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Removal of CO_2 from Natural Gas Using Membrane Separation System: Modeling and Process Design

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Abstract: Natural Gas (NG) processing is one of the major industrial separation processes. Membrane process, a relatively new technology among other available techniques, can be used for the removal of impurities like carbon dioxide from NG. Membrane performance has been described by different mathematical models over the decades. In this work, a simple mathematical model has been suggested to be incorporated with ASPEN HYSYS in order to design the membrane system for CO_2/CH_4 separation. Parameter sensitivities were analyzed by changing the operating conditions, such as feed composition and pressure and membrane properties (including selectivity of the membrane). Moreover, different configurations have been investigated for the optimized design including single stage (with and without recycle) and double stage membrane systems. It is shown that methane recovery can be improved by recycling permeate stream as well as by using double stage membrane system.

Key words: Membrane process, gas separation, natural gas processing, CO_2 removal process

INTRODUCTION

The composition of natural gas varies from source to source. Methane is the major component (75-90%), but natural gas also contains significant amounts of ethane, propane, butane and 1%-3% of other higher hydrocarbons (Baker and Lokhandwala, 2008). In some deposits, it may contain complex contaminants such as CO_2, H_2S, CO which constitutes environmental hazards and also hindered natural gas processes. The upgrading of low quality crude natural gas is an attracting interest due to the high demand for pipeline-grade gas in recent years. CO_2 needs to be removed in order to; increase the heating value of the gas, prevent corrosion of pipeline and process equipments and crystallization during liquefaction process (Bhide and Stern, 1993; Safari *et al*., 2008a, b).

CO_2 contents in the NG can vary from 4 to 50% depending upon the gas source. Before the transportation of NG, it must be pre-processed in order to meet the typical pipeline specification of 2%-5% CO (Datta and Sen, 2006). Most of the natural gas, produced in the lower 48 states of USA, contains more than 5% $C0_2$. Currently, many natural gas wells are shut due to their low production rate and low quality (i.e., high CO_2 and/or H_2S content) (Lee *et al*., 1994). Therefore, it has become necessary to develop efficient processes for the removal of CO_2 from NG.

CO_2 can be removed by a number of processes considering the factors of; capital and operating costs, gas specifications and environmental concerns. The major processes can be grouped as:

- Absorption processes (chemical and physical absorption)
- Adsorption process (solid surface)
- Hybrid solution (physical and chemical solvent)
- Physical separation (membrane. Cryogenic separation) (Maddox, 1974; Koros and Chern, 1987)

Membranes processes are commercially proven technology for natural gas processing application. Separation of CO_2 with common polymeric or inorganic (e.g., zeolite, sol-gel silica or carbon molecular sieve) membranes is achieved by differences in terms of diffusion rates and/or adsorption strengths of mixture components in the polymer matrix or the inorganic membrane pores. For a gas to permeate through a membrane surface, the gas must first dissolve in the high-pressure side of the membrane, diffuse across the membrane wall and evaporate from the low-pressure side. Gas separation therefore works on the principle that some

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gases are more soluble in and pass more readily through polymeric membrane than other gases (Ebenezer, 2006; Richard, 2004; Ismail, 2009).

In membrane process, feed gas is pretreated before entering the membrane system to ensure efficient operation. The conditioning of feed stream controls the fouling, plasticization and condensation of hydrocarbons on the membranes (Baker and Lokhandwala, 2008).

The pre-treatment equipment depends on the conditions and composition of feed gas. Usually in the case for natural gas, the feed gas is filtered, as a first step, for removal of entrained particulates or aerosols including sand, pipe scale. The feed gas is then cooled in a cooler. Any condensed liquids are removed in the gas/liquid separator. After liquid removal, the feed gas enters the feed preheater. The temperature control system is provided to maintain the gas at the desired operating temperature of the membrane fibers. Finally, the heated gas enters the membrane gas separators where it is separated into two streams; the permeate, a low pressure CO_2 stream and the non-permeate or residue, a high pressure hydrocarbon rich stream (Ebenezer, 2006).

Gas separation by membrane technology has become a major industrial application only during the last few decades but the study of gas separation has a long history (Richard, 2004).

Graham (1866) measured the permeation rates of all the gases then known through different diaphragms (Richard, 2004). Barrer (1951), Van Amerongen (1950) and played an important role in the development of solution diffusion model for the explanation of gas permeation (Richard, 2004) The first company to establish a Prism membrane was Monsanto for hydrogen separation. The success of Monsanto encouraged other companies like Cvnaoi. Separex and grace membrane systems to produce membrane plants to remove CO_2 in natural gas (Richard, 2004; Henis and Tripodi, 1980).

Datta and Sen (2006) optimized the gas processing cost of a membrane unit. It was shown that there was no unique configuration that would always be optimum irrespective of the values of carbon dioxide concentration and cost of natural gas. However, within certain ranges of the carbon dioxide concentration and the cost of natural gas. The optimum configuration might be unique and the minimum gas processing cost could be achieved by adjusting only the number of modules in each stage and the compressor power.

Wang *et al.* (2007) enhanced operational flexibility and adaptability of membrane process using an optimal method in which auto-controlling of the permeate gas flux was applied for the first time. Moreover, it was shown that the permeate gas flux could be auto-controlled through a control valve installed on the residue gas line.

Qi and Henson (1998a, b) developed the optimal design strategy for spiral membrane networks for gas separations whereas Lababidi *et al.* (1996) developed the mathematical model to optimize three configurations including single stage, two stages and the Continuous Membrane Column (CMC). The simple models for the permeability and selectivity variations of the CO_2/CH_4 system have been derived by Safari *et al.* (2008b) that included both temperature and pressure effects simultaneously.

Hao *et al.* (2008) worked on the upgrading of low quality natural gas with CO_2 selective membranes and studied process design, economics and sensitivity of membrane stage with recycle streams.

Lee *et al.* (1994) made field tests of membrane modules for the separation of carbon dioxide from low-quality natural gas. In their study, they investigated the effects of the operating variables of pressure, feed flow rate and the carbon dioxide concentration in the feed. In addition, computer models were applied for the separation of gases under perfect mixing and cross flow conditions to the analysis of the field data.

In this study, membrane processes for gas separation is studied under different configurations using ASPEN HYSYS. Since membrane unit is not a pre-defined unit operation in ASPEN HYSYS, a simple cross flow model is presented for the prediction of membrane performance in the removal of CO_2 from natural gas. The model is then included as user defined unit operation in the process simulation along with other unit operations in order to design the membrane system configuration.

MATERIALS AND METHODS

Governing equations: The study is based on the cross flow model as shown in the detailed flow diagram (Fig. 1). The model assumes no mixing in the permeate side as well as on the high pressure side. Thus the composition of permeate can be determined at any point along the membrane by the relative permeation rates of feed component at that point (Weller and Steiner, 1950; Geankoplis, 2003).

The assumptions that follow the suggested model are:

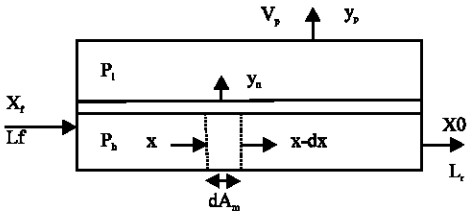

Fig. 1: Schematic diagram of cross flow membrane separation

- It holds for the binary gas mixture
- Permeability is independent of pressure and temperature of the gas stream
- It represents the whole membrane module and will not involve the details inside the module
- Pressure drop on both sides of the membrane is negligible
- The concentration polarization is assumed to be negligible

The local permeation rate at any point in the stage over a differential membrane area dA_m is:

$$ydV = \frac{P_A}{t}[p_h x - p_l y] \quad (1)$$

$$ydV = \frac{P_S}{t}[p_h(1-x) - p_l(1-y)] \quad (2)$$

Dividing Eq. 1 by Eq. 2, we get:

$$\frac{y}{1-y} = \frac{\alpha[x-(p_l-p_h)y]}{(1-x)-\left(\frac{p_l}{p_h}\right)(1-y)} \quad (3)$$

Using ingenious transformations, an analytical solution to the three equations (Eq. 1-3) have been obtained.

$$\frac{(1-\theta^*)}{(1-xf)} = \left[\frac{U_f-\frac{E}{D}}{U-\frac{E}{D}}\right]^R \left[\frac{U_f-\alpha+F}{U-\alpha+F}\right]^S \left[\frac{U_f-F}{U-F}\right]^T \quad (4)$$

where, θ^* = 1-L/L_f (L as flow rate permeated in the differential element):

$$i = \frac{x}{(1-x)}$$

$$u = -Di + (D^2i^2 + 2Ei + F^2)^{0.5}$$

$$D = 0.5\frac{(1-\alpha)p_l}{p_h} + \alpha$$

$$E = (\alpha/2)\text{-}DF$$

$$F = -0.5\frac{(1-\alpha)}{p_h}p_l - 1$$

$$R = 1/(2D\text{-}1)$$

$$S = \frac{\alpha(D\text{-}1)+F)}{(2D-1)-\left(\frac{\alpha}{2}-F\right)}$$

$$T = \frac{1}{1-D-(\frac{E}{F})}$$

The term u_f is the value of u at $i = i_f$. The value of θ^* is the fraction permeated up to the value of x. At the outlet

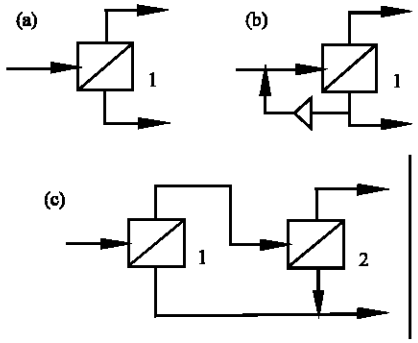

Fig. 2: Design configurations for CH_4/CO_2 separations: (a) single stage (b) Single stage with recycle and (c) two stage

where, $x = x_0$, the value of θ^* becomes equal to θ, the total fraction permeated. The composition of the permeate stream is y_p and thus can be calculated from the overall material balance.

$$yp = \frac{xf - x0(i-\theta)}{\theta} \quad (5)$$

Design configurations: The design of a membrane separation process involves (1) the configuration of permeators (2) the operating parameters of the individual permeators Different configurations have been proposed for the membrane separation as shown in Fig. 2a-c.

For moderate purity and recovery requirement, single stage system (with and without recycle) is appropriate (Schell and Houston, 1982). For more demanding separations, multiple stage system is required (Spillman, 1989; Coady and Davis, 1982). It is a conventional approach to select different configurations and then optimize the operating permeation.

RESULTS AND DISCUSSION

Model validation: Mathematical model is validated with the published experimental data for membrane separation process.

The data by Pan (1986) is based on the experiments done on sour natural gas. The feed gas contains 48.5% CO_2 that is removed in the permeate stream, with the purpose to increase the recovery of methane in the retentate stream. The temperature and pressure of the gas are 10°C and 35.28 bars respectively whereas, on the other hand, the permeate pressure is 9.28 bars. The selectivity is assumed to be 25. Figure 3a shows that the suggested model gives good approximation to the experimental data. The error may be contributed to the sensitivity of methane permeability towards high pressure. The data from Liu *et al.* (2006) is based on the study conducted on

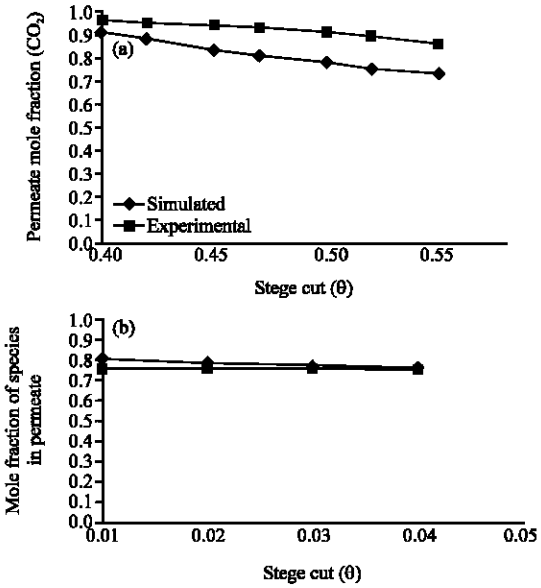

Fig. 3: Validation of mathematical model with experimental data (a) Pan (1986) and (b) Liu *et al.* (2006)

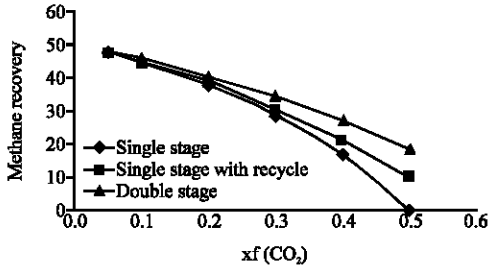

Fig. 4: Effect of feed composition on methane recovery

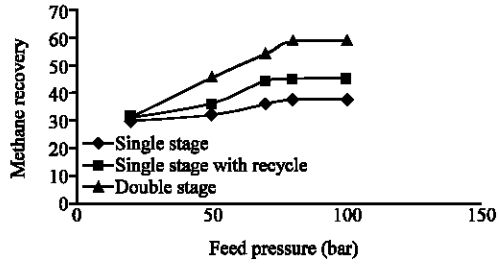

Fig. 5: Effect of feed pressure on methane recovery

propylene enrichment using cross flow membrane. Figure 3b show that the simulated data are in close agreement with the experimental data. It can also be observed that the simulated model gives better approximation with experimental data from as compared to experimental data. It might be due to the fact that the later data takes into account of the effect of pressure drop that has been assumed negligible in the suggested model.

Parametric analysis: The methane recovery is considered as the main parameter for membrane system design. The effects of feed composition, feed pressure and the selectivity of the membrane were studied on the methane recovery for different configurations using the suggested cross-flow model.

Effect of feed composition: Methane recovery decreases with the increase in CO_2 contents of the feed. At the same time, methane recovery can be improved by recycling the permeate stream as well as using double stage configuration (Schell and Houston, 1982, Spillman, 1989; Coady and Davis, 1982). It is obvious as the portion of first stage permeate that is lost is taken from first membrane module, where CO_2 is highest and hydrocarbon is lowest (Ismail, 2009).

The effect of feed composition on methane recovery for all proposed configurations, for the stage cut of 0.5 and selectivity of 25, is shown in Fig. 4. The feed pressure and permeate pressure are maintained at 100 and 4 bar respectively. It can be observed that the methane recovery is reducing with the increase of CO_2 in the feed gas. The systems without recycle, as expected, provide the lowest CH_4 recovery. It is obvious as the portion of first stage permeate that is lost is taken from the first membrane module, where feed CO_2, hence permeate CO_2 is highest and hydrocarbons are lowest. Besides, the simulated results also show that the usage of two stage system could minimize the reduction of CH_4 recovery under high CO_2 feed composition.

Effect of feed pressure: The increase in feed pressure improves methane recovery (Ismail, 2009). It is due to the fact that the increased pressure creates a greater driving force across the membrane. As a result, a net increase in permeation through the membrane increases methane recovery.

Figure 5 shows the effect of feed pressure on methane recovery for different configurations. The stage cut and selectivity is same as in previous case, whereas the feed gas contains 20% CO_2 and 80% CH_4. The increase in feed pressure increases the methane recovery, especially when is pressure is less than 70 bar. Based on the figure, the double stage configuration gives the highest recovery followed by single stage with recycle stream and single stage without recycle stream.

Effect of membrane selectivity: Membrane properties have high influence on methane recovery. Methane

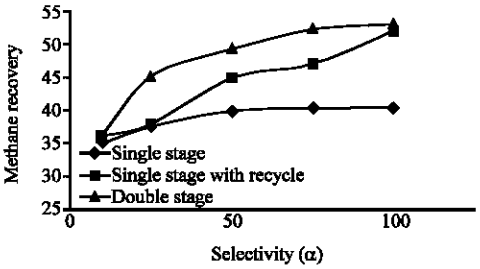

Fig. 6: Effect of membrane selectivity on methane recovery

recovery increases with the increase in selectivity of the membrane (Qi and Hensen 1998b). It is due to the reason that increased selectivity leads to higher permeation and thus improved methane recovery.

Figure 6 shows the effect of membrane selectivity on the three proposed configurations, as expected, the increase in selectivity increases CH_4 recovery, especially for the configuration with double stage and single stage with recycle stream. It can also be noted that the increment in selectivity for the single stage configuration is less significant on the methane recovery.

CONCLUSION

A systematic design strategy has been proposed for the CH_4/CO_2 separation using membrane process. The proposed cross flow model was validated with experimental data, where the simulated data exhibited good agreement with the experimental results. The design sensitivity has been investigated by changing the operating conditions and membrane properties. Different configurations including single stage (with and without recycle) and double stage membrane systems have been investigated under present study. It is shown that methane recovery can be improved by recycling the permeate stream as well as using double stage configuration. The ASPEN HYSYS user defined unit operation proposed under present study potentially to be applied for complex membrane system design and optimization.

NOMENCLATURE

x_f = Feed mole fraction
x_0 = Retentate mole fraction
y_n = Permeate mole fraction
A_m = Active membrane area (m^2)
L_f = Feed flow rate (mol sec)
L_r = Retentate flow rate (mol sec^{-1})
V_n = Permeate flow rate (mol sec^{-1})
p_h = Pressure on the high pressure side (kPa)
p_l = Pressure on the low pressure side (kPa)
P_A = Permeability of component A (mol $msec^{-1}$ Pa)
P_B = Permeability of component B (mol $msec^{-1}$ Pa)
θ = Stage Cut or fraction permeated
α = Selectivity of the membrane

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