Mechanism of Gases Transfer through Polymer Membranes and Membrane Module Calculation Model to Separate Gases

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Abstract

The given work considers gas separation process using non-porous polymer membranes. Here membrane separation of gas mixtures is based on employment of permeation-selective membranes and gases transfer mechanism through non-porous membranes has been considered. Approximate method of membrane module calculation to separate gases considering binary gas mixture, which consists of two components, has been suggested as well. As a result of the suggested methods membrane surface necessary to separate gas mixture has been found.

Keywords: polymer membrane, permeate composition, permeability, retentate, gas concentration, membrane surface.

1. Introduction

In these latter days, interest to the development of new constructions of bioenergy installations for processing organic wastes in the terms of anaerobic fermentation to produce gaseous fuel and organic fertilizers in the process of methane fermentation is growing.

Membrane technologies, having a range of advantages allow extracting the fixed component from gas mixture qualitatively, using membrane absorption in counter flow mode between liquid and gas phases of separated membranes in membrane contactor. Furthermore, membrane methods are mainly cheaper and ecologically pure.

At present membrane separation is one of the most intensively developing branches of gas separation technology. While choosing separation process to solve issues, it is necessary to take into account the impact of possible factors, employment of which is available not in all particular situations, therefore one cannot disregard specific criteria, the substantiated choice of the process should meet.

Polymer membranes, possessing high coefficient of diffusion, are not suitable for separating full, condensable gases or vapour of organic substances from permanent gases, for instance, while removing easily volatile organic components from air or evolution of higher hydrocarbons from natural gas [1]. When solving such problems in many cases it is necessary to remove small amount of great organic penetrants (easily volatile organic components or higher hydrocarbons) from mixtures with fixed gases (by air or methane). To decrease necessary area of membranes (that is, capital expenditures) and expenditures for compressing (that is, operating expenditures) membranes are required, which would be mainly permeable for gross molecules of organic vapours and practically impermeable for molecules of fixed gases. Membranes, produced from glasslike polymers are more permeable, for ‘small’ molecules of fixed gases and less permeable for ‘gross’ molecules of organic vapours that makes them useless for solving the given problems. And on the contrary, permeability of higher hydrocarbons (for instance,
propane) through rubber-like polymers is higher than for fixed gases (oxygen, nitrogen). Thus, to solve such problems as a material for membranes one ought to employ rubber like polymer materials.

2. Statement of the Problem

Usually, polymers permeability depends on working conditions, for instance, on pressure, temperature or composition of separated mixture. Let’s consider the influence of these factors on permeability coefficients, as well as coefficients of diffusion and solubility. If diffusion coefficient doesn’t depend on the concentration, and for solubility Henry’s law is realized, permeability doesn’t depend on pressure, that is flow through membrane is directly proportional to general pressure drop regardless of the value of pressure of initial mixture and permeate.

At sufficiently low pressures, the influence of penetrants on permeability coefficient is defined by dependence of coefficients penetrants properties of diffusion and solubility. With the increase of pressure, it is necessary to take into consideration the kind of sorption isotherms, concentration dependence of diffusion coefficients, and in some instances, the character of interaction of components of separated mixtures.

Selectivity of mixture separation in membrane will be defined only by diffusion factor:

$$\alpha_{ij} = \frac{M_i}{M_j}$$

where $M_i$ and $M_j$ – molecular masses of the components $i$ and $j$ correspondingly. Therefore at that it is usually impossible to achieve high degrees of separation. To get higher degree of separation cascades, consisting of several membrane modules connected among themselves should be used.

At the presence of pores of transit size in membranes, various mechanisms of transfer will be observed simultaneously. Then gas transfer through membrane can occur at the expense of both Knudsen diffusion and viscous transfer and common diffusion in pores. As a consequence, membranes will increase, but selectivity, on the contrary, will decrease. Nonporous polymer membranes can possess higher selectivity[2].

Let’s consider the mechanism of gases transfer through nonporous membranes. Diffusion of dissolved substance in the membrane is the only mechanism of transfer. Gas molecules, coming onto the membrane surface, are sorbed by this surface and dissolve. Solubility of gases in elastomers is very low. Usually Henry’s law can be used to describe solubility in amorphous highly elastic materials:

$$c = Sp$$

Here $c$ – component concentration; $p$ – its partial pressure in gaseous phase; $S$ – solubility coefficient, depending only on temperature. At increased pressures, exceeding 0,1 MPa (1 atm), for some gases at their solubility in rubbers significant deviations from this law can be observed. Henry’s law cannot be used to describe solubility of organic vapours. This law, as a rule, is also not realized at temperatures lower than glass-transition temperature. Gas diffusion in polymer is described by Fick’s first law:

$$J = -D \frac{dc}{dx}$$

Here $J$ – flow through membrane; $D$ – diffusion coefficient; $\frac{dc}{dx}$ – concentration gradient. Diffusion coefficients of various gases in polymers decrease at increasing of molecules quantity. As it is above said, solubility of gases in polymers is usually considerably low. In these conditions, diffusion coefficient practically doesn’t depend on concentration, and diffusion of various components of gas mixture flows independently. Diffusion coefficients of comparatively large organic molecules, causing polymers swelling can be comparably great. With the increase of concentration in this case diffusion coefficients usually rise.

Integration of differential equation (3) for flat membranes in the case of steady-state process gives:

$$J = \frac{D(c^l - c'^l)}{l}$$

Here $c^l$ and $c'^l$ – concentration of permeating gas through membrane at the entry to the membrane and at the output from it (at the boundaries of selective layer of membrane in the case of asymmetric and composition membranes); $l$ – membrane thickness (thickness of selective layer). Concentration can be expressed through partial pressure of the component with the help of Henry’s law. Eventually, we will get:
Thus, in the being considered case permeability equals to the product of coefficients of diffusion and solubility:

\[ \Pi = DS \]  

Selectivity of separation process of components \(i\) and \(j\) of the mixture in these conditions is defined by the ideal factor of separation:

\[ \alpha_{ij} = \frac{\Lambda_i}{\Lambda_j} = \frac{D_i}{D_j} \cdot \frac{S_i}{S_j} \]  

Permeability coefficient \(\Lambda\) can be defined by experimental way. According to numerical values of permeability coefficients of various gases one can judge whether membrane from the given material for separating one or another gas mixture is applicable.

Membrane separation of gas mixtures is based on employing permeation-selective membranes. A membrane element is the least cell of membrane mass transfer unit. Usually a membrane is a tough partition, dividing a membrane element into two operating areas. In these areas, delivery and drainage channels, various pressures and mixture compositions are maintained. From delivery channel through permeation-selective membranes all components of mixture permeate, but with different rates. The type of a membrane element is defined by the geometry of membrane surface and the scheme of gas flow motion arranging. As for carrying out liquid-phase processes, devices with flat membrane elements, tubular membrane elements, roll membrane elements as well as devices with hollow fibers are used. Schemes of flows motion arranging can be direct- and counter flow, with cross flow, with recycle of separated mixture and etc[3].

As a result of the fact, that various components permeate through membrane with different rate, mixture, coming into delivery channel, is enriched by hardly permeable components and removed from it. The mixture, enriched by components, permeating through membrane with high rate is discharged from drainage channel. Membranes for gas separation can have homogeneous structure, but asymmetric and composition membranes are used more frequently. Such membranes have thin selective layer and porous substrate, at that basic resistance to mass transfer is focused in selective layer of the membrane. Usually it is assumed that density of the flow of \(i\)-component of the mixture \(J_i\) through the membrane linearly depends on difference of partial pressures of this component above and under the membrane:

\[ J_i = \Lambda_i \frac{(p^i - p^i//)}{l} \]  

Here \(p^i\) and \(p^i//\) – partial pressures of the component near the membrane surface in delivery and drainage channels correspondingly; \(l\) – thickness of selective layer of the membrane; \(\Lambda_i\) – permeability coefficient, numerically equals to density of component flow at the value of gradient of partial pressure, equal to a unit. It is assumed that resistance to mass transfer in porous substrate can be ignored[4,6].

Separating power of the membrane can be characterized with the help of membrane separation factor:

\[ \alpha_{ij} = \frac{\Lambda_i}{\Lambda_j} \]  

Correlation of permeability \(\Lambda_i\) and \(\Lambda_j\) of pure gases \(\alpha_{ij}\) is called an ideal factor of separation.

Separation of some gas mixtures, permeabilities of components of which are essentially differed, can be realized with the help of highly permeable membranes. But if selectivity is insufficient, it is necessary to use glass like polymers with lower permeabilities for separating. As the equation shows (5), the rate of gas transfer through the membrane is inversely proportional to membrane thickness. Therefore, to increase rate of the process, efficient thickness of the membrane should be decreased.
3. Results

Let’s consider binary gas mixture, consisting of two components $i$ and $j$, which permeate through the membrane under the effect of difference of pressures $p' - p''$. Here $p'$ – gas pressure in delivery channel, $p''$ – in drainage channel. Driving force for separation process can be created or by compressing initial gas mixture with the help of compressor, or maintaining low pressure on the part of permeate with the help of vacuum pump (Fig. 1).

Simple equations can help to calculate membrane surface, necessary for gas separation.

While calculating it is usually assumed that basic resistance to mass transfer is focused in the membrane. In other words, component concentration gradient in gaseous phase, both on the part of high pressure and on the part of low one is negligible in comparison with concentration gradient in the membrane. It is explained by the fact that diffusion coefficients of permeating components in gaseous phase are higher than diffusion coefficients in the membrane. Concentration gradient in porous substrate of the membrane is also low. Besides, it is assumed that permeability coefficients of each of the components don’t depend on pressure and concentration. In other words, each of components diffuses through the membrane regardless of another one under the effect of its own concentrations gradient. We will consider that the gradient of gas pressures both in delivery one and in drainage channels can be neglected. We will assume that the component $i$ is more permeable than the component $j$.

We will define a problem on gas separation process calculation. Let’s assume that the composition of gas mixture, fed into membrane module, is known. Let’s denote molar fraction of easily permeating component through the membrane in this mixture through $x_f$. In addition, one of expenditures is known, for instance expenditure of retentate $q_r$, and composition of one of products (for instance, retentate). Molar fraction of the component $i$ in the retentate will be denoted through $x_r$. Pressures in delivery and drainage channels will be considered as known too. While calculating it is necessary to know some characteristics of the membrane. Permeability coefficient of easily permeating component $\Lambda_i$, separation factor $\alpha_{ij}$, and thickness of active layer of the membrane $l$ are known as well.

The important characteristic of membrane separation process is a share of initial mixture flow, passing through the membrane:

$$\theta = \frac{q_p}{q_f}$$  \hspace{1cm} (1)

Here $q_f$ and $q_p$ – molar expenditures of initial mixture and permeate. This quantity is usually called division coefficient of initial mixture flow. Flow division coefficient changes from 0 to 1 and defines economical efficiency of the process. While designing industrial membrane processes, as a rule, one strives for providing great values of this quantity as far as possible. With the increase of $q$ the degree of enrichment of the flow with easily permeating component decreases as a result of decrease of driving force of the process. Extraction degree of target component for binary mixture is defined as ratio of number of this component, leaving for a unit of time membrane module with the flow of permeate, and number of component, coming into the module for a unit of time with initial mixture:

$$\varphi = \frac{y_p q_p}{y_f q_f} = \theta \frac{y_p}{x_f}$$  \hspace{1cm} (2)

Here $y_p$ – molar fraction of the component $i$ in permeate.
Let’s denote concentrations (molar fractions) of the component $i$ in delivery and drainage channels correspondingly through $x$ and $y$. These concentrations change along the length of channel. Then equations, describing transfer of components through membrane surface, can be written in the following way:

$$J_i = \frac{\Lambda_i (p^i x - p^i y)}{l}$$  \hspace{1cm} (3) $$J_i = \frac{\Lambda_i [(p^i (1-x) - p^i (1-y))]}{l}$$  \hspace{1cm} (4)

It is necessary to add equations of material balance of membrane module to these equations:

$$q_f = q_p + q_r$$ \hspace{1cm} (5) $$q_{f,x} = q_p y_p + q_{r,x}$$ \hspace{1cm} (6)

Let’s assume that expenditure of initial gas mixture, delivered for separation essentially exceeds permeate expenditure[5]. In this case, change of mixture composition in delivery channel can be ignored, that is it is to be considered that compositions of initial mixture $x_f$ and retentate $x$, are roughly identical and equal to $x$. Molar fraction of the component $i$ in drainage channel $y$ in this case doesn’t change along the length of the channel and equals to $y_p$. The number of the component $i$, permeated through the membrane, can be presented as:

$$Q_i = A J_i = q_p y$$ \hspace{1cm} (7)

Here $A$—quantity of membrane surface. The number of the component $j$, permeated through the membrane, equals to:

$$Q_j = A J_j = q_p (1-y)$$ \hspace{1cm} (8)

Consequently, concentrations $x$ and $y$ are connected among themselves by the correlation:

$$y = \frac{\alpha (x - \varphi y)}{(1-x) - \varphi (1-y)}$$ \hspace{1cm} (9)

Here $\alpha = \frac{\Lambda_j}{\Lambda_i}$—division factor; $\varphi = \frac{p^i}{p}$—pressures ratio in drainage and delivery channels. The equation (9) is quadratic equation relatively $y$, solution of which is as following:

$$y = \frac{1}{2} \left( \frac{\alpha - 1}{\alpha - 1} \left( \frac{\varphi + x + 1}{\varphi - 1} \right) + \left[ \left( \frac{\alpha - 1}{\alpha - 1} \left( \frac{\varphi + x + 1}{\varphi - 1} \right) \right]^2 - \frac{4 \alpha x}{(\alpha - 1) \varphi} \right]^{1/2} \right)$$ \hspace{1cm} (10)

Fig. 2. Dependence of the permeate composition on division factors $\alpha$ various values $\varphi$.

From two solutions of quadratic equations, physical meaning has the solution, which corresponds to the symbol «minus» before square root. This expression is sufficiently lengthy, but weighty conclusion can be drawn from it. According to (10), permeate composition depends on ratio of pressures on various parts from membrane, but not on their difference.
Fig. 2 shows dependence of permeate composition \( y \) on division factor \( \alpha \) at various values \( \varphi \) and fixed value \( x \), built with the help of the formula (10). Such dependences can define what division factor of membrane should be so that permeate of the fixed composition at single stage division of mixture can be got, if correlation of pressures is specified. The same correlation can serve to find the value \( \varphi \), necessary to get permeate of the given composition, if division factor is known.

Compositions of initial mixture and retentate differ. For this reason instead of the composition of initial mixture in equation (10) for approximate calculations, it is suggested [6] to use logarithmic average value of concentration in delivery channel:

\[
\ln \left( \frac{x_f}{x_r} \right)
\]

Substituting this value in equation (10), we will define permeate composition. Then from equations of material balance, we will find initial mixture, delivered for separation, and permeate:

\[
q_f = q_r \frac{y - x_r}{y - x_f}
\]

\[
q_p = q_r \frac{x_f - x_r}{y - x_f}
\]

Membrane surface necessary for mixture separation can be then calculated with the help of equations (3), (4):

\[
A = \frac{yq_p}{\Lambda_r (p \frac{x}{x} - p \frac{y}{y})}
\]

In this correlation, value \( \chi \) is calculated by the formula (11).

4. Conclusions

The method presented here can be used for engineering calculations. If concentration of initial mixture and retentate essentially differ, calculation error can be too great. In this case, it is suggested to divide membrane module into elements conventionally, in each of which concentration in delivery channel changes not more than twice. The calculation is carried out sequentially for all elements. If the given expenditure is retentate expenditure, calculation should be begun with the last element [7].

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