Separation Devices for Gas Mixing

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When two fluid streams with different compositions mix, a significant amount of exergy is lost. Utilizing the mixing exergy of gaseous streams of different compositions can reduce equipment cost and energy consumption as well as generate electric power. Suitable modification of known separation processes such as distillation, membranes, adsorption, and absorption to convert them into efficient mixing processes is discussed in detail. Mixing may also be combined with a separation process such that the same device is used for both purposes which results in the use of the mixing exergy. This combined separation/mixing process is a single and relatively simple device with efficiencies not typically attainable in the generally used two-step method of separation followed by mixing. For such applications, some interesting results are presented for the processes using membrane, adsorption and absorption devices.

Introduction

In the chemical processing industries, and also in nature, fluids of dissimilar compositions are quite commonly mixed. While a larger volume of chemical engineering literature is devoted to increasing the energy efficiency of separation processes, systematic discussion on how to save/generate energy when the mixing of streams of different compositions takes place seems to be scarce. The objective of this article is to present a broad framework for such mixing applications utilizing the separation devices employed for separation processes such as distillation, membrane, adsorption, and absorption.

The exergy or availability of a stream is its potential to perform work with reference to an environment. Exergy is a thermodynamic state function; it is the maximum amount of work that can be derived from a stream when it is brought from its existing state to the reference state by a reversible process. The exergy of a stream can be divided into a physical component and a chemical component (Kotas, 1985). The physical component of exergy is the exergy required to take a process stream from ambient conditions T_0 and P_0 to the actual stream temperature and pressure, and can be further subdivided into the thermal component of exergy, E^T, and the pressure component of exergy, E^P. These components are given by:

$$E^T = (H - T_0 S)_{\text{at } T,P} - (H - T_0 S)_{\text{at } T_0,P} \tag{1}$$

$$E^P = (H - T_0 S)_{\text{at } T_0,P} - (H - T_0 S)_{\text{at } T_0,P_0}, \tag{2}$$

where H and S are the enthalpy and entropy of the process stream, respectively.

In this article, for simplicity, cases that do not entail chemical reaction are considered. For such cases the chemical component of exergy of a multicomponent process stream is simply the exergy due to mixing, E^m. The effect of mixing at T_0 and P_0, E^m, is the difference in the free energy of the process stream to pure components:

$$E^m = (H - T_0 S)_{\text{at } T_0,P_0} - \sum_i N_i (H_i - T_0 S_i)_{\text{at } T_0,P_0}, \tag{3}$$

where N_i is the number of moles of component i in the process stream, H_i is the enthalpy, and S_i is the entropy of pure datum component i at T_0 and P_0. The exergy of a multicomponent flow is always less than that of the same flow when unmixed. For a multicomponent process stream, which is an ideal solution of pure components, the exergy due to mixing can be written as:

$$E^m = RT_0 n \sum_i x_i \ln x_i, \tag{4}$$

where R is the universal gas constant, n is the total molar flow, and x_i is the mole fraction of component i. The equation is a good approximation for gases at low pressures. Accurate thermodynamic equations can be used to calculate E^m when the assumption of an ideal solution is not a good one.

When two or more process streams of dissimilar compositions are mixed to form a mixture, some exergy is lost. The loss of exergy can be calculated by the following equation, if (1) there are no chemical reactions or heat effects involved in the mixing process and the mixtures are ideal solutions and (2) the process streams to be mixed are at the same temperatures:

$$\Delta E^m = RT_0\left[n\sum_i x_i \ln x_i - \sum_j n_j \sum_k x_{kj} \ln x_{kj}\right], \qquad (5)$$

where n is the total number of moles of the final mixture; n_j is the moles of jth process stream being mixed; x_{kj} is the mole fraction of the kth component in the jth process stream.

Since real processes are irreversible, the total exergy flowing into any unit operation is more than the total exergy flowing out; that is, some exergy (or the potential to perform work) is lost during any unit operation. Within the constraints of cost and other process considerations, one of the objectives of a process engineer is to minimize the total exergy loss of a process, because minimal exergy loss will correspond to minimum energy input or maximum energy output, depending on the nature of the process. Exergy loss analysis around pieces of equipment can help identify critical unit operations with large losses. Such analyses can often provide clues for improvements to these critical process steps (Agrawal and Woodward, 1991; Atkinson, 1987).

In the process industry, as well as in nature, many fluids of different compositions are mixed, resulting in a great loss in exergy. For example, many chemical reaction processes involve mixing of fluids with different compositions before a reaction. It can be quite attractive to decrease such exergy loss due to mixing by recovering some of the mixing exergy to perform some useful task. There are several examples in which such recovery of the mixing exergy is achieved when mixing involves phase changes, such as vaporization of a liquid stream into a gas stream. For example, life forms use sweating, which is essentially water vaporization in the air, to regulate body temperatures. The evaporative water cooling towers widely used in the process industry work the same way. The recently invented humidified air turbine cycle also utilizes the mixing exergy of water vapor–air mixing to effectively use low-level heat for power generation (Rao, 1989). However, there are only a few examples of the utilization of mixing exergy when all the process streams being mixed are in the gas phase.

When two or more process streams of the same phase but with unequal composition are mixed, a significant fraction of the mixing exergy, which is otherwise lost, can be converted either to thermal or pressure forms of exergy. These forms of exergy can be used elsewhere in the plant, resulting in overall energy and equipment cost savings for the facility. Most of the commonly known separation devices can be suitably modified to become efficient mixing devices. In this article, use of distillation, membrane, adsorption, and absorption for mixing of two or more streams of unequal compositions will be discussed in detail. While the processes are presented for mixing of gaseous streams that are of the same phase, if needed they can be extended to the mixing of streams of different phases.

Mixing Using a Distillation Column

Atkinson and Rathbone (1989) suggested a scheme that is essentially a distillation run in reverse to convert mixing exergy to thermal exergy (Figure 1a). In this scheme components A and B are mixed in a column, which has boiler and a condenser, and mixing trays, using staged liquid–vapor equilibrium. The component with the higher boiling point, component B, is fed to the top of the column, and that with the lower boiling point, component A, is fed to the bottom of the column. Without loss of generality, we assume that both A and B are gaseous feeds. These components then mix with each other gradually on the mixing trays. Since the vapor and liquid on each tray are almost at thermodynamic equilibrium, the result is that some of the mixing exergy can be converted into thermal exergy, or rather a higher-temperature heat source (the condenser) and a lower-temperature heat sink (the boiler). Such thermal exergy can be used in the process industry. An example of such usage given by the authors is in the production of argon by air distillation. Thermal exergy produced by the mixing of oxygen and nitrogen from such a mixing column is used to supplement the energy used for argon production. Although the possibility of the commercialization of such an argon process is remote, the concept itself is rather interesting (Brugerolle, 1977).

For the mixing column of Figure 1a to operate, certain constraints must be met. These constraints can be derived from a McCabe–Thiele diagram of such a process shown in Figure 1b. The usual assumptions for drawing a McCabe–Thiele diagram for a binary distillation such as constant molar overflow have been assumed. For this mixing process to be feasible, the operating lines have to be above the equilibrium curve. The operating line for the bottom section has a slope less than one and intersects the diagonal line at $Y = Y_{BOT}$, where Y_{BOT} is the concentration of the more volatile component A in the bottom feed to the distillation column. It is essential that the point (X_1, Y_0) should not lie on the portion of the operating line that is bounded by the diagonal line and the equilibrium curve, where X_1 is the mole fraction of the liquid leaving the bottom tray and Y_0 is the mole fraction of the vapor entering the bottom tray. This implies that as long as $Y_{BOT} < 1$, that is, the bottom feed stream is not pure, the liquid from the bottom tray of the column cannot be the same composition as the bottom feed stream. As a matter of fact, the liquid from the bottom tray should have a higher concentration of the heavier component B than in the bottom feed and the constraint $f(X_1) < Y_0 < Y_{BOT}$ must be satisfied, where $Y = f(X)$ represents the equilibrium curve. Similarly, the operating line for the top section, with a slope greater than one, intersects the diagonal line at $Y = Y_{TOP}$, where Y_{TOP} is the concentration of a volatile compnent A in the top feed. Once again for $Y_{TOP} > 0$, the concentration of the more volatile component, Y_N, in the vapor leaving the top tray should be higher than the corresponding concentration in the top feed. Also, after the mixing of these two streams, Y_N should be greater than $f(X_{N+1})$, where X_{N+1} is the concentration of the more volatile component in the liquid stream entering the top tray. It is interesting to find these mixing losses at both ends of the mixing column; the only time these losses are small is when both streams to be mixed are relatively pure. There are no major surprises for the locus of the intersections of the two operating lines (the q-line) on the McCabe–Thiele diagram.

Even though not discussed by Atkinson and Rathbone (1989), the mixing column of Figure 1a can also be extended

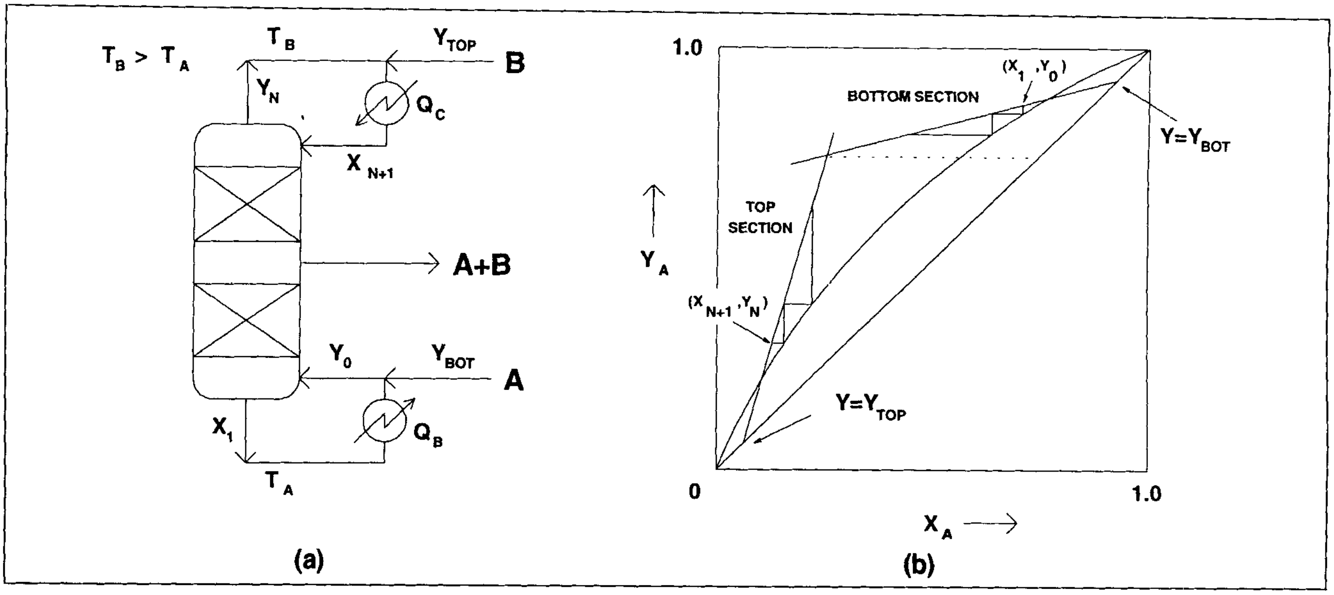


Figure 1. (a) Efficient mixing of components A and B using a mixing tower to generate thermal exergy (component A is more volatile); (b) corresponding McCabe-Thiele diagram.

to recover some of the mixing exergy as pressure exergy or mechanical energy. Figure 2 shows such a scheme. Use of a heat pump to transfer heat from a condenser to a boiler has been suggested for a distillation column (Null, 1976). Unlike a distillation column, this transfer of heat from the condenser to the boiler for the mixing column can lead to the generation of mechanical energy. In the method shown in Figure 2, the vapor from the top of the mixing column is expanded in a turboexpander, condensed by heat exchange with the liquid at the bottom of the column, and then pumped as a liquid to the top of the mixing column. The energy from the turboexpander can be recovered as electrical energy or used to compress a suitable process stream. When the energy generated by the turboexpander is more than that consumed by the pump, a net amount of energy is recovered from the mixing process. In Figure 2, for simplicity, a trimming heat exchanger needed to bring the process into overall enthalpy balance is not shown. Similar to heat pumps in distillation, alternative means to overhead vapor expansion may be used for energy recovery. The bottom liquid could be pumped and boiled by heat exchange with overhead vapor. The resulting vapor would then be expanded in a turboexpander and returned to the bottom of the mixing column. A closed-loop fluid could also be used for this purpose. Basically, any suitable cycle using the condenser as a heat source at a higher temperature and the boiler as a heat sink at a lower temperature can be used to generate work. While these ideas of using a distillation column as a mixing column to generate work are conceptually very attractive, chances of a real-life application seem to be modest at best.

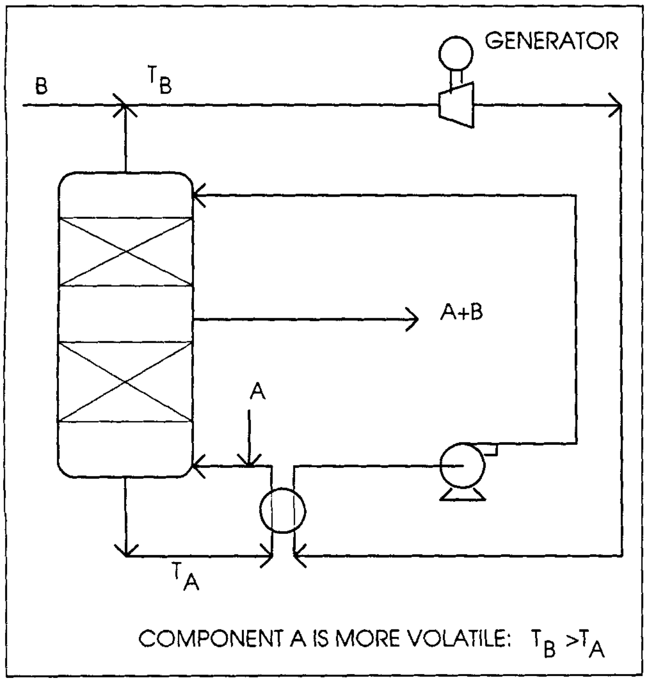


Figure 2. Efficient mixing of pure components A and B using a mixing tower: conversion of thermal exergy to mechanical energy.

Mixing Using Membranes

Membranes are primarily used for separation, and membrane processes are generally separation process (Ho and Sirkar, 1992; Matson et al., 1983). Membrane applications include gas separation, pervaporation, reverse osmosis, ultrafiltration, dialysis, and electrodialysis. Membrane-based gas separation processes have seen intense activity over the past decade (Koros and Fleming, 1993). There are several large-scale commercial processes using membrane separations and a large number of membrane materials are available today (Peterson, 1993; Robeson, 1991). Therefore, an opportunity exists to use some of these membranes for efficient mixing processes.

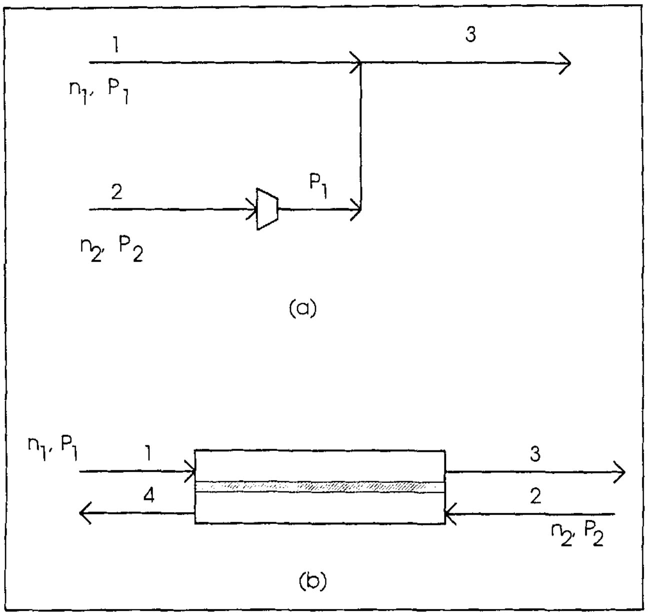


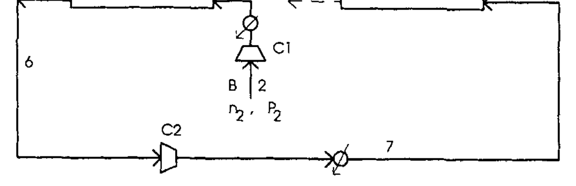
Figure 3. (a) Conventional method of mixing gaseous streams 1 and 2 with $P_1 > P_2$; (b) mixing using a semipermeable membrane (Vines, 1992).

Use of reverse-osmosis membranes to generate electric power when fresh water from a river mixes with seawater has been suggested (Norman, 1974; Loeb, 1976; Loeb et al., 1976). In this interesting application seawater is pumped to a higher pressure, which is lower than its osmotic pressure, and is then sent to one side of a reverse-osmosis membrane. The river water at atmospheric pressure is passed on the other side of the membrane. The volume of the saltwater exiting is much higher than the feed seawater; this exiting saltwater is passed through a turbine to generate electric energy. This novel application of osmosis can generate energy in an environmentally friendly manner. Even though this concept of liquid mixing using membranes has been known for some time, not much seems to have been done for gas mixing. The rest of this section provides a discussion on the mixing of gas streams using membranes.

Consider the mixing of two gaseous streams 1 and 2, with stream 1 at a pressure higher than stream 2. Generally stream 2 would be compressed and mixed with stream 1 as shown in Figure 3a. Vines (1992) suggested that in certain cases the compressor may be eliminated and a semipermeable membrane can be used for gas mixing. Since the driving force for a gas component to permeate from one side of a semipermeable membrane to the other is the difference in partial pressures, a gas may permeate from the lower-pressure side to the higher-pressure side, provided the partial pressure of that gas is higher on the lower-pressure side of the semipermeable membrane. The scheme proposed by Vines is shown in Figure 3b. In this figure the components present in stream 1 have very low permeability compared to the components in stream 2. A component present in the lower-pressure stream 2 will permeate to the higher-pressure stream 1, provided its partial pressure in stream 2 is higher than in stream 1. The maximum possible concentration of the permeable component in stream 3 is such that its partial pressure is equal to the partial pressure in stream 2. Under the partial pressure driving force, a large fraction of stream 2 can permeate and mix with stream 1, and the flow rate of stream 4 would be less than that of stream 2. Clearly, the compression energy required to mix streams 2 and 1 is eliminated or reduced, as is the compression machinery.

To analyze the problem of mixing two gaseous streams 1 and 2 that are at different pressures, first consider cases in which both gas streams are ideal gases, that is, partial pressures adequately represent the driving forces. Both streams are pure gas streams and streams 1 and 2 contain components A and B, respectively. For further simplification, assume that the semipermeable membrane is permeable to only B and pressure drop for flow on each side of the membrane is zero. Now consider the problem of mixing n_1 moles of stream 1 at pressure P_1 with n_2 moles of stream 2 at pressure P_2. For the process in Figure 3 to be useful, $P_1 > P_2$. The minimum possible pressure of stream 2, $P_{2\min}$, required to completely mix the two streams across the membrane is $[n_2/(n_1+n_2)]\ P_1$; that is, the driving force for B to permeate at the feed end of stream 2 is zero. Clearly as long as $P_{2\min} \leq P_2 < P_1$, the membrane process in Figure 3 results in energy savings when compared to the case in which only a compressor is used to boost the pressure before mixing. The use of membrane allows an effective use of exergy of mixing.

The problem when the given pressure of stream 2, P_2, is below the $P_{2\min}$ can also be analyzed for the minimization of energy consumption. Clearly in such a case, a compressor is required to boost the pressure of the permeating stream and some energy is consumed. A simple solution is to boost the pressure of stream 2 to $P_{2\min}$ before feeding it to the membrane unit. However, some interesting results are obtained when multiple stages of membrane with multiple compression stages are used. Multistage compressors with interstage cooling are often used to compress a gas stream to a higher pressure. Cooling between stages is used to minimize the work of compression. Membrane modules could be used after each stage to mix B with A. One such solution is shown as Scheme 1 in Figure 4. Here two stages of membrane, 1 and M2, are used. Stream 2, containing permeable component B, is compressed to an intermediate pressure P_5 from the given pressure P_2 and fed to membrane module M1. The low-pressure effluent from M1 is compressed to the final pressure P_7 and fed to M2 for final mixing. For this idealized semipermeable membrane, an analytical expression can be derived for the optimum pressure P_5 such that overall energy consumption in compressors C1 and C2 is minimized. The derivation is



(Scheme-1)

Figure 4. Two-stage membrane process for mixing of streams 1 and 2.

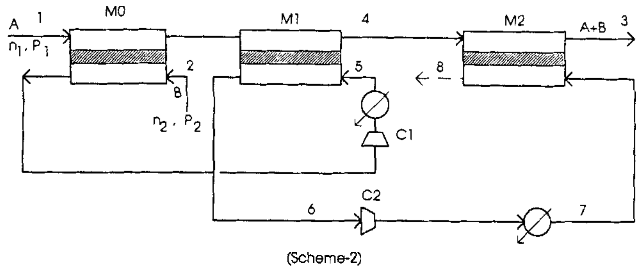


Figure 5. Three-stage membrane process for mixing of streams 1 and 2.

presented in Appendix 1 and the optimum pressure is given by the following relation:

$$1-\theta_1=\ln\frac{x_{B3}}{\theta_1}, \tag{6}$$

where

$$\theta_1=\frac{P_5}{P_1}$$

and x_{B3} is the mole fraction of B in the final mixture stream 3. It is interesting that optimum P_5 is only the function of P_1 and the composition of the final mixture; it is independent of the initial pressure of stream 2. This means that if P_2 is below the optimum pressure P_5, stream 2 should be compressed in compressor C1 to this optimum pressure; however, when P_2 is higher than the optimum P_5, compressor C1 should not be used and stream 2 should be fed directly to membrane M1.

The optimum pressure at the discharge of compressor C1 is dependent on the given initial pressure P_2 for Scheme 2 shown in Figure 5. The only difference between the two schemes is that in Scheme 2, stream 2 is first sent directly to a membrane module M0 and the effluent from this membrane is sent to compressor C1. This allows the permeation in M0 across the membrane at the given pressure P_2 of the low-pressure stream and the flow rate through compressor C1 is therefore reduced. This leads to a reduction in total energy consumption as compared to Scheme 1. Now the optimum pressure P_5, such that overall energy consumption in compressors C1 and C2 is minimized, is given by the following equation (see Appendix 2):

$$(1-\theta_2)\left\{1-\left(\frac{1-\theta_2}{\theta_2}\right)\cdot\left(\frac{\theta_0}{1-\theta_0}\right)\right\}=\ln\frac{x_{B3}}{\theta_2}, \tag{7}$$

where

$$\theta_0=\frac{P_2}{P_1}$$

$$\theta_2=\frac{P_5}{P_1}$$

As shown in Appendix 2, for a given n_1 at P_1 to be mixed with n_2 at P_2, the optimum value of θ_2 is greater than θ_1, that is, the pressure at the exhaust of compressor C1 for Scheme 2 is greater than the corresponding pressure in Scheme 1. This results from the fact that after some permeation of B has taken place across membrane M0 and its flow rate through compressor C1 is reduced, its pressure can be boosted to a higher level than for the case in which feed stream 2 is directly sent to compressor C1.

The minimum total energy consumption for Scheme 2 is always less than the minimum total energy consumption for Scheme 1, as can be seen in Appendix 2. The total energy needed to mix the two streams can be further minimized by increasing the number of stages of membrane with a compressor between each stage. As the number of membrane stages is increased, the pressure ratio across each stage is decreased and the process becomes more reversible. In the limit, as the number of stages is increased, the isothermal work becomes equal to the difference in exergy of the final mixture and the initial feed streams. However, in any given application, there is a practical limit to the number of stages of compression that can be used.

In Figures 3–5, the flows are drawn as countercurrent flows. For ideal semipermeable membranes, where only B permeates, the flow configuration is immaterial. However, most real membranes have finite permselectives. Both A and B will permeate through and it is therefore desirable to use the countercurrent flow configuration shown in these figures. For such cases, the flow rate of stream 4 in Figure 3 and stream 8 in Figures 4 and 5 will be nonzero. Some A will permeate to the lower-pressure side and the membrane discharge from the lower-pressure side of the membrane will contain A. If needed, this stream can be compressed and mixed with the high-pressure side discharge of the membrane module to provide the final mixture. Obviously, for a membrane mixing process to be attractive, the energy needed for this compression has to be significantly less than the energy needed to compress all of the low-pressure stream 2 to the pressure of stream 1. Selection of the best scheme will depend on the cost of energy consumed plus the cost of membrane modules, compressors, and other operating costs.

Figure 6 shows an example in which 10 moles of H_2 is mixed with 90 moles of methane using a membrane more permeable to H_2, but with a finite selectivity. In this scheme, as hydrogen permeates from the lower-pressure side to the higher-pressure side, some CH_4 "leaks" from the higher-pressure side to the lower-pressure side. Therefore, after a certain extent of membrane mixing, the methane-containing low-pressure hydrogen is removed form the membrane mixer and compressed to the higher pressure to mix with the effluent from the higher-pressure side. Figure 7a shows how the

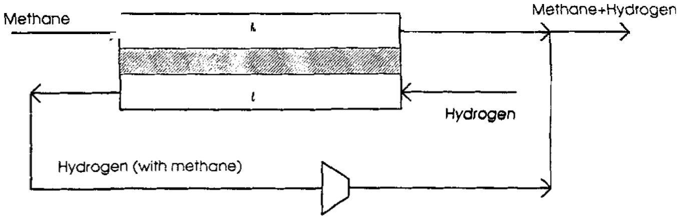


Figure 6. Mixing of a lower-pressure stream into a higher-pressure stream using a real membrane.

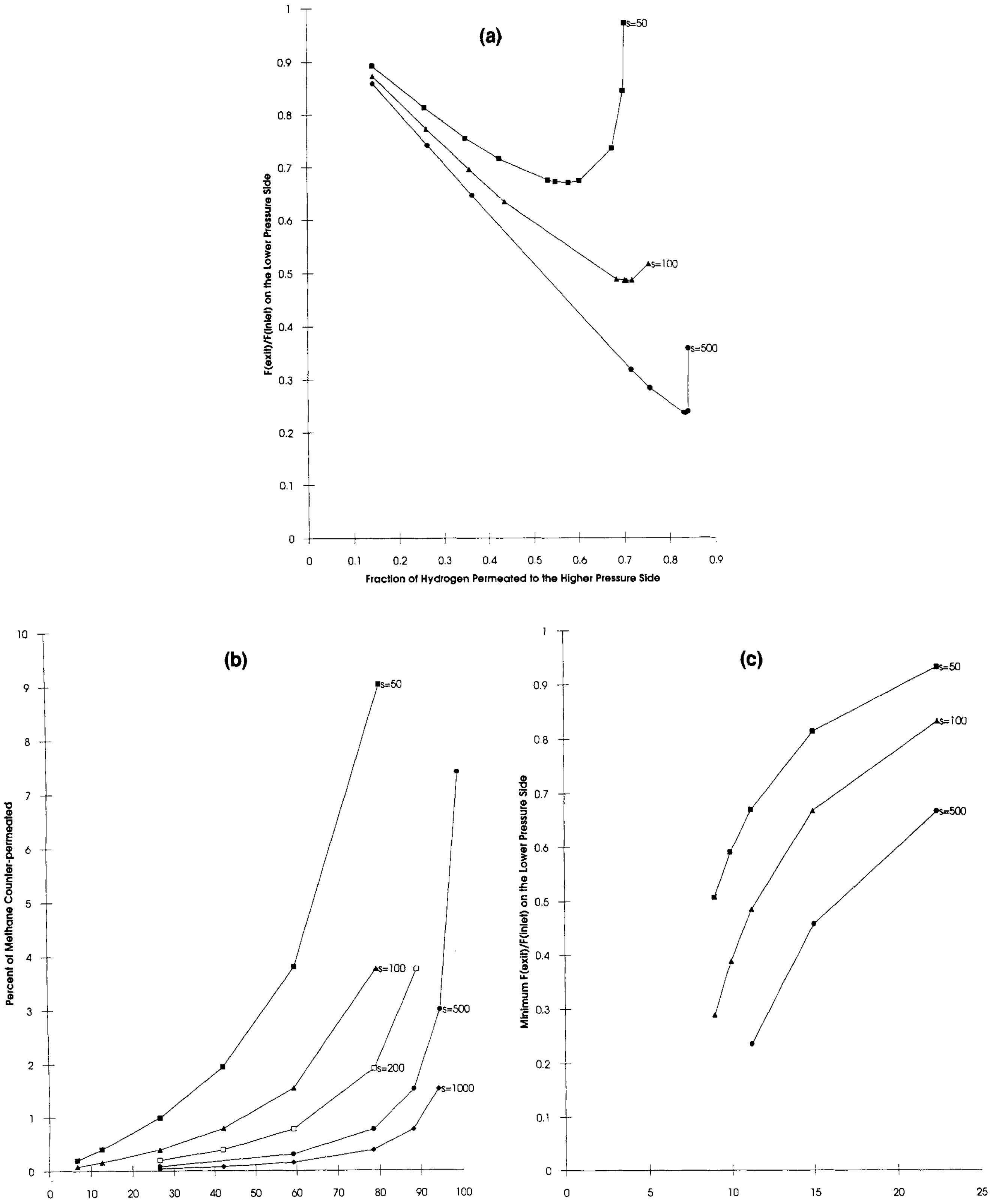


Figure 7. (a) F_{exit}/F_{inlet} on the lower-pressure side of the membrane vs. fraction of the feed hydrogen permeated to the higher-pressure side of the membrane at the pressure ratio between the two sides of the membrane $[P(h)/P(l)]$ of 11.25; (b) percent of methane counterpermeated vs. percent of hydrogen permeated at different selectivities: $P(h)/P(l) = 11.25$; (c) minimum F_{exit}/F_{inlet} on the lower-pressure side of the membrane vs. the pressure ratio $P(h)/P(l)$ at different selectivities.

ratio of lower-pressure side effluent F(exit) to the lower-pressure side feed F(inlet) varies with the fraction of hydrogen permeated, for different hydrogen to methane selectivities. As expected, the higher the selectivity, the smaller the F(exit)/F(inlet) ratio for the same fraction of hydrogen permeated. Figure 7a also shows a minimum for each curve, meaning that there is an optimal fraction of hydrogen permeated to the higher-pressure side or an optimal membrane area, beyond which more membrane mixing only hurts the efficiency. That is understandable because as hydrogen permeation proceeds, the difference in hydrogen partial pressure decreases, while that of methane partial pressure does not change in a similar magnitude. The result is that the ratio of the "leaking" rate of methane from the higher-pressure side to the lower-pressure side to the rate of hydrogen permeation increases as more hydrogen is permeated (Figure 7b). Figure 7c shows how the minimum F(exit)/F(inlet) changes with the pressure ratio $P(h)/P(l)$. As expected, the greater the pressure ratio, the less the membrane mixing process can do to reduce the flow needing compression.

Use of an asymmetric permeator to separate a ternary mixture in a single module has been analyzed by Sirkar (1980) and Sengupta and Sirkar (1987). The permeator module contains two membranes with reverse permeability values. One component of the ternary mixture is most permeable through one membrane, while another component is most permeable through the second membrane. Interesting results are obtained when such permeators are used for mixing of two streams. Consider a relatively simple case of mixing of two pure components, A and B. For the sake of simplicity, assume once again that the membranes are perfect, that is, one membrane is permeable to only one gas component. Suppose membrane M1 is permeable to A while M2 is permeable to B. The scheme shown in Figure 8 allows the mixture of A and B to have a pressure higher than those of both A and B. The maximum attainable pressure of the mixture is equal to the sum of the pressures of gases A and B. In such cases, the ratio of the mole fractions of A and B in the final mixture stream 3 follows the relationship $x_{A3}/x_{B3} = P_1/P_2$.

The concept of mixing of two pure gas streams using an asymmetric permeator containing two membranes with reverse permeabilities can be conceptually extended to mixing of more than two pure gases. Consider N pure gas streams, and assume that for each gas stream a perfect membrane that is only permeable to that component exists. Then, in principle, it is possible to design a module similar to the one shown in Figure 8 having N different membranes, with each pure gas fed to the right membrane such that the maximum possible pressure of the final mixture is the summation of each gas stream's pressure, that is, pressure of the mixture $= \Sigma_i^N P_i$. In such a case, the ratio of the mole fractions of any two gases in the final mixture will be equal to the ratio of the pressures of corresponding pure gas streams. While this concept of asymmetric permeators to mix gas streams is conceptually attractive, its immediate utility will clearly be limited by the availability of suitable membrane materials.

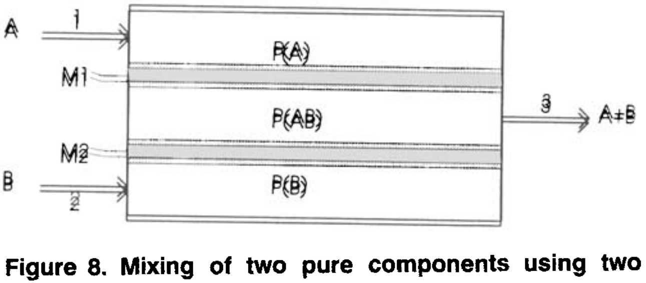


Figure 8. Mixing of two pure components using two membranes permeable to different components; M1 permeable to A, M2 permeable to B.

The membrane schemes discussed so far have been in the context of either mixing a low-pressure stream containing a more permeable component with a high-pressure stream containing a less permeable component or to mix streams such that the pressure of the final mixture is higher than the pressure of the constituent streams. Quite often streams to be mixed are at the same pressure and the final mixture is not desired to be at a higher pressure. In such cases, at least in theory, membrane mixers can be used to extract energy. For example, if the asymmetric permeator of Figure 8 is used, the final mixture, which is at a higher pressure, can be expanded in a turbine to generate electrical energy. Alternatively, the energy from the turbine could be used to compress or pump another fluid stream. There are at least two methods of extracting power with the membrane mixing module of the kind shown in Figure 3. In one alternative, the feed stream 2 containing a more permeable stream can be first expanded in an expander to a lower pressure and then fed to the membrane module for mixing with stream 1, which would be at the pressure of the final mixture. In another method, the less permeable stream 1 can be first compressed and sent to the membrane unit for mixing and then the mixture effluent can be expanded in an expander to extract the power. Since the flow of the mixture is higher than the flow through the compressor, theoretically it should be possible to extract energy from this system. However, typical isothermal efficiencies of compressors are of the order of 60–75%, and isentropic efficiencies of expanders are 75–90%; the potential to recover a significant amount of net energy is substantially diminished for the latter alternative. Because of these low machinery efficiencies, the recovery of energy by such means would generally be economically unattractive.

There are several instances in the chemical process industry in which membrane modules can be used effectively for gas mixing. An example from Vines (1992) is shown in Figure 9. This process is for the production of hydrogen using steam reforming of natural gas. A portion of the lower-pressure hydrogen product stream needs to be mixed with the higher-pressure natural gas feed stream to provide hydrogen for the desulfurization of the natural gas feed. In this process, a portion of the hydrogen product from a pressure swing adsorber, which is at a pressure lower than that of the natural gas feed, passes through one side of a semipermeable membrane that is selectively permeable to hydrogen. The feed natural gas, which is at higher pressure, passes the other side of the membrane. Since the partial pressure of hydrogen is higher on the lower-pressure side, hydrogen gas can permeate from the lower-pressure side to the higher-pressure side. Notice that in this scheme, the low-pressure side discharge from the membrane is used as a portion of the fuel stream in the reformer. This eliminates the need to compress this stream and mix it with the natural gas feed or any other higher-pressure stream. The use of membranes for mixing can be most attrac-

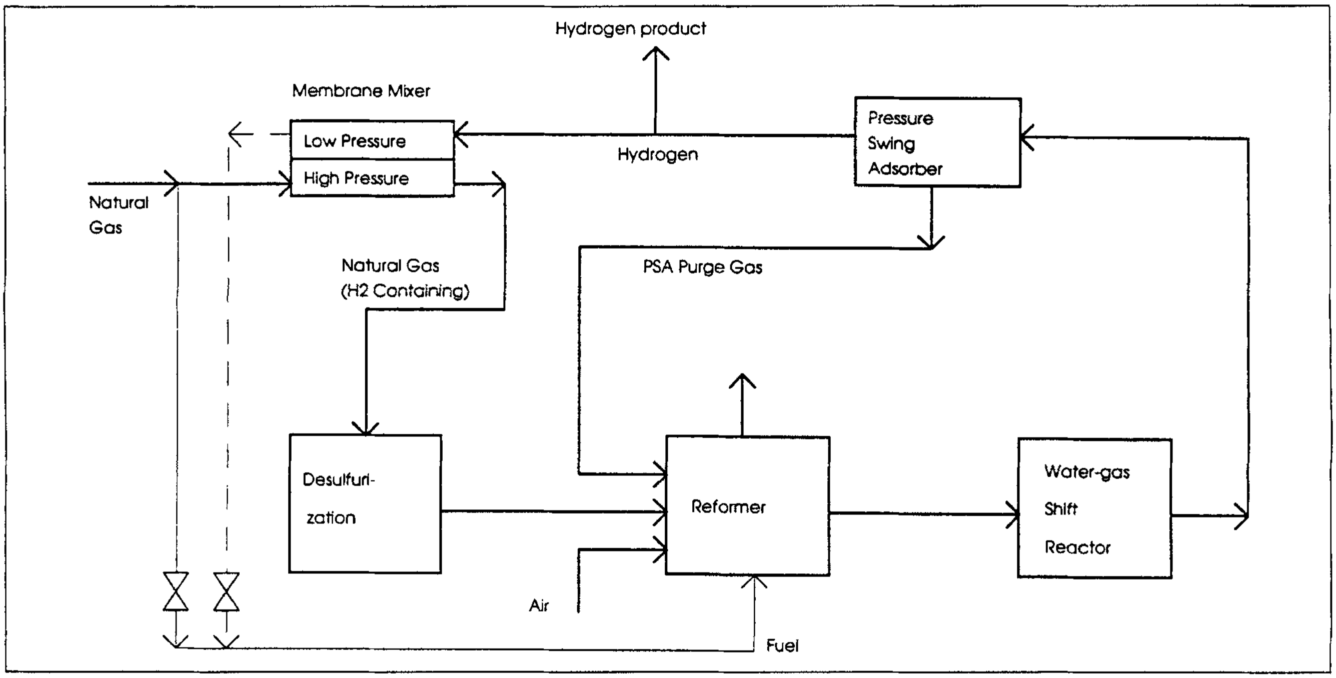


Figure 9. Hydrogen production by natural gas steam reforming; mixing of low-pressure hydrogen with high-pressure natural gas using membrane mixer (Vines, 1992).

tive in situations in which the low-pressure effluent stream from the membrane unit can be effectively utilized at its lower pressure in some other part of the overall process.

Another example can be found in steam reforming. Steam reformers typically operate in the pressure range of 15–30 atm. Consider the case of hydrogen production for ammonia synthesis, in which a steam to-carbon ratio of 3.5–4 is used. In such a case, a portion of superheated steam feed can be first expanded to a lower pressure in a turboexpander to generate power and then fed to a suitable membrane module with high water vapor permeability. The natural gas at the given high pressure is passed on the other side, and upon exiting the membrane, this stream is then directly mixed with the rest of the high-pressure steam feed. The lower-pressure side of the membrane effluent, which can contain a substantial quantity of methane, can be sent to supplement the fuel needs of the reformer. The portion of the feed steam to be mixed through the membrane module is an optimization problem. Alternatively, if low-pressure stream is already available at the plant site, it could be mixed with natural gas using a membrane module and the quantity of the higher-pressure steam needed can be reduced. Obviously, the use of this scheme is dependent on the availability of a membrane module that can operate in the temperature range of 150–250°C with high permeability for water vapor as compared to methane.

Simultaneous Separation/Mixing Using Membranes

Quite often a component is first separated from one process stream and then mixed with another stream for further processing. This is the case in almost all chemical processes using gas recycling, such as steam reforming of methane, catalytic reforming of naphtha, hydrotreating, isomerization of light hydrocarbons, and hydrocracking. In some of these cases, it is possible to carry out separation and mixing in a single step. For example, consider the mixing of stream 1 containing gas A with another gas B, but B is available in stream 2 as a gas mixture of B and C. Rather than first separating B from the mixture BC, if B has a high permselectivity through a membrane, then the process shown in Figure 10 can be used. Here the exergy of mixing is used to supplement the driving energy needed for the separation.

In Figure 10, the required pressure of stream 2 can be lower or higher than stream 1. The pressure of stream 2 has to be at least such that the partial pressure of B in stream 2 is equal to the partial pressure in stream 3 leaving the membrane. Notice that use of a sweep stream to enhance a separation has been suggested in the past (DiMartino, 1990; Prasad, 1993). In almost all of these applications, the sweep stream is at a lower pressure than the feed mixture that needs to be separated. The sweep stream exiting the membrane is often a waste stream or it is recycled for further separation. In these applications, the primary objective is not to mix two streams but to enhance separation. In general, the use of a sweep stream to facilitate a separation can be viewed as a

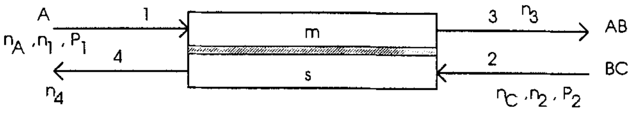


Figure 10. Separator/mixer process with a perfect membrane to separate B from a mixture BC and mix it with A to provide a desired mixture AB.

subset of a more general class of separation/mixing problems.

For a given flow rate and pressure of stream 1 in Figure 10, it is desirable to find the optimum pressure of the mixture, stream 2. This requires understanding of the pinch location in the partial-pressure driving force across the membrane. A pinch in the partial-pressure driving force means that the partial pressure of B is the same on each side of the membrane, and therefore at the location of the pinch, the difference in the partial pressure of component B across the membrane, Δp_B, is zero. This is unlike the simple mixing problem of Figure 3, where the location of the pinch is obvious: for the separation/mixing problem, the location of the pinch and the shape of the Δp_B profile along the length of the membrane module are not so obvious and need some analysis. All this information is needed so that the minimum possible pressure of stream BC required to transfer a given quantity of B across the membrane for a given pressure of stream A can be studied.

To gain an understanding of the simultaneous separation/mixing problem, a simpler problem using perfect membranes has been analyzed in detail in Appendix 3. Consider all feed and product streams to be ideal gases and the membrane to be a perfect semipermeable membrane such that only the desired component would permeate through it. Furthermore, the pressure drop due to flow on each side of the membrane is negligible. With these assumptions, in Figure 10, component B is the only permeable component and pressure drop, as streams 1 and 2 flow on either side of the membrane is zero. As shown in Appendix 3, for a given choice of stream conditions in Figure 10, it is easy to tell whether or not an extremum in Δp_B is going to occur. The location and the nature of the extremum in terms of a minimum or maximum can also be calculated. These results are dependent on the relative flow rate of nonpermeable component C (n_C), from which B is separated, to the flow rate of nonpermeable component A (n_A), in which B is going to be mixed. Clearly there are three distinct cases depending on whether n_C is equal to, less than, or greater than n_A. Once the location and the conditions under which an extremum in Δp_B occurs are known, the minimum possible pressure of stream BC required to transfer a given quantity of B across the membrane for a given pressure of stream A can be studied. The detailed derivation is given in Appendix 3 and only the relevant results will be discussed here.

First consider the case when the molar flow rate of nonpermeable component A is equal to the molar flow rate of nonpermeable component C in stream BC. For this case, the necessary condition for an extremum in Δp_B profile to occur inside the membrane is that the pressure ratio $P_2/P_1(\equiv \theta)$ across the membrane be greater than one and this extremum is always a minimum in Δp_B. The minimum possible pressure of stream BC to transfer a known quantity of B across the membrane is always given by a pinch in Δp_B at the feed end of BC. For this pinch case the pressure of stream BC is either less than or equal to that of stream A. Clearly with this pinch in Δp_B, no other minimum in Δp_B occurs inside the membrane. A case of interest is when nearly all B is transferred to A and the pressure of stream BC is only infinitesimally greater than the pressure of stream A. In this limit, if a large membrane surface is used, it is as if mixture AB is created of the same composition as BC: ideally, energy of separation equals energy of mixing and no energy is wasted. This case is worth special attention since in this process both mixing and separation are carried out with a very high efficiency in a very simple device. Such high efficiencies are not attainable with the known two-step processes in which separation and mixing are carried out independently.

Now consider the case when the flow rate of nonpermeable component A, in which B is going to mix, is greater than the flow rate of nonpermeable component C, from which B is being separated. In this case, the minimum possible pressure of stream BC to mix a known quantity of B with A is given by the pinch at the feed end of BC; under this pinch condition the pressure of stream BC is always less than the pressure of stream A. For the subcases when $P_2/P_1 \le n_C/n_A$, the partial pressure difference for component B across the membrane, Δp_B, monotonically increases as the mole fraction of B in stream BC inside the membrane, x_{BS}, decreases (Figure 11a). However, for subcases when $P_2/P_1 > n_C/n_A$ but $(P_2/P_1)(n_C/n_A) < 1$, it is sometimes possible to get a maximum in the value of Δp_B, which is located inside the membrane. As proved in Appendix 3 and shown in Figure 11b, there will always be a maximum in Δp_B whenever all of B is transferred from stream BC to stream A at the lowest possible pressure of stream BC, that is, with a pinch at the feed end of stream BC. For the subcases in which pressure of stream BC is further increased such that not only $P_2/P_1 > n_C/n_A$ but also $(P_2/P_1)(n_C/n_A) > 1$, the values of Δp_B are quite large along the length of the membrane and no pinches in Δp_B are expected; an extremum when it occurs will be a mild minimum in Δp_B.

Finally, consider the last case when the flow rate of nonpermeable component A is less than the flow rate of nonper-

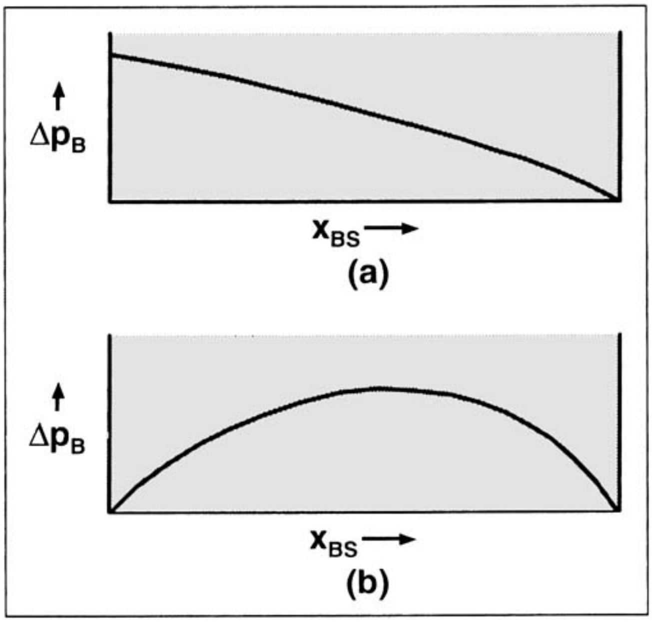


Figure 11. Typical profiles of Δp_B as a function of x_{BS} for a perfect separator/mixer when $n_C/n_A < 1$.

(a) $P_2/P_1 \le n_C/n_A$. (b) $P_2/P_1 > n_C/n_A$, $(P_2/P_1)(n_C/n_A) < 1$, and all of B is transferred from stream BC to stream A.

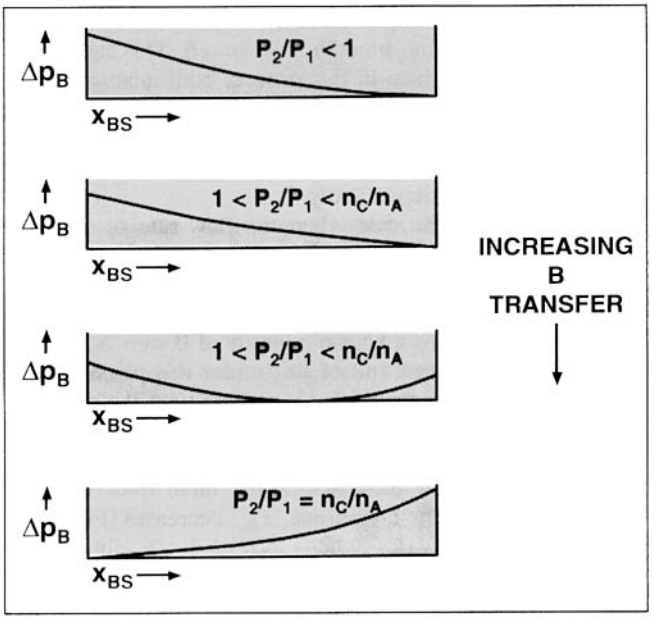


Figure 12. For $n_C/n_A > 1$, variation in the location of the pinch in Δp_B as the quantity of B transferred from stream BC to stream A is increased.

For each case, stream BC is at the minimum pressure required to transfer the desired quantity of B.

meable component C: $n_C/n_A > 1$. For this case, if an extremum in Δp_B occurs, then it is always a minimum. A necessary but not sufficient condition for a minimum in Δp_B to occur internal to the membrane is that P_2/P_1 be greater than one. For $1 < P_2/P_1 \leq n_C/n_A$, an internal minimum in Δp_B is *possible only when the mole fraction of B in stream AB exiting the membrane,* x_{B3}, *is greater than the mole fraction of B in stream BC entering the membrane,* x_{B2}. This requires a careful evaluation of the pinch in Δp_B, as it can reside inside the membrane. At the minimum operating pressure of stream BC, the location of the pinch in Δp_B is dependent on the quantity of B transferred to stream A (Figure 12). When $x_{B3} \leq x_{B2}$, the pinch is always at the feed end of BC and $P_2/P_1 \leq 1$. As more B is transferred to A and x_{B3} becomes greater than x_{B2}, initially the pinch is still at the feed end of BC but eventually moves inside the membrane with increased transfer of B. For this case $1 < P_2/P_1 < n_C/n_A$. When all of B is transferred from BC to A, the pinch in Δp_B has moved to the other end of the membrane where stream A enters and $P_2/P_1 = n_C/n_A$. Equations to identify and locate an internal minimum in the membrane and to calculate the corresponding minimum value of the pressure of stream BC are given in Appendix 3.

Now that the nature of the Δp_B profile along the length of the membrane in terms of a maximum or minimum and the location of pinch are understood for all possible values of (n_C/n_A), it is possible to devise a reversible process for the simultaneous separation and mixing of a component B under different situations. Consider, for example, a case when all of B has to be separated from BC and mixed with A. Furthermore, allow the usage of reversible isothermal expanders or compressors. For $(n_C/n_A) < 1$, one reversible process is shown in Figure 13a. Since in this case, for a given pressure of stream A, the maximum possible pressure of stream BC is dictated by a pinch at the feed end of stream BC, *multiple expanders* are required to recover energy by reducing pressure of the gas stream on the feed side of BC at multiple points. The pressure of stream C exiting the membrane module equals $(n_C/n_A)\ P_1$, where P_1 is the pressure of stream A. Of course, it is not practical to use many expanders, but whenever feasible, use of one or two expanders can reduce the energy consumption considerably. For $n_C/n_A = 1$, the situation is simple in that no intermediate expanders or compressors are required and the pressure of stream BC is infinitesimally greater than that of stream A (Figure 13b). For $n_C/n_A > 1$ and a given pressure of stream A, the maximum pressure of stream BC is dictated by a pinch at the feed end of stream A. In this case, the stream on the feed side of BC can be reversibly compressed at multiple points as shown in Figure 13c. Quite often compressors consist of multiple stages, and while the use of a large number of compressors is not feasible, use of two or more stages can result in significant energy savings.

An interesting case can be when $n_C/n_A > 1$ and not all of B is transferred from stream BC. In certain situations when the pinch is in the middle of the membrane, stream BC is first compressed and then after the pinch point it can be expanded to recover some energy.

In actual applications, the use of separator/mixer membrane processes will be subject to certain constraints. Most membranes have a finite permeability for any component present in the feed streams. Thus in Figure 10, *while component B should have the highest permeability,* components A and C can also have significant permeability values. In such cases, desired mixture AB will have some C also mixed with it; similarly some A can be lost in the C-enriched stream. For

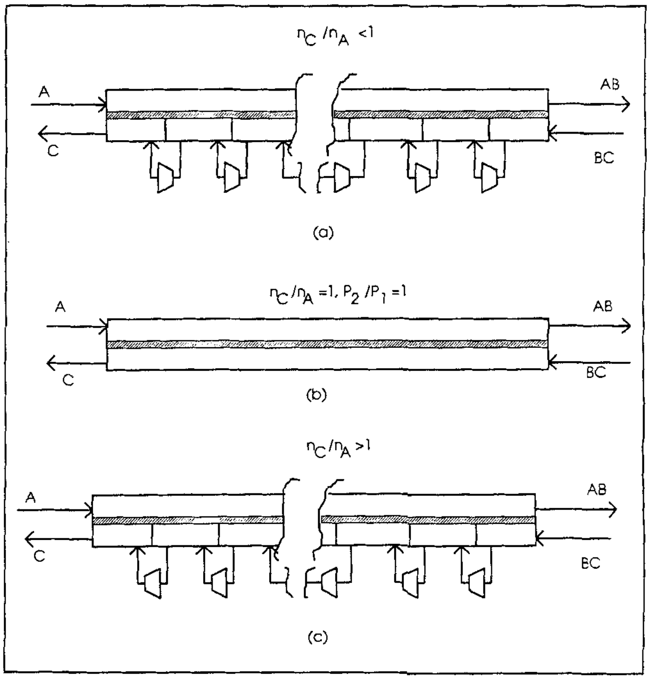


Figure 13. Suggested reversible processes for the transfer of all the B from a stream BC to a stream A for three cases.

(a) $n_C/n_A < 1$. (b) $n_C/n_A = 1$. (c) $n_C/n_A > 1$.

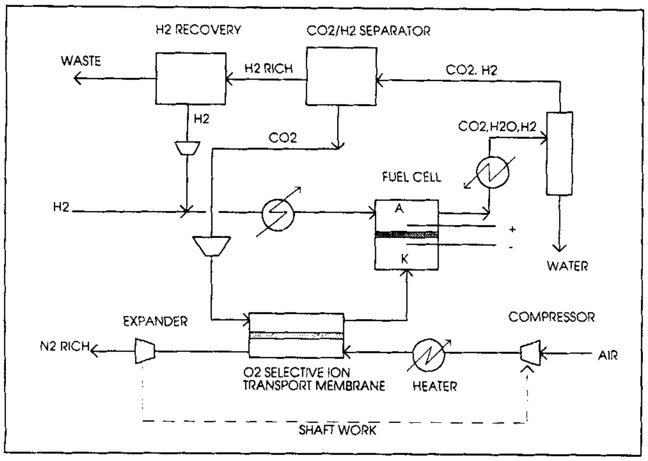


Figure 14. Application of a membrane separator/mixer in the molten carbonate fuel cell process.

these methods to be used, such secondary mixing should not have a significantly negative effect on the downstream processing of the streams exiting the membrane modules, and the loss of any one component into an undesired stream should not have damaging economic consequences. Furthermore, if the given pressure of stream A is fairly high, then depending on the quantity of B to be mixed with A, the operation of a separator/mixer membrane process can require that stream BC be also compressed to a high pressure. This implies that the pressure of a C-enriched stream exiting the membrane module should be successfully utilized in some other processing step. If the C-enriched stream is required at a high pressure, then compared to a two-step process of separation followed by mixing, the simultaneous separation/mixing process not only saves energy but can potentially eliminate the need for a separate compressor to compress either the C-enriched or B-enriched stream. On the other hand, if the C-enriched stream is not needed at the high pressure, such a separation/mixing process may not be suitable.

An example of a potential separator/mixer application is shown in Figure 14. In this process electricity is generated by a carbonate fuel cell that consumes CO_2/O_2 in its cathode cell (K). Oxygen is consumed in the cell (A) reaction by reacting with hydrogen to form water, while CO_2 is re-collected from the anode cell together with hydrogen and water. CO_2 from the anode is then separated from the hydrogen gas, recompressed to a pressure similar to that of the cathode cell, and passes through one side of a highly oxygen-selective semipermeable membrane, such as an ion transport membrane (ITM). An air stream is fed to the other side of the membrane. The selectivity of oxygen through an ITM membrane as compared to other gases involved is incredibly high (Teraoka et al., 1989a,b; Subbarao and Maiti, 1984). Oxygen in the air permeates the membrane and mixes with the CO_2 gas entering from the other side. The resultant gas on the oxygen-receiving side is the desired CO_2/O_2 mixture to be fed to the fuel cell. This process effectively utilizes the exergy of CO_2/O_2 mixing and eliminates the otherwise needed oxygen compressor and the compression power. Notice that for the CO_2/O_2 mixture to contain more than 21% oxygen, the pressure on the air side will have to be higher than that on the other side.

A second field for separator/mixer applications is hydrogen-containing systems. Hydrogen is used as a reactant or a coking suppressing agent (or both a coking suppressing agent and a reactant) in many chemical processes, such as steam reforming of hydrocarbons, catalytic reforming of naphtha, hydrocracking of gas oil, hydrotreating of hydrocarbons or other substances, isomerization of light hydrocarbons, and dehydrogenation and hydrogenation reactions. All of these processes involve the mixing of hydrogen with another feed stock such as hydrocarbons, and the separation of hydrogen from other substances after reaction. Due to its small molecular size, hydrogen can permeate many membranes that are not permeable to other molecules. A big potential therefore exists for membrane separator/mixers to be applied in such processes to reduce power consumption and equipment cost. Figure 15 shows such an example for the steam reforming of natural gas. The reformer effluent, which is rich in hydrogen, after carbon dioxide removal first goes through a hydrogen separation process in which most of the hydrogen is separated from the CO and CH_4. Since not all the hydrogen is separated in this step, the energy consumed is low, relative to more complete separation processes. The hydrogen-lean effluent stream can be fed to a membrane separator/mixer in which the remaining hydrogen is separated from the CO/CH_4 mixture. The hydrogen that permeates to the natural gas side is diluted by feed natural gas so that its partial pressure on that side is kept low and its driving force relatively high. In this process, natural gas acts as a sweep stream to enhance separation performance. In addition, hydrogen can mix with the high-pressure natural gas stream without any compression, which would otherwise have been needed if a conventional two-step process was used.

Mixing Using Adsorption/Absorption Processes

Pressure swing adsorption (PSA) or temperature swing adsorption (TSA) processes are widely used for gaseous separations (Ruthven, 1984; Yang, 1987). Several commercial PSA processes are known to exist for the separation and production of bulk gases such as hydrogen, oxygen, nitrogen, and carbon monoxide. Also, TSA and PSA processes have been used for the removal of trace components such as carbon dioxide and water from gas streams. The list of available adsorbent materials is extensive, providing a wide array of choices for many different applications. Therefore, it may be attractive to modify the known PSA and TSA processes to mix two or more streams of dissimilar compositions that are at different pressures. This can allow the use of mixing exergy to offset either part or all of the required compression energy.

To illustrate the concept, consider the mixing of a stream containing component A at pressure P_1 with a stream containing component B at pressure P_2. The pressure of the final mixed stream is to be P_1, which is greater than P_2. For the adsorption process of mixing to work, component B should be adsorbed more strongly than component A. Thus, in the simplest form, component B is adsorbed at the lower pressure P_2 until the bed is saturated. Then the high-pressure stream A is used as a purge stream at high-pressure P_1 to desorb the adsorbed component B. This will result *in the final* mixture of A and B at the higher-pressure P_1 without

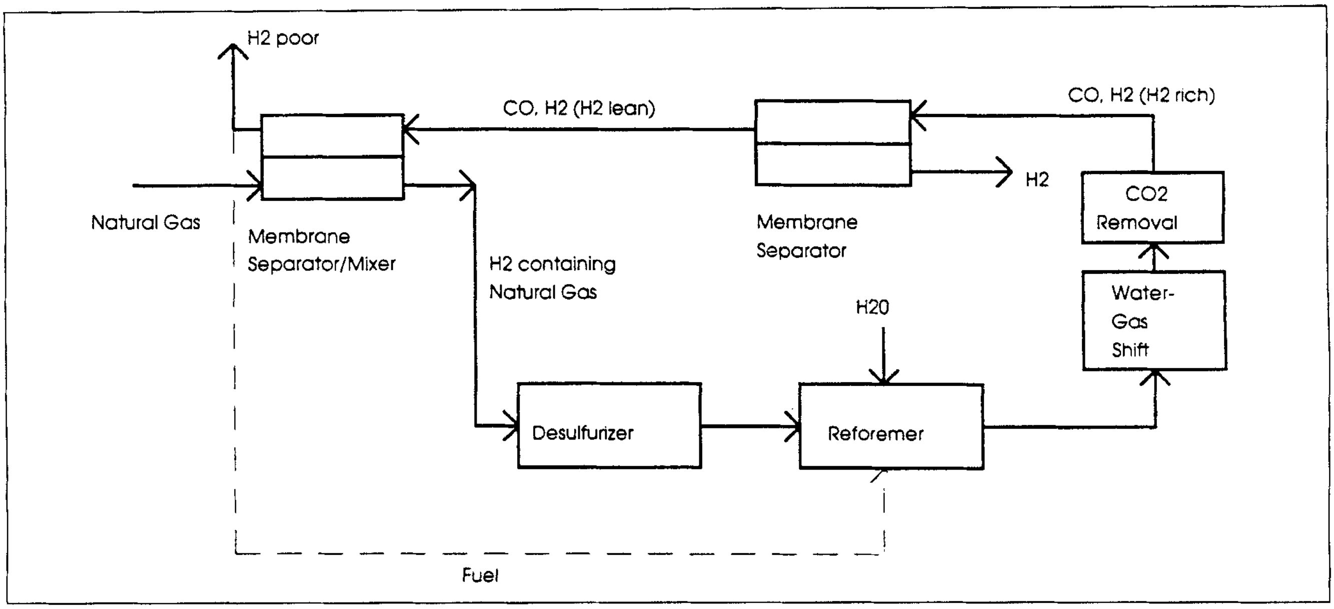


Figure 15. A membrane separator/mixer for the steam reforming of natural gas.

using any compression work. Of course, the composition of the final mixture may be limited by the adsorption properties that will determine the amount of A needed to desorb the adsorbed B.

Similar to more advanced, known adsorption processes for separation, more complicated adsorption processes for mixing can be devised to result in energy savings/decreased product loss. For example, multiple beds with pressure equalization(s) can be used. After a bed has been desorbed at the higher-pressure P_1 to yield the final mixture, it can be pressure-equalized with another bed that is ready for desorption at the higher pressure, but is at the lower pressure after the completion of the adsorption step. Once again, the use of more than two beds will allow multiple pressure equalizations, thus conserving more pressure energy. Consider, as an example, the following two-bed adsorption process for mixing, with a pressure equalization step:

(a) Adsorb component B at the lower pressure P_2.
(b) After saturation in step (a), pressure equalize with another bed to increase the pressure of this bed to an intermediate pressure between P_2 and P_1.
(c) Pressurize the bed with component A (or the final mixture) to pressure P_1.
(d) Purge at pressure P_1 with component A to obtain the final mixture stream as the effluent stream.
(e) Once B is desorbed to the desired level, stop the flow of A and depressurize to an intermediate pressure level with pressure equalization with another bed.
(f) Depressurize further to the adsorption pressure P_2 and continue step (a).

Several variations of the previously described two-bed process are possible. For example, in step (f) when the bed is depressurized from the intermediate pressure level to the adsorption pressure P_2, the bed effluent may be handled in many different ways. It may be recycled by using a booster–compressor by either mixing it with the final mixture or with component A used for purging. The recycled gas can also be used to pressurize another bed to some intermediate pressure at any suitable point in the sequence during the pressurization of the bed.

In some cases, two or more gas streams at lower pressures are desired to be mixed into a high-pressure gas stream. In such a case, the lowest-pressure gas stream can be adsorbed first, followed by the coadsorption of the next higher pressure stream. Finally, the desorption is done by the highest-pressure stream. The requirement is to choose an adsorption bed that will selectively adsorb such desired components. Such an adsorption bed could contain multiple adsorbents mixed together or in layers.

The PSA mixing process can be augmented with some temperature swing to drive the adsorption/desorption of component B. Thus, while adsorption of component B may be done at a lower temperature (at pressure P_2), its desorption may be done at a higher temperature in stream A.

An example of how the suggested method can be used to save energy is the mixing of carbon dioxide and oxygen for a carbonate fuel cell. This mixing was discussed for the separator/mixer problem using a membrane in Figure 14. Now consider the situation in which a high-pressure oxygen stream is already available from an alternative source such as a cryogenic air separation unit. Some or all of the carbon dioxide may be adsorbed on a suitable adsorbent at low pressure and then desorbed into the high-pressure oxygen stream. Some temperature swing may be needed to mix large proportions of carbon dioxide with oxygen. The mixed stream is sent to the carbonate fuel cell, leading to savings in compression energy.

As with the separator/mixer process for a membrane, adsorption-based processes can be modified to separate a component B from a mixture BC and create a new mixture AB. Which of the two components A and B should adsorb more strongly depends on the relative pressures of streams A and BC. If the pressure of stream BC is lower than that of stream

A, then it is preferable that B be adsorbed more strongly than C and A. For this case, the simplest sequence of steps will be similar to those suggested for mixing of streams A and B. First B is selectively adsorbed from the mixture BC at a given lower-pressure P_2 and then, after pressure equalization with another bed, it is desorbed using A as a purge stream at a higher-pressure P_1. In this simplest cycle, at the end of the adsorption step some C will be present in the bed that will show up in the final mixture AB. Similarly, after desorption with A and pressure equalization, some A will be present in the bed and the C-enriched stream produced during the adsorption step will contain some A. Of course, it is possible to avoid this by using more complex cycles with multiple steps and some additional energy; however, discussion of such solutions is beyond the scope of this article.

The adsorption-based separator/mixer process for the other case when the pressure of stream A is lower than that of BC has already been exploited in the literature (Fuderer, 1983; Sircar, 1990). For this case it is required that A be adsorbed more strongly than B but less strongly than C. Fuderer (1983) gives an example of producing an ammonia synthesis gas mixture of nitrogen and hydrogen from a feed stock of pure nitrogen and a synthesis gas mixture. The major constituents of a synthesis gas mixture besides hydrogen are carbon monoxide, carbon dioxide, water, and CH_4. All the components other than hydrogen are adsorbed more strongly than nitrogen on the adsorbent of choice. The essence of this process is that a saturated bed is regenerated at a lower pressure of about 100 to 700 kPa by using nitrogen as a purge gas. Nitrogen can then be further adsorbed at some intermediate pressure level. Next the bed is pressurized to the adsorption pressure level (2 to 3 MPa) and the synthesis gas mixture is passed through the bed; all other components present in the synthesis gas besides hydrogen are adsorbed and nitrogen is displaced from the bed. The effluent of the bed is a mixture of nitrogen and hydrogen. After the bed is saturated with components present in the synthesis gas, it goes through the usual step of pressure equalization with other beds and is finally purged with nitrogen at the lowest pressure. The end result of this process is a reduction in the external compression requirement for compressing low-pressure make-up nitrogen to the final product pressure of the ammonia synthesis gas.

Similar to the adsorption-based processes, absorption can also be used for mixing. Consider the mixing of A and B when a suitable solvent can be found that absorbs B selectively. B could be absorbed at a lower-pressure P_2, and the saturated solution can then be pumped to a higher-pressure P_1 followed by stripping of B with A at pressure P_1. The regenerated solution is then let down in pressure across a valve and circulated for the absorption of B. Some heat to help the stripping of absorbed B can be used. The end result is a gas mixture of A and B at the higher pressure P_1 with reduced compression energy.

Conclusion

From the preceding sections, we can see that substantial mixing exergy is involved with the mixing processes occurring in nature and in the process industry. Nature and the process industry have been using some of this mixing exergy and such applications play vital roles in life and the environment and in the process industry. However, a large portion of the mixing exergy is yet to be utilized, especially where mixing of gaseous streams of different compositions is involved. In this article, some examples of how such mixing can be utilized to either reduce the energy consumption and save equipment cost or generate power have been presented.

First, the modification of a distillation column to become a mixing column was presented. In this case, since the heavy component is fed at the top, the condenser is warmer than the boiler. Some examples of power-generating cycles with a condenser as a heat source and a boiler as a heat sink have been proposed. However, the chances of finding a real-life application for these power-generating cycles seem to be low.

Membrane devices seem to be much more amenable to the mixing of gaseous streams with unequal compositions. Several such cases have been discussed in considerable detail. A lower-pressure stream B can be mixed with a higher-pressure stream A through permeation while either eliminating or minimizing the energy of compression and the compression machinery. Two membrane cascade schemes that lead to further optimization are proposed and discussed in detail. Use of an asymmetric permeator containing two membranes with reverse permeabilities is suggested to mix two streams so that the pressure of the final mixture can be higher than the pressure of the individual streams. In the limit, this pressure is the sum of the pressures of the individual streams. The idea can easily be extended to the mixing of more than two streams.

Another interesting application that was discussed in detail is the mixing of component B from a mixture BC with component A to create another mixture AB. In these separation/mixing problems, components A and C should have much less permeability through the membrane than component B. The location of the pinch in the driving force of the partial pressures of B between the two sides of the membrane (Δp_B) is shown to primarily depend on the ratio of the flow rates of nonpermeable components C and A. This location of the pinch also depends on the quantity of B needed to be transferred from BC to A. Conditions have been identified that lead to either a maximum or a minimum in Δp_B internal to the membrane. Based on this analysis, processes with high thermodynamic efficiency have been proposed to transfer B under different molar ratios of C to A. Some interesting applications were also discussed. Such separation/mixing devices not only can recover the mixing exergy, but also perform separation in the same simple device with efficiencies not attainable in conventional separators followed by mixing.

Use of adsorption and absorption-based processes with suitable modifications for such mixing was also briefly discussed. Interesting sequences of steps can be formulated for these mixing applications using either pressure swing or temperature swing processes. Some sequences were presented to elucidate the mixing of a low-pressure stream consisting of a more absorbable component with a high-pressure stream acting as a purge stream. Also, the interesting problem of separation/mixing was briefly touched.

In summary, mixing is a very common phenomenon in nature and in the process industry. There is great potential in fully utilizing this resource to reduce equipment cost, and energy consumption or to generate energy. Suitable modification of the known separation devices can yield mixing devices for gaseous streams with unequal compositions.

Acknowledgments

R. Agrawal recalls his initial discussion on this subject with the late Harvey Vines with gratitude. Comments and encouragement provided by Dr. Keith B. Wilson of Air Products and Chemicals are highly appreciated. The permission of Air Products and Chemicals, Inc. to publish this article is gratefully acknowledged.

Notation

C_i = ith compressor
F = flow rate of a stream
M_i = ith membrane module
P_i = pressure of the ith stream
s = membrane selectivity
t = dimensionless parameter
x_{AM}, x_{BM} = mole fractions of A and B on the side of the membrane where B is mixed with A
X = mole fraction of the more volatile component in the liquid phase
θ = ratio of pressures of two streams
η = dimensionless parameter
ξ = ratio of the flow rates of nonpermeable components C and A

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Appendix 1

Calculation of the optimum pressure for the two-stage membrane mixing process of Figure 4 (Scheme 1)

Assuming that the partial pressure of B in stream 4 is equal to pressure of stream 5,

$$\frac{P_5}{P_1} = \frac{n_2 - n_6}{n_1 + (n_2 - n_6)}. \tag{A1.1}$$

Assuming both C1 and C2 have the same efficiency, α, the total energy consumption, E_T, is given by

$$\alpha\frac{E_T}{RT} = n_2 \ln\frac{P_5}{P_2} + n_6 \ln\frac{P_7}{P_5}. \tag{A1.2}$$

Once again assuming that P_7 is equal to partial pressure of B in stream 3,

$$P_7 = x_{B3}\cdot P_1. \tag{A1.3}$$

Here n_6 and P_7 can be substituted from A1.1 and A1.3 into A1.2 to give

$$\alpha\frac{E_T}{RT} = n_2 \ln\frac{P_5}{P_2} + \left\{ n_2 - \frac{n_1}{\dfrac{P_1}{P_5} - 1} \right\} \ln\frac{x_{B3}P_1}{P_5}. \tag{A1.4}$$

For a given n_1 at P_1 and n_2 at P_2 to be mixed, E_T is a function of P_5. To find an optimum value of P_5 such that E_T is minimized, $\partial E_T/\partial P_5 = 0$; the resulting value of P_5 is given by the following expression:

$$1 - \theta_1 = \ln\frac{x_{B3}}{\theta_1}, \tag{A1.5}$$

where

$$\theta_1 = \frac{P_5}{P_1}.$$

Appendix 2

Calculation of the optimum pressure for the three-stage membrane process of Figure 5 (Scheme 2)

Following the same assumptions as in Appendix 1, an expression similar to A1.4 for total energy consumption E_T can be derived:

$$\alpha \frac{E_T}{RT} = \left\{ n_2 - \frac{n_1}{\dfrac{P_1}{P_2} - 1} \right\} \ln \frac{P_5}{P_2} + \left\{ n_2 - \frac{n_1}{\dfrac{P_1}{P_5} - 1} \right\} \ln \frac{x_{B3} P_1}{P_5}. \tag{A2.1}$$

For a given n_1 at P_1 and n_2 at P_2 to be mixed, the optimum value of P_5 such that E_T is minimized is given by

$$(1-\theta_2)\left\{ 1 - \left(\frac{1-\theta_2}{\theta_2} \right) \left(\frac{\theta_0}{1-\theta_0} \right) \right\} = \ln \frac{x_{B3}}{\theta_2}, \tag{A2.2}$$

where

$$\theta_2 = \frac{P_5}{P_1}$$

$$\theta_0 = \frac{P_2}{P_1}.$$

For the cases under consideration such that the preceding equation holds,

$$0 < \theta_0 \le x_{B3}, \qquad 0 < \theta_2 \le x_{B3}.$$

Furthermore,

$$\theta_2 \ge \theta_0 \Rightarrow \left(\frac{1-\theta_2}{\theta_2} \right) \left(\frac{\theta_0}{1-\theta_0} \right) \le 1.$$

As $(1-\theta_2) > 0$; $(1-\theta_0) > 0$ clearly:

$$0 < \left(\frac{1-\theta_2}{\theta_2} \right) \left(\frac{\theta_0}{1-\theta_0} \right) \le 1$$

$$\Rightarrow 0 \le 1 - \left(\frac{1-\theta_2}{\theta_2} \right) \left(\frac{\theta_0}{1-\theta_0} \right) < 1. \tag{A2.3}$$

Let

$$\phi \equiv 1 - \left(\frac{1-\theta_2}{\theta_2} \right) \left(\frac{\theta_0}{1-\theta_0} \right). \tag{A2.4}$$

Equation A2.2 is rewritten as

$$(1-\theta_2)\phi = \ln \frac{x_{B3}}{\theta_2},$$

$$\text{where} \quad 0 \le \phi < 1. \tag{A2.5}$$

For $\phi = 1$, Eq. A2.5 becomes identical to Eq. A1.5 and $\theta_1 = \theta_2$. It is of interest to find the value of θ_2 relative to θ_1 for the other value of ϕ. For a given x_{B3}, from A2.5

$$\frac{\partial \theta_2}{\partial \phi} = \frac{(1-\theta_2)\theta_2}{\phi\theta_2 - 1}. \tag{A2.6}$$

$$\text{Since } \phi < 1 \Rightarrow \phi\theta_2 - 1 < 0 \Rightarrow \frac{\partial \theta_2}{\partial \phi} < 0. \tag{A2.7}$$

Clearly for a given x_{B3}, as the value of ϕ is decreased, the value of θ_2 increases. Since $\theta_2 = \theta_1$ at $\phi = 1$, for any other value of $0 \le \phi < 1$, $\theta_2 > \theta_1$: optimum P_5 for Scheme 2 is greater than optimum P_5 for Scheme 1. For a given P_5, the E_T calculated from Eq. A1.4 is greater than the E_T calculated from Eq. A2.1. Therefore, at the optimum value of P_5 for Scheme 1, Eq. A2.1 will give a lower value of E_T than Eq. A1.4; this value from A2.1 is greater than the value of E_T calculated at an optimum value of P_5 for Scheme 2. This concludes that the minimum power consumption for Scheme 2 is less than the minimum power consumption for Scheme 1.

Appendix 3

Equations for the membrane separator/mixer scheme, Figure 10

The difference in partial pressure of B between the two sides of the membrane is given by

$$\Delta p_B = x_{BS} P_2 - (1 - x_{AM}) P_1. \tag{A3.1}$$

All the parameters along the length of the membranes on the side where B is being separated from C are shown with subscript S, and on the other side where B is mixed with A, with subscript M. Through total and component mass balance equations across a section of the membrane, the relation between x_{AM} and x_{BS} is derived to be

$$x_{AM} = \frac{1}{1 + \xi \left(\dfrac{x_{BS}}{1 - x_{BS}} - \dfrac{x_{B4}}{1 - x_{B4}} \right)}, \tag{A3.2}$$

where

$$\xi = \frac{n_2(1 - x_{B2})}{n_1} = \frac{n_C}{n_A}, \tag{A3.3}$$

where n_C is moles of C in stream 2 or 4 and n_A is moles of A in stream 1 or 3; x_{AM} is substituted from A3.2 into A3.1. The resulting expression is differentiated with respect to x_{BS} and equated to zero to provide the location of the extremum for Δp_B. It occurs when the following condition is satisfied:

$$\eta \equiv \left(\frac{1 - x_{BM}}{1 - x_{BS}} \right)^2 = \left(\frac{x_{AM}}{x_{CS}} \right)^2 = \frac{\theta}{\xi}, \tag{A3.4}$$

where

$$\theta = \frac{P_2}{P_1}. \tag{A3.5}$$

To find when an extremum occurs, whether it is a maxima or a minima, the second derivative of Δp_B is calculated at the location of the extremum

$$\left.\frac{\partial^2 \Delta p_B}{\partial x_{BS}^2}\right|_{\text{at extremum}} = \frac{2P_1\theta}{x_{CS}}[\xi^{1/2}\theta^{1/2} - 1] \tag{A3.6}$$

clearly when

$$\theta\xi < 1 \Rightarrow \text{ a maximum in } \Delta p_B$$

$$\theta\xi > 1 \Rightarrow \text{ a minimum in } \Delta p_B.$$

For the chosen stream conditions in Figure 10, it can be shown that $\eta^{1/2}$ and therefore η is a monotonic function along the length of the membrane. Through mass balance $\eta^{1/2}$ can be expressed as

$$\eta^{1/2} \equiv \frac{x_{AM}}{x_{CS}} = \frac{n_C + n_{BS}}{\xi\{(n_A - n_{B4}) + n_{BS}\}} \tag{A3.7}$$

$$\frac{\partial \eta^{1/2}}{\partial n_{BS}} = \frac{1}{\xi\{(n_A - n_{B4}) + n_{BS}\}^2}[(n_A - n_{B4}) - n_C]$$

$$= \frac{1}{\xi\{(n_A - n_{B4}) + n_{BS}\}^2}(n_3 - n_2). \tag{A3.8}$$

For an extremum to occur for $\eta^{1/2}$, $\partial\eta^{1/2}/\partial n_{BS} = 0$:

$$\frac{\partial \eta^{1/2}}{\partial n_{BS}} = 0 \Rightarrow n_C = n_A - n_{B4} = n_A\left\{1 - \left(\frac{n_{B2} - n_{B3}}{n_A}\right)\right\}.$$

Clearly, $n_{B2} \geq n_{B3}$ and therefore for all $\xi > 1$, the preceding equation cannot be satisfied. For $\xi \leq 1$, when the preceding is substituted in Eq. A3.7, $\eta^{1/2} = 1/\xi =$ constant. In conclusion, η is either a monotonous function or for $\xi \leq 1$ it is possible to have a constant value of $\eta = 1/\xi^2$ along the length of the membrane. Furthermore, when $n_3 > n_2$, the value of η decreases along the length as the value of x_{BS} decreases, the reverse is true for $n_3 < n_2$, and it is a constant value for $n_3 = n_2$. Therefore, for a given condition of all the streams in Figure 10, the value of η can be calculated at both ends of the membrane (at the inlet end of stream 1 and the inlet end of stream 2). If these two values of η bound the value of θ/ξ, then an extremum is definitely going to occur inside the membrane at a location given by Eq. A3.4. If the value of η is equal to θ/ξ at one of the ends of the membrane, then there is no extremum inside the membrane and the maximum or minimum in the value of Δp_B occurs at that end of the membrane.

Now consider three cases: $\xi < 1$, $\xi = 1$, $\xi > 1$ separately to calculate pinch locations and the minimum possible pressure of stream BC with respect to stream A to achieve the desired task.

Case 1: $\xi < 1$. In this case $n_A > n_C \Rightarrow x_{B3} < x_{B2}$ and it can be readily proved that $x_{BM} < x_{BS}$ for all values of x_{BS}:

$$n_{B2} \geq n_{B3}$$

$$\Rightarrow n_{B2} - \Delta n \geq n_{B3} - \Delta n$$

$$\Rightarrow n_{B2} - \Delta n > \xi(n_{B3} - \Delta n)$$

$$\Rightarrow \frac{\xi n_A}{n_{B2} - \Delta n} < \frac{\xi n_A}{\xi(n_{B3} - \Delta n)} = \frac{n_A}{n_{B3} - \Delta n}$$

$$\Rightarrow \frac{1}{x_{BS}} < \frac{1}{x_{BM}}$$

$$\Rightarrow x_{BM} < x_{BS} \forall x_{BS}, \tag{A3.9}$$

where Δn is the number of moles of B transferred from the *S* side of the membrane to the *M* side of the membrane. Clearly η as defined by Eq. A3.4 will always be greater than unity. Since $x_{B3} < x_{B2}$, another conclusion can be drawn when the pinch is at the feed end of BC; in this case the partial pressure of B in streams 2 and 3 is equal:

$$\Rightarrow \theta = \frac{P_2}{P_1} = \frac{x_{B3}}{x_{B2}} < 1. \tag{A3.10}$$

From these two observations, conclusions can be drawn for the following three subcases:

$\theta \leq \xi$. Since η is always greater than unity, Eq. A3.4 cannot be satisfied for $\theta \leq \xi$; therefore, along the length of the membrane there is no extremum in the Δp_B profile. However, it is possible to have a pinch in the partial pressure driving force at the feed end of BC; in such a situation Δp_B will increase as x_{BS} decreases along the membrane.

$\theta > \xi$ and $\theta\xi < 1$. In this case it is possible to satisfy Eq. A3.4 resulting in a maximum in Δp_B. Once again it is possible to get a pinch at the feed end of BC, as θ can be less than one. However, just because $\xi < 1$ and $\theta > \xi$ and membrane is pinched at the feed end of BC such that $\theta < 1$ (therefore $\theta\xi < 1$), it does not mean that there is a maximum in the Δp_B. For the maximum to occur, Eq. A3.4 must be satisfied. It can be readily proved that when all the B from BC is transferred to A, and the membrane is pinched at the feed end of BC, a maximum in Δp_B always occurs inside the membrane:

From Eq. A3.10:

$$\theta = \frac{x_{B3}}{x_{B2}} = \frac{n_C + n_{B2}}{n_A + n_{B2}}$$

$$= \xi\left[\frac{n_A + n_{B2}/\xi}{n_A + n_{B2}}\right]. \tag{A3.11}$$

The preceding equation gives the maximum possible value of θ for which a pinch is possible at the feed end of BC. For any higher values of θ, the partial pressure of B in stream 2 will always be higher than that in stream 3. Since $n_{B2}/\xi > n_{B2}$, it follows from Eqs. A3.10 and A3.11 that when all of B is transferred from stream 2 to stream 3 and the pinch is at the feed end of BC:

$$\xi < \theta < 1.$$

Furthermore, the value of η at the feed end of BC is given by:

$$\eta = \left(\frac{x_{A3}}{x_{C2}}\right)^2 = \left[\frac{n_A}{n_A + n_{B2}} \cdot \frac{n_C + n_{B2}}{n_C}\right]^2 = \left(\frac{\theta}{\xi}\right)^2. \tag{A3.12}$$

The value of η at the feed end of stream A is one. Since $n_3 > n_2$, the value of η decreases as the value of x_{BS} decreases and therefore:

$$1 \le \eta \le \left(\frac{\theta}{\xi}\right)^2.$$

From the preceding condition it is clear that there will be a location along the length of the membrane where $\eta = \theta/\xi$ and Eq. A3.4 is satisfied. This completes the proof of a maximum in Δp_B when all of B is transferred from stream BC to stream A. Notice in this case that Δp_B is also zero at the feed end of stream A and the membrane is pinched at both ends.

$\theta > \xi$ and $\theta\xi > 1$. This is the case when θ is much larger than the value given by Eq. A3.11, and there is no pinch in the value of Δp_B. The values of Δp_B are quite large along the length of the membrane. An extremum, when it occurs, will be a minimum in Δp_B.

***Case 2:* $\xi = 1$.** In this case, $n_A = n_C$ and $n_{B3} \le n_{B2}$. By mass balance along a section of the membrane in Figure 10, it can be shown:

$$\frac{x_{AM}}{x_{CS}} = \frac{n_A + n_{BS}}{n_A - (n_{B2} - n_{B3}) + n_{BS}}, \tag{A3.13}$$

therefore, when $n_{B2} = n_{B3} \Rightarrow \eta = 1$

$$n_{B2} > n_{B3} \Rightarrow \eta > 1,$$

when $\eta > 1$, for Eq. A3.4 to be satisfied, θ must be greater than one and the extremum will be a minimum in Δp_B. For $\eta = 1$, it can be shown below that there is no extremum in Δp_B. Consider a case when almost all of the B is transferred to A, such that $x_{B4}/(1 - x_{B4})$ is very small; Eq. A3.2 can then be substituted in Eq. A3.1 and rearranged to give the following approximate relation:

$$\Delta p_B \cong (P_2 - P_1)x_{BS} + \left(\frac{x_{B4}}{1 - x_{B4}}\right)(1 - x_{BS})^2 P_1. \tag{A3.14}$$

Clearly, for $\eta = 1$, when x_{B4} is zero, Δp_B is a monotonous function of x_{BS} with no extremum. This equation also shows that when $P_2 < P_1$, $x_{B4} \ne 0$; otherwise, Δp_B will be less than zero. When $\theta = 1$ and x_{B4} approaches zero,

$$\Delta p_B \approx \left(\frac{x_{B4}}{1 - x_{B4}}\right)(1 - x_{BS})^2 P_1$$

We can thus conclude $\lim_{x_{B4} \to 0} \Delta p_B|_{\xi=1,\theta=1} = 0$.

Whenever there is a pinch in Δp_B at the feed end of BC, it follows from Eq. A3.10 that $\theta \le 1$ and there is no extremum in the value of Δp_B.

***Case 3:* $\xi > 1$.** In this case $n_C > n_A$; $n_3 < n_2 \Rightarrow \eta$ will always increase as x_{BS} is reduced along the length of the membrane. There are three subcases of interest:

$\theta \le 1$. Since $P_1 x_{B3} \le P_2 x_{B2}$, it implies that for $\theta \le 1$, $x_{B3} \le x_{B2}$. Therefore at the feed end of BC, the value of $\eta \ge 1$; this value will further increase as x_{BS} is reduced. But $\theta/\xi < 1$, and as a result, Eq. A3.4 cannot be satisfied. There is no extremum in the value of Δp_B for this subcase. The pinch in the value of Δp_B, when it occurs, will take place at the feed end of stream BC.

$1 < \theta \le \xi$. Since $\theta\xi > 1$, whenever an extremum in Δp_B occurs, it will always be a minimum. Once again for $x_{B3} \le x_{B2}$, $\eta \ge 1$ and $\theta/\xi \le 1$, and there is no extremum in the value of Δp_B inside the membrane; the value of Δp_B increases monotonically as x_{BS} is decreased. However, for $x_{B3} > x_{B2}$, it is possible to have a minimum in the value of Δp_B.

For $x_{B3} \le x_{B2}$, the pinch in Δp_B is always at the feed end of BC. However, for $x_{B3} > x_{B2}$, the pinch can be *inside* the membrane. To calculate the minimum possible θ to achieve a given task, it is desirable to derive an equation relating the location of pinch x_{BS}^1 to θ and ξ. For such a pinch, both Eqs. A3.1, with $\Delta p_B = 0$, and A3.4 will be simultaneously satisfied, combining the two results:

$$\left(\frac{1 - \theta x_{BS}^1}{1 - x_{BS}^1}\right)^2 = \frac{\theta}{\xi}. \tag{A3.15}$$

Define

$$t \equiv \left(\frac{\theta}{\xi}\right)^{1/2}. \tag{A3.16}$$

Rearrangement of Eq. A3.15 gives

$$\xi x_{BS}^1 t^2 + (1 - x_{BS}^1)t - 1 = 0. \tag{A3.17}$$

For $\theta = \xi$, $x_{BS}^1 = 0$, and pinch is at the feed end of stream A when all of the B has been removed from BC. Therefore, pinch in the middle of the membrane can only occur for $1 < \theta < \xi$. For a given x_{B2} and ξ, use of Eq. A3.17 provides an upper value of x_{B3} called x_{B3}^1, below which pinch is always at the feed end of stream BC. Whenever x_{B3} is chosen to be higher than the calculated upper value of x_{B3}^1, the pinch is inside the membrane. Such an upper value of x_{B3}^1 is calculated by substituting x_{BS}^1 equal to the given x_{B2} in Eq. A3.17 and solving for t. Once t and therefore θ (called θ^1) have been calculated, the value of $x_{B3}^1 = \theta^1 x_{B2}$. If $x_{B3} = x_{B3}^1$ and

$\theta = \theta^1$, then Eq. A3.4 is satisfied at the feed end of BC and pinch in Δp_B is also at this end. As the value of x_{B3} is increased above x_{B3}^1, the value of η at the feed end of BC is decreased; while the value of θ needs to be higher than θ^1, which means θ/ξ increases, this means Eq. A3.4 will be satisfied inside the membrane at some $x_{BS} < x_{B2}$; in this case, the pinch is inside the membrane. On the other hand, as x_{B3} is decreased below x_{B3}^1, the value of η at the feed end of BC is increased; while the value of θ is lower than θ^1, which means θ/ξ decreases, this means Eq. A3.4 cannot be satisfied; in this case pinch is at the feed end of BC. This means that a quick method to estimate whether pinch is internal to the membrane module or not is to assume that the pinch is at the feed end of BC and calculate the corresponding value of θ; if this value of θ is such that $\theta^1 < \theta < \xi$, then the pinch is internally located; otherwise, it is at the feed end of stream BC.

For a given x_{B3} and x_{B2}, once the presence of an internal pinch has been established, its location can be calculated. If Δn is the moles of B transferred from stream 2 before pinch takes place, then Eq. A3.4 gives

$$\frac{n_C + n_{B2} - \Delta n}{n_A + n_{B3} - \Delta n} = (\theta\xi)^{1/2}. \tag{A3.18}$$

Equation A3.1 with $\Delta p_B = 0$ gives

$$\frac{n_{B2} - \Delta n}{n_C + (n_{B2} - \Delta n)} \cdot \theta = \frac{n_{B3} - \Delta n}{n_A + (n_{B3} - \Delta n)}. \tag{A3.19}$$

From the preceding two equations, two expressions for Δn can be derived:

$$\Delta n = \frac{(\theta/\xi)^{1/2} n_{B2} - n_{B3}}{(\theta/\xi)^{1/2} - 1} \tag{A3.20}$$

$$\Delta n = \frac{n_2 - n_3(\theta\xi)^{1/2}}{1 - (\theta\xi)^{1/2}}. \tag{A3.21}$$

If for this internal pinch, along with n_{B2}, n_{B3}, n_2, and ξ the value of θ was known, then the corresponding location of pinch can be readily calculated by either Eq. A3.20 or Eq. A3.21. Quite often, n_{B2}, n_{B3}, n_2, and ξ are known, and it is required to find the minimum value of θ for internal pinch. For this purpose, Δn is eliminated from Eqs. A3.20 and A3.21, and all the flow rates are related to mole fractions; after some algebraic manipulation the following relation is derived:

$$t^2\{\xi^2 x_{B2} x_{A3} - \xi x_{C2}\} + t\xi\{x_{C2} + x_{A3} - x_{B3} x_{C2} - x_{B2} x_{A3}\} - \xi x_{A3} + x_{B3} x_{C2} = 0, \tag{A3.22}$$

where t is defined by Eq. A3.16. Thus for a given ξ and mole fractions in the streams, the corresponding value of θ for an internal pinch can be calculated.

Finally, it is of interest to find the location of pinch when all of B is transferred and mixed with A. In this case, $n_{B2} = n_{B3}$, and from Eq. A3.20, $\Delta n = n_{B2}$; that is, pinch will take place at the feed end of stream A with $x_{B4} = 0$. As stated earlier, for this situation $\theta = \xi$ from Eq. A3.17.

$\underline{\xi < \theta}$. For this case it follows from the preceding discussion that there is no pinch in Δp_B except at the feed end of stream A. Otherwise, its value is always greater than zero throughout the membrane. Mathematically, the value of x_{BS}^1 calculated from Eq. A3.17 is negative, which means that Δp_B cannot have a zero value inside the membrane. Since the value of η increases uniformly along the length of the membrane, it is possible to satisfy Eq. A3.4 for any given value of x_{B3} and x_{B2}; therefore, the occurrence of a minimum in Δp_B does not solely depend on whether x_{B3} is greater than, equal to, or less than x_{B2}.

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