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March 27, 2000

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Dear Ms. Kuzniar:

Enclosed is a copy of our Final Report on DOE Grant, DE-FG21-91MC28072, "Upgrading Natural Gas via Membrane Separation Processes". We hope that you will find the report satisfactory.

We greatly appreciate your support of this project and your patience in waiting for this report.

Sincerely,

Philip A. Rice
Professor

PAR:rrd

Cc: Mary Ann Holmquist, Sponsored Programs

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JAN 29 2004

**UPGRADING NATURAL GAS VIA MEMBRANE SEPARATION PROCESSES
DE-FG21-91MC28072**

COMPREHENSIVE TECHNICAL REPORT

by

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MEMBRANE PROCESSES FOR THE UPGRADING OF LOW-QUALITY NATURAL GAS

I. INTRODUCTION

1. Objective of Study

The objective of the present study is to assess the potential usefulness of membrane separation processes for removing CO₂ and H₂S from *low-quality* natural gas containing substantial amounts of both these "acid" gases, e.g., up to 40 mole-% CO₂ and 10 mole-% H₂S. The membrane processes must be capable of upgrading the crude natural gas to pipeline specifications (≤ 2 mole-% CO₂, ≤ 4 ppm H₂S). Moreover, these processes must also be economically competitive with the conventional separation techniques, such as gas absorption, utilized for this purpose by the gas industry.

2. General Considerations

Natural gas is one of the three major energy resources in the United States together with oil and coal. The natural gas demand in 1995 was 22.25 quadrillion Btu, or about 25.5 % of the total energy consumption and just below the demand for oil [1]. According to the Gas Research Institute (GRI) of Chicago, IL, the demand for natural gas will increase steadily and may reach 27% of the total energy consumption in 2015 [2].

Crude natural gas containing substantial amounts of CO₂ (but only small amounts of H₂S) is being increasingly upgraded to pipeline specifications by means of membrane separation processes [3-7]. These processes offer a number of important advantages over the conventional techniques of gas separation. Thus, membrane processes are inherently energy-efficient and, due to their modular design, can be easily scaled up or operated at reduced capacity. Moreover, these processes offer good space and weight efficiency and adjust readily to variations in feed gas composition and flow rate.

Membrane processes for the upgrading of natural gas are, in addition, environmentally safe and usually operate at ambient temperature, thereby avoiding the energy losses associated with heat exchange [7-10]. Also, membrane plants can be used to process natural gas at wellheads instead of at a central plant [7].

Until recently, large-scale membrane processes for the upgrading of natural gas utilized membranes made from *cellulose acetate*, which have a relatively modest CO₂/CH₄ selectivity, cf. ref. [11]. These processes are economically competitive only when used for the treatment of natural gas containing over 10-20 mole-% CO₂, depending on the wellhead pressure. In the last few years new types of *polyimide* membranes with much higher CO₂/CH₄ selectivities and equal or larger permeabilities to CO₂ were developed at Syracuse University [12] and elsewhere. The new membranes will substantially improve the economics of membrane processes for the upgrading of natural gas and extend their ranges of applications.

In view of the expected growth in the demand for natural gas, increasing attention is being devoted by the U.S. Department of Energy and by the gas industry to the upgrading of *low-quality* natural gas containing substantial amounts of *both* H₂S and CO₂.

Consequently, a membrane process that could economically reduce the concentrations of these "acid" gases to pipeline specifications will require polymer membranes that exhibit both high H_2S/CH_4 and CO_2/CH_4 selectivities. However, neither the cellulose acetate membranes nor the newly developed polyimide membranes exhibit a sufficiently high H_2S/CH_4 selectivity for this application. Recent studies have shown that certain *polyurethane* block polymers are very promising membrane materials for the removal of H_2S from natural gas. Thus, the H_2S/CH_4 selectivity of a poly(ether urethane urea) membrane synthesized at Syracuse University and designated hereafter as PU4 is about 4 times higher than that of cellulose acetate membranes [at 95°F (35°C) and 147 psia (10.14 bars)] [13]. Even more impressive is the fact that the permeability of the PU4 membranes to H_2S is 93 times higher than that of cellulose acetate membranes under the same conditions. However, the CO_2/CH_4 selectivity of PU4 membranes is relatively low.

The above results suggest that it may be possible to develop membrane processes for the upgrading of low-quality natural gas by utilizing both highly CO_2 -selective membranes, such as the new polyimide membranes mentioned above, and highly H_2S -selective membranes, such as the newly-developed PU4 membranes. Comprehensive membrane process simulations and economic evaluations have been completed in order to identify the process configurations that will most effectively combine the two types of membranes mentioned above. It is also important to determine if the pipeline specifications for H_2S and CO_2 can be met by means of a simpler membrane process utilizing only the highly H_2S -selective PU4 membranes, at least for some ranges of acid gas concentrations in natural gas.

Both types of membranes considered in this study are much more permeable to H_2S and CO_2 than to CH_4 . Consequently, in the membrane processes under consideration the two acid gases will concentrate in the *permeate* (low-pressure) stream, whereas the CH_4 will concentrate in the *retentate* (high-pressure) stream, i.e., in the fraction of natural gas (the "feed") not permeating through the membranes. Hence, the retentate is the desired product, i.e., the upgraded natural gas. These are very favorable process conditions because the retentate will be obtained at almost wellhead pressure. The main pressure loss in the retentate stream will be caused by the pressure drop inside the membrane modules, which is generally very small compared to the pressure drop across the membranes.

II. MEMBRANE PROCESS DESIGN

1. Operating Conditions and Economic Parameters

Computer simulations and economic assessments of membrane separation processes for the upgrading of low-quality natural gas were performed for natural gas "feeds" containing up to 40 mole-% CO_2 as well as up to 10 mole-% H_2S , the balance being CH_4 . It is assumed that in all cases the concentrations of CO_2 and H_2S in the retentate stream (the desired product) will meet pipeline specifications. It should be noted that the pipeline specifications for H_2S are much more stringent than those for CO_2 (≤ 4 ppm H_2S , ≤ 2 mole-% CO_2).

The separation performance of eight different membrane process configurations without or with recycle, and utilizing either CO_2 - or H_2S -selective membranes or both,

has been investigated [15]. The process configurations are described in a following section.

The assumed operating conditions (the "base-case" conditions) are typical for a medium-sized acid gas removal plant with a feed flow rate of 35 MMSCFD. The feed pressure was taken to be 800 psia (55.14 bars) and the permeate pressure as 20 psia (1.38 bars). Other assumed operating conditions and the selected economic parameters are listed in Tables 1-3.

The CH₄, CO₂, and H₂S concentrations in the retentate and permeate product streams will depend on the selectivities of the membranes to these gases, on the feed composition, and on the selected operating conditions. The effects of varying feed flow rate, feed pressure, membrane module cost, and price of CH₄ on the process economics have also been examined in a "sensitivity" study.

It should be noted that polymer membranes are only partially selective to gases. As a result, some CH₄ in the feed stream will permeate through the membranes together with the CO₂ and H₂S, and consequently will be lost (unless otherwise recovered). Hence, the cost of the CH₄ lost in the permeate must be included in the processing cost of crude natural gas.

2. Membrane Process Configurations

In the following discussion a "membrane process configuration" is taken to consist of a single permeation stage or of two permeation stages connected in *series* or *cascade*. The "permeation stage" is the basic membrane separation unit and consists, in turn, of a single membrane module or of two or more modules connected in *parallel*, depending on the feed flow rate and module size.

The membrane process configurations may or may not be provided with *recycle streams*, depending on the desired objective. For example, recycle streams may be used to reduce the loss of a valuable feed component, such as CH₄, in the permeate.

In the present study it is assumed that the membrane modules are of the "spiral-wound" type and utilize "composite" membrane in sheet form, with an effective thickness of 1,000 Å (3.93×10^{-3} mil) [3,7,9,10]. Consequently, the cost of membrane modules for the "base-case" conditions was taken to be that of spiral-wound modules, cf. Table 3.

The membranes considered for use are, as mentioned above, some of the highly CO₂-selective, fluorine-containing polyimide membranes [12] and the highly H₂S-selective poly(ether urethane urea) PU4 membranes [13].

A. Membrane Processes without Recycle

Five different membrane process configurations *without recycle streams* have been examined and optimized by computer simulations. These process configurations are illustrated in Figures 1-5 and comprise:

- 1) *A single membrane permeation stage* utilizing only the highly H₂S-selective membranes, cf. Figure 1 ;
- 2) *A single membrane permeation stage* utilizing only the highly CO₂-selective membranes, cf., Figure 2 ;
- 3) *A single membrane permeation stage* utilizing both the H₂S-selective and CO₂-selective membranes, cf., Figure 3;

4) *Two membrane permeation stages connected in series*, the first stage utilizing only the H₂S-selective membranes and the second stage only the CO₂-selective membranes, cf., Figure 4 ; and

5) *Two membrane permeation stages connected in series*, the first stage utilizing only the CO₂-selective membranes and the second stage only the H₂S-selective membranes, cf., Figure 5.

The ratio of areas of the CO₂- and H₂S-selective membranes required in the last three process configurations will depend on the relative concentrations of the two acid gases in the natural gas feed and on the selected operating conditions.

B. Membrane Processes with Recycle

Three membrane process configurations with recycle have been simulated and optimized in a preliminary way via a computer program. The three membrane process configurations that have been partially studied are:

1) *Two permeation stages in cascade with recycle*, both stages utilizing only the H₂S-selective membranes, cf., Figure 6;

2) *Two permeation stages in cascade with recycle*, the first stage utilizing only the H₂S-selective membranes and the second stage only the CO₂-selective membranes, cf., Figure 7;

3) *Two permeation stages in cascade with recycle*, both stages utilizing only the CO₂-selective membranes, cf., Figure 8.

III. OPTIMIZATION METHODOLOGY

The mathematical derivation and the theoretical background for the single permeation stage with one selective membrane (H₂S-selective or CO₂-selective) and for the single permeation stage with both H₂S- and CO₂-selective membranes are given in the Appendix I. The membrane configuration of two stages in *series or cascade* (Figures 4 to 8) is just two single-permeation stages connected in *series or cascade* and its mathematical derivation for each stage is similar to that of the single stage. Therefore the mathematical derivation of two stages in *series or cascade* (Figures 4 to 8) is not presented in here.

1. Problem Formulation and Analysis

The operating conditions in all membrane process configurations studied were optimized so as to yield the lowest processing costs, i.e., the lowest cost of upgrading the crude natural gas to pipeline specifications. In view of the complex nature of the membrane process design involved, several different optimization methods were employed for this purpose.

The *objective function* in the present process design study is the processing cost and the *optimization constraints* are the product purity. The objective function and constraints can be expressed as follows:

Objective function:

$$\text{Processing cost, } f(\theta_1, \dots, \theta_i, \dots, \theta_n, \beta_1, \dots, \beta_i, \dots, \beta_n),$$

$$1 \leq i \leq n; \quad 0 \leq \theta_i \leq 1; \quad 0 \leq \beta_i \leq 1;$$

where the decision variable θ_i is the stage-cut in stage i , and the decision variable β_i is the area-fraction of the H₂S-selective membrane in stage i , i.e., the ratio $\text{Area}_{\text{H}_2\text{S}}/(\text{Area}_{\text{H}_2\text{S}} + \text{Area}_{\text{CO}_2})$. The terms "Area_{H₂S}" and "Area_{CO₂}" designate the areas of the H₂S- and CO₂-selective membranes, respectively, in a permeation stage. The "stage-cut" is the fraction of feed allowed to permeate through the membrane in a given permeation stage, i.e., the ratio of permeate-to-feed flow rates. It should be noted that if stage i contains *only one type* of selective membrane, β_i has the limiting value of either 0 (if the membrane is CO₂-selective) or of 1 (if the membrane is H₂S-selective).

Constraints:

Pipeline specification for CO₂: $x_{\text{CO}_2} \leq 2$ mole-%

Pipeline specification for H₂S: $x_{\text{H}_2\text{S}} \leq 4$ ppm

These constraints are implicit and cannot be expressed in terms of the decision variables θ_i and β_i . The objective function for the processing cost, $f(\theta_1, \dots, \theta_n, \beta_1, \dots, \beta_n)$, is also implicit and dependent on the membrane process configuration and feed composition. No unique and explicit expression is available for the processing cost. Moreover, the number of variables (θ and β) to be optimized is determined by the selected membrane process configuration.

For a given feed composition, the objective of the present study is to find not only the optimum values of the decision variables for a specified process configuration but also the optimum configuration. Therefore, the optimization procedure is a two-step problem. For any given feed composition, each process configuration has a set of optimum decision variables (i.e., $\theta \dots \theta \dots \theta \beta \dots \beta \dots \beta$) which yield a minimum processing cost. The process configuration that yields the lowest overall processing cost for that feed composition can then be determined by comparing the processing costs for all the optimized process configurations studied.

2. Optimization Methods

For a single permeation stage incorporating only CO₂- or H₂S-selective membranes, only one decision variable needs to be optimized, namely, the stage-cut θ . In this case, it is possible to use any of the classic optimization methods (e.g., region elimination, quadratic estimation, etc.) to find the optimum value of θ . However, it was found that the processing cost increases with an increase in the stage-cut θ . Therefore, for the single-stage configuration with a single type of selective membrane, the optimum decision variable θ is the minimum stage-cut that can produce pipeline-quality natural gas, that is, the stage cut where either one or both constraints are active. (Here active means the sign of the constraint is equal. For example, for the constraint $x_{\text{CO}_2} \leq 2$ mole-%, if $x_{\text{CO}_2} = 2$ mole-% in the product, the constraint is active; if $x_{\text{CO}_2} < 2$ mole-% in the product, the constraint is inactive.) It is advantageous to use the desired product purity as a criterion for finding the optimum stage cut θ .

Reference is now made to the membrane configurations shown in Figure 3 (*a single stage utilizing both H₂S- and CO₂-selective membranes*) and in Figures 4 - 8 (*two stages connected in series or cascade, each stage utilizing only one type of selective membranes*), cf., Section II.2. Only two decision variables need to be optimized for these

configurations, namely, θ β for the configuration of Figure 3, and θ_1 , θ_2 for the configurations of Figures 4 to 8. The two-variable optimization problem can be reduced to two one-variable problems. Then any of one-variable optimization method for the single stage with one selective membrane can be used to find the optimum decision variables (θ and β or θ_1 and θ_2). The one-variable optimization method used in this study is the *Golden Section* method [14], which is one of the most effective region-elimination methods for the unimodal problems. An example of this method is presented in Appendix II.

IV. RESULTS AND DISCUSSIONS

1. Membrane Processes without Recycle

A. Processing Costs for Base-Case Conditions

1). Single Permeation Stage with H₂S-Selective Membranes

The total processing cost of crude natural gas consists of three parts: (a) the capital-related, or investment, cost (CRC), (b) the variable operating and maintenance cost (VOM), and (c) the cost of CH₄ lost in the permeate stream (CH₄LS). The processing cost is reported in this study as the cost per MSCF (1,000 standard cubic feet) of *product*, i.e., of natural gas upgraded to pipeline specifications (≤ 2 mole-% CO₂ and ≤ 4 ppm H₂S).

The dependence of the processing costs on the concentration of CO₂ in the crude natural gas feed (0-40 mole-% CO₂) is illustrated in Figure 9 for a constant concentration of 1 mole-% H₂S in the feed. The data in this figure were obtained for the process design configuration shown in Figure 1, namely, a single permeation stage utilizing only the highly H₂S-selective poly(ether urethane urea) PU4 membranes.

The plot in Figure 9 shows that, for a constant H₂S concentration in the feed stream, the processing cost first *decreases*, reaches a *minimum*, and finally *increases* with increasing CO₂ concentration in the feed. The minimum results from the intersection of two curves denoted A and B. The two curves represent the costs of membrane processes that will reduce the CO₂ and H₂S concentrations in the *retentate stream* to the following levels:

(a) At all CO₂ concentrations in the feed *lower* than that at the intersection point, i.e., along curve A, the retentate will contain a *constant* amount of 4 ppm H₂S, which is the pipeline specification for H₂S, and < 2 mole-% CO₂, which is *less* than the pipeline specification for this gas. As the CO₂ concentration in the feed increases (and, therefore, that of CH₄ decreases), the concentration of CO₂ in the retentate also increases, *but remains below 2 mole-%*.

The processing cost *decreases* under these conditions because of the decrease in the CH₄ losses in the permeate (per MSCF of product gas). Also, the increase in the partial pressure of CO₂ caused by the increasing concentration of this gas in the feed, and the corresponding increase in the driving force of CO₂ across the membrane, results in a decrease in the required membrane area, and therefore in the capital investment cost of the process.

The processing costs for the conditions represented by curve A are controlled by the cost of H₂S removal, i.e., the cost of reducing the concentration of H₂S to 4 ppm and maintaining it constant at this concentration ;

(b) At the *minimum* of the plot in Figure 9, i.e., at the intersection of curves A and B, the concentrations of *both* CO₂ and H₂S in the retentate have just reached their pipeline specifications of 2 mole-% and 4 ppm, respectively;

(c) At all CO₂ concentrations in the feed *higher* than that at the above-mentioned intersection, i.e., along curve B, the retentate (the desired product) will contain a *constant* amount of 2 mole-% CO₂, which is the pipeline specification for CO₂, and < 4 ppm H₂S, which is *less* than the specification for H₂S. As the CO₂ concentration in the feed stream increases, the concentration of H₂S in the retentate further decreases below 4 ppm.

The processing cost *increases* in this case with increasing CO₂ concentration in the feed because of an increase in both the CH₄ losses in the permeate and in the membrane area required to maintain the CO₂ concentration in the retentate stream at 2 mole-%. The increase in membrane area exceeds the savings in membrane area resulting from the increase in the partial pressure of CO₂ and in the driving force of this gas across the membranes.

The processing costs for the conditions represented by curve B are controlled by the cost of CO₂ removal, i.e., the cost of reducing the concentration of CO₂ to 2 mole-% and maintaining it constant at this concentration.

The dashed extensions of curves A and B below their intersection represent conditions where the concentration of either CO₂ or of H₂S does not meet pipeline specifications.

The processing costs shown in Figure 9 are limited to natural gas feeds containing 0-40 mole-% CO₂ but only 1 mole-% H₂S. When other H₂S concentrations in the feed are considered, the plots representing the processing cost versus the CO₂ concentration in the feed remain similar in shape to those in Figure 9. However, at higher H₂S concentrations in the feed, the intersection in these plots is shifted toward higher CO₂ concentrations and higher processing costs.

This behavior is illustrated in Figure 10, which is a three dimensional plot of the processing costs versus the CO₂ and H₂S concentrations in the feed (0-40 mole-% CO₂ and 1 ppm- 10 mole-% H₂S). The solid curve which connects all the intersection points of the processing costs corresponds to the product stream containing 2 mole-% CO₂ and 4 ppm H₂S. At any given H₂S concentration, if CO₂ concentrations in the feed are lower than those at the intersection points, the processing cost is controlled by the H₂S removal; if CO₂ concentrations in the feed are higher than those at the intersection points, the processing cost is controlled by the CO₂ removal.

2). Single Permeation Stage with CO₂-Selective Membranes

Figure 11 exhibits the processing costs obtained with a *single permeation stage with CO₂-selective membranes only* (cf., Figure 2) as a function of H₂S in the crude natural gas feed (1 ppm to 10 mole-% H₂S) at 20 mole-% CO₂. The processing cost first increases slowly, then reaches an intersection point, and finally increases rapidly with increasing H₂S concentration in the feed. Similar to Figure 9, the dashed extensions of curves A and B below their intersection represent conditions where the pipeline specification for either H₂S or CO₂ is not met. However, the retentate (the desired

product) compositions on curves A and B are different from those in Figure 6 and can be explained as following:

(a) At all H₂S concentrations in the feed lower than those at the intersection of curves A and B, i.e., along curve A, the product stream will contain 2 mole-% CO₂ and < 4 ppm H₂S. The processing cost remains nearly constant with increasing H₂S concentration in the feed. This is due to the fact that the separation is controlled by the CO₂ removal and the CO₂ concentration in the feed is constant. Furthermore, the increase of the H₂S concentration in this region is quite small (less than 7 ppm), therefore it has little effect on the CH₄ concentration in the feed (the balance of CO₂ and H₂S) and the change of the CH₄ lost in the permeate is negligible;

(b) At the intersection, the product stream contains exactly 2 mole-% CO₂ and 4 ppm H₂S;

(c) At all H₂S concentrations in the feed higher than those at the intersection point, i.e., along curve B, the product stream will contain 4 ppm H₂S and < 2 mole-% CO₂ and the separation is controlled by the H₂S removal. The processing cost increases rapidly with the increase of H₂S concentration in the feed. This is because even the most highly CO₂-selective membranes have a much lower H₂S/CH₄ selectivity than the highly H₂S-selective poly(ether urethane urea) PU4 membranes considered in this study. As a result, considerably more CH₄ is lost with a process configuration utilizing only CO₂-selective membranes than with one utilizing only the H₂S-selective membranes or both CO₂- and H₂S-selective membranes. Moreover, the permeability to H₂S of the CO₂-selective membranes is about 1/100th of that of the H₂S-selective membranes. Therefore, the membrane area required to meet pipeline specifications with a process configuration utilizing only the CO₂-selective membranes is commensurately larger.

Figure 12 is a three dimensional plot of the processing costs versus the CO₂ and H₂S concentrations in the feed (0-40 mole-% CO₂ and 1 ppm- 10 mole-% H₂S). The solid curve which connects all the intersection points corresponds to the product stream containing 2 mole-% CO₂ and 4 ppm H₂S. At any given CO₂ concentration, if the H₂S concentrations in the feed are lower than those at the intersection points, the processing cost is controlled by the CO₂ removal; if the H₂S concentrations in the feed are higher than those at the intersection points, the processing cost is controlled by the H₂S removal.

3). Permeation Stage(s) with both CO₂- and H₂S- Selective Membranes

As discussed in Section II.2.A, three different membrane process configurations utilizing both CO₂- and H₂S-selective membranes have been considered in this study, cf., Figures 3, 4, and 5. The processing costs obtained with these configurations for the "base-case" conditions are compared in Figure 13 with those for the single-stage process configuration utilizing the H₂S-selective membranes only. The comparison is made for a range of CO₂ concentrations in the feed from 0 to 40 mole-% and an H₂S concentration in the feed of 1 mole-%.

The plot shown in Figure 13 by a full heavy line is identical with that in Figure 9. It is seen that at CO₂ concentrations *lower* than the one at the minimum of the plot, i.e., along curve A, *the processing costs are the same for all membrane process configurations utilizing H₂S-selective membranes singly or in conjunction with CO₂-selective membranes*, cf., Figures 1,3-5. This is because, for the conditions represented by curve A, the processing costs are controlled entirely by the cost of reducing the H₂S

concentration in the retentate to 4 ppm. As a result, the processing costs are minimized only when the area of the CO₂-selective membranes is reduced to zero. The process configurations utilizing both CO₂- and H₂S-selective membranes are thus reduced to the single-stage configuration with H₂S-selective membranes, which is the optimum configuration for these conditions.

By contrast, at CO₂ concentrations in the feed *higher* than those at the minimum of the plot each of the membrane process configurations studied yields different processing costs, which are represented by curves B and C. Under these conditions the processing costs are controlled by:

(a) For the process configuration utilizing only the H₂S-selective membranes: the cost of reducing the CO₂ concentration in the retentate to 2 mole-%, cf., curve B and Figure 1. It should be noted that in this case the concentration of H₂S will be reduced to less than 4 ppm;

(b) For the process configurations utilizing both the CO₂- and H₂S-selective membranes: the cost of reducing the CO₂ and H₂S concentrations to 2 mole-% and 4 ppm, respectively, cf., curves C and Figures 3-5.

The processing costs for the membrane process configurations incorporating CO₂-selective membranes as well as H₂S-selective membranes (curves C) are all lower than the costs incurred with the process configuration utilizing only the latter membranes (curve B). The lowest processing costs of natural gas containing a higher concentration of CO₂ in the feed than that at the minimum of the plot in Figure 13 is obtained with a process configuration consisting of two permeation stages in series, the first stage utilizing only the H₂S-selective membranes and the second stage utilizing only the CO₂-selective membranes, cf., Figure 4.

Figure 14 shows the fraction of CH₄ recovered in the product stream as a function of CO₂ concentrations in the feed from 0 to 40 mole-% and an H₂S concentration in the feed of 1 mole-%. The membrane configuration of Figure 4 (two permeation stages in series, the first stage utilizing only the H₂S-selective membranes and the second stage utilizing only the CO₂-selective membranes) has the highest fraction of CH₄ recovered in the product. Since the processing cost is dominated by the cost of CH₄ lost in the permeate stream (to be discussed at Section IV.5), the membrane configuration of Figure 4 has the lowest processing cost (cf. Figure 13).

Our objective is to find the optimum membrane configurations at different feed concentrations. The processing costs shown in Figure 13 are limited to natural gas feeds containing 0-40 mole-% CO₂ but only 1 mole-% H₂S. For the crude natural gas containing 0-40 mole-% CO₂ and 1 ppm -10 mole-% H₂S, the processing costs for the optimum membrane configuration are presented in Figure 15. *At any given H₂S concentration, if CO₂ concentrations in the feed are lower than those at the intersection points of the single stage with H₂S-selective membranes (cf. Figure 10), the lowest processing costs are obtained, as mentioned before, with a single permeation stage provided with H₂S-selective membranes only. At any given CO₂ concentration, if H₂S concentrations in the feed are lower than those at the intersection points of the single stage with CO₂-selective membranes (cf. Figure 12), the lowest processing costs are obtained for the membrane configuration of a single permeation stage provided with CO₂-selective membranes only. For the feed concentrations between the intersection*

points of the single stage with H₂S-selective membranes and the intersection points of the single stage with CO₂-selective membranes, the optimum process configuration is that consisting of two permeation stages in series with H₂S-selective membranes in the first stage and CO₂-selective membranes in the second stage.

4). Adjustment of CO₂ and H₂S Concentrations in Retentate

For a given feed flow rate, composition, and pressure, the desired CO₂ and/or H₂S concentration in the retentate, e.g., ≤ 2 mole-% CO₂ and ≤ 4 ppm H₂S, is obtained as follows:

(a) For the single-stage configuration utilizing H₂S-selective membranes only: by adjusting the "stage-cut", i.e., the fraction of feed which is allowed to permeate through the membranes. For a given feed flow rate and pressure, the desired stage-cut is obtained by adjusting the membrane area: an increase in membrane area will increase the stage-cut.

In this case it is not possible to adjust the CO₂ and H₂S concentrations in the retentate independently of one another. For example, under the conditions shown in Figure 9, it is possible to reduce the H₂S concentration in the retentate to 4 ppm by maintaining the CO₂ concentration at < 2 mole-% (curve A), or to reduce the CO₂ concentration in the retentate to 2 mole-% by maintaining the H₂S concentration at < 4 ppm (curve B). The actual concentration of CO₂ in the former case and of H₂S in the latter case will depend on the feed compositions and the operating conditions used;

(b) For the two-stage configuration utilizing H₂S-selective membranes in the first stage and CO₂-selective membranes in the second stage: by adjusting the stage-cuts in the two stages. This can be achieved by adjusting the ratio of membrane areas in the two stages, i.e., the respective membrane areas.

In this case it is possible to adjust the CO₂ and H₂S concentrations in the retentate independently of one another, for example, to obtain 2 mole-% CO₂ and 4 ppm H₂S in the retentate. In all cases discussed above it is assumed that the permeate pressure is maintained constant.

5). Components of Total Processing Costs

It was mentioned above that the total processing costs consist of three main components, namely, capital-related, or investment, costs, variable operating and maintenance costs, and the cost of CH₄ losses in the permeate. The relative magnitudes of these costs are given in Figure 16. This figure shows the lowest total processing costs and their components as a function of the CO₂ concentration in the feed and for an H₂S concentration in the feed of 1 mole-%. The costs on the left of the minima of the processing cost in the plots are for a single permeation stage utilizing only H₂S-selective membranes. The costs on the right of the minima of the processing cost are for two permeation stages in series with H₂S-selective membranes in the first stage and CO₂-selective membranes in the second stage. All cost data are for the "base-case" conditions listed in Table 3.

Figure 16 shows that the CH₄ losses in the permeate constitute by far the largest component of the total processing costs. The large CH₄ losses are due to two factors: (a) The membrane configurations considered so far are all the configurations without recycle and therefore a significant amount of CH₄ is lost in the permeate stream; (b) The gas permeability of the H₂S-selective poly(ether urethane urea) PU4 membranes considered

for use (PU4 is a "rubbery" polymer) is very large [13]. Therefore the membrane area requirement is low and thus CRC and VOM only comprise a small fraction in the total processing cost.

B. Effects of Operating and Economic Parameters on Processing Cost

The basis to use both the H₂S-selective membrane and the CO₂-selective membrane in the process configuration is that the H₂S-selective membrane exhibits higher H₂S/CH₄ selectivity and the CO₂-selective membrane higher CO₂/CH₄ selectivity. However, the permeabilities of the CO₂-selective membrane to CO₂, H₂S and CH₄ are lower than those of the H₂S-selective membrane. For any membrane configuration, using CO₂-selective membranes to separate the same crude natural gas into pipeline-quality natural gas requires a larger membrane area than using H₂S-selective membranes. Consequently the CRC and VOM of the membrane configuration using the CO₂-selective membrane are higher than those using the H₂S-selective membrane. The advantage of using CO₂-selective membrane to upgrade the crude natural gas is that it can recover CH₄ effectively if the feed stream mainly contains CH₄ and CO₂. However when the processing cost is dominated by the CRC and VOM, there is no need to use the CO₂-selective membrane in the membrane process configurations. Specifically, if the feed stream only contains CO₂ and CH₄ and the processing cost of a single stage with CO₂-selective membranes is higher than that of a single stage with H₂S-selective membranes, there is no basis to use the CO₂-selective membrane in the membrane process configurations.

The processing cost depends on many factors. Among these factors, the feed flow rate, membrane module cost, wellhead cost and feed pressure are the most important. The effects of these factors on the processing cost for the optimum membrane configuration will be illustrated in the following section.

1) Effect of Feed Flow Rate

For the membrane process configurations without recycle (Figures 1-5), the effect of feed flow rate on the processing cost of is straightforward. The membrane area requirement and labor cost are proportional to the feed flow rate, and the costs of utilities and the compressor module are not present in the membrane process configurations without recycle. Therefore the total plant investment and annual variable operating and maintenance cost are proportional to the feed flow rate. The annual cost of CH₄ lost is also proportional to the feed flow rate but the fraction of CH₄ lost in the permeate is independent of feed flow rate. Since CRC, VOM and CH₄LS are all defined as cost per MSCF of product, these costs are all independent of the feed flow rate. Consequently the processing cost (\$/MSCF of product) is independent of feed flow rate.

2) Effect of Wellhead Price of Natural Gas

The wellhead price of natural gas mainly depends on the market and is very hard to predict. For example the wellhead price peaked at \$2.66/MSCF (1 MSCF of natural gas \cong 1000 Btu) in 1984 and dropped to \$1.59/MSCF in 1995. However, in the first half of 1996, the wellhead cost increased to \$2.16/MSCF. Due to the unpredictability of the wellhead price, the wellhead cost in this study is considered to be in the range of \$1 to \$5 per MMBTU (million btu).

Figure 17 shows the effect of wellhead price on processing cost for the optimum

membrane configuration as a function of CO_2 concentration in the feed at 1 mole-% H_2S . The effect of wellhead price on processing cost for the optimum membrane configuration as a function of H_2S concentration in the feed at 20 mole-% CO_2 is exhibited in Figure 18. At any given H_2S and CO_2 concentrations in the feed, the processing cost increases proportionally with increasing wellhead price. However, at different H_2S and CO_2 concentrations in the feed, the gradient of this increase is different.

In the range of \$1 to \$5/MMBTU wellhead price, the CRC and VOM are independent of wellhead price. This is because the optimum membrane area requirement is independent of the wellhead price. Furthermore for the membrane process configurations utilizing both H_2S - and CO_2 -selective membranes (Figures 3-5), the optimum membrane area ratio of the H_2S -selective membrane to the CO_2 -selective membrane is also independent of the wellhead price. Although CH₄LS increases with the wellhead price, the fraction of CH_4 recovered in the product stream is independent of the wellhead price.

3) Effect of Membrane Module Cost

The membrane module cost is studied in the range of \$5 to \$70 per square feet and the membrane replacement cost is assumed to be one half of the membrane module cost. Figure 19 exhibits the effect of the membrane module cost on the processing cost for the optimum membrane configuration as a function of the CO_2 concentration in the feed at 1 mole-% H_2S . The effect of the membrane module cost on processing cost for the optimum membrane configuration as a function of the H_2S concentration in the feed at 20 mole-% CO_2 is shown in Figure 20.

If the membrane module cost is \geq \$60 per square feet, it was found that even for the natural gas feed containing 0 mole-% H_2S and 20 mole-% CO_2 , the processing cost of the single stage with the CO_2 -selective membrane is higher than that of single stage with the H_2S -selective membrane. There is no economic reason to use the CO_2 -selective membrane in any of the process configurations because of its higher membrane area requirement. All five configurations without recycle (Figures 1-5) are reduced to a single stage with the H_2S -selective membrane at this membrane module cost.

If the membrane module cost is \leq \$50 per square feet, to upgrade crude natural gas containing 0 mole-% H_2S and 20 mole-% CO_2 to the pipeline specifications, the processing cost of a single stage with the CO_2 -selective membrane is lower than that of single stage with the H_2S -selective membrane, and therefore the CO_2 -selective membrane should be considered in the membrane process configurations. In this membrane module cost range, although the CRC and VOM depend on the membrane module cost, the optimum total membrane area requirement and optimum membrane area ratio of the H_2S -selective membrane to the CO_2 -selective membrane of the two-membrane configuration (Figures 3 to 5) are independent of the membrane module cost. Moreover, CH₄LS and the fraction of CH_4 recovered in the product stream are also independent of the membrane module cost.

4) Effect of Feed Pressure

The feed pressure in this study is considered in the range of 200 to 1600 psia, which includes the pressure of the most natural basins discovered so far. Feed pressure has a significant effect on membrane area requirement and the fraction of CH_4 recovered in the product. Consequently CRC, VOM, CH₄LS and processing cost change greatly

with the feed pressure.

(a) Figures 21 and 22 exhibit the processing cost as a function of CO_2 concentration in the feed at 1 mole-% H_2S . At 200 psia feed pressure, the optimum configuration is the single stage with the H_2S -selective membrane because of the enormous membrane area requirement when the CO_2 -selective membrane is used in the membrane configurations.

For feed pressures ≥ 400 psia, similar to the base-case, there is a minimum processing cost at a given pressure for the single stage with H_2S -selective membranes. The minimum point moves to a lower CO_2 concentration as the feed pressure increases. At all CO_2 concentrations in the feed lower than the CO_2 concentration at the minima, the optimum configuration is the single stage with the H_2S -selective membrane. At all CO_2 concentrations in the feed higher than the CO_2 concentration at the minima, the membrane configuration utilizing both H_2S - and CO_2 -selective membranes is better than one membrane configuration (single stage with only H_2S -selective membranes or single stage with only CO_2 -selective membranes).

(b) Figures 23 to 24 show the processing cost as a function of H_2S concentration in the feed at 20 mole-% CO_2 . For the single stage with the CO_2 -selective membrane, similar to the base-case, there are an intersection point at a given pressure. With increasing feed pressure, the intersection points move to lower H_2S concentrations.

For feed pressures ≥ 400 psia, the optimum membrane process configuration at different H_2S concentrations in the feed can be summarized as following:

- i) At all H_2S concentrations in the feed lower than the H_2S concentration at the break point of the curves for a single stage with CO_2 -selective membranes, the best membrane process configuration is the single stage with the CO_2 -selective membranes;
- ii) At all H_2S concentrations in the feed higher than the H_2S concentration at the break point of the curves for a single stage with H_2S -selective membranes, the best membrane process configuration is the single stage with the H_2S -selective membranes;
- iii) At all H_2S concentrations in the feed higher than the H_2S concentration at the break point of the curves for a single stage with CO_2 -selective membrane and lower than the H_2S concentration at the break point of the curves for a single stage with H_2S -selective membrane, the membrane configuration utilizing both H_2S - and CO_2 -selective membranes is better than either one membrane configuration (single stage with the H_2S -selective membrane or single stage with the CO_2 -selective membrane).

2. Membrane Process Configurations with Recycle

Three configurations of two stages in a cascade with recycle (Figures 6 to 8) were partially studied and compared with the *optimum* membrane process configuration without recycle (Figures 1 to 5). For the two stages in cascade with recycle, the permeate of the first stage is compressed and fed to the second stage. The retentate of the second stage is recycled to the first stage, and thus a substantial amount of CH_4 is recovered.

Figure 25 shows the plots of processing cost as a function of CO_2 concentration in the crude natural gas feed (0-40 mole-% CO_2) at 1 mole-% H_2S . Similar plots were also obtained for 0.1 mole-%, 0.5 mole-%, 5 mole-%, and 10 mole-% H_2S in the crude natural gas. At the base-case operating conditions with the economic parameters listed in Tables 1-3, the following results were obtained:

1) For the *two stages in cascade with recycle, both stages utilizing the H₂S-selective membrane*, the processing cost increases quickly with increasing CO₂ concentration in the feed. At lower CO₂ concentration in the feed, the processing cost is lower than that of optimum membrane configuration without recycle. At higher CO₂ concentration in the feed, due to the large increase of the compressor module cost and utility cost, the processing cost is higher than that of the optimum membrane configuration without recycle.

2) For the *two stages in cascade with recycle, the first stage utilizing the H₂S-selective membrane and the second stage utilizing the CO₂-selective membrane*, the processing cost increases greatly with increasing of CO₂ concentration in the feed. In contrast with *two stages in cascade with recycle, both stages utilizing the H₂S-selective membrane*, it was found that the processing cost of this configuration is higher at the lower CO₂ concentration in the feed and lower at higher CO₂ concentration in the feed. However at higher CO₂ concentrations in the feed, the processing cost of this configuration is still higher than that of the optimum membrane processing configuration *without recycle*.

In the base-case, when crude natural gas does not contain the H₂S, our previous study has shown that *a single stage with CO₂-selective membranes* is the best configuration among the five membrane configurations without recycle (Figures 1-5). However, for the CO₂-selective membrane with high CO₂/CH₄ selectivity (e.g. polyimides developed in our lab), the question remains whether there are any CO₂ concentrations where it is advantageous to use two stages in cascade with recycle. The answer is decided by the two contradicting factors: the cost of CH₄ loss, and the costs of the compressor and utilities (electricity for the compressor).

a). For the *single stage with CO₂-selective membranes*, a relatively larger amount of CH₄ is lost in the permeate stream but there are no costs for the compressor and utilities;

b). For the *two stages in cascade with recycle, both stages utilizing CO₂-selective membranes*, the second stage recovers most of CH₄ in the permeate stream of first stage, but with the added costs for the compressor and utilities.

Figure 26 exhibits the processing costs of *single stage with CO₂-selective membranes* and *two stages in cascade with recycle, both stages utilizing CO₂-selective membranes*. At all CO₂ concentrations in the feed higher than 2 mole-%, the processing cost of *single stage with CO₂-selective membranes* is lower than that of *two stages in cascade with recycle, both stages utilizing CO₂-selective membranes*.

Since the pipeline specification for CO₂ is not very stringent (2 mole-% CO₂), and the selectivity of CO₂ to CH₄ is very high for the polyimide membranes (the selectivity, α , is about 60), only a relatively small fraction of CH₄ is lost in the permeate stream when using *a single stage with CO₂-selective membranes* to upgrade the crude natural gas. The cost of the compressor and utilities for the two stages in cascade with recycle is proportional to the permeate flow rate of the first stage and increases greatly with the increase CO₂ concentration in the feed. However, even at lower CO₂ concentration in the feed, the cost of the compressor and utilities surpasses the cost of CH₄ that this configuration could recover. Therefore, for the base-case, *a single stage with CO₂-selective membranes* is better than *two stages in cascade with recycle, both stages*

utilizing CO_2 -selective membranes when the crude natural gas does not contain H_2S .

3. Comparison of Membrane Process without Recycle and Adsorption

Figure 27 shows the processing cost as a function of total acid gas concentration in feed for optimum membrane process configurations and gas absorption. Since diethanolamine is the chemical solvent and has equal selectivity to H_2S and CO_2 , the processing cost only changes with the total amount of acid gas [16]. The selectivities of CO_2 -selective membranes and H_2S -selective membranes vary widely and have a significant impact on the processing cost. The plot of Figure 27 can be summarized as follows:

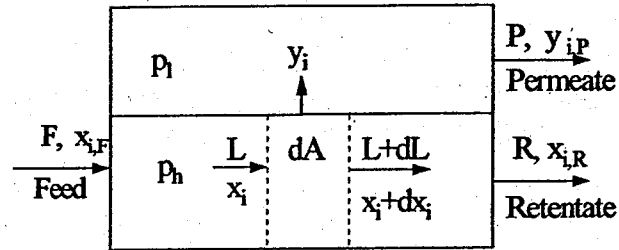
1). For the crude natural gas containing 0 mole-% H_2S , the processing cost for the membrane process configuration is lower than that of gas absorption. This is because the pipeline specification for the CO_2 (≤ 2 mole-%) is not very stringent and CO_2/CH_4 selectivity of CO_2 -selective membrane is very high. Therefore the membrane requirement is low and only a small portion of CH_4 is lost in the permeate stream.

2). For the crude natural gas containing some amount of H_2S (0.1 to 10 mole-%), the processing cost plots of the membrane process intersect with that of gas absorption. At higher H_2S concentrations in the feed, the intersection points move to higher processing costs. At all acid gas concentrations in the feed lower than that at the intersection point, the processing costs are higher than that of gas absorption. This is because a large amount of CH_4 is lost in the permeate stream and the energy requirement of the stripper in the gas absorption process is not high. At all acid gas concentration in the feed higher than that at the intersection point, the cost of regenerating diethanolamine solvent is so significant that the processing cost of the gas absorption is higher than that of the membrane process.

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APPENDIX I

Mathematical Derivation of Membrane Separation1. Single Stage with H₂S-Selective (or CO₂-Selective) Membrane

Material balance for *component i* is:

$$(L + dL) \cdot (x_i + dx_i) + dA \cdot J_i = L \cdot x_i \quad (1)$$

Equation (1) can be written into

$$L \cdot dx_i + x_i \cdot dL + dL \cdot dx_i + dA \cdot \frac{\bar{P}_i}{\sigma} (p_h \cdot x_i - p_l \cdot y_i) = 0 \quad (2)$$

One can neglect second order differential and simplify equation (2) into

$$d(L \cdot x_i) + dA \cdot \frac{\bar{P}_i}{\sigma} (p_h \cdot x_i - p_l \cdot y_i) = 0 \quad (3)$$

For the material balance of *n* components, one can obtain

$$dL + dA \cdot \sum_{i=1}^n \frac{\bar{P}_i}{\sigma} (p_h \cdot x_i - p_l \cdot y_i) = 0 \quad (4)$$

Since

$$d(L \cdot x_i) = x_i \cdot dL + L \cdot dx_i$$

one can obtain

$$\frac{dx_i}{dA} = \frac{1}{L} \left[\frac{d(Lx_i)}{dA} - x_i \frac{dL}{dA} \right] \quad (5)$$

Substituting equations (3) and (4) into equation (5), one can obtain

$$\frac{dx_i}{dA} = -\frac{1}{L} \left[\frac{\bar{P}_i}{\sigma} (p_h \cdot x_i - p_l \cdot y_i) - x_i \sum_{j=1}^n \frac{\bar{P}_j}{\sigma} (p_h \cdot x_j - p_l \cdot y_j) \right] \quad (6)$$

From equation (6) and equation (4), one obtains

$$\frac{dx_i}{dL} = \frac{\left[\frac{\bar{P}_i}{\sigma} (p_h \cdot x_i - p_l \cdot y_i) - x_i \sum_{j=1}^n \frac{\bar{P}_j}{\sigma} (p_h \cdot x_j - p_l \cdot y_j) \right]}{L \cdot \sum_{j=1}^n \frac{\bar{P}_j}{\sigma} (p_h \cdot x_j - p_l \cdot y_j)} \quad (7)$$

Since the flow pattern is assumed to be cross-flow, the permeate side mole fractions at any point are given by the ratio of the local component flux to the total local flux,

$$y_i = \frac{J_i}{\sum_{j=1}^n J_j} = \frac{\frac{\bar{P}_i}{\delta} (p_h \cdot x_i - p_l \cdot y_i)}{\sum_{j=1}^n \frac{\bar{P}_j}{\delta} (p_h \cdot x_j - p_l \cdot y_j)} \quad (8)$$

Therefore, equation (7) can be rewritten into:

$$\frac{dx_i}{dL} = \frac{y_i - x_i}{L} \quad (9)$$

The definition of stage cut θ is

$$\theta = \frac{F - L}{F}$$

So

$$dL = -F \cdot d\theta \quad (10)$$

Substituting equation (10) to equation (9), one obtains

$$\frac{dx_i}{d\theta} = -\frac{y_i - x_i}{(1 - \theta)} \quad (11)$$

where $x_i = x_{i,F}$ at $\theta = 0$

Similarly, one can substitute equation (10) to equation (4) and obtain

$$\frac{dA}{d\theta} = \frac{F}{\sum_{j=1}^n \frac{\bar{P}_j}{\sigma} (p_h \cdot x_j - p_l \cdot y_j)} \quad (12)$$

where $A=0$ at $\theta = 0$

The overall or outlet permeate composition, $y_{i,P}$, can be obtained from the material balance over the entire module:

$$F \cdot x_{i,F} = P \cdot y_{i,P} + R \cdot x_{i,R} \quad (13)$$

From the definition of stage cut, the above equation can be rewritten into:

$$y_{i,P} = \frac{x_{i,F} - (1-\theta) \cdot x_{i,R}}{\theta} \quad (14)$$

where $x_{i,R}$ is the mole fraction of component i in the overall or outlet retentate stream.

It should be noted that numerical (Runge-Kutta) method was used to solve equations (11) and (12). In equations (11) and (12), y_i is calculated by trial and error method. For the feed containing CH_4 , CO_2 and H_2S , the detail steps of calculating y_i are as follows, where subscript 0 represents CH_4 , 1 represents CO_2 and 2 represents H_2S .

1). Assuming y_{CH_4} (y_1) a given value;

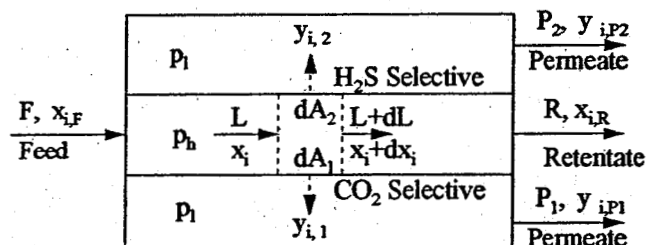
2). For the cross-flow, one can have $y_i = \frac{J_i}{\sum_{j=1}^2 J_j}$

$$\text{Therefore } \frac{y_1}{y_i} = \frac{J_1}{J_i} = \frac{J_1}{(\overline{P}_i/\sigma) \cdot (p_h \cdot x_i - p_l \cdot y_i)}$$

$$y_i = \frac{(\overline{P}_i/\sigma) \cdot p_h \cdot y_1 \cdot x_i}{J_1 + (\overline{P}_i/\sigma) \cdot p_l \cdot y_1} \quad \text{where } i=2 \text{ and } 3$$

From above equation, one can calculate y_2 and y_3 . Since $\sum_{j=1}^3 y_j = 1$, one can check and recalculate y_1 , and repeat above steps until satisfied accuracy is achieved.

2. Single Stage with both H₂S- and CO₂-Selective Membranes



Membrane area ratio:

$dA_2/dA_1 = \text{H}_2\text{S-Selective Membrane Area}/\text{CO}_2\text{-Selective membrane Area}$

Material balance for component i is:

$$(L + dL) \cdot (x_i + dx_i) + dA_1 \cdot J_{i,1} + dA_2 \cdot J_{i,2} = L \cdot x_i \quad (1)$$

Let $\alpha = dA_2/dA_1$ and $\beta = dA_2/(dA_1 + dA_2)$, then $\beta = \frac{\alpha}{1 + \alpha}$ and equation (1) can be

written into

$$L \cdot dx_i + x_i \cdot dL + dL \cdot dx_i + dA_1 \cdot (J_{i,1} + \alpha \cdot J_{i,2}) = 0 \quad (2)$$

One can neglect second order differential and simplify equation (2) into

$$d(L \cdot x_i) + \frac{dA}{1 + \alpha} (J_{i,1} + \alpha \cdot J_{i,2}) = 0 \quad (3)$$

where $dA = dA_1 + dA_2 = (1 + \alpha)dA_1$

For the material balance of n components, one can obtain

$$dL + \frac{dA}{1 + \alpha} \sum_{i=1}^n (J_{i,1} + \alpha \cdot J_{i,2}) = 0 \quad (4)$$

Since

$$d(L \cdot x_i) = x_i \cdot dL + L \cdot dx_i$$

one can obtain

$$\frac{dx_i}{dA} = \frac{1}{L} \left[\frac{d(Lx_i)}{dA} - x_i \frac{dL}{dA} \right] \quad (5)$$

Substituting equations (3) and (4) into equation (5), one can obtain

$$\frac{dx_i}{dA} = -\frac{1}{L} \frac{1}{1+\alpha} \left[(J_{i,1} + \alpha \cdot J_{i,2}) - x_i \sum_{j=1}^n (J_{j,1} + \alpha \cdot J_{j,2}) \right] \quad (6)$$

From equation (6) and equation (4), one obtains

$$\frac{dx_i}{dL} = \frac{\left[(J_{i,1} + \alpha \cdot J_{i,2}) - x_i \sum_{j=1}^n (J_{j,1} + \alpha \cdot J_{j,2}) \right]}{L \cdot \sum_{j=1}^n (J_{j,1} + \alpha \cdot J_{j,2})} \quad (7)$$

The definition of stage cut θ is

$$\theta = \frac{F - L}{F}$$

So

$$dL = -F \cdot d\theta \quad (8)$$

Substituting equation (8) to equation (7), one obtains

$$\begin{aligned} \frac{dx_i}{d\theta} &= -\frac{\left[(J_{i,1} + \alpha \cdot J_{i,2}) - x_i \sum_{j=1}^n (J_{j,1} + \alpha \cdot J_{j,2}) \right]}{(1-\theta) \cdot \sum_{j=1}^n (J_{j,1} + \alpha \cdot J_{j,2})} \\ &= -\frac{\left[(J_{i,1} + \beta/(1-\beta) \cdot J_{i,2}) - x_i \sum_{j=1}^n (J_{j,1} + \beta/(1-\beta) \cdot J_{j,2}) \right]}{(1-\theta) \cdot \sum_{j=1}^n (J_{j,1} + \beta/(1-\beta) \cdot J_{j,2})} \end{aligned} \quad (9)$$

where $x_i = x_{i,F}$ at $\theta = 0$

One can substitute equation (8) to equation (4) and obtain

$$\begin{aligned} \frac{dA}{d\theta} &= \frac{F \cdot (1+\alpha)}{\sum_{j=1}^n (J_{j,1} + \alpha \cdot J_{j,2})} \\ &= \frac{F}{\sum_{j=1}^n (J_{j,1} \cdot (1-\beta) + \beta \cdot J_{j,2})} \end{aligned} \quad (10)$$

where $A=0$ at $\theta = 0$

It should be noted that the increment of stage cut of CO_2 -selective membrane

$$d\theta_1 = \frac{\sum_{j=1}^n J_{j,1} dA_1}{\sum_{j=1}^n (J_{j,1} dA_1 + J_{j,2} dA_2)} d\theta = \frac{\sum_{j=1}^n J_{j,1}}{\sum_{j=1}^n (J_{j,1} + \alpha \cdot J_{j,2})} d\theta \quad (11)$$

The increment of flow rate of *component i* in the permeate side of CO_2 -selective membrane

$$dP_{i,1} = F \cdot y_{i,1} \cdot d\theta_1 \quad (12)$$

The increment of stage cut of H_2S -selective membrane

$$d\theta_2 = \frac{\sum_{j=1}^n \alpha \cdot J_{j,2}}{\sum_{j=1}^n (J_{j,1} + \alpha \cdot J_{j,2})} d\theta \quad (13)$$

The increment of flow rate of *component i* in the permeate side of H_2S -selective membrane

$$dP_{i,2} = F \cdot y_{i,2} \cdot d\theta_2 \quad (14)$$

For the cross-flow pattern, the permeate side mole fractions at any point are given by the ratio of the local component flux to the total local flux,

$$y_{i,1} = \frac{J_{i,1}}{\sum_{j=1}^n J_{j,1}} = \frac{\bar{P}_i (p_h \cdot x_i - p_l \cdot y_{i,1})}{\sum_{j=1}^n \bar{P}_j (p_h \cdot x_j - p_l \cdot y_{j,1})} \quad (15)$$

$$y_{i,2} = \frac{J_{i,2}}{\sum_{j=1}^n J_{j,2}} = \frac{\bar{P}_i (p_h \cdot x_i - p_l \cdot y_{i,2})}{\sum_{j=1}^n \bar{P}_j (p_h \cdot x_j - p_l \cdot y_{j,2})} \quad (16)$$

The *overall or outlet permeate composition*, $y_{i,P}$, can be obtained from the material balance over the entire module:

$$y_{i,P} = \frac{x_{i,F} - (1 - \theta) \cdot x_{i,R}}{\theta}$$

where $x_{i,R}$ is the mole fraction of component *i* in the *overall or outlet retentate stream*.

APPENDIX II

Optimization Methodology

It was mentioned in Section III.B that the *one-variable* optimization method used in this study to find the optimum decision variables was the *Golden Section* method [15], which is one of the most effective "region-elimination" methods for the unimodal problems. As an example of this method, the steps that must be used to optimize the decision variables θ and β for process configuration 3, i.e., the single stage with both H₂S- and CO₂-selective membranes, are listed below:

- 1) Find the bracket of β that contains the optimum β , i.e., the lower bound β_L and the upper bound β_U ; (note: $\beta_L \geq 0$ and $\beta_U \leq 1$)
- 2) Use the Golden Section method to find the new points $\beta_{LU} = \beta_L + 0.318 * (\beta_U - \beta_L)$, and $\beta_{UL} = \beta_U - 0.318 * (\beta_U - \beta_L)$;
- 3) Find the optimum values of θ at β_L , β_{LU} , β_{UL} , and β_U , respectively; calculate the processing cost at these four points;
- 4) Reduce the bracket of β . If the processing cost at β_L is larger than that at β_U , then set $\beta_L = \beta_{LU}$, $\beta_{LU} = \beta_{UL}$ and calculate the new β_{UL} from step 2; otherwise set $\beta_U = \beta_{UL}$, $\beta_{UL} = \beta_{LU}$ and calculate the new β_{LU} from step 2;
- 5) Find the optimum values of θ at new β_{UL} (or β_{LU}) and calculate the processing cost at this point;
- 6) Check the bracket length ($\beta_U - \beta_L$) to see if the desired termination criterion is met or not. If the criterion is met, terminate; if not, go to step 4.

It should be noted that the optimum θ is the *minimum stage-cut* that can produce pipeline-quality natural gas (either one or both constraints are active). Based on this criterion, implementation of the above step 3 is straightforward. Furthermore, extensive calculation results have proven that processing cost is unimodal to β at optimum θ .

TABLES

Table 1

Operating and Feed Conditions Used in Process Simulations

Feed composition: 0.1-10 mole-% H ₂ S, 0-40 mole-% of CO ₂ , balance CH ₄
Product purity target: ≤ 2 mole-% CO ₂ and ≤ 4 ppm H ₂ S
Feed flow rate: 35 MMSCFD (million standard ft ³ /day)
Feed pressure: 800 psia (54 atm); Permeate pressure: 20 psia (1.4 atm)
Flow pattern inside permeator module: Cross-flow
Effective membrane thickness: 1000 Å

Table 2

Permeability and Selectivity Values Used in Process Simulations

Polymer Membranes	\bar{P} (CH ₄)*	CO ₂ /CH ₄ Selectivity	H ₂ S/CH ₄ Selectivity
H ₂ S Selective (PU4)	2×10^{-10}	16	75
CO ₂ Selective (Polyimide)	0.1×10^{-10}	60	15

* Units of permeability coefficients \bar{P} : [cm³ · (STP) · cm]/(s · cm² · cmHg)

Given temperature: 95°F (35°C)

Table 3**Economic Parameters and Assumptions****Total Plant Investment(TPI):**

Membrane module cost(MC): \$10/ft² (include cost of membrane element)

Compressor module cost(CC): $\$8650 \times (HP/\eta)^{0.82}$

Fixed cost(FC) =MC+CC

Base plant cost(BPC)=1.12×FC (includes home office cost = 0.12×FC)

Project contingency (PC)=0.20×BPC

Total facilities investment(TFI)=BPC+PC

Start-up cost (SC)=0.10×VOM(see below for the explanation of VOM)

Total Plant Investment(TPI)=TFI+SC

Annual Variable Operating & Maintenance Cost(VOM):

Contract & material maintenance cost(CMC)=0.05×TFI

Local taxes & insurance (LTI)=0.015×TFI

Direct labor cost(DL): 8 hr./day per 25 MMSCFD of feed (hourly wage: \$15)

Labor overhead cost(LOC)=1.15×DL

Membrane replacement cost(MRC): \$5/ft²

Utility cost(UC):\$0.07/KWHr

Variable Operating & Maintenance Cost(VOM):

$$VOM = CMC + LTI + DL + LOC + MRC + UC$$

Gas Processing Cost(GPC):

Annual capital related cost(CRC)=0.2×TPI (5-year payout period)

Feed gas cost(or Cost of CH₄ losses) (CH₄LS):\$2.0/MMBTU

Annual variable operating & maintenance cost(VOM) (see above)

Gas process cost(GPC) = CRC + CH₄LS + VOM (/MSCF of product)

Other Assumptions:

Membrane life: 4 year

On-Stream factor: 96%

Compressor efficiency (η): 80%

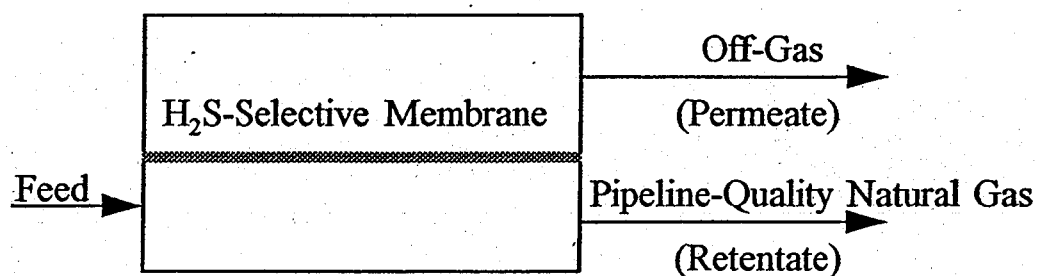


Figure 1: Single Permeation Stage with H₂S-Selective Membranes

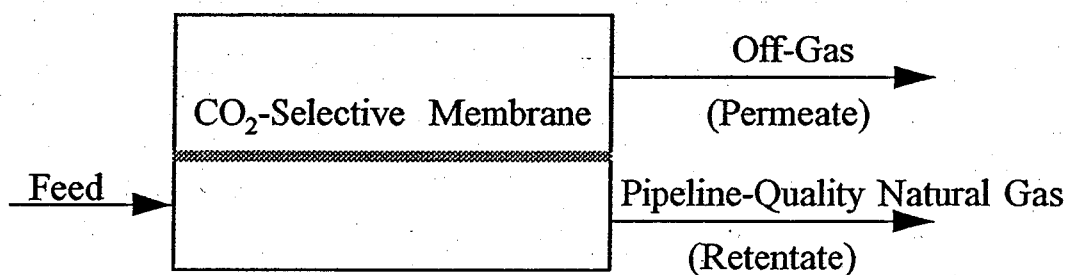


Figure 2: Single Permeation Stage with CO₂-Selective Membranes

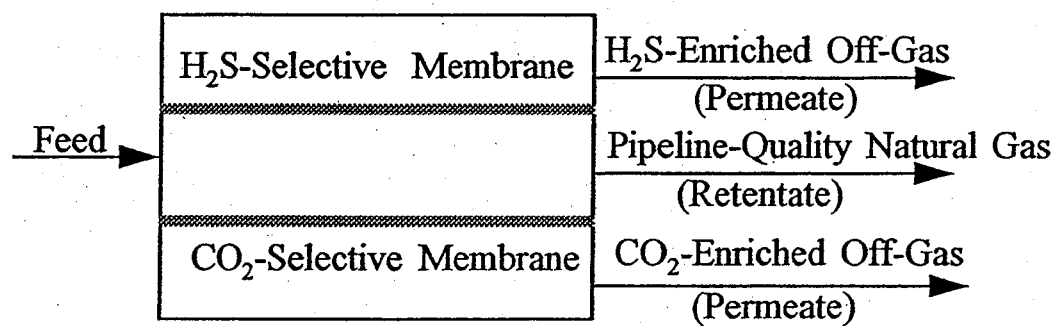


Figure 3: Single Permeation Stage with both H₂S- and CO₂-Selective Membranes

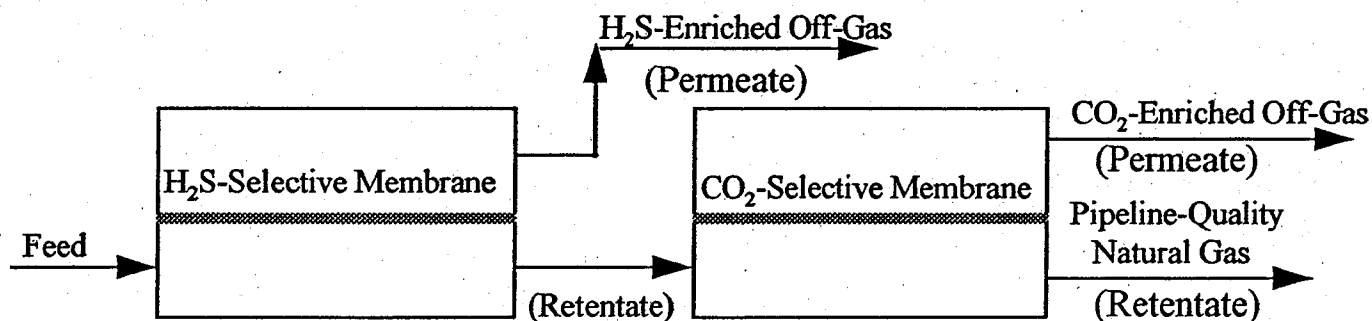


Figure 4: Two Permeation Stages in Series with H₂S-Selective Membranes in the First Stage and CO₂-Selective Membranes in the Second Stage

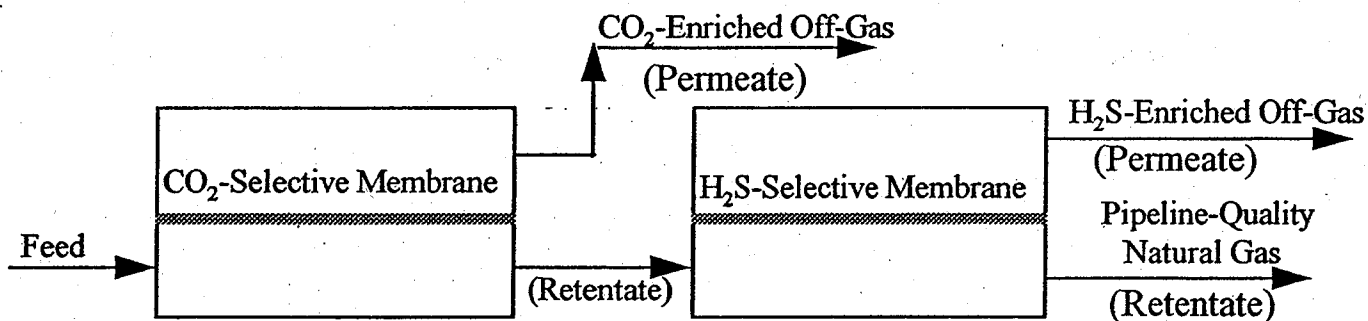


Figure 5: Two Permeation Stages in Series with CO₂-Selective Membranes in the First Stage and H₂S-Selective Membranes in the Second Stage

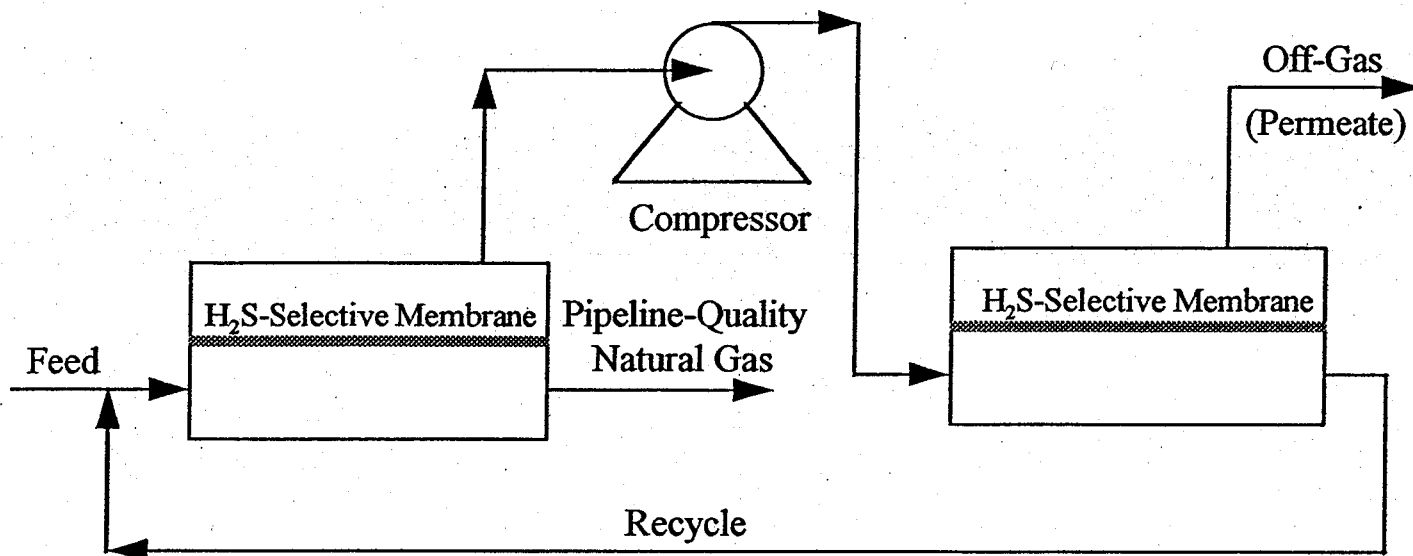


Figure 6: Two Permeation Stages in Cascade with Recycle, Both Stages Utilizing H₂S-Selective Membranes

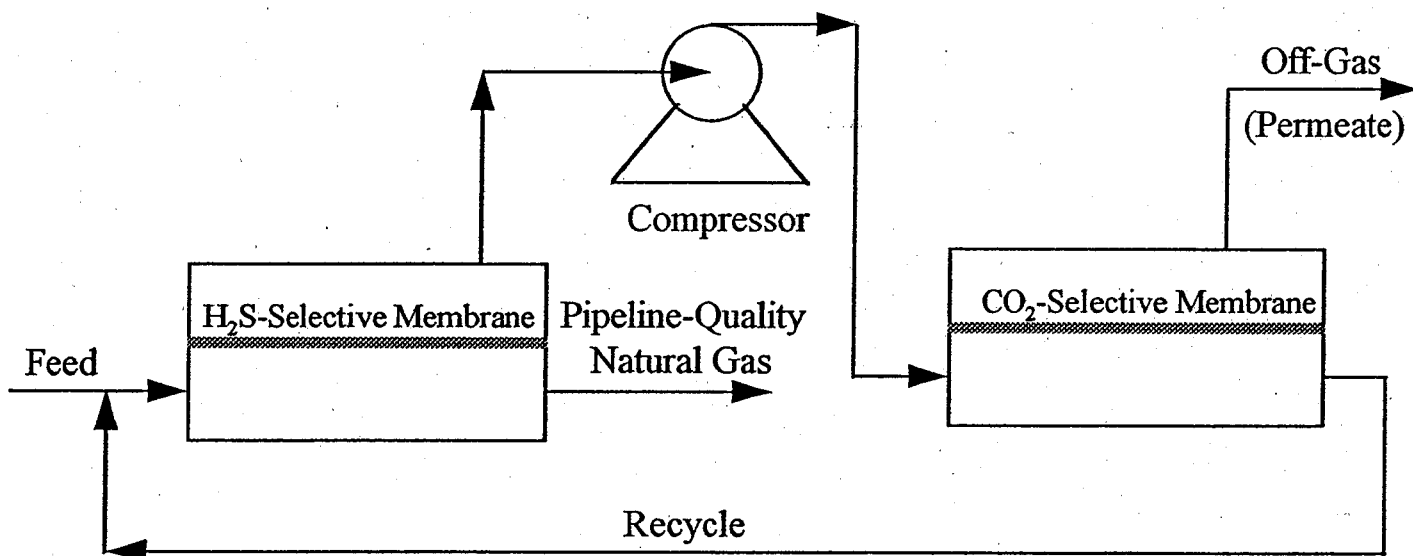


Figure 7: Two Permeation Stages in Cascade with Recycle, First Stages Utilizing H₂S-Selective Membranes and Second Stage Utilizing CO₂-Selective Membranes

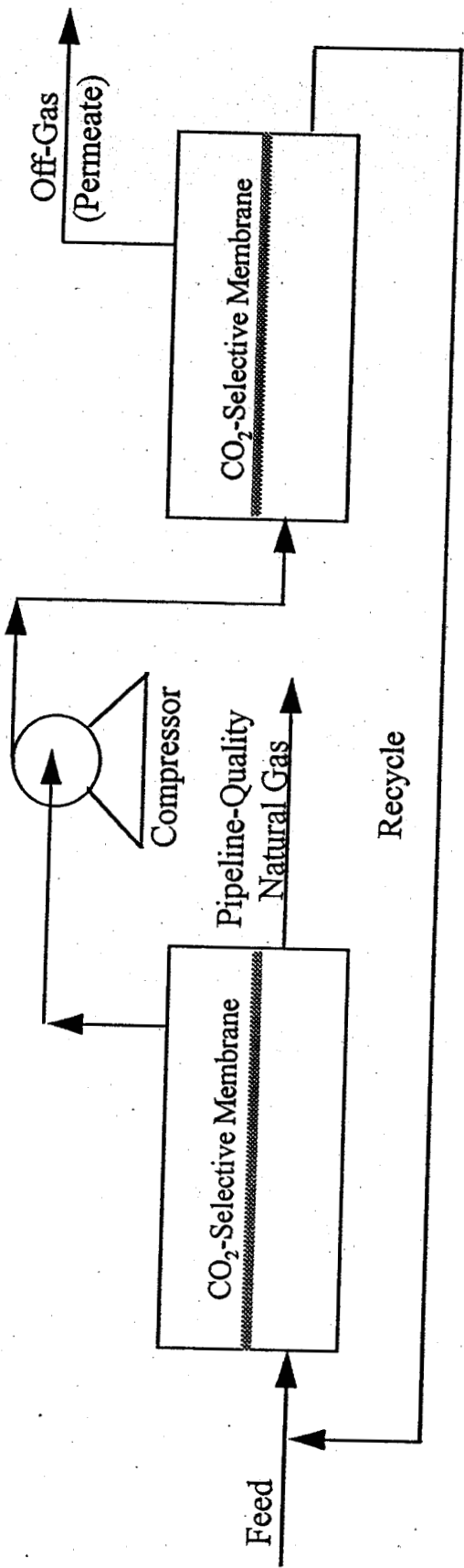


Figure 8: Two Permeation Stages in Cascade with Recycle, Both Stages Utilizing CO₂-Selective Membranes

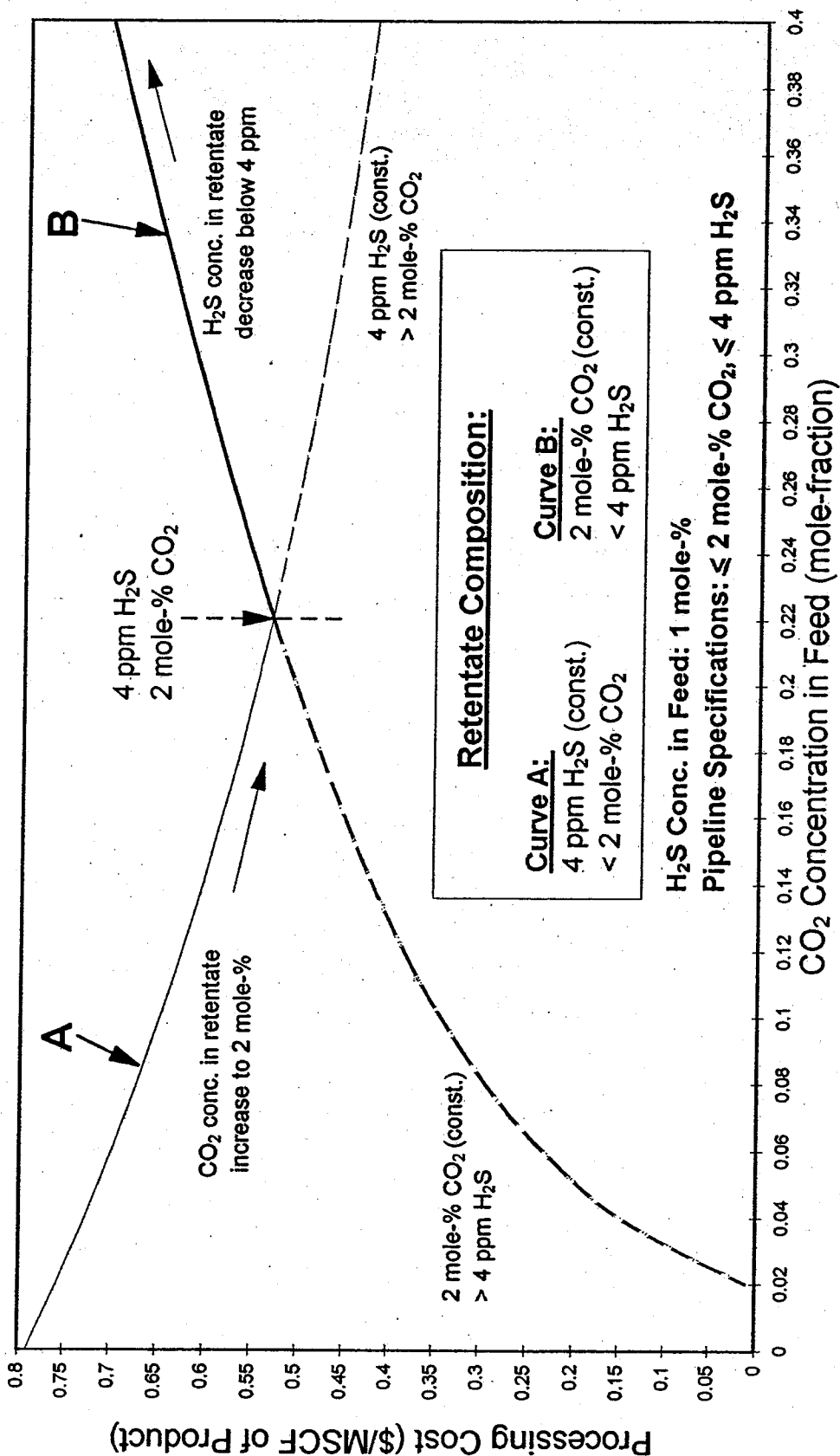


Figure 9: Processing Costs as a Function of CO₂ Concentration in Feed for a Single Stage with H₂S-Selective Membranes (Membrane Configuration 1)

For the conditions represented by Curve A, the processing cost is controlled by the cost of H₂S removal from the feed. For the conditions represented by Curve B, the processing cost is controlled by the cost of CO₂ removal from the feed. The retentate compositions for the conditions represented by the extensions of Curves A and B (dashed) below their intersection do not meet pipeline specifications.

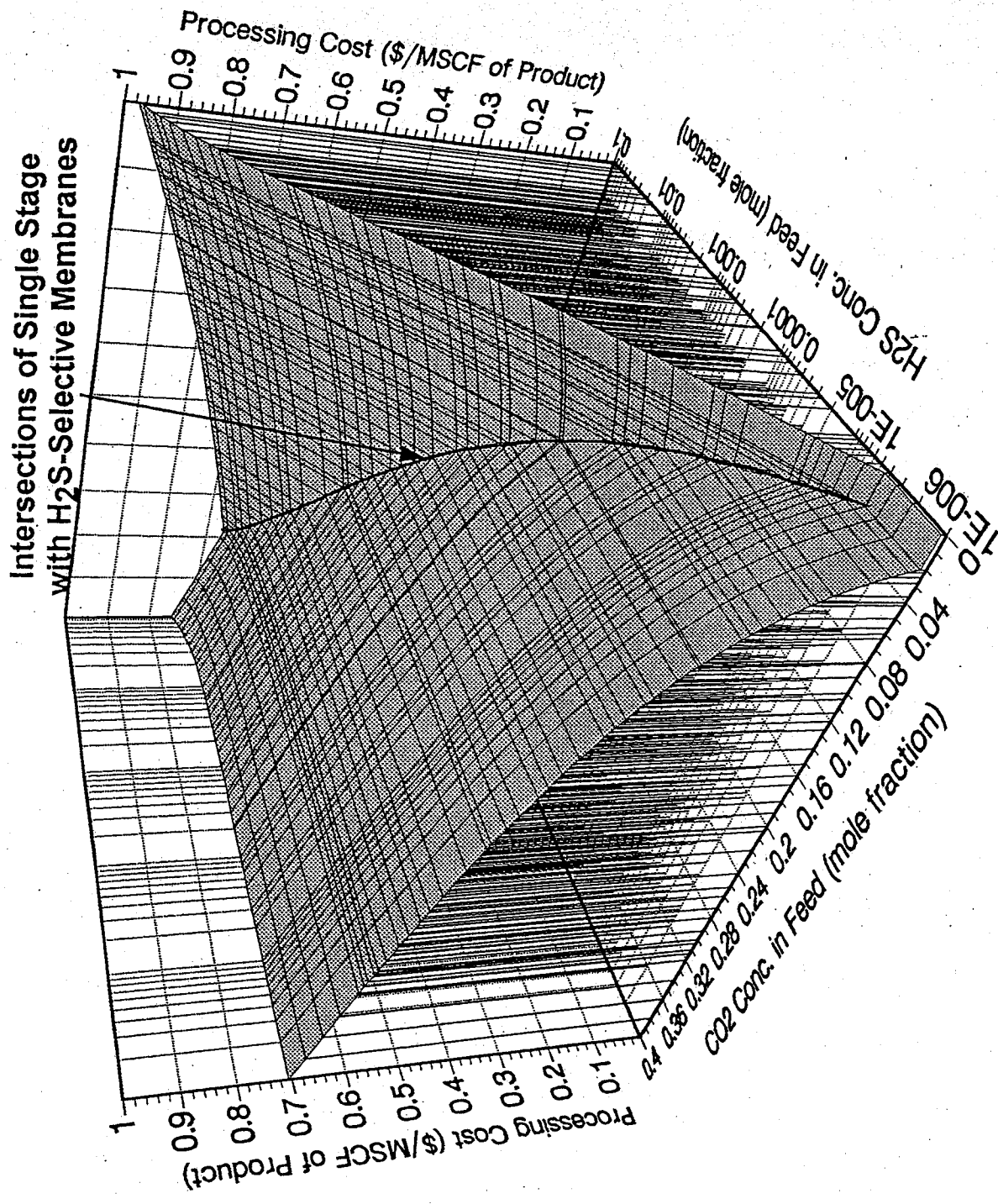


Figure 10: Processing Cost for Upgrading Low-Quality Natural Gas to Pipeline Specifications
Membrane Configuration: Single Permeation Stage with H₂S-Selective Membranes

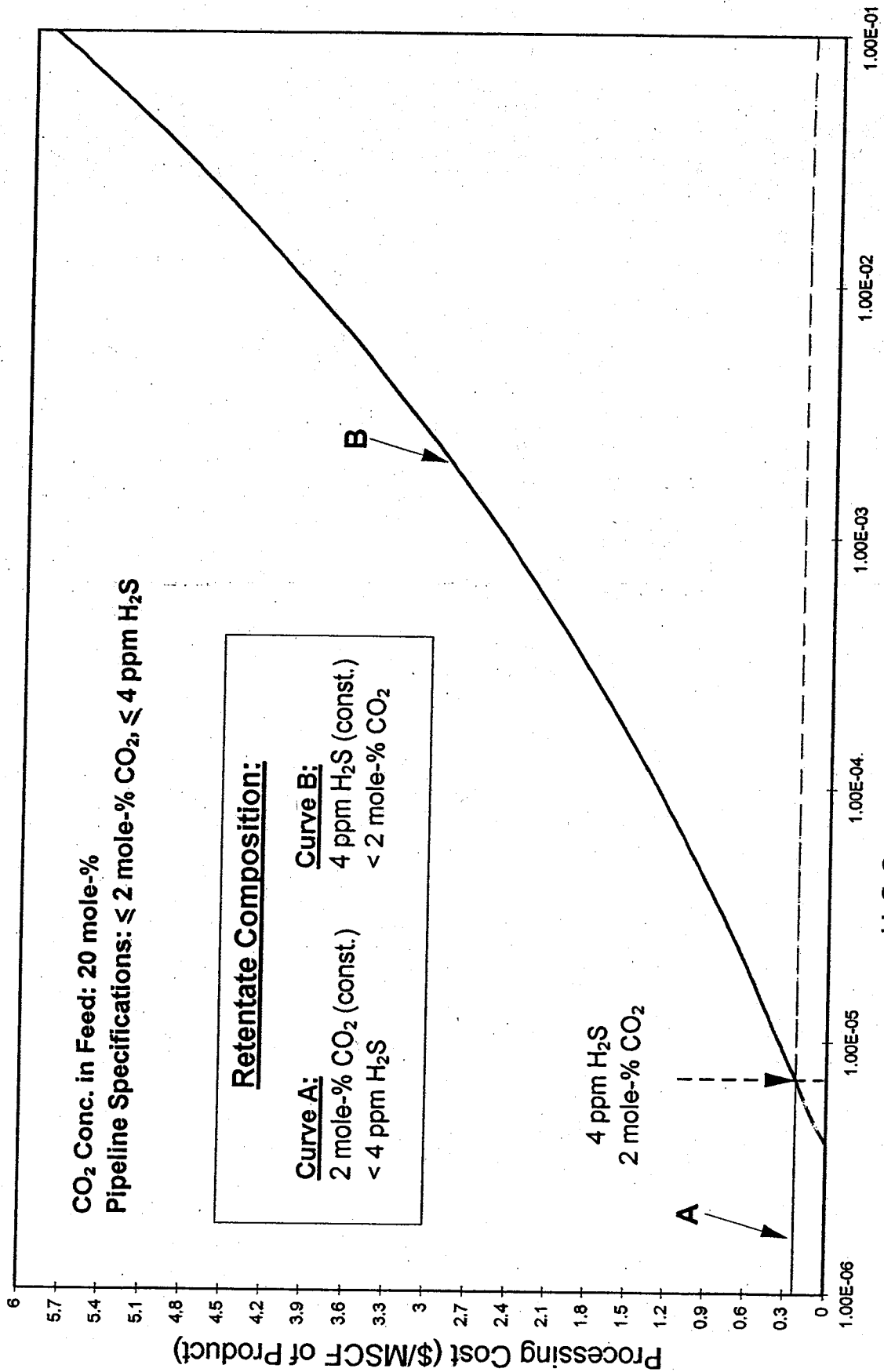


Figure 11: Processing Costs as a Function of CO₂ Concentration in Feed for a Single Stage with CO₂-Selective Membranes (Membrane Configuration 2)

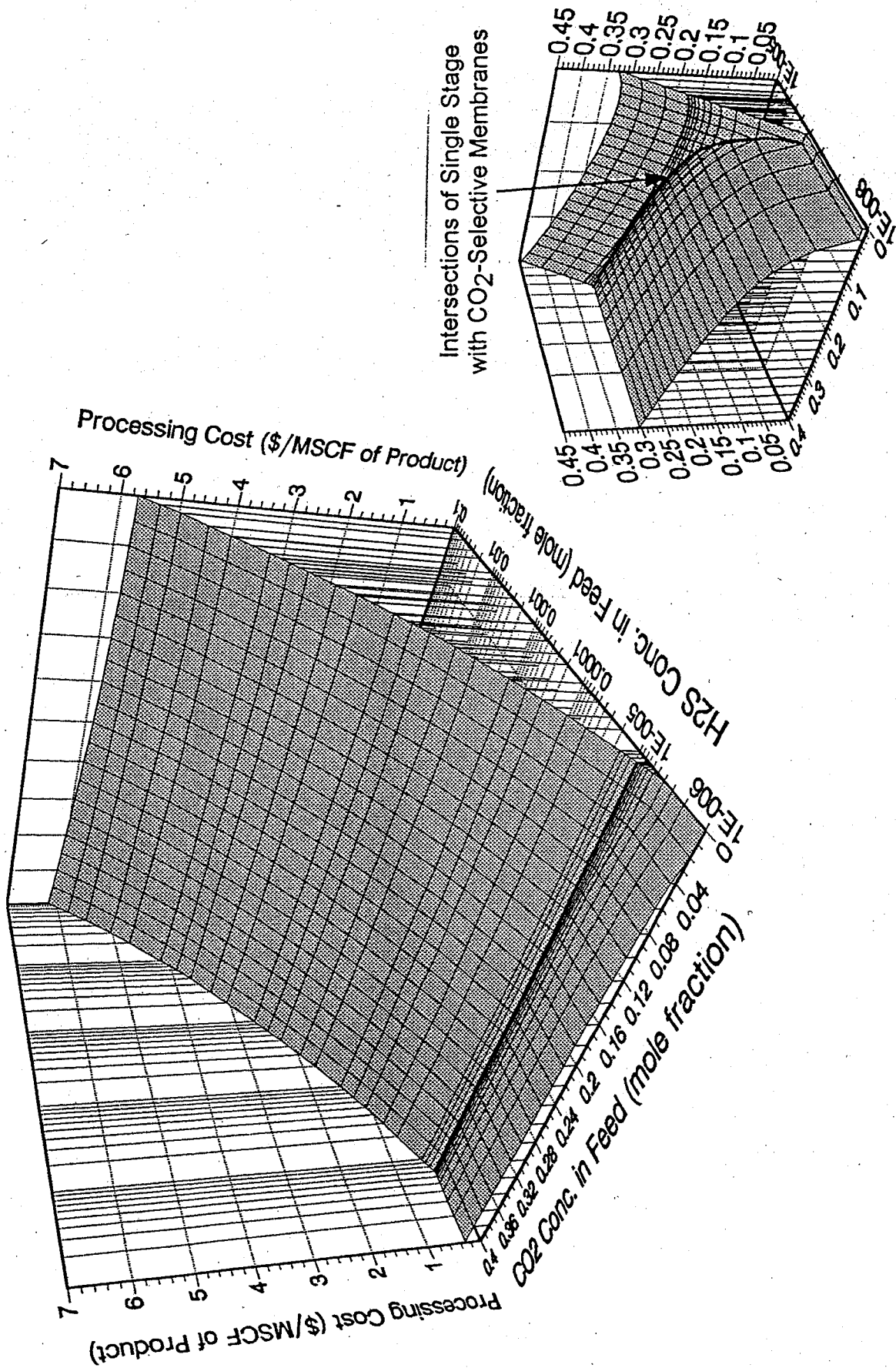


Figure 12: Processing Cost for Upgrading Low-Quality Natural Gas to Pipeline Specifications
Membrane Configuration: Single Permeation Stage with CO₂-Selective Membranes

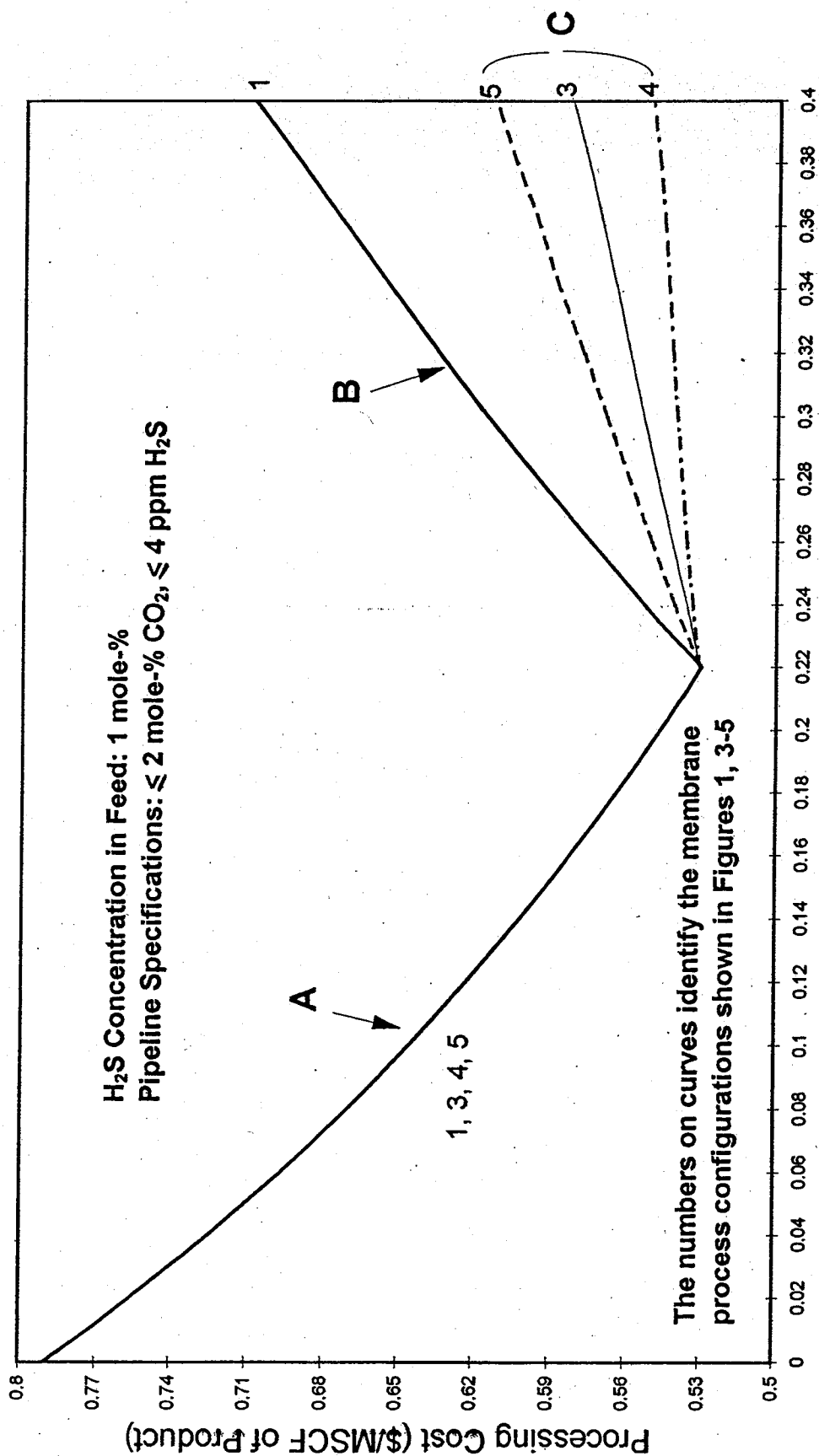


Figure 13: Processing Costs for as a Function of CO₂ Concentration in Feed for Different Membrane Process Configurations

For the CO₂ concentrations spanned by curve A, all process configurations yield the same processing costs. For the CO₂ concentrations spanned by curves B and C, the lowest processing costs are obtained with Process Configuration 4 (two permeation stages in series with H₂S-selective membranes in the first stage and CO₂-selective membranes in the second stage). The pipeline specifications for H₂S and CO₂ are met for all the conditions shown in Figure 7. For the conditions represented by curves A and B, the concentrations of H₂S and CO₂ in the retentate are the same as shown in Figure 6. For all conditions represented by curves C, the retentate will contain 4 ppm H₂S and 2 mole-% CO₂.

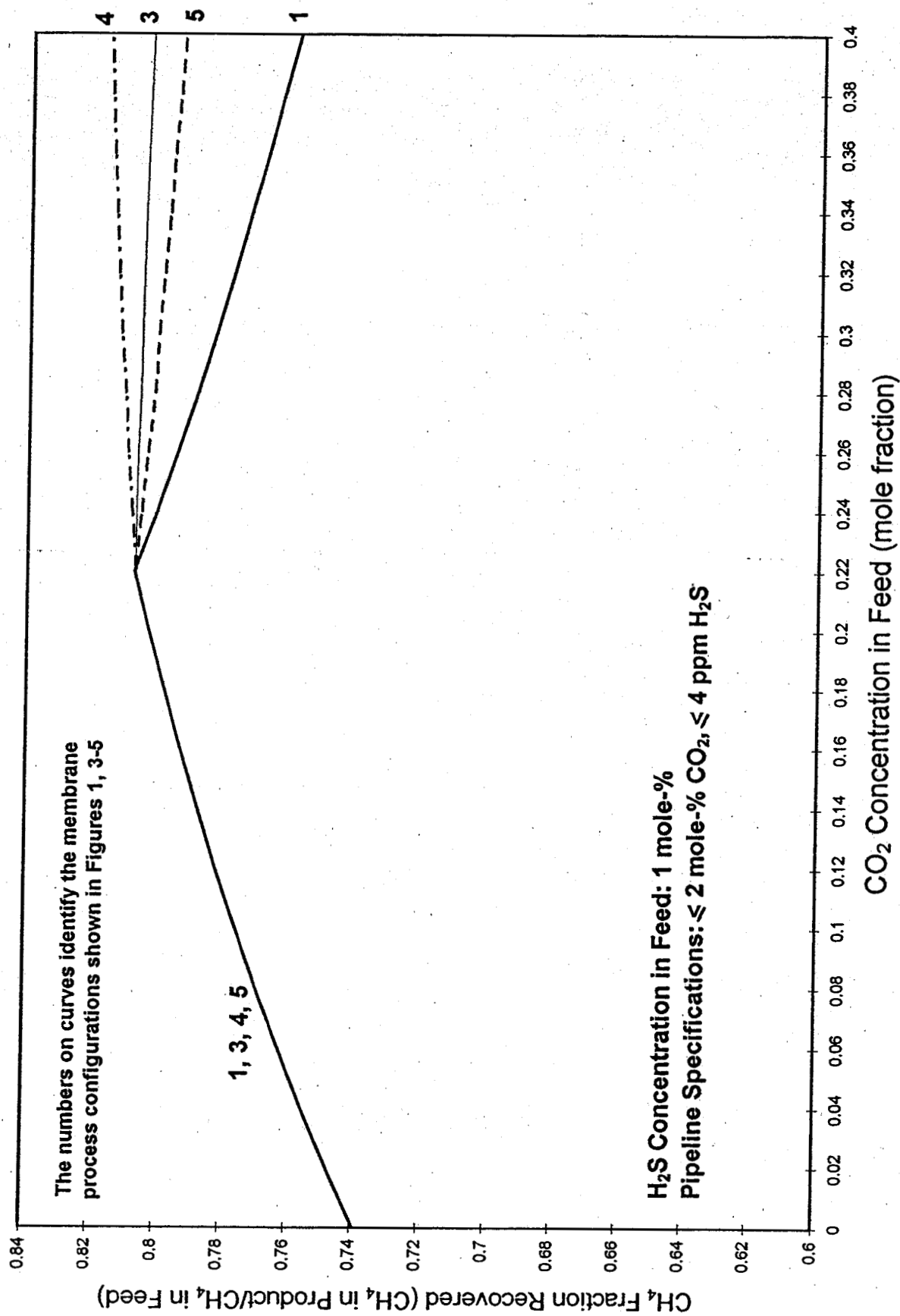


Figure 14: Fraction of CH₄ in Feed Recovered in Product Stream for Different Membrane Process Configurations without Recycle

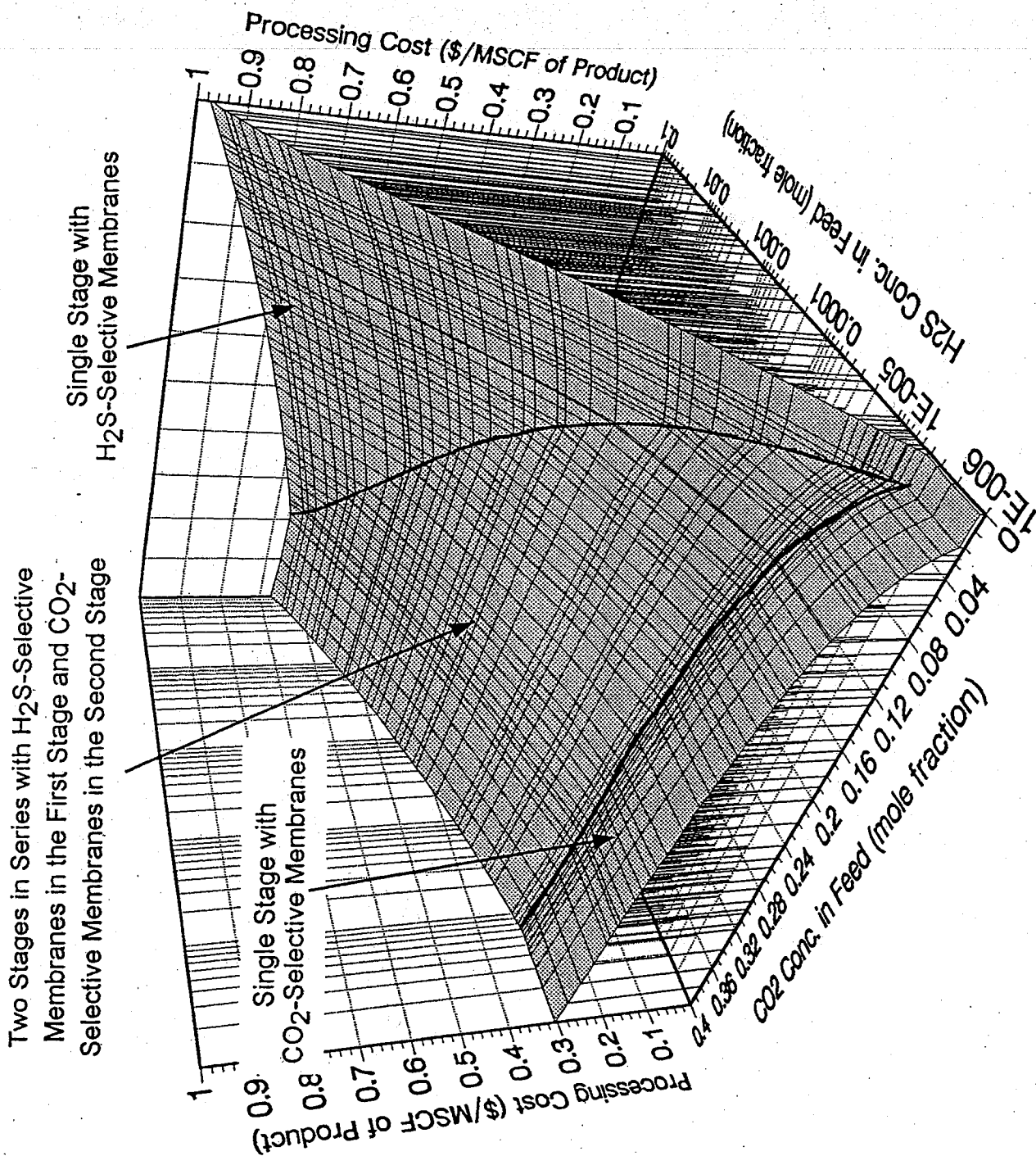


Figure 15: Processing Cost for Upgrading Low-Quality Natural Gas to pipeline specifications by Optimum Membrane Configurations without Recycle

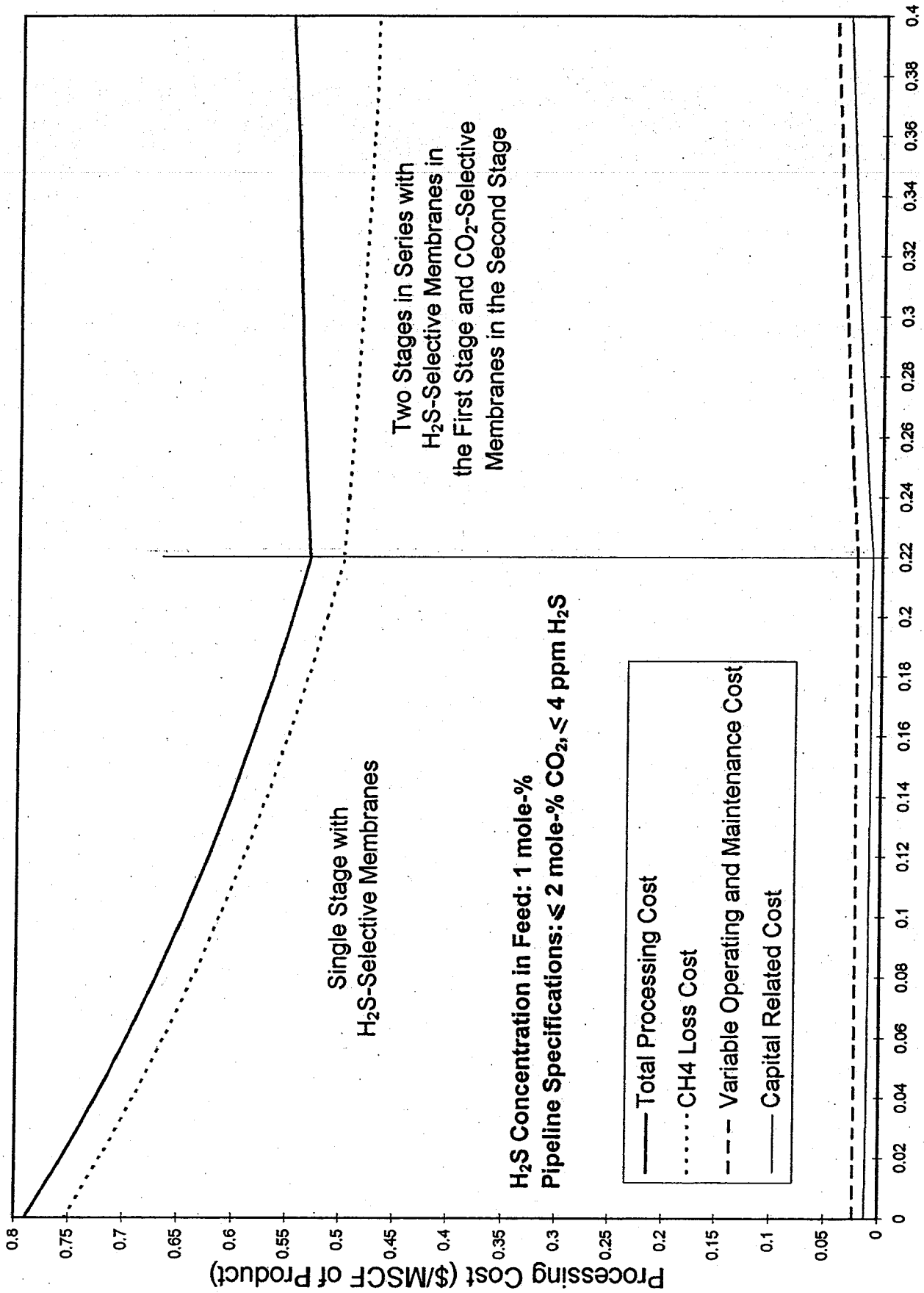


Figure 16: Effect of CO₂ Concentration in Feed on Processing Cost for Optimum Membrane Configurations

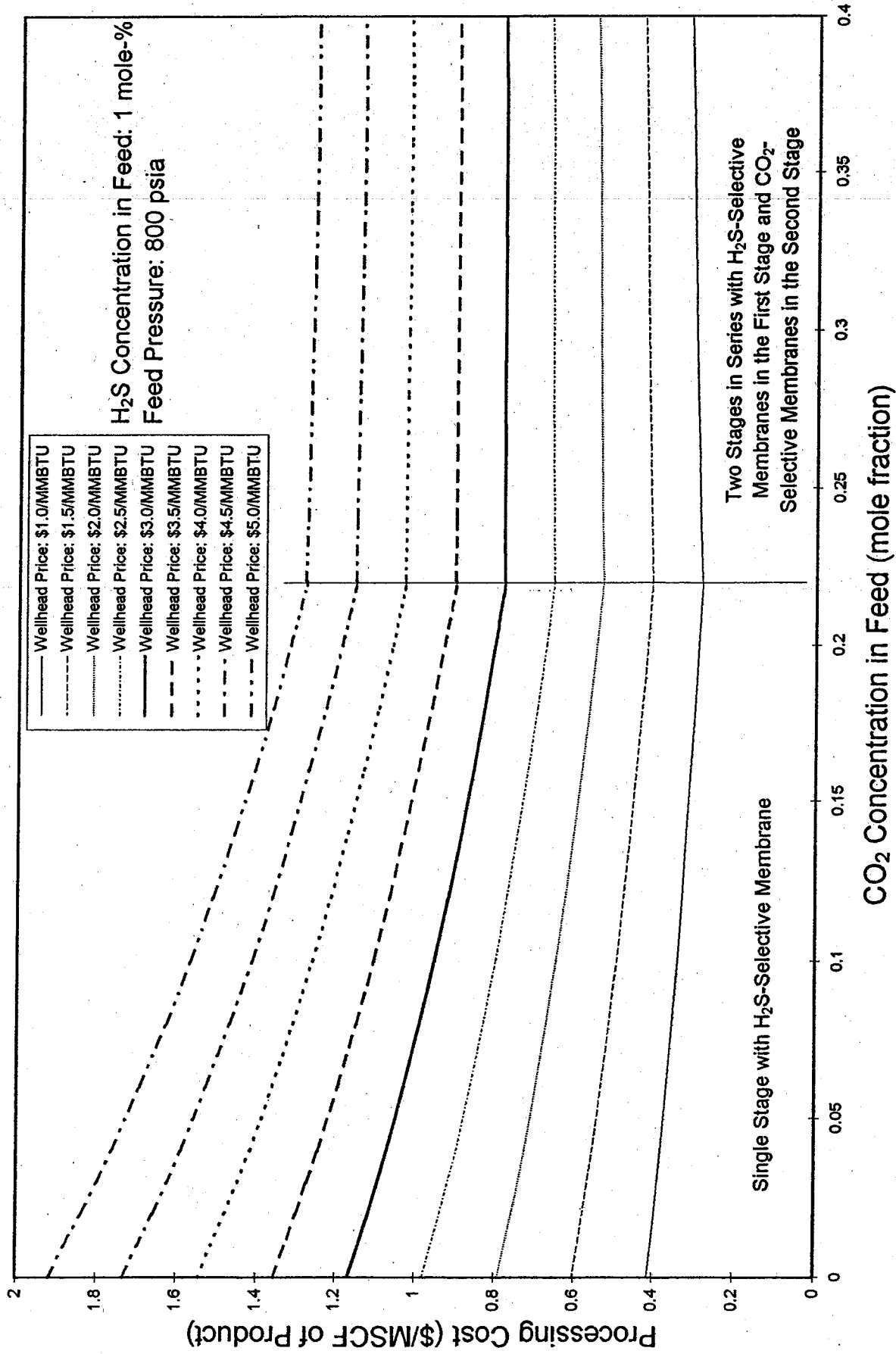


Figure 17: Effect of Wellhead Price and CO₂ Concentration in the Feed on Processing Cost for Optimum Membrane Process Configuration without Recycle

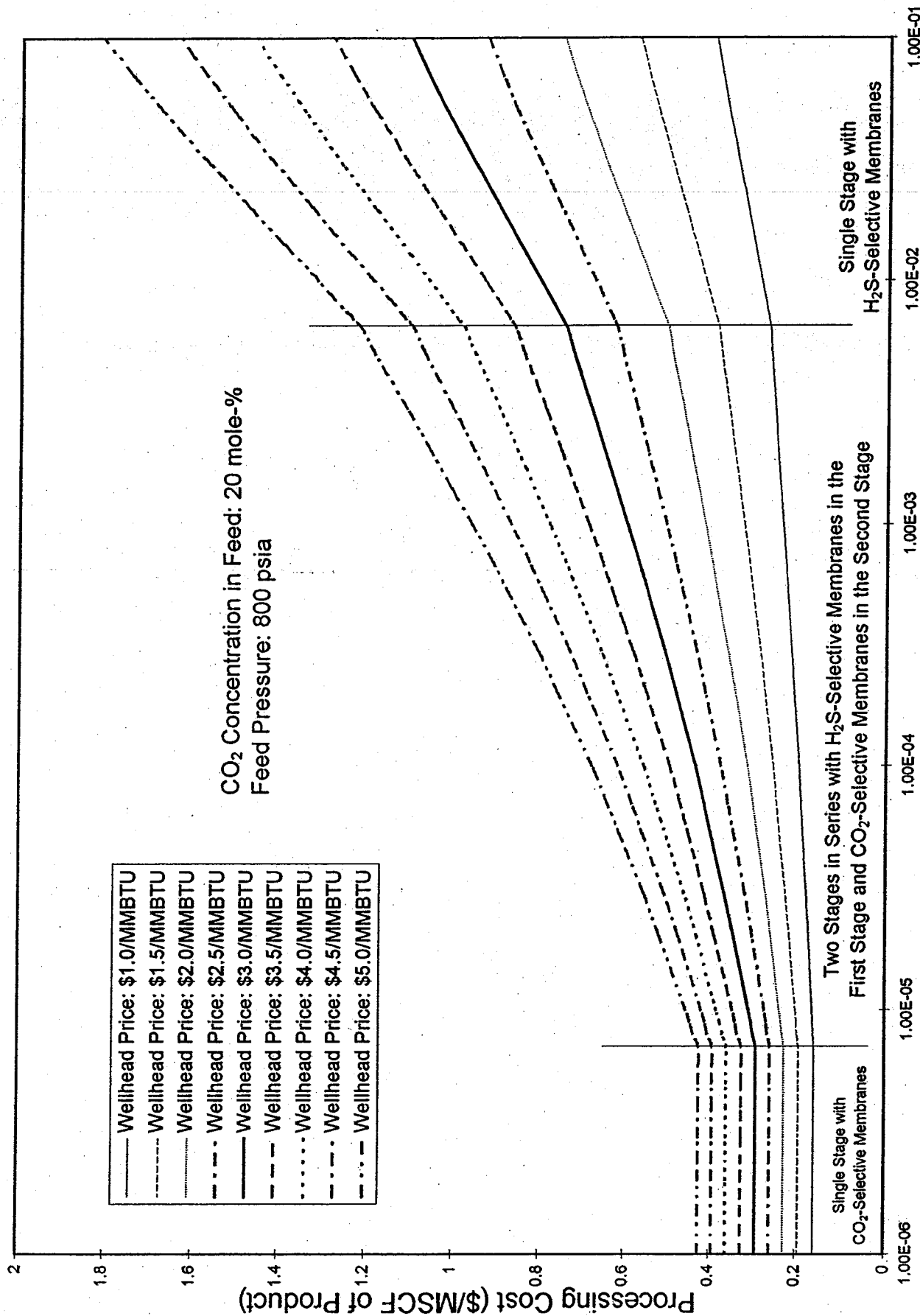


Figure 18: Effect of Wellhead Price and H₂S Concentration in the Feed on Processing Cost for Optimum Membrane Configurations without Recycle

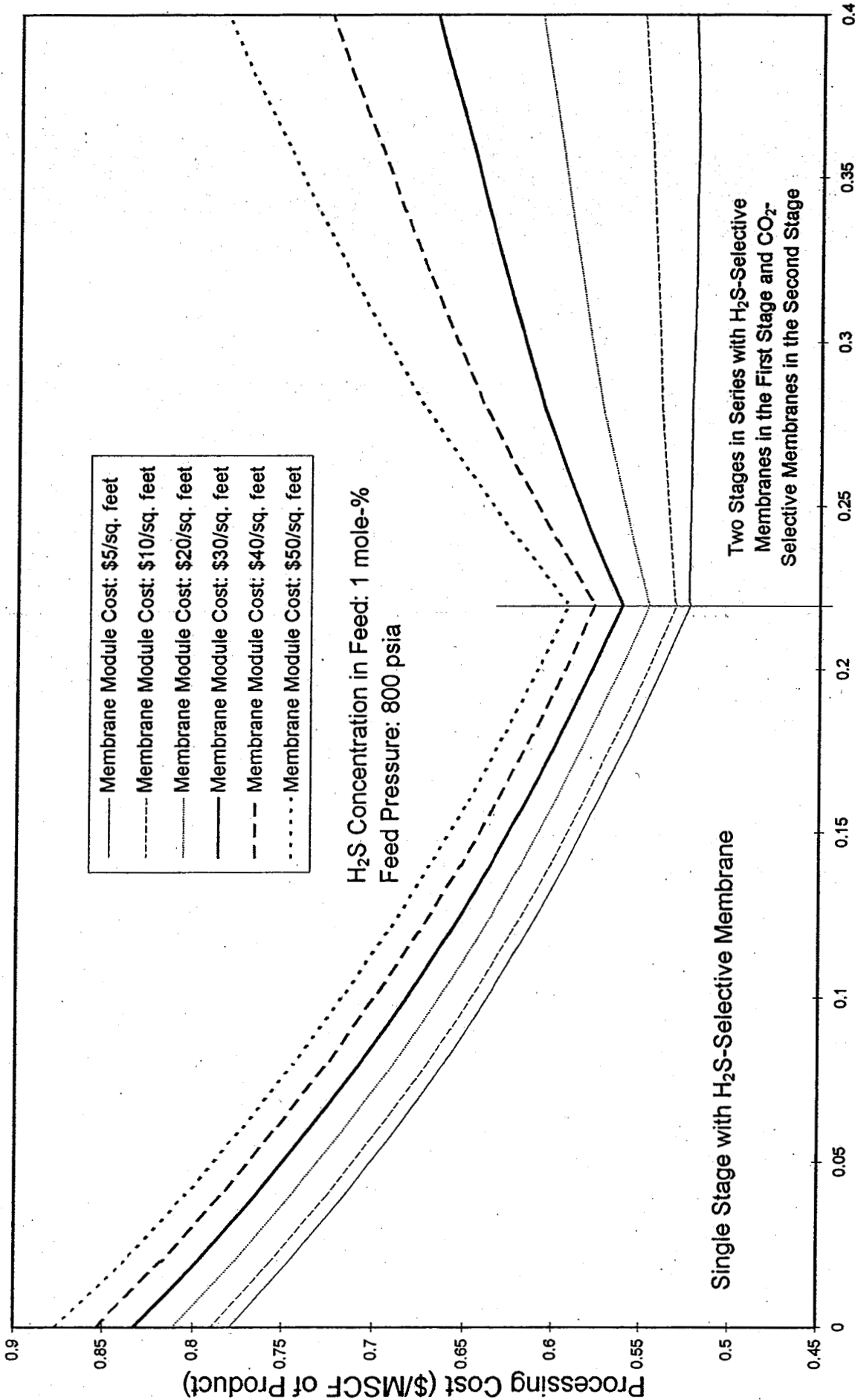


Figure 19: Effect of Membrane Module Cost and CO₂ Concentration in the Feed on Processing Cost for Membrane Process Configurations without Recycle

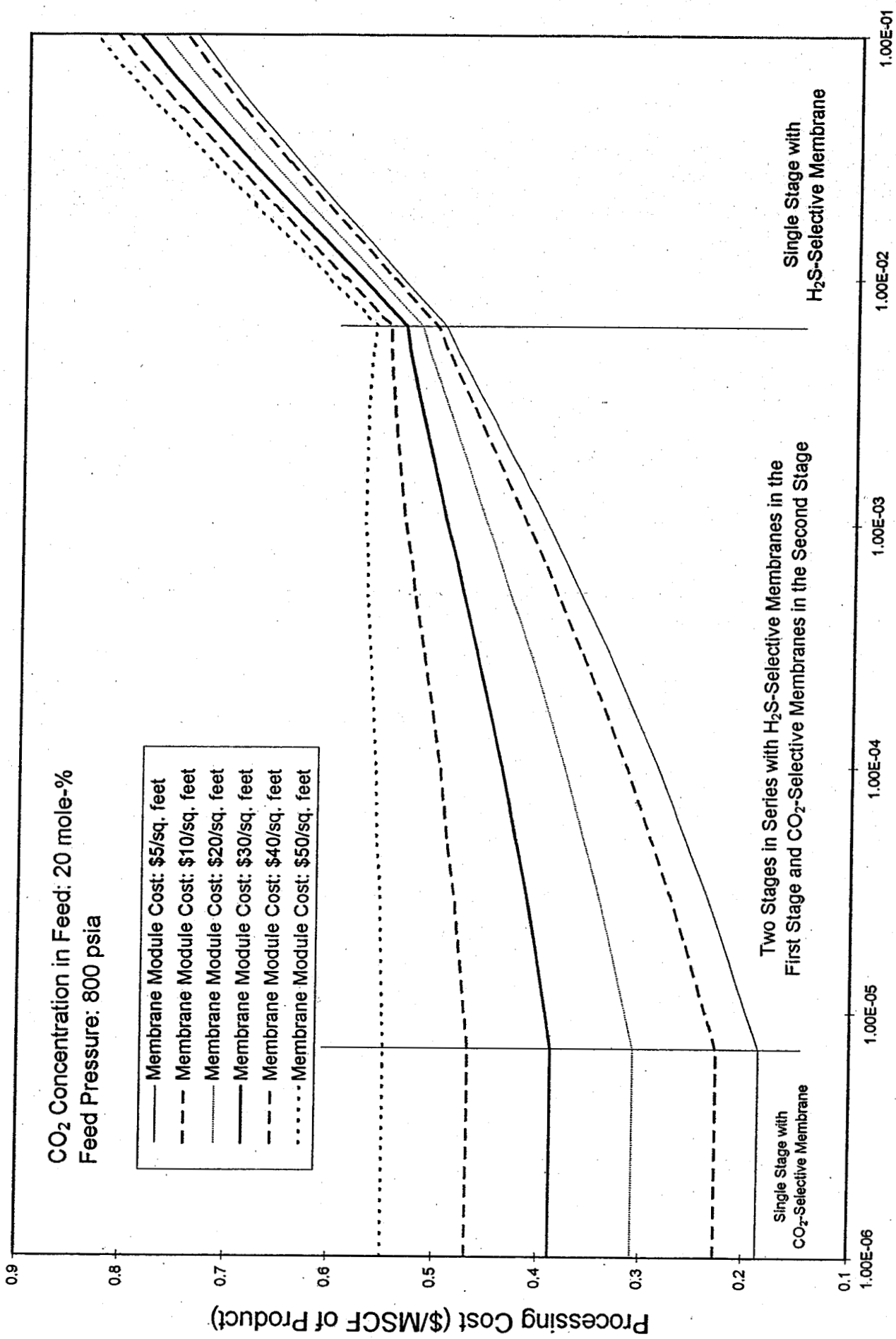


Figure 20: Effect of Membrane Module Cost and H₂S Concentration in the Feed on Processing Cost for Optimum Membrane Process Configurations without Recycle

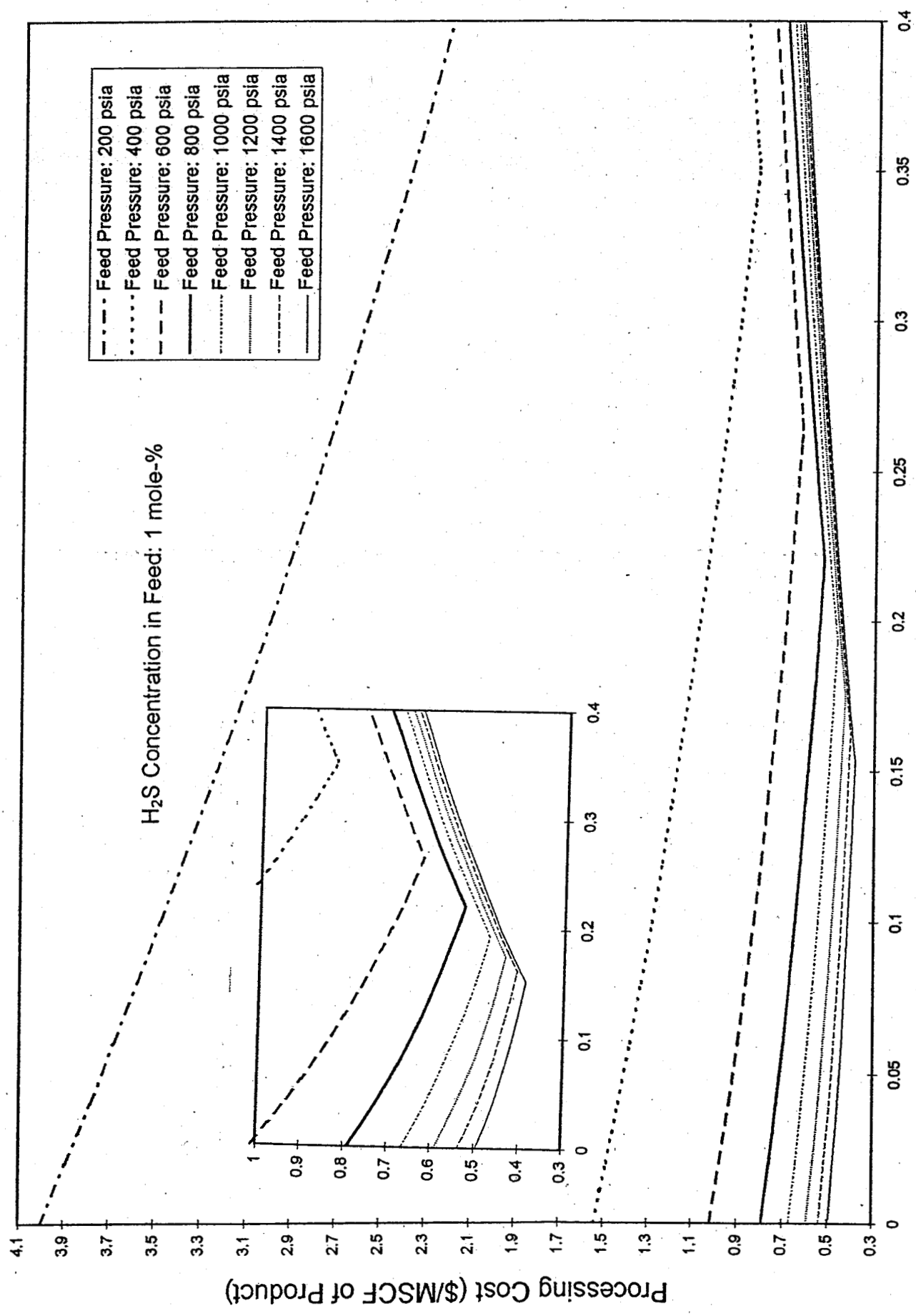


Figure 21: Effect of Feed Pressure and CO₂ Concentration in the Feed on Processing Cost
Configuration: Single Stage with H₂S-Selective Membranes without Recycle

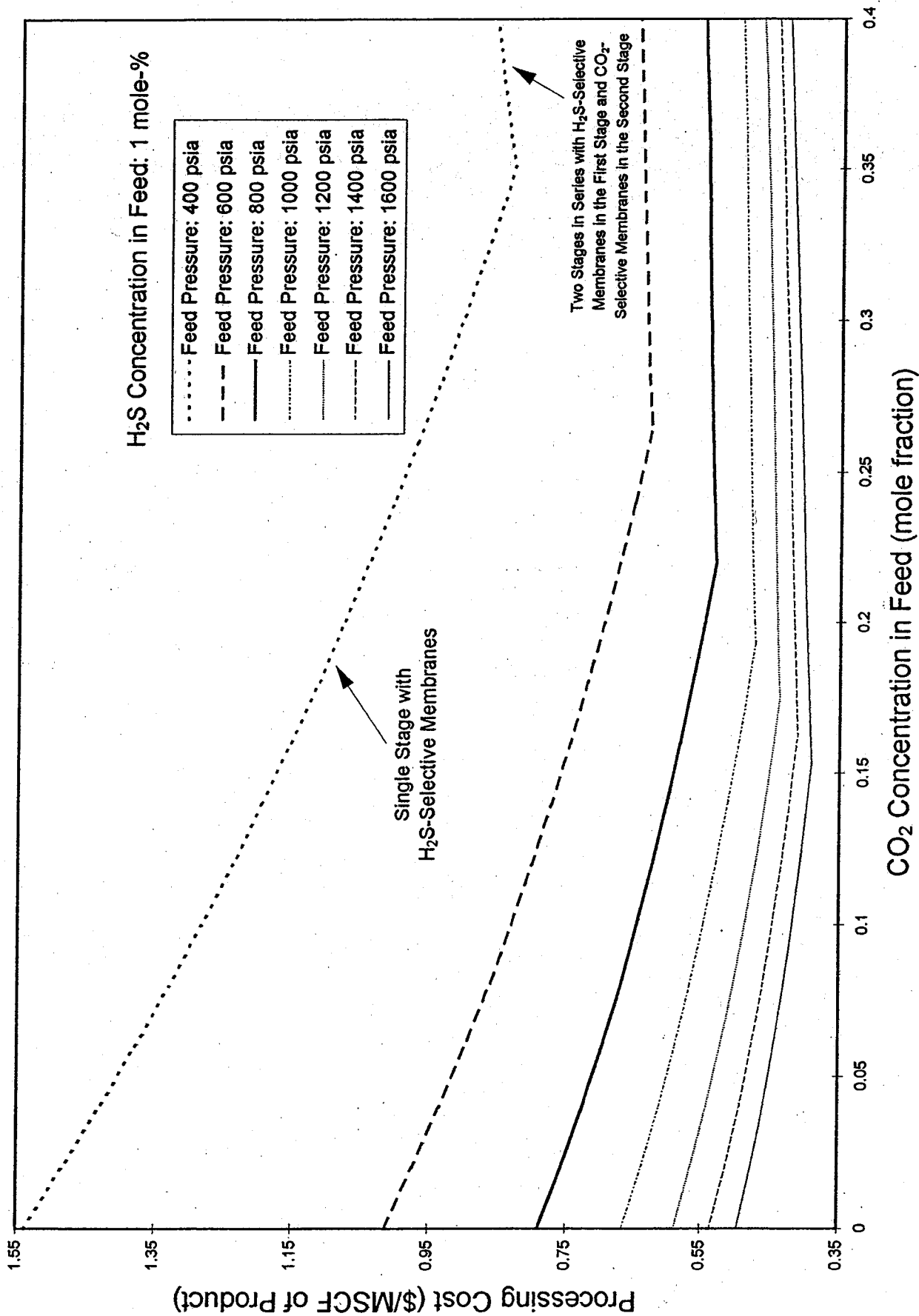
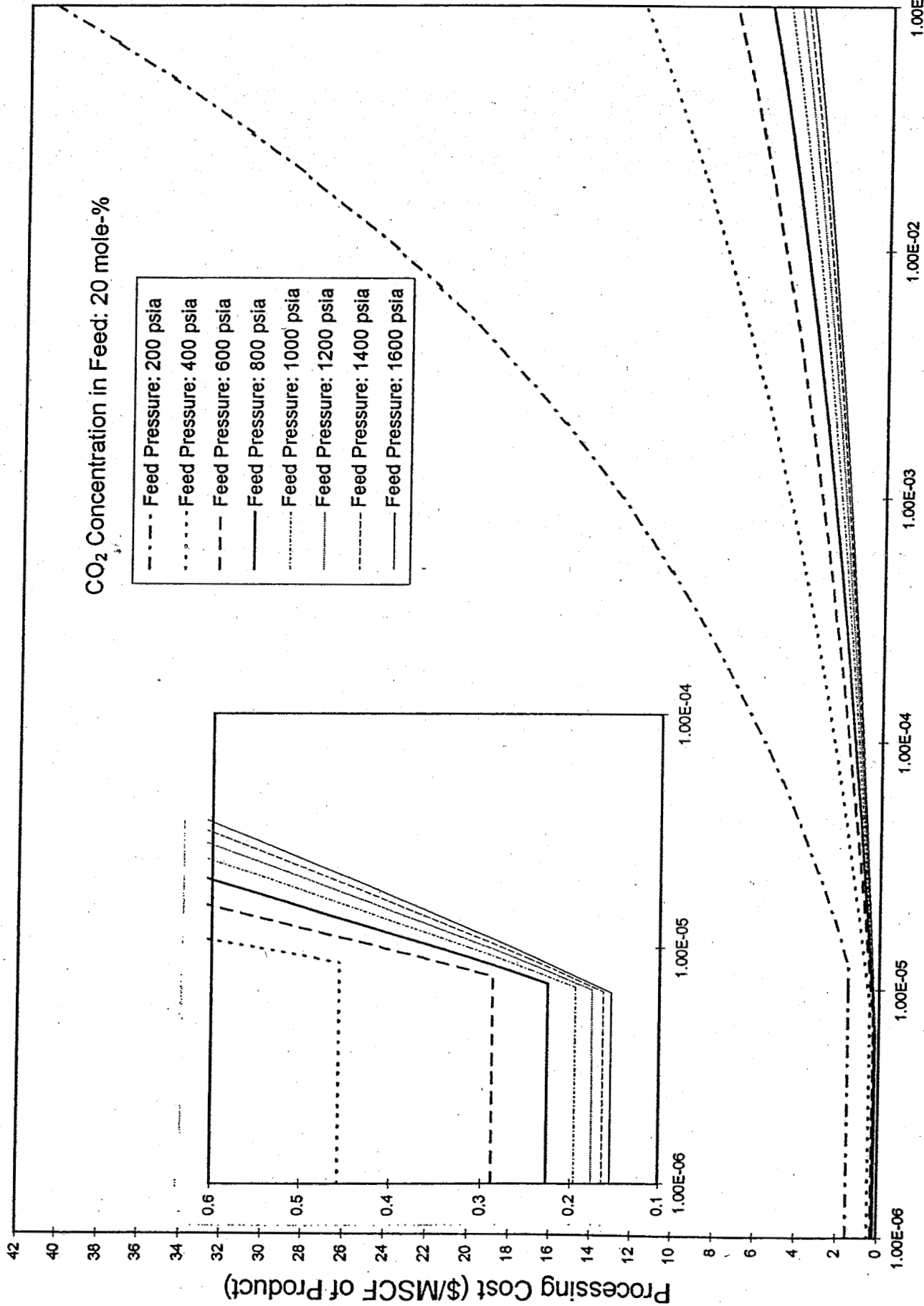


Figure 22: Effect of Feed Pressure and CO₂ Concentration in Feed on Processing Cost for Optimum Membrane Process Configurations without Recycle



H₂S Concentration in Feed (mole fraction)

Figure 23: Effect of Feed Pressure and H₂S Concentration in the Feed on Processing Cost
Configuration: Single Stage with CO₂-Selective Membranes without Recycle

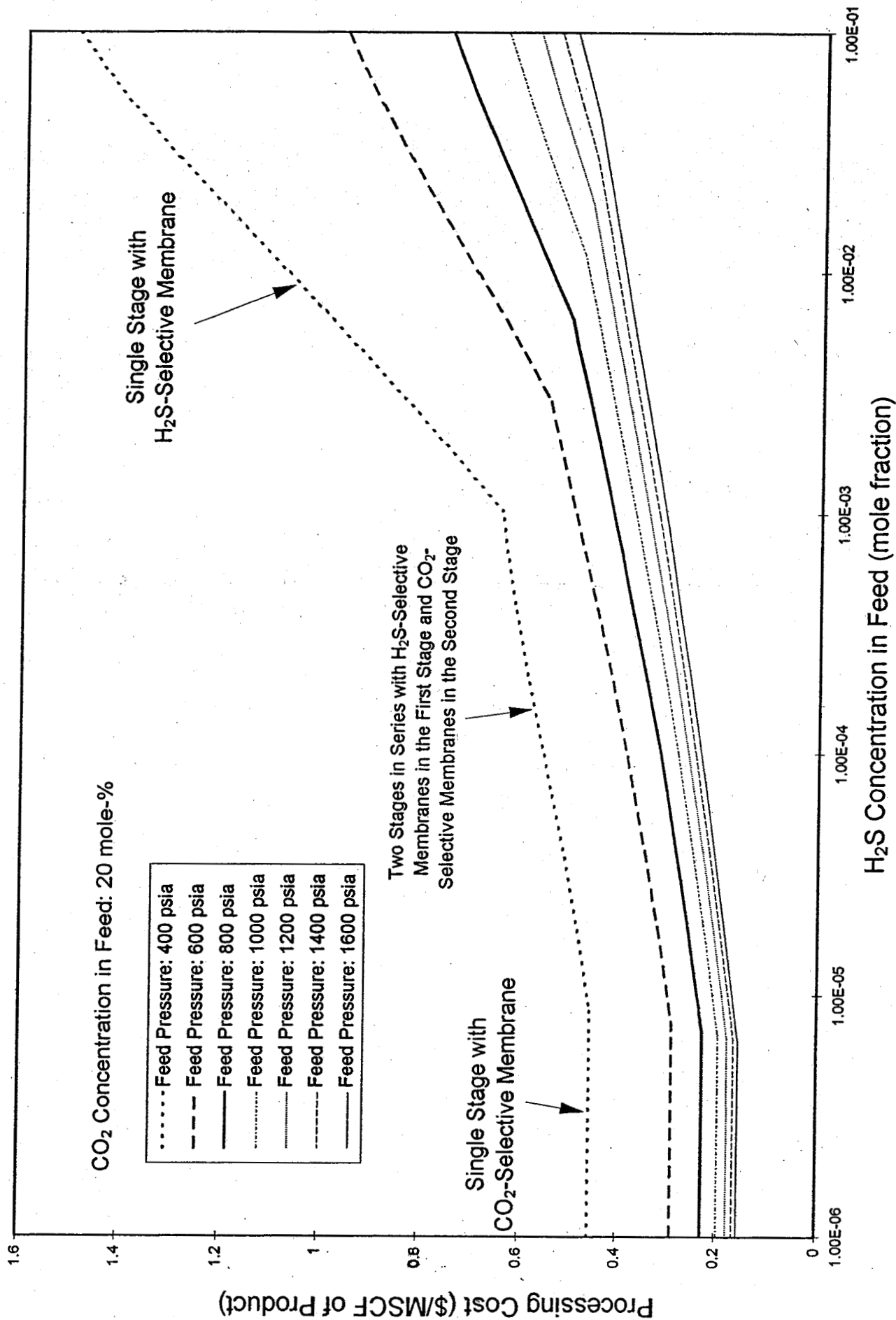


Figure 24: Effect of Feed Pressure and H₂S Concentration in the Feed on Processing Cost for Optimum Membrane Process Configurations without Recycle

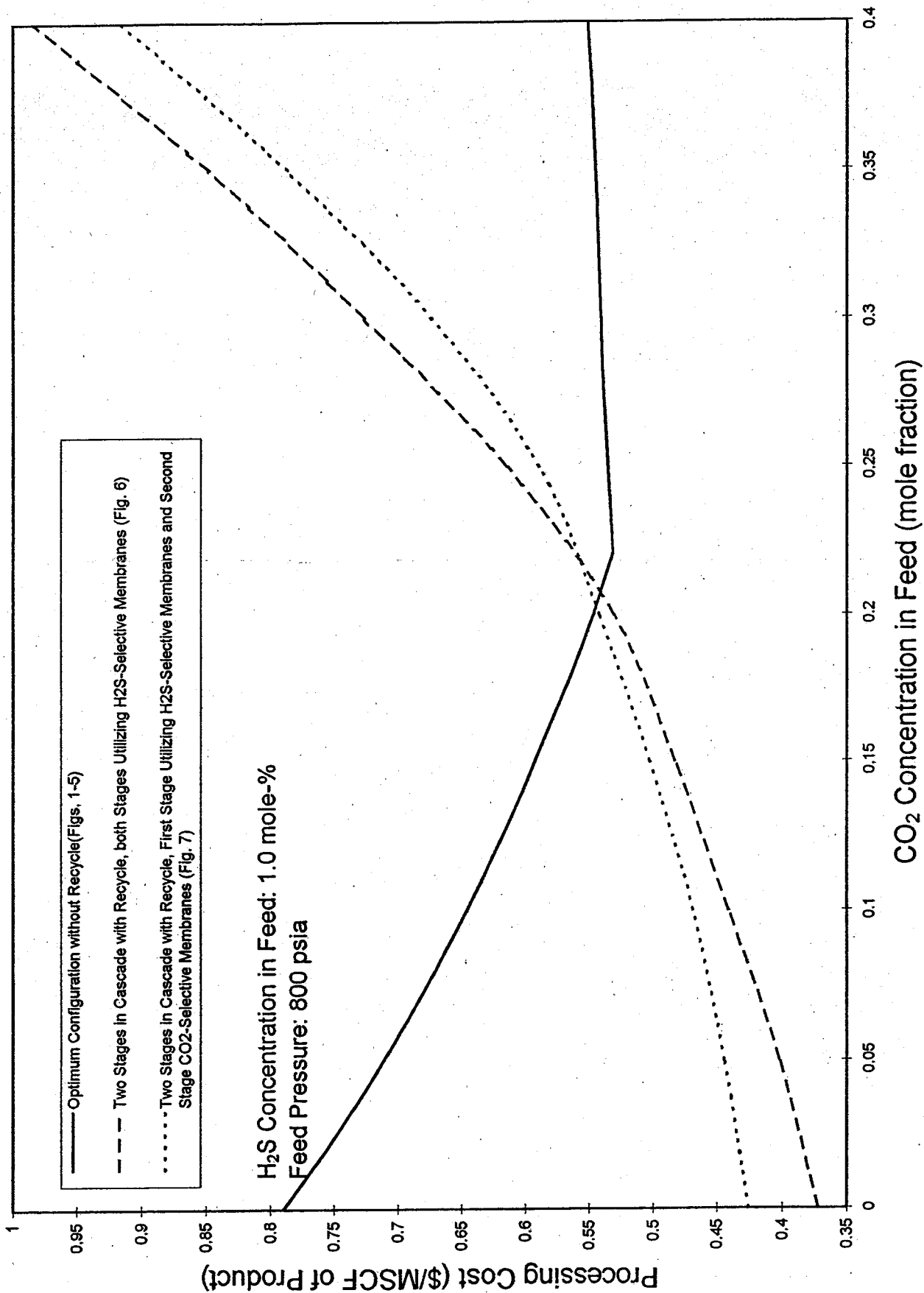


Figure 25: Processing Costs for Different Membrane Process Configurations

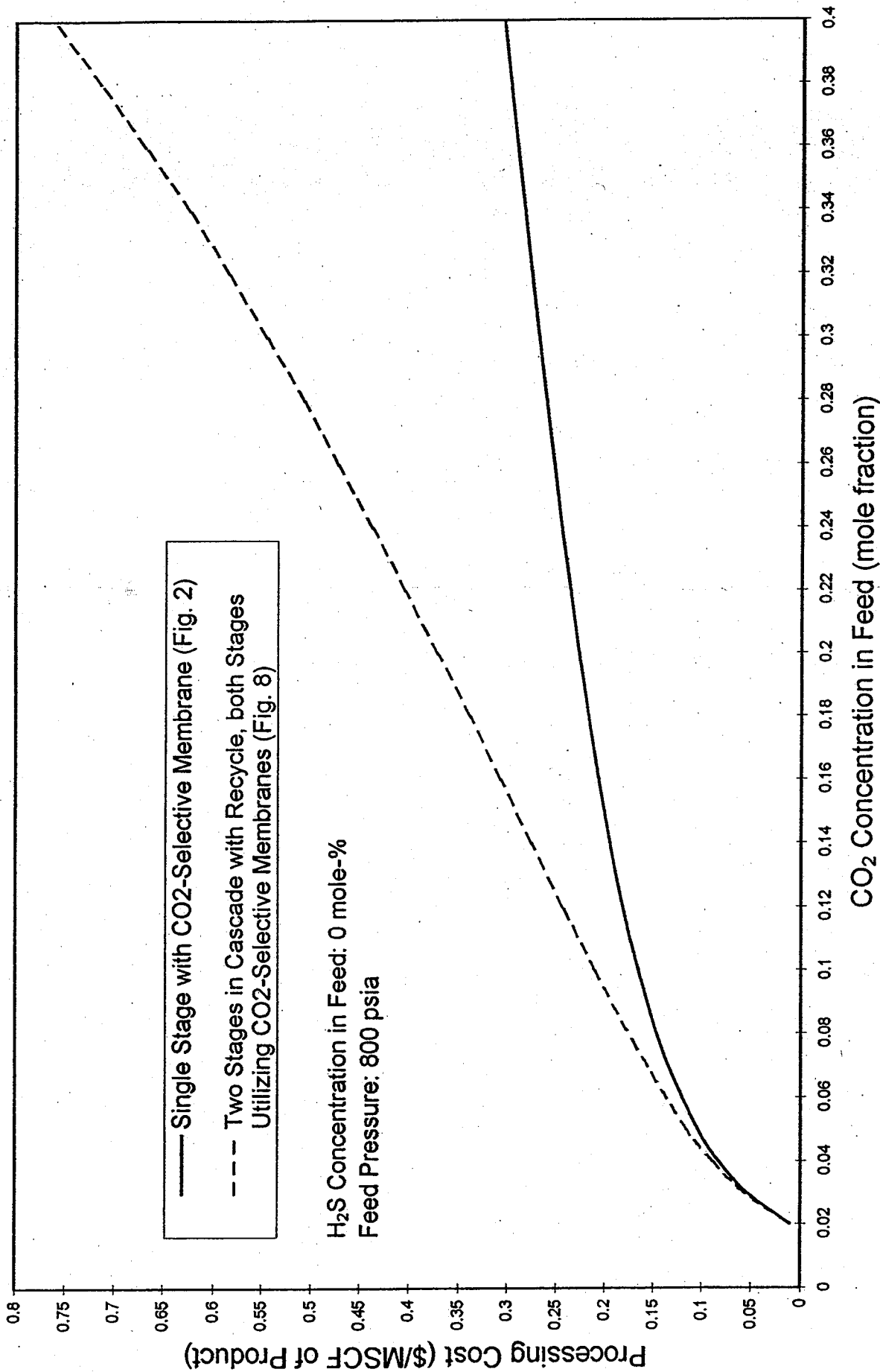


Figure 26: Comparison of Processing Costs of Upgrading Low-Quality Natural Gas Containing CO₂ to Pipeline Specifications for Membrane Configurations with and without Recycle

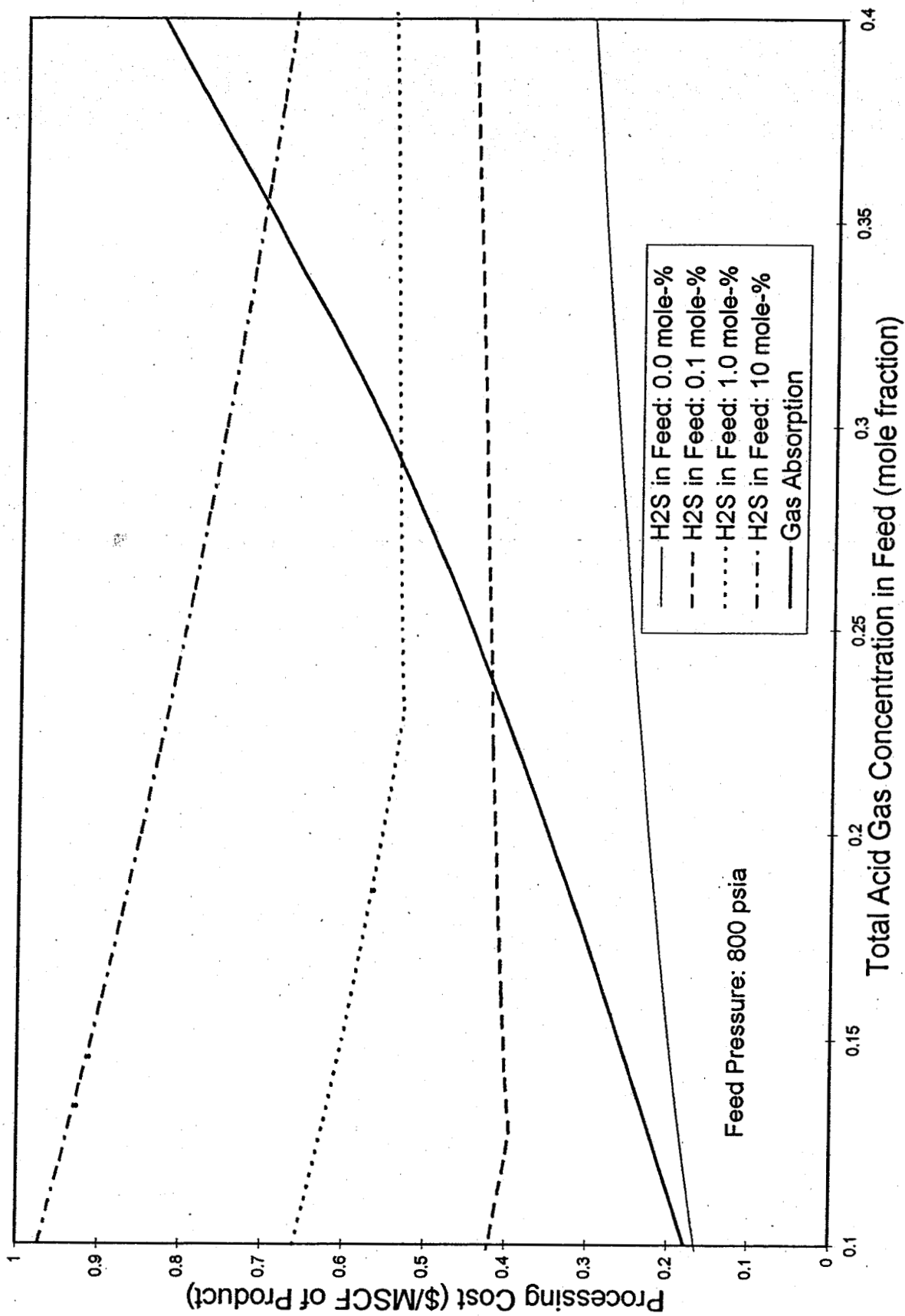


Figure 27: Processing Costs as a Function of Total Acid Gas Concentration in the Feed for the Optimum Membrane Process without Recycle and Gas Absorption