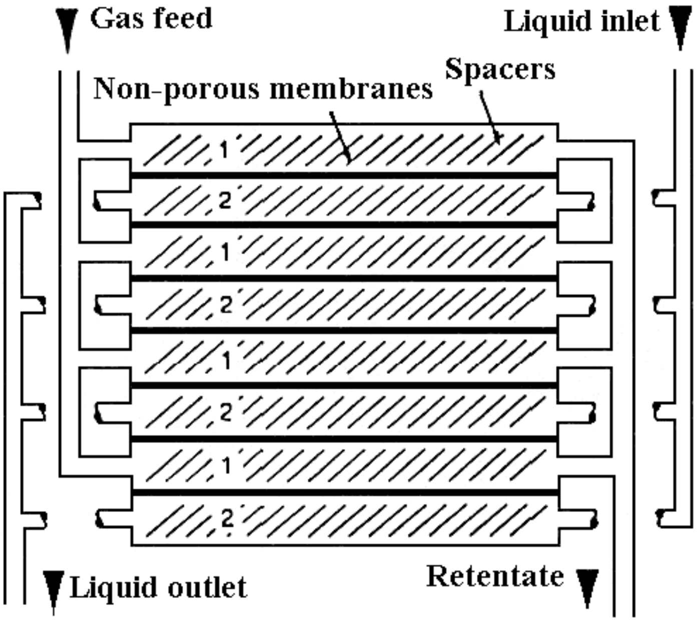


Figure 4. Schematic diagram of the membrane-liquid module: 1, gas channels; 2, liquid channels.

Materials and Experimental Setup. To obtain highest efficiency from the absorber and stripper in the minimum equipment, we used a multimembrane module consisting of 24 chambers as shown in Fig 4. This compact assembly measured 200 mm*150*12 mm, providing a membrane surface area of 0,6 m^2. The thickness of the layer of flowing silver nitrate solution and gas between the membrane was 0.45 mm. Figure 5 a,b shows how the membranes were place the absorber (a) and in the stripper (b).

The membrane module was compressed between two blocks of stainless steel (Figure 6). Each block had two branch pipes (one for the entry and one for the exit of gas or liquid) and nine ports, through which gas (or liquid) was fed to contact the membranes. Turbulence-promoter spacers between the membranes decreased the resistance of the liquid film to gas permeation. We used polymeric netlike turbulence promoters that were stable in silver nitrate solution to enhance mass transfer. The net-type spacers were square-meshed with a two-level structure in which the cross strands were welded on top of the others. The mesh size was 0.42 mm, and the diameter of the strands was 0.22 mm. In these studies, the absorber and stripper modules were set up in circulation mode, and the total surface of the membrane area in the stripper module ranged from 0.57 to 1.14 m^2. A peristaltic pump (Masterflex pump controller, Cole-Parmer Instrument Co.) was used to feed silver nitrate solution into the system. Silver nitrate of analytical grade was obtained from Merck Ltd. Nitrogen was used as a sweep gas in the desorption module. The experimental liquid-membrane system used for separation of olefins is shown in Figure 7.

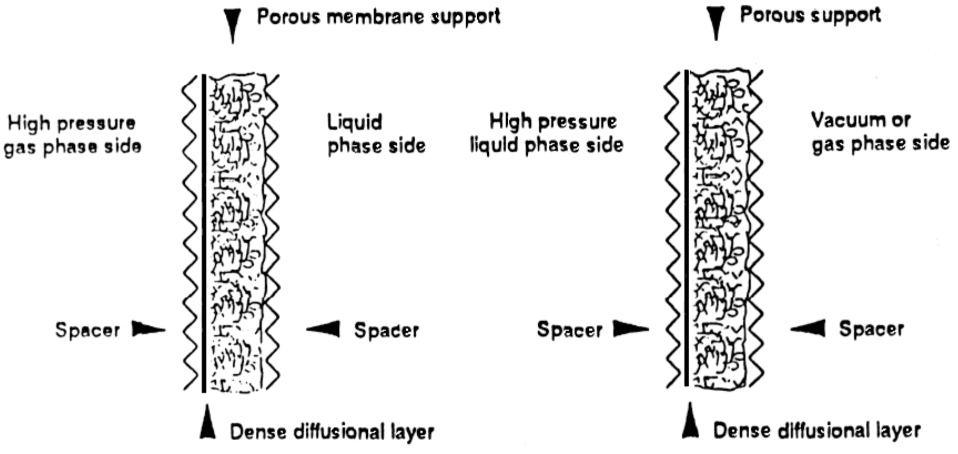


Figure 5. Position of the asymmetric membrane in the (a) absorption and (b) desorption modules.

GC Measurements and Data Analysis. The flow rates of gas and liquid were controlled by rotameters. The temperature of the flowing-liquid absorbent wag observed by means of two thermometers (on the inlets of the absorber and desorber modules). The hydrocarbon concentration in the retentate and desorbate streams was determined with a Varinn gas chromatograph (model 3700) at room temperature. FID and glass capillary alumina oxide-coated columns that were 25 m long were used. The carrier gas was helium. The separation data were recorded by в Hewlett-Packard (3380A) integrator. The initial feed mixture contained 64/36 vol % of ethylene and ethane, respectively, supplied as a mixture in a gas cylinder by Afrox.

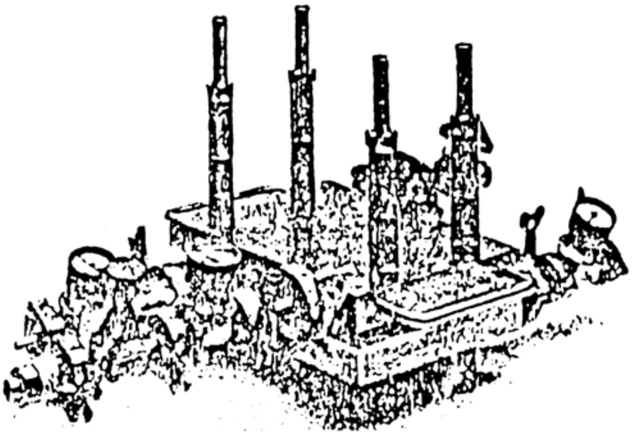


Figure 6. Membrane absorption (desorption) module of the membrane permabsorber.

The productivity Q (cm^3/cm^2 s cmHg) of the membrane desorber (stripper) was calculated using the equation

$$Q = \frac{v\gamma}{A\Delta p} \quad (2)$$

where v is the volume flow rate of the sweep gas, γ is the fraction of the hydrocarbon obtained from the GC calibration curve, A is the total surface area of the membrane, and Δp is the partial pressure difference (here assumed to have the value $\Delta p = 1$ atm because o the rather high nitrogen flow rate). All data in the tables are presented as relative volume percent without consideration of the nitrogen content. Since we used nitrogen as a strip gas in the permeate side of the desorber as a model replacement for vacuum stripping the exiting product stream contained nitrogen. The actual concentration of nitrogen in the exiting gas mixture from the desorber module was varied from 81 to 97 vol %.

The ideal separation factors α_1 [C_2H_6/C_2H_4] and α_2 [C_2H_4/C_2H_6] were calculated in this case with the equation

$$\alpha = \frac{Y_A / Y_B}{X_A / X_B} \quad (3)$$

where Y_a and Y_b are the concentrations of the gas components (A and B) in the desorber stream or in retentate and X_a and X_b are the concentrations of the gas components in the feed.

Results and Discussion

Four series of experiments were conducted. Three are equal-membrane-area mode, and one is non-equal-membrane-area mode.

Equal-Membrane-Area Mode. Three series of experiments were done with membranes of equal surface area in the absorber and in the desorber so that $A_{abs} = A_{des} = 0.57$ m^2. The feed-gas mixture and the sweep gas (N_2) were passed countercurrently to the liquid absorbent in the absorber and in the desorber modules of the permabsorber, respectively. The flow rate of the sweep gas (N_2) was 40 ml/s. The flow rate of the feed, measured at the outlet of the absorber, was constant at 3.2 mL/s. The experimental conditions were as follows. (1) The concentration of the $AgNO_3$ water solution was 15.4 wt %, the temperature of the liquid solution in the desorber module was 45 ^{o}C, and the temperature of the liquid solution in the absorber module was 20 ^{o}C. (2) The concentration of the $AgNO_3$ water solution won 26.7 wt %, and the temperature of the liquid solution in the desorber module was the same as that in the absorber (25 ^oC). (3) The concentration of the $AgNO_3$ water solution was 26.7 wt %, and temperatures of the liquid solution in the desorber module and in the absorber were as they were in series 1.

Table 1 shows the dependence of the productivity and purity of the ethylene in the desorber on the experimental variables (flow rate, concentration, and temperature of the silver nitrate solution).

Non-Equal-Membrane-Area Mode. In these experiments, the membrane area in the desorber was 1.14 m2 and the membrane area in the absorber was 0.57 m^2. The experimental conditions were as follows: (4) The concentration of the $AgNO_3$ water solution was 15.4 wt %, the temperature of the liquid solution in the desorber module was 45 °C, and the temperature of the liquid solution in the absorber module was 20 ^oC.

Table 1. Experimental Parameter of C_2H_4 Separation in the Desorber

Silver nitrate flow rate (mL/s)	Productivity $cm^3(STP)/cm^2$ s*cmHg	CH_4 Vol%	Ideal separation factor, α C_2H_4/C_2H_6	Temperature, °C	
				Absorber	Desorber
Series 1: $A_{abs}=A_{des}=0,57$ m^2, 15,4 wt% $AgNO_3$					
0.8	$4.7*10^{-4}$	98.9	51	59	45
1.8	$4.9*10^{-4}$	96.2	14		
2.5	$4,1*10^{-4}$	96	13.5		
5	$3.1*10^{-4}$	91.2	9		
Series 1: $A_{abs}=A_{des}=0,57$ m^2, 26.7 wt% $AgNO_3$					
0.5	$2.9*10^{-4}$	93	56	25	25
2	$3.1*10^{-4}$	97.6	23		
4	$3.5*10^{-4}$	91.8	10		
5	$2.3*10^{-4}$	91.5	9.6		
Series 1: $A_{abs}=A_{des}=0,57$ m^2, 26.7 wt% $AgNO_3$					
0.5	$4.2*10^{-4}$	99.9	562	20	45
0.8	$8.0*10^{-4}$	99.4	93		
2.5	$6.7*10^{-4}$	97.9	26		
5	$5.8*10^{-4}$	94.8	10		

Table 2 shows the experimental dependencies of the productivity and purity of the ethylene in the desorber on the silver nitrate solution flow rate. Table 2 shows that there was no maximum productivity of the system for the range of liquid-flow rates used. The purity of ethylene also decreased with an increase in the liquid-flow rate.

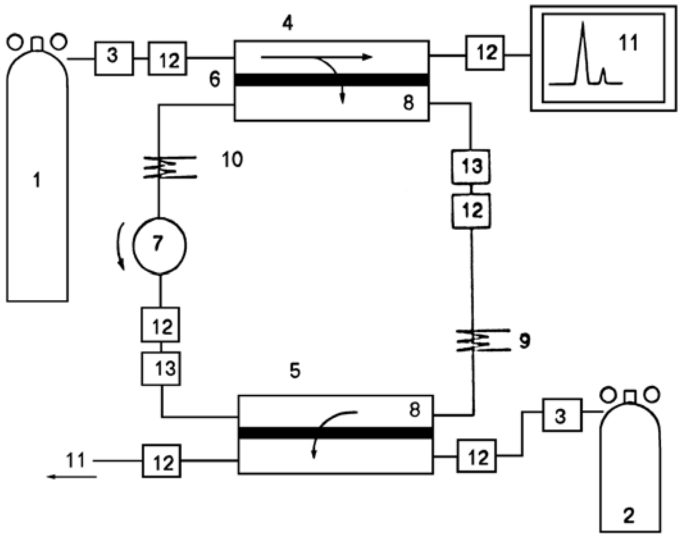


Figure 7. Diagram of the experimental setup for C_2H_4/C_2H_6 separation: 1, gas cylinder with the feed; 2, gas cylinder with the sweep gas (nitrogen), 3. gas regulators; 4, membrane absorber; 5, membrane desorber (stripper); 6, polymeric membranes; 7, peristaltic pump; 8, flowing-liquid absorbent; 9, heating; 10, cooling; 11, gas chromatograph; 12, rotameters; 13, thermometers.

The absence of a maximum productivity in the desorber in this mode of operation may be explained by the greater efficiency of the degassing processes in the desorber. The data in Table 1 show that the productivity increased with an increase in the temperature of the liquid flowing in the desorber module. Table 1 shows that in all cases, the maximum productivity depended upon the flow rate of the solution of silver nitrate. In all cases, the purity of the ethylene decreased with an increase in the flow rate of the liquid solution. The maximum of the separation factor was near the low values of the solution-flow rates. The same results were obtained in a study CO_2/CH_4 separation by means of a membrane permeabsorber (Shelekhin and Beckman, 1992) containing flowing monoethanolamine solutions.

Table 1 shows that the efficiency of the separation factor increased with an increase in the concentration of silver nitrate in the solution. It is reasonable to expect an increase in selectivity, if the concentration of the selective complex reagent increases. It is a well-known phenomenon that the solubility coefficient of C_2H_6 decreases in ionic solutions because of the salting-out effect; therefore, the increase in separation efficiency is determined by two factors acting in opposite directions. This interesting solution arises, accompanying the determination of the optimal concentration of the silver nitrate in such a system. One may assume that the further increase in the concentration of the silver ions in the solution would determine the low solubility of C_2H_6.

Table 2. Experimental Parameters of C_2H_4 Separation in the Desorber

Silver nitrate flow rate (mL/s)	Productivity cm^3(STP)/cm^2 s*cmHg	C_2H_4 Vol%	Ideal separation factor, α C_2H_4/C_2H_6	Temperature, °C	
				Absorber	Desorber
0.5	1.7*10-4	99.8	280	20	45
1.5	2.5*10-4	99.6	140		
2.5	2.6*10-4	99.1	62		
5	3.0*10-4	97.9	26		
8	3.3*10-4	96.5	15.5		

Model of Mass Transfer. When the diffusion of gas through the membrane is in the steady state, the mass balance describing the performance of the membrane permabsorber/stripper system for single gas A can be represented by the following dimensionless equations (Shelekhin and Beckman, 1992; Beckman, 1994):

$$\theta_a \frac{d\Psi_{la}}{d\xi} = 1 - \Psi_{La} \quad 0 \le \xi \le 1 \tag{4a}$$

$$\theta_d \frac{d\Psi_{ld}}{d\xi} = -\Psi_{Ld} \quad 1 \le \xi \le \eta \tag{4b}$$

where

$$\Psi_{La} = C_{La}/C_0 \tag{5a}$$

$$\Psi_{Ld} = C_{Ld}/C_0 \tag{5b}$$

$$\theta_a = \frac{S_L \Omega}{Q_{Ma} A_{Ma}} \tag{6a}$$

$$\theta_d = \frac{S_L \Omega}{Q_{Md} A_{Md}} \tag{6b}$$

$$C_0 = Smp_0 \tag{7c}$$

The analytical solutions of the ordinary differential equations (4a,b) with the boundary conditions for the circulation mode

$$C_{La(\xi=1)} = C_{Ld(\xi=1)},\ C_{La(\xi=0)} = C_{Ld(\xi=\eta)}$$

lead to the following limits for the separation factor (a) for gases A and B:

$$\lim_{\Omega \to 0} \alpha = \frac{S_L^A}{S_L^B} \tag{8}$$

$$\lim_{\Omega \to \infty} \alpha = \frac{Q_M^A}{S_M^B} \tag{9}$$

The limit (8) for the low flow rate of the liquid shows that the efficiency of the separation process is determined by the selectivity of the absorption liquid. The limit (9) for the high flow rate of the liquid shows that the efficiency of the separation process is determined by the selectivity of the membrane. This simple phenomenological analysis may explain our experimental results; a higher separation factor corresponds to the lower liquid-flow rate and vice versa. This means that at low rates of flow of liquid absorbent, the selectivity of the process is determined by the properties of the selective liquid absorbent, whereas at high rates of flow of absorbent, the system operates as a simple membrane module.

The same simple theoretical analysis can be used to explain the increase of productivity that accompanies the increase of the volumetric flow rate of the liquid. As expected from the theoretical analysis, in our experiments, an increase in absorbent flow rate caused an increase in the permeation rates for both C_2H_4 and C_2H_6 while the selectivity decreased simultaneously (Tables 1 and 2).

Even though this plug-flow model of mass transfer in the membrane permabsorber is very simple and does not take into account reversible chemical complexation between gas and liquid or resistance to mass transfer of the liquid film, both of which occurred in this study, it predicts the main features of the system and explains some experimental results. At the same time, the model does not explain the maximum productivity upon the liquid-flow rate.

Bessarabov and Beckman (1993a,b) and Bessarabov et al. (1994b) have proposed a system of differential equations which has an analytical solution and considers reversible chemical complexation of the gas component and the liquid:

$$A+C \underset{k_2}{\overset{k_1}{\rightleftarrows}} AC$$

The mass balance equations for the absorber module can be written as

$$\Omega L\frac{dC_L^A}{dy}=\frac{DA}{lS_L}\left(C_g^A S_L-C_L^A S_m\right)-V\left(k_1^* C_L^A-k_2 C_L^{AC}\right) \qquad (10a)$$

$$\Omega L\frac{dC_L^{AC}}{dy}=V\left(k_1^* C_L^A-k_2 C_L^{AC}\right)$$

where $k_1{*}=k_1C_L^C$.

An analogous system of equations can be written for the desorber module. The boundary conditions for the circulation mode are as follows:

$$C^A_{Ld(y=L)}=C^A_{La(y=L)};\quad C^{AC}_{Ld(y=L)}=C^{AC}_{La(y=L)};\quad C^A_{Ld(y=L+d)}=C^A_{La(y=0)};\quad C^{AC}_{Ld(y=L+Ld)}=C^{AC}_{La(y=0)}$$
(11)

The system of the differential equations (10 a,b) assumes that the feed composition does not change in the channels of the absorption module. This is reasonable when pure feed gas is used. However, the composition of the gas usually changes in the module, and this may influence both productivity and selectivity. If the feed composition changes in the channels of the absorption module with permeable membranes, it is necessary to consider a feed pressure drop and a change in the flow rate along the channels (Olson, 1949; Berman, 1953; Pan, 1983). In order to take this into account, it is necessary to add a phenomenological equation for the feed-gas composition with necessary boundary conditions to the system of equations (l0 a.b). This equation could be written as follows:

$$\Omega_g L\frac{dC_g^A}{dy}=-\frac{DA}{lS_L}\left(C_g^A S_L-C_L^A S_m\right)-C_g^A L\frac{d\Omega_g}{dy} \qquad (10c)$$

In that case, the system (10a-c) of the phenomenological equations requires additional equations which considerably complicate the process of obtaining an analytical solution. Since we assume that complete degassing takes place in the desorption module, i.e. $C^A_{gd(y=Ld)}=C^A_{gd(y=L+Ld)}=0$, it is possible to use equations (10 a,b) for the qualitative estimation of the separation parameters in the stripper.

Two different modes of operation of the membrane permabsorber, namely, continuous-flow and circulation-flow modes, were reported by Shelekhin and Beckman (1992). It was shown that the maximum of desorber productivity (Q_d) at certain liquid-flow rates could appear if the system was operated in the continuous-flow mode. The difference between the continuous-flow and circulation-flow modes is expressed by the boundary conditions. The boundary conditions for the continuous-flow mode of operation are as follows:

$$C^{A}_{Ld(y=L)} = C^{A}_{La(y=L)};\; C^{AC}_{Ld(y=L)} = C^{AC}_{La(y=L)};\; C^{A}_{La(y=0)} = 0;\; C^{AC}_{La(y=0)} = 0 \qquad (12)$$

The same boundary conditions could be used for the system (10a,b) for the circulation mode of operation of the membrane permabsorber if we assume that complete degassing of the liquid absorbent takes place in the stripper. In other words, the liquid absorbent exiting stripper does not contain dissolved gas. In that case, the so-called “quasicirculation mode” can be realized (Bessarabov and Beckman, 1993b). This assumtion may explain the observed maximum of productivi in the desorber. The maximum of productivity in the desorber in the non-equal-membrane-area mode operation may be shifted to a higher liquid-flow rate range and cannot be observed at the given range oft flow rates. The rate constants of the reversible reaction between gas and the liquid carrier also limit the efficiency of the degassing process in the desorber.

We shall discuss this system of equations (10 a-c) a their analytical solution in detail in our next papier. Nevertheless, it is useful to mention here that the analytical solution of these’ systems for an over transfer rate (Q_d) of gas A in the desorber with the experimental variables can give maximum values under certain conditions, which may explain the experimentally observed productivity maximum at certain liquid flow rates and total membrane area.

Module Stability and Water Content in Ethelene. Nitrogen was used as a strip gas in our separation experiments. It is possible to apply a vacuum in the permeate side of the desorber to enhance separation efficiency. In that case, the problem of module stabilities may arise. It was shown (Bessarabov et al., 1994c) that the performance of the module was stable when the vacuum of -1050 mbar was applied in the permeate side of the desorber.

The silver nitrate solution in the system did the change color over a period of three weeks, and the separation process was stable for the same period time. Our experiments show that the overall productivity of the stripper increased with the increase in temperature of the silver nitrate solution loaded ethylene. Therefore, to enhance the separation efficiency, it is necessary to maintain a temperature gradient in the silver nitrate solution in the system this case, the problem of pervaporation of water in product stream arises. The significant amount of water was determined at 55 °C in the outlets of the desorber. We did not measure water content quantitatively at the temperature. In the case of the “cool” (25-35 °C) liquid absorbent flowing in the system, the purified ethyl did not contain a significant amount of water that was detected by means of a cooling trap. Since the production of the separation could not be considered as water-free, additional measurements have been done.

In order to estimate the water content in the desorption stream, the transfer rate of water vapor through composite PDMS/PPSQ membrane has been measured by means of additional vacuum pervaporation experiments. Distilled water with a conductivity of $4.0 * 10^{-6}$ S/cm was used in the experiments. A leakage-experimental cell containing a membrane sample with a membrane area of 37 cm^2 was used. The temperature of the water was 38 °C in all the experiments. Distillate water circulated in the pervaporation cell along dense side of the composite membrane under non-pressure. The flow rates of water ranged from 0. 2.0 mL/s. The vacuum of -1050 mbar was maintain in the permeate side of the cell. The permeate site the cell was connected with a trap that was cooled liquid nitrogen. These pervaporation experiment lowed for the determination of the water vapor productivity of $6.3 * 10^{-6}$ g/cm^2 s under the given pressure difference and temperature. Additionally, the humidly of the nitrogen, exiting the desorber module circulating distilled water, was measured by means a dew point hygrometer (EG&G, model 880). The point was +25 °C under the given condition, showing saturation of nitrogen with water vapors. These experiments showed that the water vapor permeation through the nonporous membranes in such a system limits the purity of the products and the temperature that could be applied in the desorber module. The permeability of the vapor of an absorbent in membranes should be taken into account in such systems. The condensation of the water vapor in the system may decrease the effective membrane area and therefore decrease the productivity.

As for the retentate composition, measurements at rather low feed-flow rates measured at the outlet of the absorber (3.2 ml/s) showed that under the given conditions, the retentate contained from 99.6 to 99.8 vol % of ethane and did not depend strongly on the above-mentioned concentrations of silver nitrate and flow rates of the solution or on the temperature differences in the absorber and desorber. The separation factor in the absorber module ranged from 443 to 887. The same dependence of the retentate upon the liquid flow rate was shown by Shelekhin and Beckman (1992).

Estimation of the Liquid Boundary Layer Resistance. The results show that the overall mass transfer rate of the liquid-membrane system is near that of the single PDMS/PPSQ membrane if we assume that the productivity of ethylene is approximately the same as that of ethane with the PDMS/PPSQ membrane. The data for ethylene separation obtained by means of the PDMS/PPSQ-coated membranes and flowing-water solutions of silver nitrate present an interesting means for the estimation of the resistance to transport by the boundary liquid layer. The overall transport resistance of the membrane ($1/K_{OV}$) is given by the sum of membrane resistance ($1/K_M$), gas phase resistance ($1/K_G$), and resistance of the boundary liquid layer ($1/K_L$)

$$\frac{1}{K_{OV}}=\frac{1}{K_G}+\frac{1}{K_M}+\frac{1}{mEK_L} \qquad (13)$$

The mass transfer coefficients of the gas and liquid phases, $1/K_G$ and $1/K_L$, are determined by convection and diffusion. The mass transfer coefficient of the membrane depends on the structure of the membrane. E is the enhancement factor, which can be defined as the effect of the chemical reaction on the absorption; m is the distributional coefficient (Kreulen, 1993).

It is assumed that the effect of the gas phase resistance is negligible because of the presence of the turbulence-promoter spacers in the gas phase of the system. In this case, $1/K_{ov}$ is given by

$$\frac{1}{K_{OV}}=\frac{1}{K_M}+\frac{1}{mEK_L} \qquad (14)$$

The influence of the liquid-film resistance to gas transport can be estimated by means of the following equation (Yasuda ct al., 1972)

$$\frac{1}{Q_{OV}}=\frac{1}{Q_L}+\frac{1}{Q_M} \qquad (15)$$

where Q is the productivity (cm^3 (STP)/cm^2 s cmHg). This equation can be used if the membrane absorber and stripper arc operated in the steady state in the circulation mode. In our studies, all measurements were done at different liquid-flow rates when the steady state of operation was detected in the stripper or absorber.

By using the minimum data from Table 1 for desorber productivity and data for the productivity of the membrane for ethane (Sidorenko, 1991), we can calculate that the liquid-film resistance can be 50% of the transport resistance.

We did not determine specifically the influence of the spacers on the mass transfer in the membrane perm-absorber. It is believed that the presence of the spacers allowed gas and liquid phases to be well-mixed. It is important to mention here that the same membrane system with the PVTMS asymmetric membrane was evaluated for bubble-free oxygenation and low-temperature deoxygenating of water (Bessarabov et al., 1994b,c). It was shown that the overall mass transfer coefficients were strongly dependent on the water-flow rate.

Use of Pure Water as я Liquid Absorbent. To estimate the influence of the enhancement factor E of the chemical reaction on the efficiency of the process, ethylene and ethane were separated from the mixture by using pure water as the absorption liquid. The experimental conditions were as follows: The temperatures of the water in the desorber and absorber modules were 45 and 20 ^{o}C, respectively. The flow rates of water ranged from 0.5 to 2.5 mL/s. The productivity measured on a water-flow rate of 1.0 mL/s was $3.5*10^{-6}$ cm^3 (STPVcm^2 s cmHg with a value of selectivity [C_2H_4/C_2H_6] of 1.5. In this case, liquid-film resistance comprised more than 90% of the transport resistance to gas permeation.

Comparison of the experimental data shows that the mass transfer in such a system takes place with a minimum of liquid-film resistance if the absorption is accompanied by a fast chemical reaction. The tables show that it is possible to vary the efficiency of the separation process by varying the flow rate of the liquid absorbent, the temperature of the liquid, and the concentration of the selective carrier in the liquid.

Conclusions

Evaluation of the new configuration for a membrane permabsorber for ethylene/ethane separation using nonporous gas-separation flat-sheet asymmetric composite membranes with a diffusional layer made of PDMS/PPSQ block «polymer with water solutions of the silver nitrate flowing along turbulence-promoter spacers between membranes led to the following conclusions. The membrane permabsorber permitted separation for both the components of the feed, retentate and desorbate, simultaneously. The efficiency of the separation process variables can be changed by altering the liquid-flow rate, the concentration of the selective carrier in the liquid, the temperature of the liquid absorbent, and the total membrane area. The pervaporation of water through the nonporous membranes limits the purity of the products at a high temperature range.

Acknowledgment

The asymmetric composite gas-separation membranes with a trade name “LESTOSIL” were used in this work. These membranes were kindly provided by Dr. S. I.” Semenova (NPO Polymersintez) whose present address is Yokohama National University, Department of Material Science & Chemical Engineering, Yokohama 240, Japan.

Nomenclature

A = membrane area, m^2
C = concentration, cm^3 (STP)/cm^3
D = diffusion coefficient, cm^2/s
E = enhancement factor
K = mass transfer coefficient, cm/s
k_1 - rate constant, C^{-1} t^{-1}, where C is concentration, t is time
k_2 = rate constant, t^{-1}
h = length, cm
l = membrane thickness, cm
m = distribution coefficient
p_0 = pressure, cmHg
Q = productivity, cm^3 (STP)/cm^2 s cmHg
S = solubility coefficient s m^3 (STP)/cm^3 cmHg
V — volume, cm^3
y = coordinate along membrane

Greek Symbols
α = separation factor
Ω = liquid-flow rate, cm^3/s
Ω_g = feed-gas flow rate, cm^3/s
Ψ = dimensionless concentration
θ - dimensionless parameter
ξ = dimensionless distance ,
v = gas flow rate, cm^3/s

Superscripts
A, B = components of gas mixture
C = selective carrier
AC = reversible complex of gas A with carrier C

Subscripts
a = absorber
d = desorber
g=gas
L = liquid
M = membrane
OV = overall

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