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# ASSESSMENT OF THE POTENTIAL FOR REFINERY APPLICATIONS OF INORGANIC MEMBRANE TECHNOLOGY-AN IDENTIFICATION AND SCREENING ANALYSIS

## Final Report

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# Glossary & Abbreviations

| | |
|---|---|
| b, bbl | barrel |
| BOC | British Oxygen Company |
| BTU | British Thermal Units (1 BTU = 0.252 kilocalories) |
| CAA | U.S. Clean Air Act |
| CPI | chemical process industry |
| d, D | day |
| DEA | diethanol amine |
| DIPA | diisopropanol amine |
| DOE | U.S. Department of Energy |
| E&C | engineering and construction |
| EOR | enhanced oil recovery |
| °F | temperature, degrees Fahrenheit |
| FCC | fluid catalytic cracking |
| ft | feet |
| HDS | hydrodesulfurization |
| hr | hour |
| kg | kilogram |
| kW | kilowatt (1,000 watts), based on electrical output unless otherwise stated |
| kWh | kilowatt-hour |
| lb | pound (1 lb = 454 grams) |
| lt | long ton (1 lt = 2,240 pounds or 1,016 kg) |
| m | meter |
| M | thousand |
| MDEA | methyl diethanol amine |
| MEA | monoethanol amine |
| MM | million |
| NEA | nitrogen enhanced air |
| NMP | N-methyl-2-pyrolidone |
| NPRA | National Petroleum Refiners Association |
| OEA | oxygen enhanced air |

| | |
|---|---|
| ppmv | parts per million by volume |
| PSA | pressure swing adsorption |
| psia | pounds per square inch absolute |
| psig | pounds per square inch gauge |
| Q&A | NPRA Question and Answer Session |
| R&D | research and development |
| scf | standard cubic feet (gas measured at 60°F, 1 atmospheric pressure) |
| sd | stream day (330 stream days per calendar year unless noted otherwise) |
| SMR | steam methane reforming |
| TEA | triethanol amine |
| wt% | weight percent |
| vol% | volume percent |
| yr | year |
| % | percent |
| $ | U.S. dollar |
| & | and |

# SECTION 1

# EXECUTIVE SUMMARY

# Section 1

# Executive Summary

## Introduction

Commercial application of membrane technology in the separation of gas, liquid, and solid streams has grown to a business with worldwide revenues exceeding $1 billion annually. Use of organic membranes for industrial gas separation, particularly in the refining industry, is one of the major growth areas. However, organic membranes based on polymeric separation barriers, are susceptible to damage by liquids, and careful precautions must be taken to retain the system integrity. Researchers are currently developing small pore sized inorganic membranes which may substantially increase the efficiency and economics in selected refinery separation applications. Expected advantages of these *advanced* inorganic membranes include high permeability, high selectivity, and low manufacturing cost.

SFA Pacific conducted a screening analysis to identify applications for inorganic membrane technology in the petroleum refining industry and their potential cost advantages over competing separation systems. Two meetings were held in connection with this project. Copies of Viewgraphs presented by SFA Pacific at these meetings are attached in Appendices A and C.

Potential high priority applications and market impacts of *advanced* inorganic membrane technology in the refining industry are addressed in this report, and include the following areas:

- Competitive separation technologies
- Application of those technologies
- Incentives for inorganic membranes
- Market benefits and impacts of inorganic membranes

## Application of Separation Technologies in the Refining Industry

Separation technology is extremely important to the refining industry. Capital investment for separation equipment is commonly over half of that for the battery limits, and associated operating costs often exceed half of those for the total site. Separation technologies used include organic membranes, pressure swing adsorption (PSA), cryogenics, liquid scrubbing, and distillation.

### *Organic Membranes*

Separation via organic membranes is a solution-diffusion process based on the difference in permeation rates among stream components in relation to properties of the membrane material. In industrial gas separations, membranes are primarily based on organic polymers such as cellulose acetate, polysulfone, and polyimide. Membrane separators use either one of two geometries--flat-film or hollow-fiber. These geometries are arranged as bundles and packaged in modules as either spiral-wound (formed by wrapping layers of flat-film membranes separated by spacers around a perforated collector tube) or hollow-fiber (arranged similar to shell and tube heat exchangers) separator systems. These systems are supplied as skid-mounted modules which are compact, simple, light-weight, have few moving parts, and are available in short delivery time.

Membrane separation produces two streams--the permeate and the residue. The permeate stream consists of gas components which have dissolved and diffused through the membrane. The permeate is obtained at pressure substantially lower than the feed. The residue consists of the gas components not permeating the membrane, and is recovered at a pressure only slightly below that of the feed. The performance of membrane systems is influenced by several factors, including feed and permeate pressure, feed flow rate, targeted product purity and recovery, and membrane area. The pressure differential between the feed and permeate streams has the greatest impact on system performance.

Widespread use of organic membranes for gas separation has occurred within the last ten to fifteen years. Vendors of organic membranes for gas separation to the refining industry include Air Products (PRISM), W.R. Grace, Hoechst Celanese (Separex), L' Air Liquide/Du Pont (MEDAL), UBE Industries, and UOP. For the period 1977 to 1993, there are 219 organic membrane units in refining applications installed worldwide. PRISM units account for over 60% the total. The refining applications include:

- $H_2$ recovery from hydrotreater, hydrocracker, and catalytic reformer purge streams, and refinery vent gases.
- $H_2$ recovery from ammonia, methanol, and other petrochemical plant purge streams.
- Adjustment of the $H_2/CO$ synthesis gas ratio in stream methane reformers.
- Separation of $CO_2$ from light hydrocarbon streams in enhanced oil recovery operations.

Refiners using organic membrane separation technology are increasingly satisfied, and economic justification for application of the technology is easily demonstrated. Increased refinery hydrogen requirements due to changing processing strategies can be met using organic membrane separators for hydrogen recovery. Modularity, compact system size, and minimal required operator attention contribute to low operating and maintenance costs for these separators. However, damage by liquids and generation of the permeate at low pressure are major drawbacks for this technology. Users and vendors note the importance of removing any entrained liquids in pretreatment steps ahead of the membranes. If the permeate stream must be recompressed to high pressure, significant recompression costs must be included in the membrane system economics. Future improvements in organic membrane technology focus on selectivity, productivity, and operational reliability through innovations related to the polymeric material.

### *Pressure Swing Adsorption*

Pressure swing adsorption (PSA) is a separation technology based on the capacity of high surface area adsorbents to selectively remove more of certain components at high gas-phase partial pressure than at low gas-phase partial pressure. This separation is achieved in multiple fixed-bed adsorbers in two basic cyclic steps--adsorption and regeneration. The adsorbent is selected on the basis of the separation requirements, and is either organic (e.g., active carbon, carbon molecular sieves) or inorganic (e.g., silica gel, zeolites). Since the process is cyclic with each cycle requiring discrete increments of time, PSA systems commonly consist of multiple beds (5 to 10). The timing of bed switching is controlled through a network of elaborate valves.

Separation via PSA produces two streams--the product and the tail gas. The product stream is of extremely high purity, and contains only ppm levels of the less-strongly adsorbed feed components. It is delivered at essentially feed pressure. The tail gas is composed of components which were adsorbed from the feed, and is obtained at pressures as low as possible, typically between 2 and 5 psig. The performance of PSA systems is measured in terms of desired product gas recovery and purity, feed quantity, feed and tail gas pressure, and adsorbent life. The driving force for separation is the partial pressure difference between the feed stream and the tail gas, and a minimum ratio of 4:1 is generally required for economic operation. Product recoveries of 80 to 92% with product purities of 99 to 99+% are typical.

A large variety of binary and multi-component gas mixtures are commercially separated in PSA systems. Widespread use of PSA units for gas separation in the refining industry has occurred in last 25 years. Vendors of PSA technology include Air Products (Gemini), Dow (Generon), Linde AG, Mitsubishi Heavy Industries, Nippon Kokan K.K., Toyo Engineering, and UOP (Polybed). UOP's technology dominates refining applications in the United States. For the period 1966 to 1993, 417 Polybed PSA units were installed worldwide for the following refining applications:

- $H_2$ recovery from hydrotreater, hydrocracker, and catalytic reformer purge streams, and refinery vent gases.

- $H_2$ recovery from ammonia, ethylene, methanol, and other petrochemical plant purge streams.

- Adjustment of the $H_2/CO$ synthesis gas ratio in stream methane reformers.

The PSA technology is accepted within the refining industry for production of high-purity, high-pressure gas streams. However, refiners are somewhat apprehensive regarding its use due to the technology's complexity and possibility of valve failures. The capital investment and maintenance, and operating costs are higher than for organic membrane systems. Future advances in PSA technology include the following:

- Innovations in system configuration allowing for recovery of multiple high-purity, high-pressure product streams

- Improvements in technology reliability through improvements in valves and their control

- Development of improved adsorbents, and attainment of a better understanding of gas-solid interactions

### *Cryogenic Separation*

Separation via cryogenics relies on the phase separation of stream components due to large differences in relative volatilities at extremely low temperatures. This technology is well established for recovering multiple components from gas streams. These systems include phase separators, aluminum plate-fin heat exchangers, and pressure expanders. The driving force for the separation is the temperature drop of the gas due to the Joule-Thomson effect associated with expansion. Design of these systems employs sophisticated thermodynamic correlations. The feed stream is typically cooled to -200 to -250°F.

Cryogenic systems are best for bulk quantity of industrial gases (greater than 50 MMscf/d). These systems are used in recovery of valuable components from natural gas, upgrading the heat content of fuel gas, air separation, purifying various process and waste streams, and producing ethylene. Cryogenic systems are used for upgrading streams of low hydrogen purity (less than 50 vol%), that also contain recoverable quantities of other valuable components. The technology is more efficient than organic membrane and PSA systems, but is more capital intensive. Inorganic membrane technology may best be suited for use in hybrid applications with cryogenic separators. Several vendors market cryogenic technology including Air Products, KTI, Linde AG, and UOP.

### *Liquid Scrubbing*

Liquid scrubbing is generally used for bulk removal of acid gases by using various solvents, and can be categorized into three types--chemical, physical, and hybrid solvent systems. These are typically big systems and require large capital investments. Inorganic membrane technology is best suited for use in hybrid applications with liquid scrubbing systems, adding more flexibility in separation technology selection and downstream process options.

With chemical solvents, acid gas removal depends on chemical reaction. Process solvents are based on either amines or potassium carbonates. Processes of interest include the amine-based UOP process, and the hot potassium carbonate-based Benfield HiPure process. With physical solvents, removal depends on physical solubility of the acid gas. These solvents are best used at high acid gas partial pressure and exhibit substantially higher solubility for $H_2S$ than $CO_2$. Processes of interest include glycol-based Selexol, pyrolidone-based Purisol, and methanol-based Rectisol. Hybrid solvents combine the characteristics of both chemical and physical systems. The best known and most widely used of this type is the Sulfinol process which uses an amine in a mixture with sulfolane and water.

### *Distillation*

Distillation is the most important separation technology used in the petroleum refining industry. It is the basic process used for atmospheric and vacuum crude separation. Distillation is also used to recover valuable components from various refinery process unit streams. Separation is based on differences in relative volatilities of stream components. This technology is primarily for large gas capacities recovering valuable components such as $C_3$-$C_6$s from various gas streams generated in refineries such as crude distillation units, cokers, catalytic crackers, reformers, and hydrocrackers. For large gas streams, distillation systems require large capital investment and generally occupy large portions of space. As with liquid scrubbing, inorganic membranes are best used in hybrid applications allowing more flexibility in optimizing distillation technology and downstream processing.

## Incentives for Inorganic Membranes Technology

Several key systems warrant initial testing on the *advanced* inorganic membrane technology. The systems include $H_2/CH_4$ separation, enrichment of $H_2S$ in $H_2S/CO_2$ mixtures, sulfur/aromatic removal from kerosene and diesel fuels, normal hexane/cyclohexane separation, and $O_2/N_2$ air separation. These are all important refinery separations, and there are significant incentives to demonstrate application of inorganic membrane technology on these systems. The incentives are estimated by assuming a performance improvement attributed to use of inorganic membrane technology relative to a base case.

Hydrogen separation from hydrocarbon gases (e.g., $H_2/CH_4$ separation) is extremely important in the refining industry. The current cost for conventional hydrogen manufacture (from stream methane reforming) is about $2.50/Mscf, while costs for hydrogen recovery from organic membrane and PSA systems range from about $0.75 to 1.05/Mscf (depending upon the recovery percentage and permeate pressure). Inorganic membranes offer a large cost incentive provided systems are developed with a hydrogen separation factor and permeability considerably greater than that for competitive organic membranes. This feature will allow inorganic membrane systems to be appropriately designed to maximize the permeate pressure, and minimize the recompression cost of the permeate to high pressures. The recompression cost may often be larger than the membrane operating cost. The impact of permeate pressure on $H_2$ cost is clearly shown in Appendix C-2/Viewgraph 7. This application can also be expanded to hydrogen manufacture, where the goal is $H_2/CO_2$ separation.

The partial oxidation process converts hydrocarbon feeds (such as methane, light and heavy liquids, and solids) to synthesis gas--mostly CO and $H_2$, with small amounts of acid gases $CO_2$, $H_2S$, and COS. Expensive acid gas removal processes (such as Rectisol) are often used to separate $H_2S$ and $CO_2$ from $H_2$ in the syngas. Less expensive acid gas removal processes are available (such as UOP Amine and hot potassium carbonate), but the mixture of $H_2S$ and $CO_2$ produced cannot be processed in a normal Claus plant for production of sulfur. Inorganic membranes may be used to enrich $H_2S$ separation from $CO_2$, and permit use of the cheaper acid gas removal processes. These savings can be as much as $0.54/Mscf. However, the cost for use of inorganic membranes must also be included. Assuming inorganic membranes cost twice as much as organic membranes for $H_2$ recovery, the cost of applying inorganic membranes would be $0.13/Mscf. The potential savings is therefore $0.54 - 0.13 = $0.41/Mscf. This value still represents a large incentive.

New federal environmental standards on diesel necessitate reduction of sulfur to a 0.05 wt% maximum and require cetane index of at least 40 (this limits aromatics to about 35-40 vol%). In addition, in California, aromatics are limited to 10 vol% or the equivalent tail pipe emissions. Upgrading diesel to these new standards results in significant increases in hydrotreating severity (higher reactor pressures and more hydrogen consumed) and resultant costs. Both federal and California standards are estimated to increase diesel treating by over $3/bbl. Inorganic membrane technology could provide a simple and effective technique for treating diesel to remove extra increments of aromatics and sulfur compounds. This is not possible with organic membrane technology due to its susceptibility to damage by liquids. This application of inorganic membranes may also be used in treating other refinery liquid streams such as catalytic naphthas, jet fuels, lube oils, and higher boiling gas oils which are of higher value and more abundant than diesel fuel.

Performance targets for experimental programs on the systems discussed above are attached in Appendix B. Additional refinery separation applications which are important potential users of inorganic membrane technology include the following:

- Separation of benzene from refinery wastewater in compliance with federal clean air standards for hazardous air pollutants.
- Catalytic membranes reactors that combine reaction and separation permitting higher conversion per pass, less severe operating conditions, less recycle, and reduced equipment capital investment.

However, these systems are not evaluated in this report due to absence of a frame basis for the base case or reliability of the technical concept and performance. Application of inorganic membrane technology to these systems warrants further study and are beyond the scope of refining processes evaluated in this project.

Additionally, this screening analysis primarily examines areas where the organic membranes may have marketing potential due to their unique or distinct capabilities. It does not address potential markets applications where inorganic membranes may ultimately directly compete with organic membranes on a cost, performance and/or durability basis. Nor does it address any possible benefits from hot gas (1,100°F+) separation and clean up.

## Market Benefits and Impacts of Inorganic Membranes Technology

The overall impact of inorganic membranes in refinery applications is assessed by projecting the growth and penetration of the field in competition with other separation methods, and by determining the economic advantage achieved by their use. A scenario must be assumed to estimate when inorganic membranes become commercially available, and how fast they penetrate the market. SFA Pacific estimated overall benefits and impacts for inorganic membranes to the U.S. refining industry with the following results:

- $H_2$ recovery from purge gases: By 2001, a single year savings of about $65 million/year is achieved in additional $H_2$ manufacture needed to treat diesel and heavy catalytic naphtha. In subsequent years as $H_2$ use grows and inorganic membranes acquire a larger share of the market, the incentive/year will be greater. This assumes that purge gases represent 20% of $H_2$ production, and by 1996, 20% of these purges are processed in inorganic membranes (with a pressure advantage over organic membranes of $0.15/Mscf due to development of inorganic membranes of higher permeability to hydrogen than organic membranes).

- $H_2S$ enrichment from $CO_2$: By 2001, a single year savings of about $85 million/year results from additional $H_2$ manufacture needed to treat diesel and heavy catalytic naphtha. This assumes that partial oxidation accounts for 20% of new $H_2$ manufacture, and by 1996 inorganic membranes have begun to be used commercially in connection with hot potassium carbonate acid gas separation (with a credit of $0.25/Mscf). This reflects the large credits for using inorganic membranes in both the manufacturing and separation steps.

- Sulfur/aromatics removal from diesel: Savings of $132 million/year is achieved by treating diesel. This assumes a U.S. diesel production rate of 2 MM bbl/d, that sulfur and aromatics are reduced from 0.05 to 0.01 wt% and 35 to 20 vol%, respectively, and that 20% of the diesel is treated with inorganic membranes (with a credit of about $1.00/bbl).

Experimental data on inorganic membrane performance on these applications may permit consideration of a wider range of refining applications, including the following: $H_2/CO_2$ separation in $H_2$ manufacture, application to ammonia and methanol manufacture, sulfur/aromatics removal from other liquid streams (catalytically cracked gas oils, lube oils, and jet fuel), and expansion to worldwide operations. Experimental data should also be obtain on $O_2/N_2$ separation and filtration of 2-10 micron catalyst particles from cat cracker bottoms at 350-650°F to ascertain potential for applications in these areas.

# SECTION 2

# INTRODUCTION

# Section 2
# Introduction

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## Background

Industrial applications of membranes in the separation of liquid and liquid/solid streams have been practiced for many years (e.g., reverse osmosis, ultrafiltration, microfiltration, and other membrane-based processes). Membrane technology has expanded to a business with worldwide revenues exceeding $1 billion annually [1]. One of the major growth areas for this business is the use of organic membranes for industrial gas separations. Such membrane systems are being used increasingly in separations involving hydrogen recovery and purification, acid gas removal, and air separation due to material and technology advances achieved in the past fifteen years.

Organic membrane systems consist of polymeric barriers to achieve the desired separation. However, in separating refinery gas streams, polymeric membranes are often damaged by entrained hydrocarbon liquids, and careful precautions must be taken to retain the integrity of the membrane system. Researchers are developing *advanced* small-pore-sized inorganic membranes which may substantially increase the efficiency and economics of separation processes for selected refining applications. Expected advantages of the *advanced* inorganic membranes are high permeability (1,000 to 10,000 times organic membrane permeability), high selectivity, and a low cost, simple, versatile manufacturing process. Additional inherent advantages of inorganic membranes include high durability and reliability, processing capability in hostile corrosive, erosive, and high temperature environments, and chemical reactor potential. These inorganic membranes are less susceptible to damage by liquids, and may accomplish desired separations in systems requiring less capital investment than current competitive systems.

## Objective

This report addresses the potential high priority applications and market impacts of *advanced* inorganic membrane technology in the petroleum refining industry. Emphasis is given to refinery down-stream applications.

There are a total of six sections in the report, including the Executive Summary (Section 1) and Introduction (Section 2). References are included at the end of each section. Sections 3 through 6 are summarized below:

> Section 3 (Competitive Separation Technologies) reviews the commercial separation technologies of organic membrane, pressure swing adsorption, cryogenics, liquid scrubbing, and distillation.
>
> Section 4 (Application of Separation Technologies in the Refining Industry) discusses current commercial use, strengths, weaknesses, and R&D trends associated with organic membrane and pressure swing adsorption technologies in refineries.
>
> Section 5 (Incentives for Inorganic Membrane Technology in the Refining Industry) provides a screening analysis of the cost and performance characteristics for use of inorganic membranes on selected market entry and growth refining applications.
>
> Section 6 (Market Benefits and Impacts of Inorganic Membrane Technology) presents a discussion of the potential U.S. and worldwide market benefits and impacts of inorganic membranes to the refining industry.

Also included at the end of the report are appendices containing the following additional material developed by SFA Pacific:

| | |
|---|---|
| Appendix A | Viewgraphs from Kick-Off Meeting |
| Appendix B | Key Separation Performance Targets |
| Appendix C | Viewgraphs from Mid-Course Review Meeting |

## References

1. A.M. Crull, "The Evolving Membrane Industry Picture," in The 1988 Sixth Annual Membrane Technology/Planning Conference Proceedings, Business Communications Company, Inc., Cambridge, MA, 1988.

# SECTION 3

# COMPETITIVE SEPARATION TECHNOLOGIES

# Section 3

# Competitive Separation Technologies

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## Introduction

The efficient and economical separation of gas, liquid, and solid intermediate and product streams is crucial to the chemical processing and petroleum refining industries. Capital investment for separation equipment is commonly over half of the battery limits investment. Additionally, operating costs associated with stream separation often exceeds half of those for the total site. It is desirable to identify areas where inorganic membranes can be used as a replacement technology or in conjunction with other technologies to reduce investments and costs related to separation.

Several separation processes are used in the petroleum refining industry, depending upon various stream characteristics and its ultimate destination. Technologies used include the following:

- Organic membranes
- Pressure swing adsorption (PSA)
- Cryogenics
- Liquid scrubbing
- Distillation

A discussion of these technologies was presented at the Kick-Off Meeting on June 23-24, 1992. Viewgraphs from the meeting are presented in Appendix A. Supplemental information on these separation technologies, emphasizing organic membrane and PSA technology is presented below.

## Organic Membranes

Industrial application of membranes for the separation of liquid-liquid and liquid-solid streams has been practiced for many years in processes such as reverse osmosis, ultrafiltration, microfiltration, and dialysis. Advances in material and membrane technology have led to the development of organic membranes suitable for industrial gas separation, applicable to the petroleum refining industry.

### *Separation by Solution-Diffusion*

Membranes are thin barriers that allow preferential passage of selected substances. In industrial gas separations, membranes are primarily based on organic polymers. Separation via organic membranes is a solution-diffusion technology based on the difference in permeation rates among stream components in relation to properties of membrane material. Gas permeation rates are affected by both the solubility and diffusion rates of the gases to be separated. Gas solubilities depend primarily on the chemical composition of the polymer, while the diffusivities depend on the structure of the polymer. Gases can have high permeation rates due to high solubilities, high diffusivities, or both.

Relative permeabilities for selected gases through different membranes are illustrated in Table 3-1. Gases that have high permeation rates are termed *fast* gases, and those with low permeation rates are termed *slow* gases. The relative permeation rates range from fast for $H_2O$, $H_2$, He, and $H_2S$, to intermediate for $CO_2$, and $O_2$, to slow for CO, $CH_4$, and $N_2$. The fast gases have low molecular weight ($H_2$, He) or are polar structures ($H_2O$, $H_2S$), while the slow gases have high molecular weight or are symmetrical molecules. It can be seen that gas permeabilities vary among polymers, and also that the relative permeabilities of any two gases may vary for different polymers.

## Table 3-1

## Relative Permeabilities of Various Gases for Several Organic Membranes

(Permeability relative to $O_2$ separation across Polysulfone)

Fast---------------------------------------------------------------------------->Slow

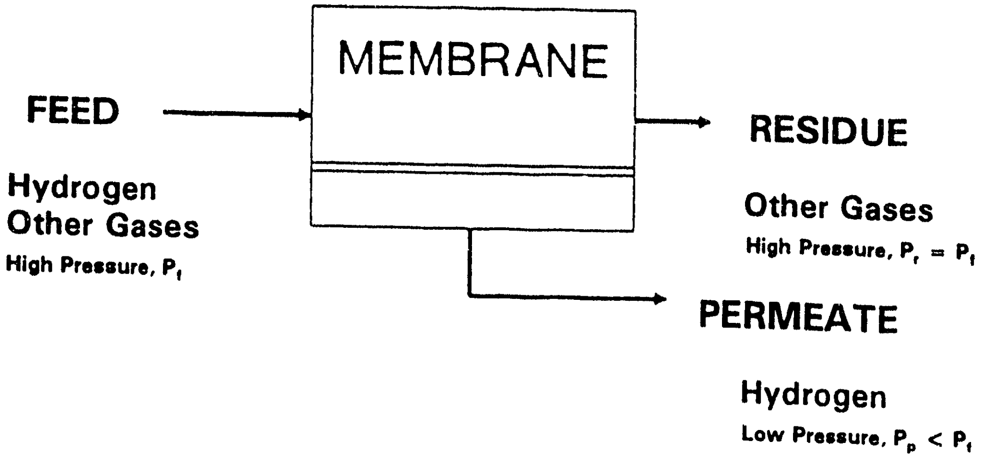
| Membrane | $H_2O$ | $H_2$ | He | $H_2S$ | $CO_2$ | $O_2$ | Ar | CO | $CH_4$ | $N_2$ | $C_2H$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Polysulfone | - | 13 | - | - | 6 | 1 | - | - | 0.22 | 0.2 | - |
| Cellulose Acetate | 120 | 12 | - | 10 | 6 | 1 | - | 0.30 | 0.20 | 0.17 | 0.10 |
| Polyamide | - | 9 | - | - | - | 0.5 | - | - | 0.05 | 0.05 | - |
| Dow Product | - | 136 | - | - | 93 | 32 | - | - | - | 8 | - |
| Permea Product | - | 22 | - | - | 9 | 2.3 | - | - | 0.4 | 0.4 | - |
| Polydimethylsiloxan | - | 649 | - | - | 1070 | 604 | - | - | 3230 | 281 | - |

Source: References 1 & 2

The idealized separation of two gases by a membrane is illustrated in Figure 3-1. The gas passing through the membrane is the *permeate*, while that remaining behind is the *residue* (or retentate). Complete separation is shown in the figure, although in fact this never occurs. The degree of separation is defined by the selectivity of the membrane as well as the conditions of the separation (such as feed pressure, feed composition, etc. discussed in detail later).

**Figure 3-1**

**Idealized Separation in an Organic Membrane**



Source: Reference 3

The separation process involves two sequential steps: the permeable gas first dissolves into the membrane, then it diffuses through the membrane to the permeate side. This is also referred to as solution-diffusion. The driving force for the separation is the partial pressure difference across the membrane between the feed and permeate sides. This is represented using Fick's Law of Diffusion according to the following equation:

$$Q_i = P_i A(P_f - P_p)/L \qquad (3.1)$$

where $Q_i$ is the flux rate for each gaseous component, $P_i$ is the permeability coefficient for each component, A is the membrane area, $P_f$ is the feed partial pressure, $P_p$ is the permeate partial pressure, and L is the thickness of the membrane. Transport across the membrane can be assumed to consist of a solution of molecules at the high partial pressure surface, diffusion across the membrane due to the pressure gradient, and desorption at the low partial pressure surface. Thus, the permeability of each component is a function of solubility and diffusion coefficients.

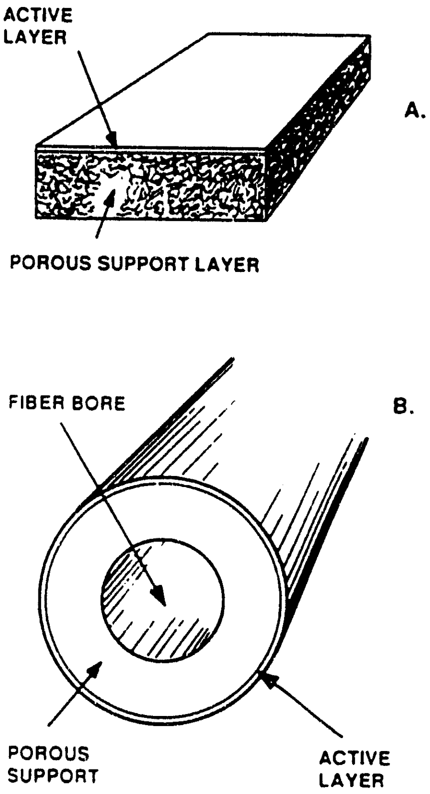
The gas component with the higher relative permeability will permeate at a higher rate. The other gas components will permeate at lower rates, and will remain concentrated in the residue. The residue gas is recovered at a pressure only slightly below feed pressure. The permeation rate is increased by both an increased pressure drop and by an increased partial pressure ratio across the membrane (between the feed and permeate sides). Permeate recovery and purity are functions of the pressure differential, the area of membrane surface, and the potential staging of the membrane modules. However, if the permeate gas is needed at a high pressure and must be recompressed, the optimum permeate gas pressure is one of the variables to be optimized.

### *Organic Membrane System Design*

Organic membranes are made from a variety of polymers including polyethylene, polyamide, polyimide, polydimethylsiloxan, cellulose acetate, polysulfone, polyaramide, polycarbonate, and depending upon the system manufacturer. Polymeric membranes are classified as symmetric or asymmetric depending on whether membrane morphology is the same across the entire thickness of the membrane. Commercial solution-diffusion membranes are of the asymmetric type--do not have a uniform density across their thickness--as shown in Figure 3-2. The membrane consists of a porous support layer and a thin polymeric layer. The support layer provides mechanical strength and allows the membrane to tolerate both the manufacturing process and the pressure differentials imposed during operation. On one side of the support layer is the active polymeric layer (or skin) which governs the molecular transport rate and achieves the separation. This active layer consists of either a single polymer system (two layers of a single polymer), or a composite system (a separation polymer coated very thinly on a different substrate polymer). The rate of gas transport across the membrane is inversely proportional to the thickness of the active layer as indicated in Equation 3.1. The thinner the membrane the higher the gas flux, but the weaker the membrane itself.

Figure 3-2

Schematic Representation of Asymmetric Membranes



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A: Flat-film membrane
B: Hollow-fiber membrane

Source: Reference 4

As shown in Figure 3-2, the two geometries of asymmetric membranes are flat-film and hollow-fiber. These systems are generally fabricated by casting films or spinning fibers from polymer solution. Commercially available membranes show a wide variation in properties, based on both the range of polymers used and the membrane structures achieved. These geometries are arranged as bundles and packaged in modules as either spiral-wound or hollow-fiber separator systems. Spiral-wound and hollow-fiber membrane separators are depicted in Appendix A/Viewgraph 8 [3,5]. Spiral-wound systems are formed by wrapping layers of flat-film membranes separated by spacers around a perforated collector tube. Hollow-fiber systems consists of many small capillaries, typically ranging in diameter from 30 to 500 microns, arranged in a form similar to that of a shell and tube heat exchanger.

The majority of commercial membrane systems are the hollow-fiber type, but the use of the spiral-wound type is increasing. Hollow-fiber membranes are less robust, but have larger area/volume ratio, while spiral-wound units tend to have higher permeability. Spiral-wound modules have a packing density of 1,500 $m^2/m^3$ surface, compared with about 9,000 $m^2/m^3$ for hollow fiber membranes [1]. Hollow fiber membrane systems have the advantage that a larger surface area can be packaged in a given number of modules. In either case, modular packaging allows for standardization of equipment.

Generally, separation with organic membrane systems requires multiple stages, the first stage for bulk removal, and subsequent stages for increased purification and hydrocarbon recovery. These systems are compact, simple, light-weight, have few moving parts, and are available in short delivery time. Membrane systems are supplied as skid-mounted modules, resulting in low initial investment for smaller throughput plants. Since the relationship between throughput and investment is linear, the economies of scale for organic membrane systems are less than those for processes in which larger modules can be used; therefore, higher capacities lead to a less competitive process.

Organic membrane systems also require auxiliary compressors for boosting the low-pressure permeate back to higher pressure. This is a disadvantage due to the considerable amount of energy required for product compression. Optimization of the variables involved in membrane system design is a sophisticated calculation, and many membrane vendors have developed computer models for selecting the appropriate system for a given application.

### *Performance Criterion for Organic Membranes*

The performance of membrane systems is influenced by several factors, including feed and permeate pressure, feed flow rate, targeted product purity and recovery, and membrane area. However, the pressure differential between the feed and permeate streams has by far the greatest impact on a particular membrane's performance [3]. The amount of membrane area required, and the volume and composition of the residue and permeate streams are all impacted by this pressure differential.

The three key performance characteristics that affect the economics for a given membrane separation application are selectivity, permeability, and membrane life. Selectivity directly impacts the recovery of the process and indirectly impacts membrane area and feed gas flow requirements. The permeability (or membrane flux) simply dictates the amount of membrane required. The life of the membrane affects the maintenance and replacement costs. Shown in Table 3-2 are ranges of permeabilities and selectivities for commercial polymeric gas separation membranes. Manufacturers do not normally disclose performance properties for their products, and the specific permeation and selectivity properties of most commercial membranes cannot be readily determined. But in general, membranes with higher permeability coefficients possess lower selectivities [4]. The life expectancy of membrane systems is usually about five to ten years, after which time bundles are typically replaced.

## Table 3-2

## Estimated Ranges of Membrane Properties in Commercially Available Gas Separation Membranes

| *Membrane Type and Property* | *Value* (1) |
|---|---|
| *Hydrogen Separation Membranes* | |
| Hydrogen permeability coefficient | 30 to 500 GPU |
| Hydrogen/methane selectivity | 30 to 250 |
| *Carbon Dioxide Separation Membranes* | |
| Carbon dioxide permeability coefficient | 10 to 200 GPU |
| Carbon dioxide/methane selectivity | 5 to 30 |
| *Air Separation Membranes* | |
| Oxygen permeability coefficient | 5 to 250 GPU |
| Oxygen/nitrogen selectivity | 3 to 7 |

---

(1) 1 GPU = $10^{-6}$ $cm^3$ (STP)/$cm^2 \cdot s \cdot$ cm Hg

Source: Reference 4

Other factors relating to organic membrane system performance are summarized as follows:

- Residue stream purity increases with increasing pressure differential, and membrane area requirements are reduced. However, pressure differential alone does not define membrane performance, since the absolute permeate pressure (or pressure ratio) is also important.

- Organic membranes perform very effectively on high pressure (250 to 2,000 psig) and moderate temperature (30 to 150°F) feed streams. Good feed temperature control is important because operation at higher temperatures increases permeability at the expense of selectivity, and the membrane itself can be damaged by high temperatures.

- Increases in feed impurity concentrations result in increases in product impurity concentrations. The product purity can be maintained for small feed composition changes by adjusting the feed-to-permeate pressure ratio, but the relatively strong impact of product recovery can be significantly affected.

- Feed flow rate impacts the residue product purity, but has relatively little impact on the total permeate flow rate. Higher feed rates reduce residue purity but the permeate recovery is increased. Low to moderate volume flow rates (0.15 to 20 MMscf/d) are best suited for separation with membranes.

- Increasing the membrane area results in a purer residue, while decreasing the membrane area results in a purer permeate. And in both cases, recovery will decrease as the purity requirement increases.

- Organic membrane units are not particularly applicable if separate residue streams rich in specific hydrocarbon fractions are desired.

- The capital investment required for membrane units are approximately \$7/ft$^2$. This cost is not subject to economies of scale, since capital investment for membranes increase linearly with gas throughput. Given the specific separation application, the three important elements to be considered in an economic assessment of organic membrane systems are (1) the required capital investment of the membrane system itself, (2) the associated operating costs (including capital and operating charges, feed costs, and fuel credits), and (3) charges for recompression of the permeate stream (if necessary). In the economic assessment, it is important to design a process that will balance these elements for a particular application.

Gas separation applications most suited for organic membranes meet one or more of the following criteria [1]:

- The feed stream contains moderate concentrations (10 to 85 vol%) of the more permeable gas, so that a reasonable feed-side partial pressure of the more permeable gas is readily achieved.
- The feed gas pressure is high, and either the fast gas product is required at low pressure or the slow gas product is required at high pressure.
- The product gas is not required at absolute purity or 100% recovery, since this is not readily achieved with membrane technology.
- A combination of high purity and high recovery is not required.
- The flow rates are relatively small.
- The selectivity of the membrane can be matched with the desired duty.
- The gas does not attack or alter the performance of the membrane.

It is important to note that there are pretreatment requirements for organic membrane systems since certain membrane materials can be permanently damaged by contaminants (such as dust, corrosive materials, organic solvents, and hydrocarbon mist). In fact, entrained liquids in the feed, even from relatively short-term upsets, can damage an entire unit because of the large amount of feed gas processed per module. Saturated feedstocks are normally pretreated in a knock-out drum with mist eliminator, coalescing filter, and/or a heater (to approximately 20°F above its dew point) prior to separation in a membrane unit. Organic membranes also should not be subjected to high temperatures.

It is also important to note that certain feed components cannot be completely removed via processing in organic membranes. Additional pre- or post-treatment may be necessary if these contaminants are not acceptable in the product stream. Specific examples include $H_2S$, CO, and $CO_2$ which cannot normally be reduced to ppmv levels by processing in organic membranes alone. Compatibility of a polyimide membrane to various chemical components is shown in Table 3-3. Other issues affecting separation with organic membranes involve their durability and include solvent and chemical resistance, pore size distribution, stability and narrowness of the polymer, mechanical stability of the system, fouling characteristics (ease of cleaning), and system life (possibility of regeneration). Durability enhances the flexibility and ease of operation of membrane systems to accept unconditioned feeds.

Modularity is a key advantage for membrane systems, especially for processing variable flow rates. Membrane systems are extremely flexible and are normally capable of maintaining product purity at rates from 30 to 100+% of design. Modular systems are ideally suited for expansion, since expansion usually only requires the addition of identical modules. Membrane systems are delivered skid-mounted, simple to operate and very reliable, with high on-stream factors. Refining industry operating experience with organic membrane systems is discussed in Section 4.

It is important to note that the most economic gas separation application of organic membranes is often one in which the product recovery rate may be lower than that of a competing process. In some cases, the most economical choice may be a combination of processes since membrane systems may be coupled with other separation technologies when high product purity and recovery are required.

## Table 3-3

## Chemical Compatibility Of A Commercial Polyimide Membrane

| | Volume Percent in Feed Gas (1) | | | | | |
|---|---|---|---|---|---|---|
| Component | 0.01 | 0.1 | 1 | 3 | 5 | 10 |
| $H_2O$ | A | A | A | A | A | A |
| $H_2S$ | A | A | A | A | B | B |
| HCl | A | A | A | A | B | B |
| NH3 | A | B | C | C | C | C |
| $CH_3OH$ | A | A | A | A | A | B |
| $CH_3OCH_3$ | A | A | A | A | A | B |
| $CH_3CHO$ | A | A | A | A | B | B |
| BTX (2) | A | A | A | B | B | B |
| Gasoline | A | A | A | A | A | B |

---

(1) Legend

A: The membrane can be used satisfactorily for an extended period of time.

B: The membrane can withstand the condition in this range for a short period of time. However, long-term operation in this range is not recommended, otherwise some performance decline will result.

C: Operation in this range is to be avoided. The membrane will be irreversibly damaged.

(2) BTX = benzene/toluene/xylenes.

Source: UBE Industries

### Pressure Swing Adsorption

The pressure swing adsorption (PSA) process has been used extensively in the fractionation of air and other gases. It is used for the dehydration, purification, and detoxification of air, as well as for the separation of air into oxygen and nitrogen, and has been successfully applied to the purification of hydrogen and natural gas, and in coal gas bulk separation. The first and most numerous applications of PSA systems were for drying compressed air at gasoline service stations.

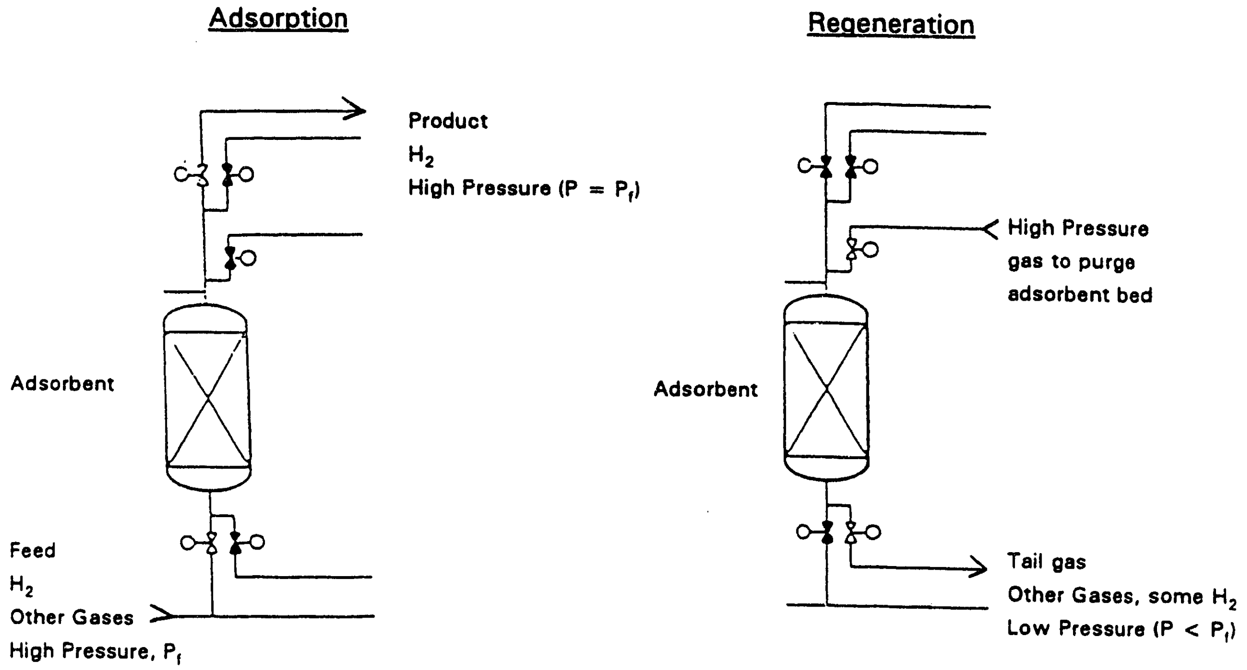
### *Separation by Adsorption*

PSA is a separation technology for treating gas streams based on the capacity of adsorbents to selectively remove more of certain components at high gas-phase partial pressure than at low gas-phase partial pressure. PSA systems are fixed-bed, cyclic processes having two basic steps--adsorption and regeneration, as illustrated in Figure 3-3. A multi-component gas stream at high pressure flows through a vessel containing a fixed-bed of adsorbents producing a product gas stream essentially free of impurities. The product gas pressure is available at essentially feed pressure, with a nominal 10 psi pressure drop. Gases are adsorbed at different rates, as shown in Table 3-4. Non-polar gases like $H_2$, $N_2$, Ar are not tightly bound in adsorbents when compared to components like CO, $CO_2$, $CH_4$, and $H_2O$. The product gas will contain only the less-strongly adsorbed components of the feed in detectable levels.

The feed gas flows through the bed until the adsorbent is loaded with impurities, and at that time the feed gas flow is switched to another adsorber. The loaded adsorber is then regenerated by desorbing impurities by *swinging* the adsorber pressure from the feed pressure to the tail gas pressure. The remaining adsorbed components are removed by flushing with high-pressure, high-purity gas. The purge exhaust is referred to as the tail gas, and is vented from the system. There are no significant changes in temperature, except for those caused by the heats of adsorption and desorption. As shown in Appendix A/Viewgraph 11, multiple adsorber beds are operated on a cyclic basis to provide constant feed, product, and tail gas flows. Automatic control devices time the changeover of the beds so that contaminant components of the feed stream never emerge from the on-stream bed and sufficient regeneration of the off-stream adsorbent bed is accomplished.

## Figure 3-3

## Simplified PSA Process



Source: SFA Pacific, Inc.

## Table 3-4

## Relative Strength of Adsorption of Typical Gas Stream Components

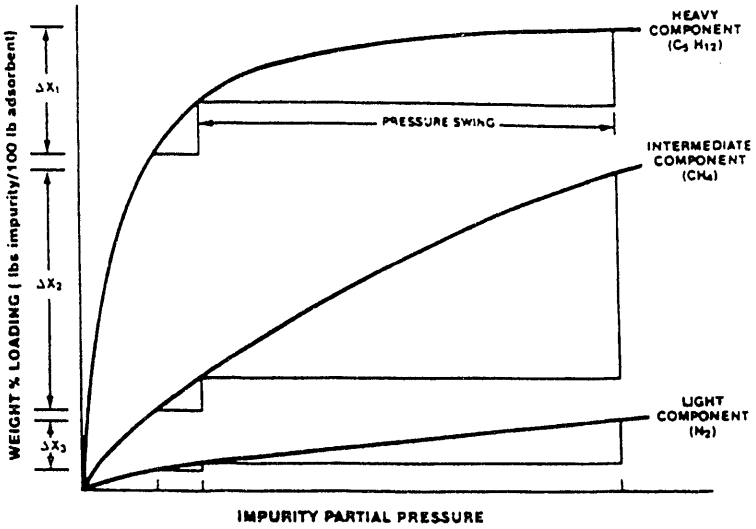
| Non-Adsorbed | Light | Intermediate | Heavy |
|---|---|---|---|
| $H_2$ | $O_2$ | CO | $C_3H_6$ |
| He | $N_2$ | $CH_4$ | $C_4H_{10}$ |
|  | Ar | $C_2H_6$ | $C_5+$ |
|  |  | $CO_2$ | $H_2S$ |
|  |  | $C_3H_8$ | $NH_3$ |
|  |  | $C_2H_4$ | BTX |
|  |  |  | $H_2O$ |

Source: Reference 6

The driving force for PSA separation is the partial pressure difference between the feed stream and the tail gas. This is illustrated by the adsorption isotherms shown in Figure 3-4. The absolute pressures of the feed stream and tail gas are also important, particularly for recovery of hydrogen. The optimum feed pressure range for PSA units in refinery applications is 200 to 500 psig. The optimum tail gas pressure is as low as possible, typically between 2 and 5 psig, and as high as 65 to 75 psig. Two psig is appropriate when the tail gas is to be compressed, and 5 psig is appropriate when the tail gas is sent directly to fuel burners. As indicated in Figure 3-5, PSA process performance is much more sensitive to tail gas pressure than feed gas pressure.

**Figure 3-4**

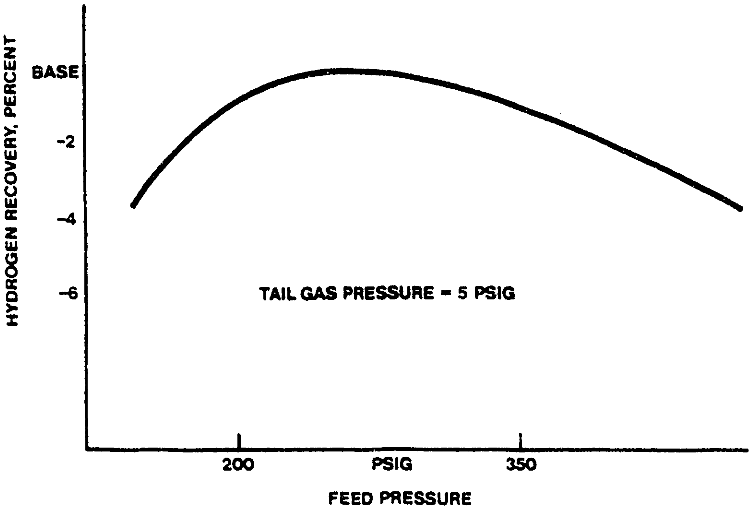
**PSA Adsorption Isotherms**

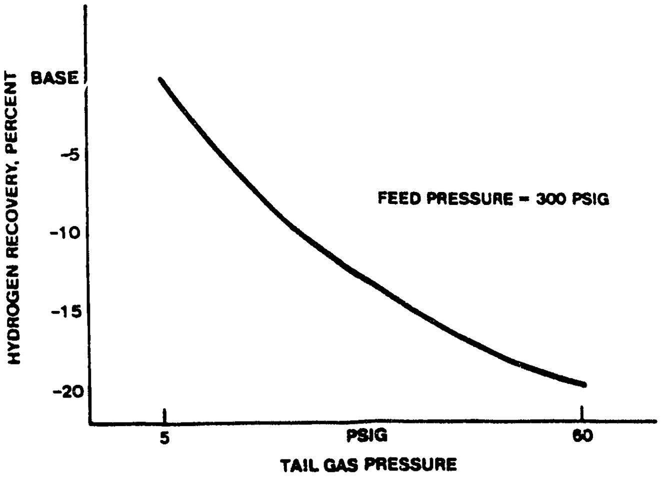


Source: Reference 6

## Figure 3-5

## Effect of Pressure Levels on PSA System Recovery





Source: Reference 6

### *PSA System Design*

PSA systems consists of two or more pressure vessels containing the appropriate adsorbent (adsorbent beds) with interconnecting piping and valving, and automatic control devices. The adsorbents possess high surface area, and are from organic and inorganic groups. Organic adsorbents include active carbon and carbon molecular sieves, and inorganic adsorbents include silica gel and zeolites. The particular adsorbent is selected on the basis of the requirements of the gas separation.

Since the PSA process is cyclic, and each cycle requires a discrete amount of time, PSA systems commonly consist of multiple beds (5 to 10). In general, the more beds in the system, the higher the recovery available due to more equalization steps between beds and the smoother the flow of product gas. The number of beds in a PSA system is subject to the following limitations:

- A greater number of vessels results in increased investment costs
- The minimum number of vessels is limited by the maximum size that can be manufactured
- Available pressure
- Greater feed quantities require a greater number of vessels

The three critical considerations in the design of a PSA system are the adsorbent bed pressure gradient, the bed volume, and the regeneration purge. A minimum pressure ratio of about 4:1 between feed stream and tail gas pressures is usually required, particularly for hydrogen separations. A characteristic of the pressure swing cycles is a loss of recovery caused by blowdown, and purging losses depending on the pressure differential between feed and tail gas and the cycling rate. Purging losses are a function of, and approximate, the ratio of the tail gas pressure to the feed pressure.

### *Performance Criterion for PSA*

The overall efficiency of the system is measured in terms of the following characteristics:

- Desired product gas recovery and purity--product recoveries of 80 to 92% are typically achieved with product purities of 99 to 99.99+%.
- Feed stream concentration of desired component--for $H_2$ recovery the optimum feed composition is in the range of 60 to 90 vol%. Feed stream impurities also impact system efficiency.
- Feed stream pressure--optimum for moderate pressures in the range of 200 to 600 psig. PSA process performance is much more sensitive to tail gas pressure than feed gas pressure.
- Tail gas pressure--optimum tail gas pressure is as low as possible. This sets the minimum pressure for the regeneration step and can have the most influence on the efficiency of the system. As shown in Figure 3-5, $H_2$ recovery increases as tail gas pressure decreases.
- Ratio of feed stream to tail gas pressure--a minimum ratio of 4:1 is generally required for economic operation, ratios above 7 are preferred.
- Quantity of gas processed--optimum for moderate rates in the range of 10 to 80 MMscf/d.
- Temperature--optimum range is 80 to 100°F.
- PSA systems are also evaluated in terms of the operating power requirement, the system size, reliability of components, and life of the adsorbent.

PSA units are often built as complete skid-mounted packages containing the adsorbent vessels, valve racks, and controls completely assembled and piped together. The adsorbers and piping are typically carbon steel. Operation of PSA units are completely automatic and unattended. Other than small quantities of instrument air and power, no utilities are required. The automatic valves are the only moving parts of the system.

The feed to PSA units must be fully characterized since some minor constituents can have effects disproportionate to their concentrations. High boiling components are strongly adsorbed and will require more purge gas to regenerate the bed, reducing recovery. It may be necessary to remove the high boiling point components via condensation and adsorption in a carbon bed. Since liquid carryover can also damage the adsorbents, a good phase separator should be installed upstream of the unit. Any oxygen in the feed stream should be removed prior to the PSA system to eliminate the possibility of concentrating it to the point where a flammable mixture exists.

PSA systems have recently become popular for hydrogen purification for two reasons: the development of reliable flow-control valves, and the use of microcomputers to control the actuation sequence of the flow-control valves. PSA systems are very advantageous for producing very high purity hydrogen (99.9+%) with the ability to remove impurities to any level (e.g., ppmv levels if desired). Feed stream impurities such as $CO_2$, $CH_4$, and $C_2$ to $C_5$ aliphatic hydrocarbons are the easiest to adsorb, $N_2$ and CO are more difficult. Removal of troublesome impurities such as CO and $CO_2$ down to levels such as 0.1 to 10 ppmv is common. The tail gas is almost always used as fuel, and economics of PSA technology strongly depend on the ability to use the tail gas at low pressure. PSA systems also have a low energy investment. Refining industry application of PSA systems are presented in Section 4.

The major limitation of PSA technology centers on the characteristics of the adsorbents themselves. Heavy molecules may be strongly adsorbed and, possibly, form coke -- deactivating the adsorbent. Some undesirable side reactions may also occur. For example in natural gas sweetening some sieves promote the formation of COS from $CO_2$ and $H_2S$, which is not as easily removed as $H_2S$. Like organic membranes, PSA systems are not suited for by-product hydrocarbon recovery. However, PSA systems may be coupled with other separation technologies when by-product recovery is required.

## Cryogenic Separation

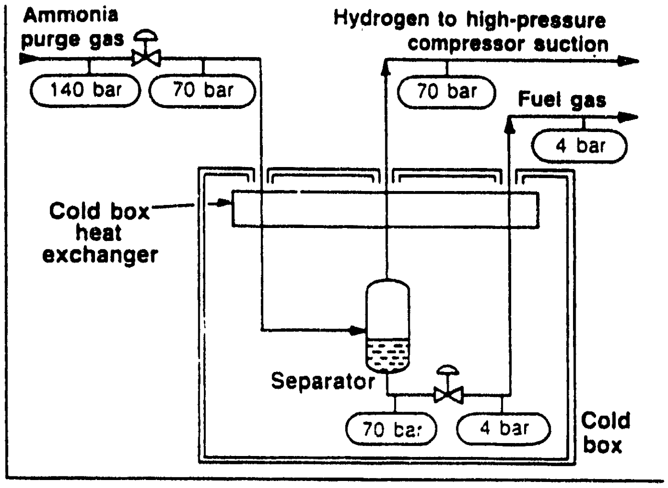
Cryogenic separation is well-established in the chemical processing and petroleum refining industries for recovering valuable components from natural gas streams, upgrading the heat content of fuel gas, air separation, purifying various process and waste streams, and producing ethylene.

### *Separation by Relative Volatility Difference at Low Temperatures*

Separation via cryogenics relies on the phase separation of stream components due to large differences in relative volatilities at extremely low temperatures. A simplified diagram illustrating separation via cryogenics is shown in Figure 3-6. The lighter gas component is recovered by cooling and partially condensing the feed stream. The lighter component remains in vapor form and is recovered at essentially feed pressure. The heavier gas component is separated out in liquid form and is expanded from high pressure to low pressure. The driving force for the separation is the temperature drop due to the Joule-Thomson effect when the condensed liquid is reduced in pressure. This provides the refrigeration for partial condensation of the feed stream.

**Figure 3-6**

**Simplified Cryogenic Processing Unit**



Source: Reference 7

### *Cryogenic Separator System Design*

Separation via cryogenics is based on the well-known chemical engineering principles of heat exchange, rotating machinery, separation, and distillation, the differences being that the temperatures are very low, and efficiencies are very high. The feed stream is cooled to about -200 to -250°F at 200 to 500 psig, which results in gas and liquid phase formation. The major equipment used in cryogenic separator systems are phase separators (or fractionators), aluminum plate-fin heat exchangers, and pressure expanders. Design of these systems requires very accurate thermodynamic correlations for the properties of the stream components, which affects the size of the equipment used. A small change in the relative volatility prediction can affect the size of the phase separator significantly. Overall process efficiency can be extremely high, with very close temperature differences achievable in the range of about 2 to 3°C.

Aluminum plate-fin exchangers take advantage of metal conduction to transfer heat to non adjacent streams (indirect heat exchange), thus remaining efficient on a multi-stream duty. These exchangers can process six or seven streams in a single block, thus making them ideal for multi-product or multi-feed plants.

Several process configurations are possible, with varying degrees of complexity. Cryogenic separator systems often consist of two stages of cooling and partial condensation. Sometimes three stages are used if higher product purity is required. In hydrogen recovery, the primary and secondary stages of cooling and condensation are used to remove the heavier constituents from the hydrogen-rich gas mixture, thereby attaining the correct hydrogen purity.

Cryogenic separation can only be used in systems that are acid-gas-free. Typically, the concentration of $CO_2$ must be less than 20 ppm to prevent plugging problems caused by $CO_2$ freezing. Pretreatment of the feed stream is very critical in the steady operation of the cryogenic systems. Typical trace contaminants, such as water, high-boiling hydrocarbons, $CO_2$, $H_2S$, are routinely removed using either molecular sieve adsorption or strong amine washing to prevent heat exchanger plugging. A special removal step is also required if mercury is present since mercury has been found to corrode aluminum heat exchangers in the presence of moisture. Mercury is usually removed by using sulfur impregnated adsorbents.

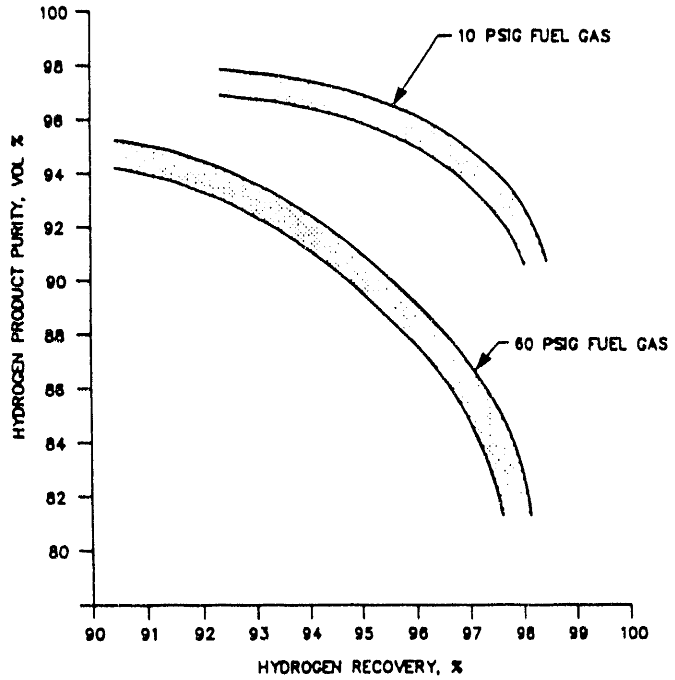
In some cases, a turbo-expander compressor is incorporated in the cryogenic separator system design for additional refrigeration (as shown in Appendix A/Viewgraph 13). These turbo-expanders are basically of a similar design to centrifugal compressors with lubrication and seal gas systems. The compressor (or brake) is attached by a fixed shaft to the expander rotor; thus, while one is expanding process gas through the expander wheel, the compressor or brake can compress another process stream (or the same process stream at different conditions). The shaft runs on oil lubricated bearings with a process seal gas preventing contact between cold process gas and warm oil, thus avoiding contamination and freezing, respectively. These items currently achieve expansion efficiencies of up to 86% for moderate to large machines, hence producing large amount of refrigeration for the process.

### *Performance Criterion for Cryogenic Separation*

Cryogenic separator systems are suitable for bulk quantity production of industrial gas and are most appropriate for relatively large feed streams, greater than 50 MMscf/d. This technology is most advantageous when recovery of multiple streams in high purity is desired. A product of 98.5 vol% purity is typically achieved. Hydrogen recovery versus purity for cryogenic systems is illustrated in Figure 3-7. The penalty on recovery for increased $H_2$ purity is less dramatic than for organic membrane systems.

**Figure 3-7**

**Hydrogen Recovery vs. Purity for Cryogenic Systems**



Source: Reference 6

Overall, cryogenic separation technology is more efficient than organic membrane and PSA systems, and like PSA, generates the product at feed pressure. The technology is desirable for upgrading streams which contain low feed concentrations of hydrogen (< 50 vol%). The system possess good economies of scale and is compatible with other systems.

Weaknesses of cryogenic separator technology include both high capital investment and capital costs, and pretreatment requirements. Presence of high value by-products are needed to justify use of cryogenic technology. The high refrigeration costs add to utilities, but this can be offset by absence of recompression cost.

Cryogenic separator systems are available from several process vendors, including Air Products and Chemicals, KTI, Linde AG, and UOP. It is not felt that inorganic membrane technology will compete directly with these systems. Rather, inorganic membrane systems are best suited for use in hybrid systems in conjunction with cryogenic separation systems.

## Liquid Scrubbing

Liquid scrubbing is generally used for bulk removal of acid gases employing various solvents, whereas organic membranes, PSA, and cryogenic separation systems are used for stream enrichment. Liquid scrubbing can be categorized into three types, based on the solvent used--chemical solvents, physical solvents, and hybrid solvents (physical and chemical). In liquid scrubbing with chemical solvents, the removal of acid gases is dependant upon chemical reaction with the solvent, while in liquid scrubbing with physical solvents, the removal is dependant on the physical solubility of the acid gas in the solvent. Inorganic membrane technology is not viewed as a replacement for this technology, but rather will best be suited for use in hybrid applications allowing more flexibility in the selection of appropriate liquid scrubbing technology.

### *Chemical Solvents*

There are basically two types of chemical solvent systems--one based on amine solvents, and one based on potassium carbonates. These systems find wide application in all types of gas processing. In a typical aqueous amine process, the solvent contacts the gas in a packed or trayed absorption tower, as shown in Appendix A/Viewgraph 16. The loaded solvent is then regenerated in an amine stripper, from which the lean solvent returns to the absorber. The rich solvent is preheated with the lean solvent by heat exchange between the absorber and the stripper. The lean solvent from the heat exchanger is then cooled before entering the absorption tower. Solvent degradation products are usually rejected through a batch-type solvent reclaimer [8].

Amines which are being used include the following: monoethanol amine (MEA), diethanol amine (DEA), diisopropanol amine (DIPA), and methyl diethanol amine (MDEA). These amines are being used for cleanup of natural gas and synthesis gas, with MEA and DEA being used most frequently. However, DIPA and MDEA have been supplanting MEA and DEA in some applications.

The hot potassium carbonate process *(Hot Pot)* is shown in Appendix A/Viewgraph 17. The *Hot Pot* name derives from the fact that it operates at approximately 200°F. This high-temperature operation allows the solvent to be stripped with less heat than conventional amine systems and eliminates the need for a rich/lean solvent heat exchanger. The principal application of this process has been for $CO_2$ removal at high partial pressures with little or no $H_2S$. The most frequent application of the process has been in treating gases from steam reforming in the manufacture of hydrogen and ammonia. It has generally not been competitive with amine systems for removal of significant amounts of $H_2S$.

### *Physical Solvents*

Physical solvents are best used at high acid gas partial pressures. The carrying capacity of the physical solvent is higher at higher pressures and lower temperatures, thus these solvents are often prechilled to attain the desired acid gas removal, which requires a refrigeration system. Physical solvents are usually easy to regenerate, which is often accomplished with just flashing and minor temperature increase. Their ease of regeneration, combined with their low absorption heat, often result in low overall process heat requirements.

Physical solvents that show substantially higher solubility for $H_2S$ than $CO_2$ can be used for selective removal of $H_2S$. These include dimethyl ether of polyethylene glycol--the Selexol process solvent, N-methyl-2-pyrolidone (NMP)--the Purisol process solvent, and methanol--the Rectisol process solvent. Several plants have been constructed which incorporate these systems.

### *Hybrid Solvents*

A number of processes use a mixture of chemical and physical solvents to combine the characteristics of both. Perhaps the best known and most widely used of this genre is the Shell Sulfinol process. This process uses DIPA or MDEA in a mixture with sulfolane and water. The respective names of the processes are Sulfinol-D and Sulfinol-M, depending on whether the former or the latter amine is used in the mixture. There are numerous Sulfinol process commercial installations that treat both natural gas and synthesis gas.

### Distillation

The process of distillation is probably better developed technically than any other major separation process. Distillation technology is used to recover valuable components such as $C_3$-$C_6$ components from the various gas streams generated by such refinery process units as crude distillation, cokers, catalytic crackers, reformers, and hydrocrackers. This technology is primarily for big gas recovery units for bulk separation. As with liquid scrubbing, inorganic membrane technology will best be used in hybrid applications to allow more flexibility in optimizing the distillation technology selection.

Separation via distillation is based on the differences in relative volatilities of feed stream components. Heating and condensation are use to separate fractions. The fractionation occurs in a series of distillation columns, which are either packed or trayed columns. A sample distillation process is shown in appendix A/Viewgraph 19. Distillation requires high capital investment and generally takes up large portions of space.

Distillation technology is extremely energy intensive, since it involves supplying the latent heat of vaporization to much, if not all of the feed, and in most cases much more than the latent heat. Estimates place the yearly energy usage by distillation in the United States at about two quadrillion Btu in 1976, or about three percent of the national energy usage in that year [9]. As such, distillation required more energy than that used by the entire commercial aviation industry in the same year [9]. It has also been shown that the actual energy consumptions for even well-run distillation processes are many times--typically 10 to 100 times or more--the values for the minimum work of separation.

Both the capital and utility operating costs rise as the relative volatility decreases. The important point is that the increase in both costs become quite precipitous below a relative volatility of about 2 and especially below about 1.5 [9]. In scaling down to smaller sizes distillation can sometimes lose its economic edge to other processes. A major cause of this situation is that investment drops less than proportionally to a capacity decrease. The smaller a distillation column is for a given separation, the more capital-intensive it will be per unit of throughput.

System design for distillation systems is affected by the following constraints: reflux ratio, feed rate, feed composition, distillate composition, bottoms composition, and operating pressure. Distillation is not appropriate under the following circumstances:

- The need for ultra-high purity
- The lack of necessity for high recovery of the desired product
- The ability to use the high pressure of a gas feed to supply all of the energy for the separation

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# SECTION 4

# APPLICATION OF SEPARATION TECHNOLOGIES IN THE REFINING INDUSTRY

# Section 4

# Application of Separation Technologies in the Refining Industry

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## Introduction

This section identifies current commercial uses, strengths, weaknesses, and research and development (R&D) trends associated with organic membrane and pressure swing adsorption technologies in the refining industry. This information is based on SFA Pacific's extensive review of separation literature and discussions with technology experts, vendors, and users. Discussion of these applications was presented at the Mid-Course Review Meeting, on September 1, 1992. Copies of viewgraphs from that presentation are presented in Appendix C-1. Supplemental information is presented below.

## Selection of Separation Technology is Case Specific

As discussed in Section 3, there are several separation technologies at the disposal of the refining industry. Application of the appropriate technology is based on many factors, including stream phase, size, composition, temperature, pressure, ultimate destination, etc. Separation options are examined relative to specific refining circumstances. In many cases refiners are apt to continue use of separation technologies in which they have previous operating experience. Refiners are very conservative with regard to technology change. However, they are willing to use newer technologies if economic justification and system operation are easily demonstrated.

Many engineering and construction (E&C) companies are now getting involved in projects earlier by assuming some of the process, engineering, and planning responsibilities traditionally conducted by the refiner. This early involvement is necessary because most refining companies have downsized their process and engineering staffs in recent years. In many cases, E&C

companies participate in selection of the separation technology, as well as the specific vendor of that selected technology. A list of major E&C companies servicing the refining industry is shown in Table 4-1.

## Organic Membranes are Gaining Acceptance

The concept of separating gases with polymeric membranes is more than 100 years old [1]. Processes using membranes for separating hydrogen from hydrogenation tail gas, enrichment of refinery gas, air separation, and helium recovery from natural gas were considered as early as 1950 [2]. However, the widespread use of organic membranes for gas separation has occurred only recently within the last 10 to 15 years.

The use of Monsanto's PRISM technology for adjustment of $H_2$/CO ratio in 1977 and recovery of hydrogen from chemical plant purge gases in 1978 were the first commercial applications of polymeric organic membranes for gas separation. Since then, organic membrane systems have experienced significant material and performance improvements which have led to commercialization of systems for numerous gas-mixture separations. These advances, combined with increased competition in the separation industry, have greatly improved the price/ performance of organic membrane processes.

Since Monsanto's first application of organic membranes for industrial gas separation, the number of suppliers and applications of these systems has greatly increased. A list of commercial organic membrane system suppliers is shown in Table 4-2. Several of the suppliers are joint ventures between chemical process industry (CPI) and industrial gas companies. CPI companies typically contribute expertise in polymer technology and membrane fabrication, while gas companies contribute knowledge of customer needs and have established customer networks. Two such joint ventures include Generon Systems--a joint venture of Airco Industrial Gases (a subsidiary of the British Oxygen Company (BOC) Group) and Dow Chemical, and MEDAL Membrane Systems--a limited partnership joint venture between Du Pont and members of the L'Air Liquide Group.

## Table 4-1

## Major E&C Companies Serving the Refining Industry

**ABB Lummus Crest, Inc.**
1515 Broad Street
Bloomfield, NJ 07003
Tel: 201-893-1515
Fax: 201-893-2000

**The Badger Co., Inc.**
One Broadway
Cambridge, MA 02142
Tel: 617-494-7713
Fax: 617-494-7258

**Bechtel Corp.**
50 Beale Street
San Francisco, CA 94105
Tel: 415-768-1234
Fax: 415-768-9038

**John Brown E & C Inc.**
7909 Parkwood Circle Drive
Houston, TX 77036
Tel: 713-988-2002
Fax: 713-772-4673

**Brown & Root Braun**
4100 Clinton Drive
Houston, TX 77020-6299
Tel: 713-676-3632
Fax: 713-676-3769

**Fluor Daniel, Inc.**
3333 Michaelson Drive
Irvine, CA 92730
Tel: 714-975-5000
Fax: 714-975-5981

**Foster Wheeler Corp.**
Perryville Corporate Park
Clinton, NJ 08809-4000
Tel: 908-730-4000
Fax: 908-730-5315

**Howe-Baker Engineers, Inc.**
3102 E. Fifth Street
P.O. Box 956
Tyler, TX 75750
Tel: 903-597-0311

**Jacobs Engineering Group, Inc.**
251 South Lake Avenue
Pasadena, CA 91101-3063
Tel: 818-449-2171
Fax: 818-578-6916

**The M.W. Kellogg Co.**
601 Jefferson Avenue
Houston, TX 77210-4557
Tel: 713-753-2000
Fax: 713-753-5353

**Kinetics Technology International Corp. (KTI)**
650 Cienega Avenue
San Dimas, CA 91773
Tel: 714-592-4455
Fax: 714-592-3399

**Litwin Engineers & Constructors, Inc.**
1250 W. Sam Houston Pkwy. So.
Houston, TX 77042
Tel: 713-268-8200
Fax: 713-268-7469

**The Ralph M. Parsons Co.**
100 West Walnut Street
Pasadena, CA 91124
Tel: 818-440-2000
Fax: 818-440-2630

**Stone & Webster Engineering Corp.**
330 Barker Cypress Road
Houston, TX 77253
Tel: 713-492-4000
Fax: 713-492-4001

Source: Chemical Engineering

## Table 4-2

## Commercial Organic Membrane Suppliers

| Company | $CO_2$ | $H_2$ | Air<br>$O_2$ | <br>$N_2$ | Other[1] |
|---|---|---|---|---|---|
| A/G Technology (AVIR) | X | | X | X | |
| Air Products (PRISM) | X | X | X | X | X |
| Asahi Glass (HISEP) | | | X | X | |
| Cynara (Dow) | X | | | | |
| Dow (Generon) | | | X | X | |
| DuPont/L'Air Liquide (MEDAL) | | X | | X | |
| Grace Membrane Systems | X | X | | | X |
| Hoechst Celanese (Separex) | X | X | | | X |
| International Permeation | X | | | | X |
| Membrane Technology & Research | | | | | X |
| Nippon Kokan K.K. | | | | | X |
| Osaka Gas | | | X | | |
| Oxygen Enrichment Co. | | | X | | |
| Perma Pure | | | | | X |
| Techmashexport (USSR) | | | X | | |
| Teijin Ltd. | | | X | | |
| Toyobo | | | X | | |
| UBE Industries | | X | X | X | X |
| Union Carbide (Linde) | X | X | X | | |
| UOP/Union Carbide | X | | | | |

---

(1) Includes solvent vapor recovery, dehumidification and/or helium recovery membranes.

Source: Adapted and updated from Reference 3

Ownership of organic membrane technology has also changed. The PRISM technology (owned by Permea Inc.) was acquired by Air Products in 1991 from Monsanto. This technology is also licensed by UOP. The Separex technology (Separex was originally an independent company, then became a part of Perry Gas, and then acquired by Air Products in 1986) was acquired by Hoechst Celanese in 1990 from Air Products.

The differences among system vendors are basically the membrane material used depending on separation application and the system configuration chosen (i.e., hollow fiber or spiral wound technology). System suppliers do not necessarily disclose the membrane material used in their units. However, it is known that the PRISM hollow fiber systems use polysulfone (coated with a layer of siloxane), Grace and Separex spiral wound systems use cellulose acetate, MEDAL hollow fiber systems use polyaramide, and UBE hollow fiber systems use polyimide. Generon hollow fiber systems are believed to be based on poly(4-methyl 1-pentene) [4].

### *The Market for Organic Membranes in Gas Separations is Increasing*

The current market for all commercial membranes systems is about $750 million in the United States, and $691 million in Europe (market information for Japan is not available) [5,6]. Estimated growth rates range from 5 to 10% per year. It is anticipated that gas separation applications will be one of the major growth areas. Membrane systems for gas separation applications in the U.S. are projected to grow annually from $45 million/year in 1990 to $278 million/year by 2000 [7]. Growth in membrane technology applications is attributed to the development of third and fourth generation membranes and hybrid systems which are acquiring increasing portions of PSA and cryogenic technologies market share [8].

The United States is a world leader in supply of and research on membrane-based gas separation systems. However, this dominant position is beginning to erode due to the increased activity by European and Japanese companies, governments, and institutions. Increased R&D activity on membrane-based gas separation will increase the probability that the next generation technology for high-performance, ultrathin membranes will be controlled by the United States [9]. This will make membrane-based gas separation even more competitive with other separation technologies over a broader spectrum of applications. The justification for use of organic membrane technology must be frequently updated to include new developments that improve economics in comparison with other separation technologies. However, membranes do not neatly replace other processes in many situations, requiring other process changes that directly impact the cost of the separation.

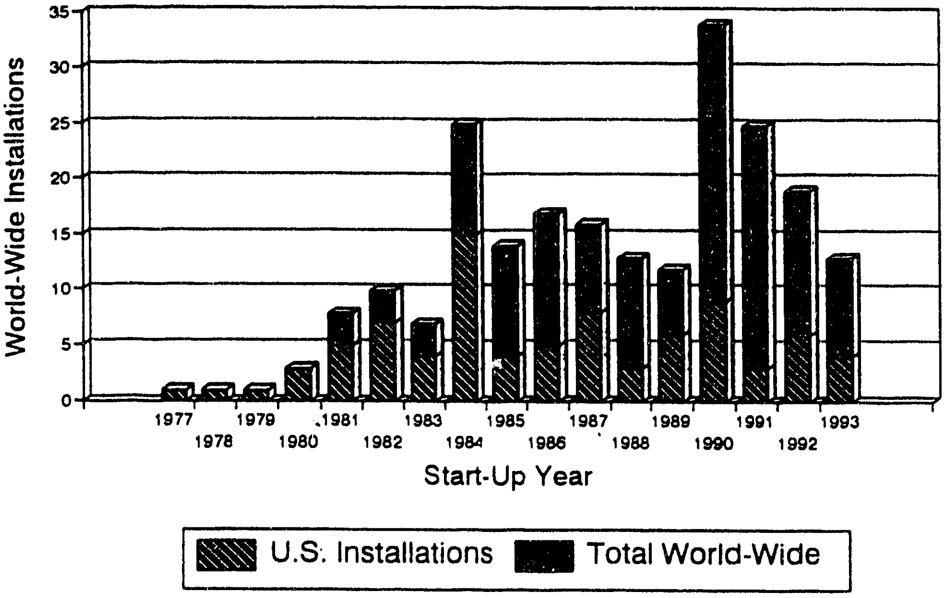
### *Refining Industry Experience with Organic Membranes*

Organic membranes are now commonly used in areas of gas processing such as hydrogen recovery and purification, helium recovery, acid gas removal (primarily $CO_2$ separation from hydrocarbons either for natural gas purification or reinjection in enhanced oil recovery (EOR) operations), inert gas generation, and air separation.

The distribution of organic membrane installations for the period 1977 to 1993 is shown in Figure 4-1. These units represent installations that are in the engineering and planning stages, as well as those currently in operation based on information supplied by technology vendors. Organic membrane vendors contacted by SFA Pacific are listed in Table 4-3. Of the total of 219 worldwide installations of organic membrane units in refining applications, 85 systems are installed in the United States. As indicated in Table 4-4, the bulk of organic membrane systems installed are PRISM units.

**Figure 4-1**

**Organic Membrane Installations**
**(219 Installations Worldwide)**



Source: SFA Pacific, Inc.

## Table 4-3

## Separation Technology Vendor Contacts

Generon Membrane Systems
R. Fleischman
Generon Systems
515 West Greens Road, Suite 100
Houston, TX 77067
Tel: 713-873-5100
Fax: 713-876-4255

Grace Membrane Systems
T. E. Cooley
W.R. Grace & Co.
7125 W. Tidwell Road, Suite L-104
Houston, TX 77092
Tel: 713-690-4488
Fax: 713-690-3082

MEDAL Membrane Systems
G.E. Dupuis
Liquid Air Engineering Corporation
2121 N. California Blvd., Suite 350
Walnut Creek, CA 94596
Tel: 510-746-6381
Fax: 510-977-6590

PRISM Separators
P. O'Brien
Permea Inc.
11444 Lackland Road
St. Louis, MO 63146
Tel: 314-995-3499
Fax: 314-995-3500

Separex Membrane Systems
J.J. Vari
Hoechst Celanese Corporation
13800 South Lakes Drive
Charlotte, NC 28273
Tel: 704-587-8558
Fax: 704-587-8600

UBE Membrane Systems
K.S. McGinn
UBE Industries (America), Inc.
16001 Park Ten Place, Suite 430
Houston, TX 77218
Tel: 713-492-8333
Fax: 713-492-2180

UOP Advanced Membrane Systems & Polybed PSA
R.J. Fumose
UOP
13105 N.W. Freeway, Suite 600
Houston, TX 77040
Tel: 713-744-2871
Fax: 713-744-2880

Source: SFA Pacific, Inc.

## Table 4-4

## Vendor Break-Down of Organic Membrane Installations

| Vendor | Installations | Percent of Total |
|---|---|---|
| Grace Membrane Systems | 1 | 0.5 |
| MEDAL | 26 | 11.9 |
| PRISM | 137 | 62.6 |
| Separex | 22 | 10.0 |
| UBE | 22 | 10.0 |
| UOP | 11 | 5.0 |
| Total | 219 | 100 |

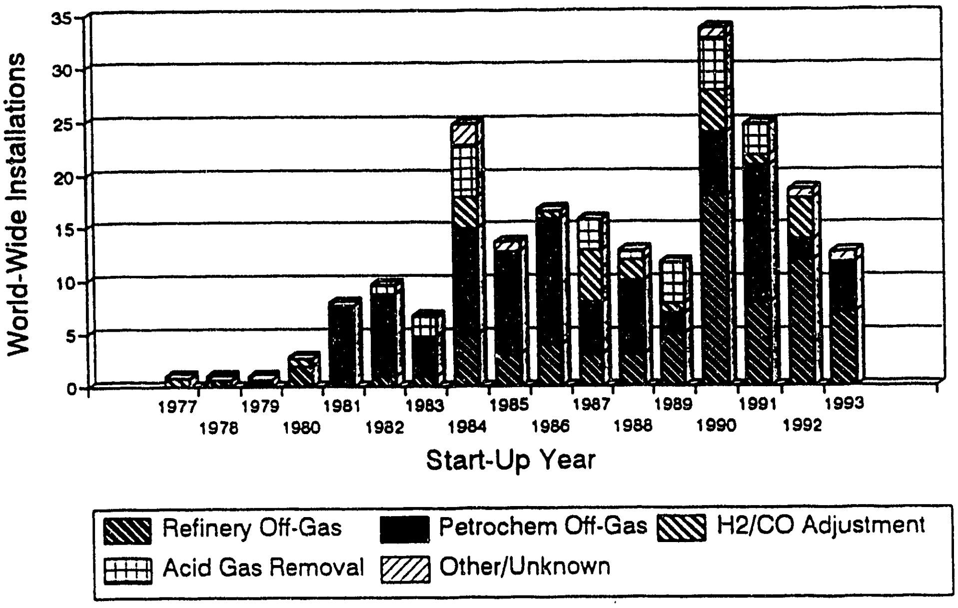
Source: SFA Pacific, Inc.

The distribution of organic membrane installations by application is shown in Figure 4-2. These units process streams in the following refining/petrochemical applications:

- Refinery off-gases: hydrotreater, hydrocracker, catalytic reformer purge, and refinery vent gases; primarily $H_2$ recovery from light hydrocarbon streams.
- Petrochemical off-gases: ammonia purge, methanol purge, and other petrochemical plant streams; primarily $H_2$ recovery from $N_2$ and light hydrocarbon streams.
- $H_2$/CO ratio adjustment: separation of $H_2$ from synthesis gas.
- Acid gas removal: separation of $CO_2$ from light hydrocarbon streams, such as in EOR operations; does not include separation from bio- and landfill gas streams.
- Other/unknown: some type of refinery application, but stream identity is unclear; does not include air separation systems.

Figure 4-2

Organic Membrane Installations
(by application)



Source: SFA Pacific, Inc.

Refiners using organic membranes for gas separations are increasingly satisfied with the technology. Applications of organic membrane technology has been discussed at recent National Petroleum Refiners Association (NPRA) question and answer (Q&A) sessions [10,11]. Use of membranes to enhance hydrogen supply was one of the topics of discussion during the 1992 NPRA Q&A meeting.

Conoco's use of a MEDAL membrane since 1987 at their Ponca City, Oklahoma refinery is well documented in the literature [12]. A high purity $H_2$ stream (98% purity) from a 15 MMscf/d HDS purge stream (75% $H_2$) is generated, achieving a simple payback for the system in 1.7 years. Similarly, Exxon's operation of an UBE membrane unit in Japan since 1989 for recovery and purification of hydrogen from about 22 MMscf/d hydrorefiner offgas also demonstrates the effectiveness of these systems [13].

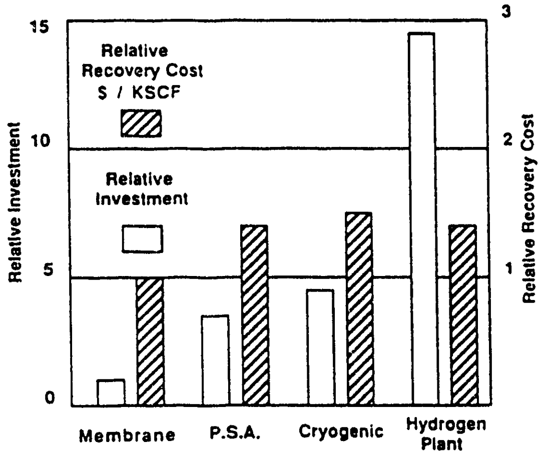
PRISM technology has been in use at ARCO's Los Angeles, California refinery since 1981 to aid in maintaining refinery hydrogen balance. In 1986, operation of a PRISM unit to recover hydrogen from a 22-28 MMscf/d high pressure HDS purge stream began. After several years of operation it was discovered that hydrogen recovery was low due to liquid carry-over damage to the membrane unit. This was caused by use of an under-sized knock-out pot ahead of the separator. ARCO also noted a problem associated with the automatic by-pass system activated during reduced capacity operation. The system automatically by-passed selected membrane modules when flow rate decreased, but required manual over-ride upon return to normal flow rates. The time delay between periods of low and high flows resulted in too much gas being processed through portions of the separation unit. This also damaged membrane material and decreased system efficiency. ARCO is now experiencing excellent operation of the PRISM unit since the membrane bundles have been replaced, the knock-out pot resized, and the valve control sequence reconfigured [14].

Economic justification for application of organic membrane technology is easily demonstrated. Relative investment and product recovery costs for membrane systems are compared to those for PSA, cryogenic, and hydrogen plant systems in Figure 4-3. Modularity, compact system size, and minimal required operator attention contribute to keeping operating and maintenance costs low for organic membrane technology in gas purification and recovery applications. Installation factors of 2 are commonly used for these systems.

Major drawbacks to organic membrane technology are system susceptibility to liquids and generation of the permeate at low pressure. Refiners and technology vendors reinforce the importance of using properly-sized knock-out pots, mist eliminators, and/or heaters ahead of actual membrane modules to removed liquids such as $H_2O$, $NH_3$, condensible hydrocarbons, and methanol. Such simple pre-treatment steps aid in extending membrane life. Use of the permeate at low pressure is desirable, otherwise this stream must be recompressed to high pressure. Recompression results in significant costs affecting economics for membrane systems.

## Figure 4-3

## Recovery Costs for Alternative Separation Technologies



Source: Reference 15

### *Improvements in Selection, Productivity, and Reliability*

Membrane technology is advancing at a pace faster than that for other separation technologies. The advancement to the next generation of organic membranes will focus on selectivity, productivity, and operational reliability [9]. R&D is concentrating on methods for making better, high-performance membranes, and dealing with membrane materials with improved selectivity and permeability. Membrane systems now on the market are based on polymers specifically designed and synthesized for their permeability properties, whereas in the past, the membrane systems were prepared from polymers developed for other purposes. Organic membranes face competition from breakthroughs in new materials, such as inorganic membranes, zeolites, and molecular sieve membranes, since most of the limitations of present gas separation technology arise from the polymeric membrane material. The new performance materials should also allow their use at higher temperatures (above 212°F), provided that potting materials are capable of high temperature operation are also developed.

Materials R&D continue with the goal of improving gas separation via organic membranes. In 96 membrane-related patents issued by the U.S. Patent Office in the period running from late June to mid-September, 1991, gas separation accounted for 26 patents (the largest single category), while reverse osmosis, ultra-filtration, and micro-filtration together accounted for 25, various types of membrane preparation systems accounted for 16, prevaporation accounted for 10, and the remaining categories accounted for a few apiece [8].

Patent activity in organic membranes for gas separations is being dominated by Air Products, who has been devoting a substantial effort to the development of better membrane materials for oxygen/nitrogen separation. Developers have also been investigating surface treatment to improve membrane properties which result in a more selective, but less permeable, polymer skin layer. This is exemplified by R&D at the University of California at Los Angeles where the use of polyaniline synthesized via a special doping technique yielding very selective polymeric membranes for gas separations are being investigated [16].

### Pressure Swing Adsorption is Routinely Used in the Refining Industry

The PSA process was developed by Union Carbide in the early 1960s. The first U.S. patent for a PSA process was issued to Skarstrom in 1960 [17]. Current commercial PSA technology is based on improvements and modifications to the original technology. A large variety of binary and multi-component gas mixtures are commercially being separated using PSA technology. These applications include gas drying, air separation, $CO_2/CH_4$ separation, alcohol dehydration, ozone enrichment, solvent vapor removal and recovery, and CO, $CO_2$, $H_2$, and ammonia production [18].

The growth in PSA has been aided by the introduction of a large spectrum of commercial adsorbents with different pore structures, surface polarities, and adsorption characteristics such as capacities, kinetics, selectivities, heats of adsorption, etc [19]. Total 1991 U.S. sales for PSA systems were $99 million, and sales are projected to increase to $123 million in 1996 and $155 million in 2001 [8]. UOP, a joint venture of Union Carbide and Allied-Signal Inc., market Polybed PSA systems, which is the dominant technology for refinery applications in the United

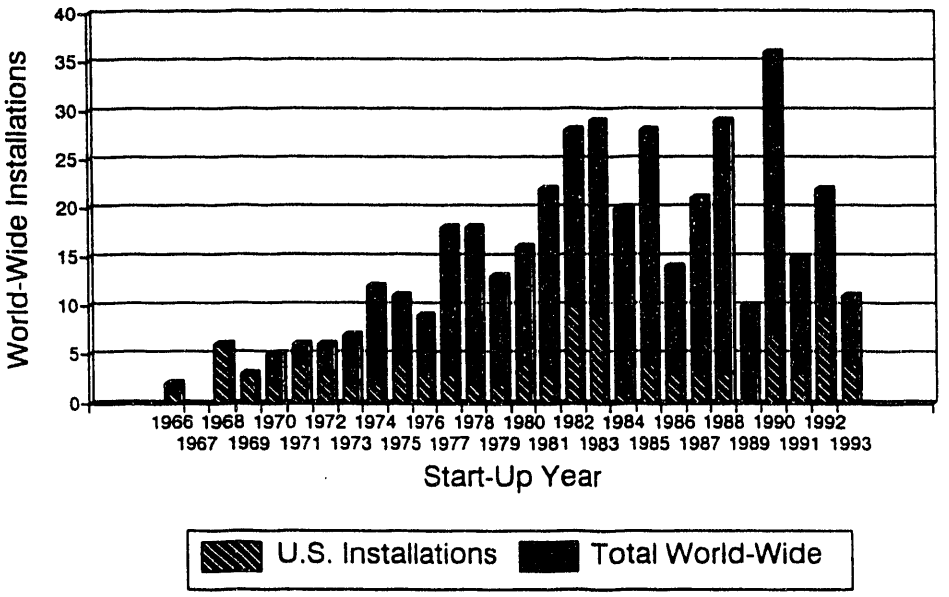
States. For air separation, other U.S. vendors such as Air Products (Gemini) and Dow (Generon) provide PSA technology. In Europe and Japan, UOP receives competition from several other vendors of PSA technology such as Linde AG, Mitsubishi Heavy Industries, Nippon Kokan K.K., and Toyo Engineering Corp.

### *Refining Experience with PSA*

The first commercial application of PSA technology in the refining/petrochemical industry was in Canada in 1966. Since that time, the number of installation has grown steadily. The distribution of UOP Polybed PSA installations for the period 1966 to 1993 is shown in Figure 4-4. This figure includes installations that are currently in operation as well as those that are in the engineering and planning stages based on information supplied by the vendor. The UOP PSA contact is indicated in Table 4-3. Of the total of 417 worldwide installations of PSA units in refining applications, 100 systems are installed in the United States.

**Figure 4-4**

**UOP Polybed PSA Installations**
**(417 Installations Worldwide)**



Source: SFA Pacific, Inc.

The distribution of UOP Polybed PSA installations by application is shown in Figure 4-5. These units process streams in the following refining/petrochemical applications:

- Refinery off-gases: hydrotreater, hydrocracker, catalytic reformer purge, hydrodealkylation, and refinery vent gases; primarily $H_2$ recovery from light hydrocarbon streams.

- Petrochemical off-gases: ethylene purge, ammonia purge, methanol purge, and other petrochemical plant streams; primarily $H_2$ recovery from $N_2$ and light hydrocarbon streams.

- $H_2$/CO ratio adjustment: separation of $H_2$ from synthesis gas.

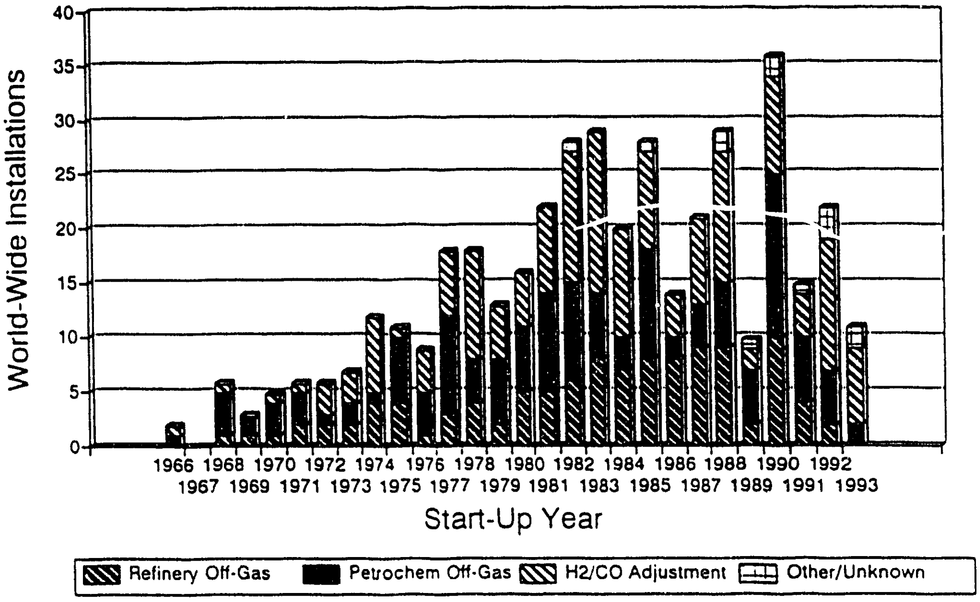
- Other/unknown: some type of refinery application, but stream identity is unclear; does not include air separation systems.

Refiners using PSA systems are increasingly satisfied with the technology. Application of PSA technology also has been discussed at recent NPRA Q&A sessions [10,11]. Use of PSA technology to enhance hydrogen supply, experience with valve failures, and adsorbent dust carryover in the residue gas were topics of discussion during the 1992 NPRA Q&A meeting.

Texaco has experience with changing adsorbents in PSA units operating for hydrogen recovery [11]. Unit beds are taken off-line, purged with nitrogen, then the adsorbent is vacuumed out. New adsorbent is reloaded under atmospheric conditions. Criterion for adsorbent change is poor hydrogen recovery and contamination of the adsorbent caused by amine, heavy hydrocarbon, and lube oil carryover to the unit.

**Figure 4-5**

**UOP Polybed PSA Installations**
**(by application)**



Source: SFA Pacific, Inc.

Like organic membranes, PSA technology is relatively easy to economically justify for hydrogen purification and recovery. A higher purity product is obtained at pressure equivalent to the feed, while the residue gas is produced at reduced pressure. The mechanical complexity of PSA systems caused apprehension about their use, since valve failures were common and more operator attention may have been required. However, this is no longer the case. Installation cost factors of 3 are commonly associated with these systems. The higher total capital investment result in higher capital, maintenance, and operating costs than membrane systems.

### *Improvements in System Configurations, Reliability, and Adsorbents*

The major technological improvements in PSA technology have focused on the economics of larger-scale operations and adsorbent performance. These improvements have lead to increased product purity and recovery, and decreased adsorbent inventory. PSA has become an accepted technology in steam methane reforming for synthesis gas ratio adjustment, as well as a low-cost system for production of enhanced nitrogen and oxygen streams from air.

Advances in PSA technology for the future include innovations in system configuration, reliability, and adsorbents. Complex PSA configurations are being investigated that may result in the possibility of recovering multiple, high-purity, high-pressure product streams [19]. Improvements in valve control will affect system reliability, and reduce user apprehensions about system failures. Design of PSA systems is improving as new adsorbents are being developed and a better understanding of multi-component gas-solid interactions (thermodynamic and kinetic) is being gained.

### References

1. W.S.W. Ho and K.K. Sirkar (Editors), *Membrane Handbook*, Van Nostrand Reinhold, 1992.
2. S. Weller and W.A. Steiner, "Engineering aspects of separation gases: fractional permeation through membranes," *Chemical Engineering Progress*, Volume 46, Number 11, 1950, pp 585-590.
3. R. Spillman, "Economics of Gas Separation Membranes," *Chemical Engineering Progress*, January 1989, pp 41-62.
4. J. Haggin, New Generation of Membranes Developed for Industrial Separations," *Chemical and Engineering News*, June 6, 1988, pp 7-16.
5. "Membranes Rise in Future For Europeans, *Chemical Marketing Reporter*, July 6, 1992.
6. "Demand for Membrane Separations Growing, *Chemical Marketing Reporter*, April 20, 1992.

7. T. Wett, "Technology Galore," *Chemical Marketing Reporter*, December 9, 1991.

8. North American Membrane Society, *Membrane Quarterly*, January/April 1992.

9. R.W. Baker, et al., "Membrane Separation Systems: A Research Needs Assessment," DOE Report ER/30133-H1, April 1990.

10. *1990 NPRA Q&A Session on Refining and Petrochemical Technology*, October 3-5, 1991.

11. *1991 NPRA Q&A Session on Refining and Petrochemical Technology*, October 16-18, 1991.

12. K.G. Shaver, G.L. Poffenbarger, and D.R. Grotewold, "Membranes recover hydrogen," *Hydrocarbon Process*, June 1991, pp 77-80.

13. Tonen Technology K.K. (Exxon Engineering Co.) and UBE Industries, "UBE Polyimide Membrane System for Hydrogen Recovery and Purification of Hydrorefiner Offgas," March 16, 1990.

14. SFA Pacific, Inc. site visit to ARCO Los Angeles Refinery, August 26, 1992.

15. J. Heyd, "Hydrogen recovery using membranes in refining applications," presented at NPRA Annual Meeting, Los Angeles, CA, March 1986.

16. M.R. Anderson, et al., "Conjugated Polymer Films for Gas Separations," *Science*, June 7, 1991, pp 1412-1415.

17. C.W. Skarstrom, U.S. Patent 2,944,627, 1960.

18. S. Sircar, "Pressure Swing Adsorption," presented at the NATO Advanced Study Institute on Adsorption Science & Technology, Vimerio, Portugal, July 17-29, 1988.

19. S. Sircar, "Recent Trends in Pressure Swing Adsorption," from proceedings of Symposium on Adsorptive Processes, Chung-Li, Taiwan, ROC, 1992, pp 47-54.

# SECTION 5

# INCENTIVES FOR INORGANIC MEMBRANES IN REFINING INDUSTRY

# Section 5

# Incentives For Inorganic Membranes In The Refining Industry

## Introduction

At the Kick-Off Meeting on June 23-24, 1992, SFA Pacific provided the technical rationale for selecting several key systems for initial testing with *advanced* inorganic membranes. Viewgraphs from the meeting are presented in Appendix A. The key systems identified include the following:

- Separation of $H_2$ from $CH_4$
- Enrichment of $H_2S$ in $H_2S/CO_2$ mixtures
- Sulfur and aromatic removal from kerosene and diesel fuels
- Separation of normal hexane from cyclohexane
- $O_2/N_2$ separation

These systems represent potential refinery applications of inorganic membrane technology which possess high pay-off, and transferability for which both technical and economic feasibility can be evaluated or demonstrated in the near-term. During the Kick-Off Meeting discussion, the following three additional applications were identified:

- Separation of benzene from water
- Catalytic membrane reactors
- Separation of catalyst fines from cat cracker bottoms

Subsequently, as requested by DOE personnel at the meeting, SFA Pacific expanded its technical rationale and recommended some general performance targets for consideration by DOE staff in development of the proposed experimental program. These performance targets are explored in detail Appendix B.

SFA Pacific has developed some quantitative incentives for use of inorganic membrane technology on key systems of interest to the refining industry, emphasizing down-stream petroleum processing. These incentives were presented at the Mid-Course Review Meeting, on September 1, 1992. Viewgraphs from this presentation are attached in Appendix C-2.

Major incentives for the following three systems are summarized in this section:

- $H_2/CH_4$
- $H_2S/CO_2$
- Sulfur/Aromatics from Diesel

The incentives can be applied to a wider range of applications once actual experimental data are available for analysis.

## Incentives Defined By Comparing Current Costs With Potential Improvements

Calculating incentives for process improvements has been compared to *quantifying wishful thinking*. The general approach is to first evaluate the current practice, or the base case. The second step is to assume some general performance of the inorganic membrane and see how it can be incorporated in the process to improve the performance and reduce the costs. The reduction in cost is called the *incentive*.

Since both the performance and cost of the *advanced* inorganic membranes is speculative at this point, SFA Pacific has tested a range of performance and identified the key economic factors which can be used to guide experimental testing.

It is important to be able to establish the *base case* accurately, in order to calculate a quantitative incentive. Such information is available on the three key systems evaluated below. For the other systems, such as benzene/water separation and catalytic membrane reactors, there is no frame basis for the base case or information whether the technical concept and performance is reliable.

## Hydrogen Separation From Methane Is An Excellent Application Of Inorganic Membrane Technology

The recovery of hydrogen from hydrocarbon gases is an important application in the refining industry today. Refiners generate large quantities of hydrogen for use in improving the quality of fuels or in improving feed quality for various processes. In using the hydrogen, light hydrocarbon gases are produced, which must be purged from the reaction system. As a result, the accompanying hydrogen generally amounts to 20% of the total hydrogen generated. In the past, these purge gases were used as refinery fuel. Today, with hydrogen in short supply, attention is turning to application of organic membrane and PSA systems to recover this hydrogen (as discussed in Section 3 and 4), rather than the more expensive step of manufacturing more hydrogen.

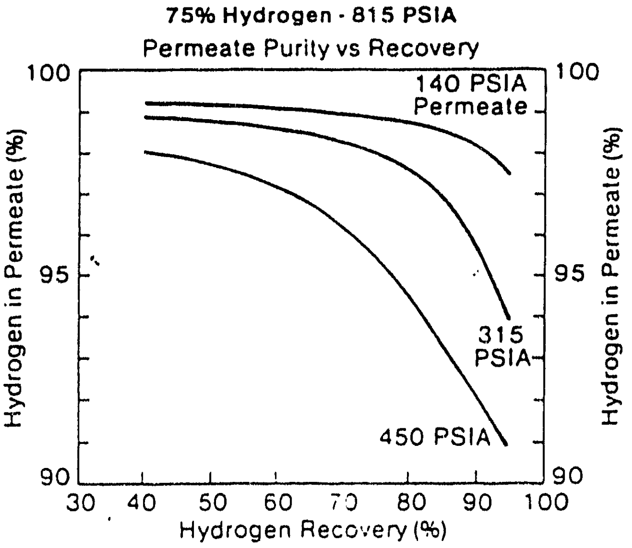
Currently the cost of manufacturing hydrogen from natural gas (valued at $2.50/MM Btu) is about $2.50/Mscf, equivalent to about $8.00/MM Btu [1]. Thus there is a major gap--or incentive--to recover hydrogen rather than burn it as fuel.

Currently, several companies market organic membrane systems used to recover hydrogen from refinery purge gases (typically 70-80% $H_2$) recovered from high pressure hydrotreaters at 700-800 psig. The recovery of $H_2$ and its purity are generally high, and are controlled by adjusting the low pressure on the permeate. An example of one unit is shown in Figure 5-1 [2].

Extremely good recoveries are obtained as the permeate pressure drops below about 500 psig. However, there is an economic debit for lowering pressure, since the hydrogen must be recompressed to 2,500-3,000 psig for use in the high pressure reactors. This cost can be high, as shown in Figure 5-2, derived from studies conducted for DOE [3,4]. Hydrogen compression cost details are given in Appendix C-2/Viewgraph 3, assuming a power cost of $0.05/kWh and a capital charge of 20% investment per year. The costs represent the cost of compressing

**Figure 5-1**

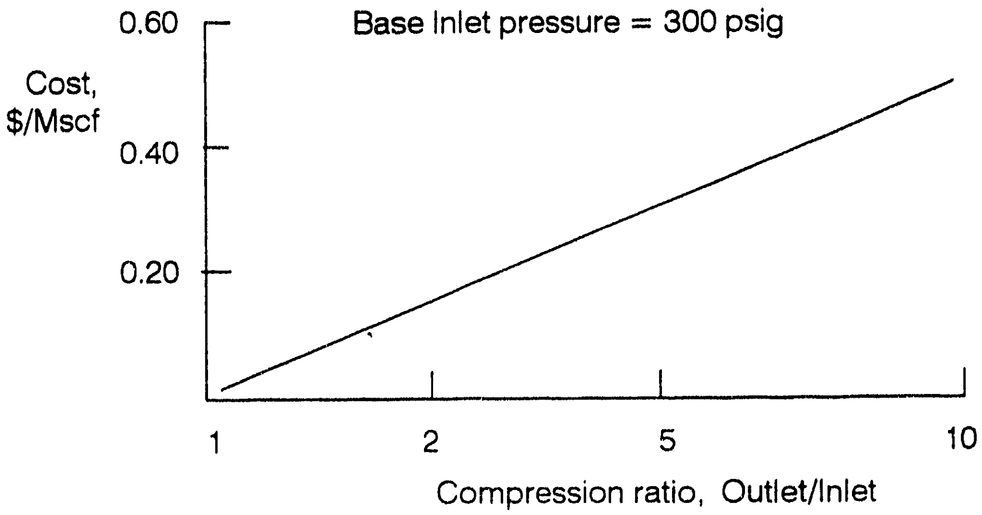
**Recovery of Hydrogen from Hydrotreater Purge Gases**



Source: Conoco

**Figure 5-2**

**Compression Costs Can Be High**



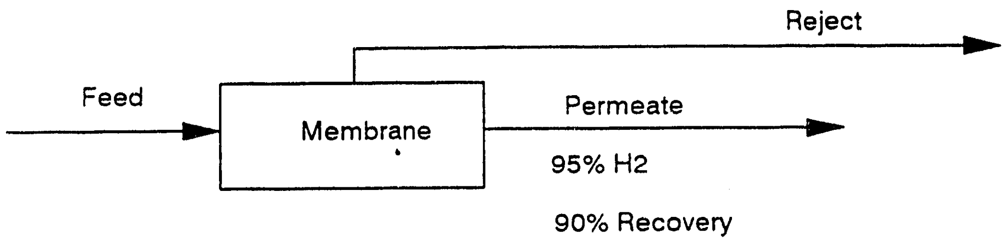
Source: SFA Pacific, Inc.

hydrogen from 300 psig to any final pressure. For example, for a compression ratio of 2 (2 x 315 - 15 = 615 psig), the cost is about \$0.15/Mscf. If a permeate stream is produced at 150 psig, the cost of compressing it to 615 psig (compression ratio = (615 + 15)/(150 + 15) = 3.8) is \$0.29/Mscf.

A typical material balance for 90% hydrogen recovery of 95% hydrogen purity from a feed stream of 75% $H_2$ and 25% $CH_4$ is given is Figure 5-3.

**Figure 5-3**

**Sample Material Balance for $H_2/CH_4$ Separation**



| | | | |
|---|---|---|---|
| Scf | | | |
| H2 | 75 | 67.50 | 7.50 |
| CH4 | 25 | 3.55 | 21.45 |
| | 100 | 71.05 | 28.95 |
| Btu | | | |
| H2 | 23,250 | 20,925 | 2,325 |
| CH4 | 25,250 | 3,585 | 21,665 |
| | 48,500 | 24,510 | 23,990 |

Source: SFA Pacific, Inc.

In SFA Pacific's multisponsored study on Hydrogen Manufacture and Recovery, costs for organic membranes to achieve a similar type of separation were obtained [1]. The basic economics for recovering the permeate at 300 psig are illustrated in Table 5-1.

**Table 5-1**

**Sample Economics for Membranes**

Basis:

| | |
|---|---|
| Feed rate, MMscf/sd | 10 |
| $H_2$ in feed, % | 75 |
| $H_2$ in permeate, % | 95 |
| $H_2$ recovery, % | 90 |
| Permeate pressure, psig | 300 |
| Total Investment, $MM | 1.2 |

| | $/Mscf $H_2$(100%) |
|---|---|
| Fuel value @ $2.50/MM Btu | |
| - Feed | 1.80 |
| - Reject | (0.89) |
| - $CH_4$ in permeate | (0.13) |
| Subtotal | 0.78 |
| Operating Costs | 0.03 |
| Capital Cost @ 20%/year | 0.08 |
| Total Cost | 0.89 |

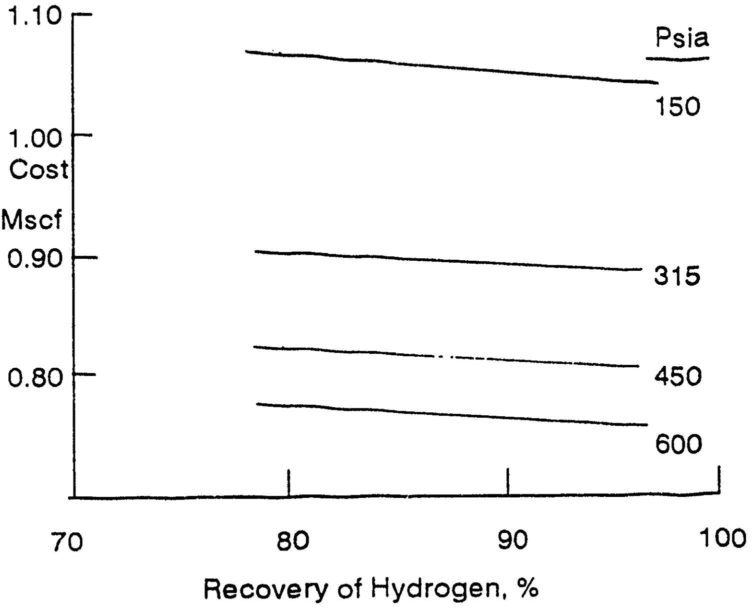
Source: SFA Pacific, Inc.

Note that the total cost of the membranes is only $0.11/Mscf.

The cost of recovering hydrogen at pressures other than 300 psig (relative to the cost at 300 psig) is shown in Figure 5-4.

Figure 5-4

**High Permeate Pressure Is Main Goal**



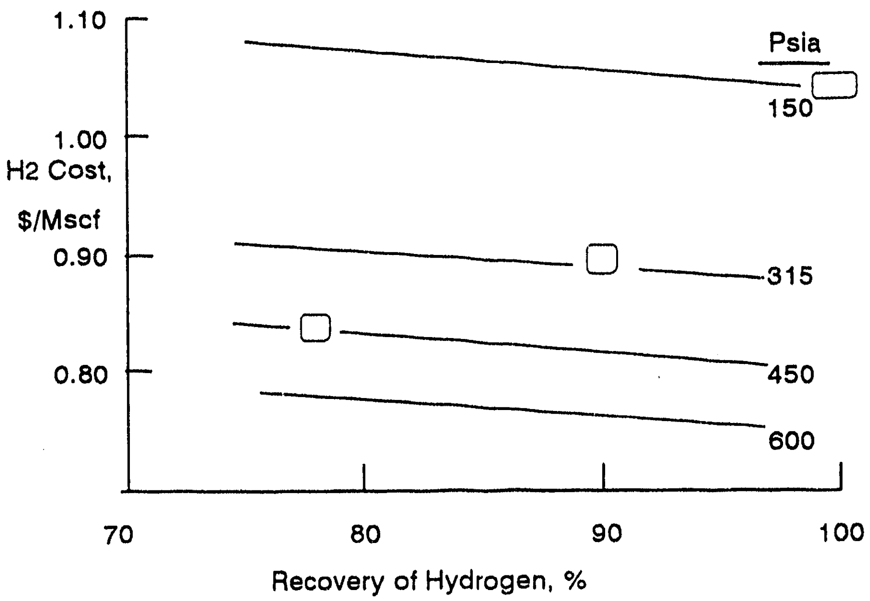
Source: SFA Pacific, Inc.

Clearly, it is advantageous to maintain as high a permeate pressure as practical, even if some loss of yield occurs. The impact of the range of pressures is about $0.25/Mscf, which is more than the cost associated with the membrane itself. The performance of the actual membrane system shown in Figure 5-1 for a permeate having 95% hydrogen can be superimposed on this general graph to verify this conclusion. This is shown in Figure 5-5, where the actual performance is indicated by the open squares.

The advantage for the high pressure is clear, even though the yield loss is substantial. If a refiner were very short on hydrogen, it might be preferable to take the higher yield, even though the cost rises. This is part of the flexibility and advantage of membrane separation technology.

## Figure 5-5

## Actual Performance Shows Value Of High Pressure



Source: SFA Pacific, Inc.

Separation via membranes, whether organic or inorganic, is a function of material properties and the pressure driving force. Materials with similar separation factors and permeabilities will achieve similar separation given similar operating pressures. If *advanced* inorganic membranes are developed such that the hydrogen separation factor and permeability are *considerably* greater than those for organic membranes, it may be possible to achieve comparable *separation* of hydrogen at higher permeate pressures. This would result in lower compression costs. Thus, the general advantage of inorganic membranes would be in achieving high separation factors and permeabilities to hydrogen, so as to maintain a high permeate pressure.

If *advanced* inorganic membranes are found to be more selective and more permeable to hydrogen than competitive organic membranes, their application to the *manufacture* of hydrogen should also be practical. The goal in this case is to separate $H_2$ from $CO_2$, while achieving only a low pressure drop on the hydrogen permeate.

## $H_2S$ Enrichment From $CO_2$ Will Provide Cheap Hydrogen From Partial Oxidation

The partial oxidation process is used to convert a hydrocarbon feed, steam, and oxygen to synthesis gas, mostly CO and $H_2$, with small amounts of acid gases $CO_2$, $H_2S$, and COS. The process can handle a wide range of hydrocarbon feeds: methane, light and heavy liquids, and solids (such as petroleum coke and coal). The synthesis gas can be used to make hydrogen, methanol, oxo-alcohols, ammonia, and many other products. More than 200 partial oxidation plants have been constructed worldwide--particularly in areas where natural gas is expensive or not available. It is environmentally advantageous, providing excellent control of sulfur, no formation of nitrogen oxides, and a vitreous slag of metals (nickel and vanadium) which is not hazardous. The main drawback to the process has been economics. The Rectisol process (which uses refrigerated methanol) for separating the $H_2S$ and $CO_2$ from the hydrogen is extremely expensive.

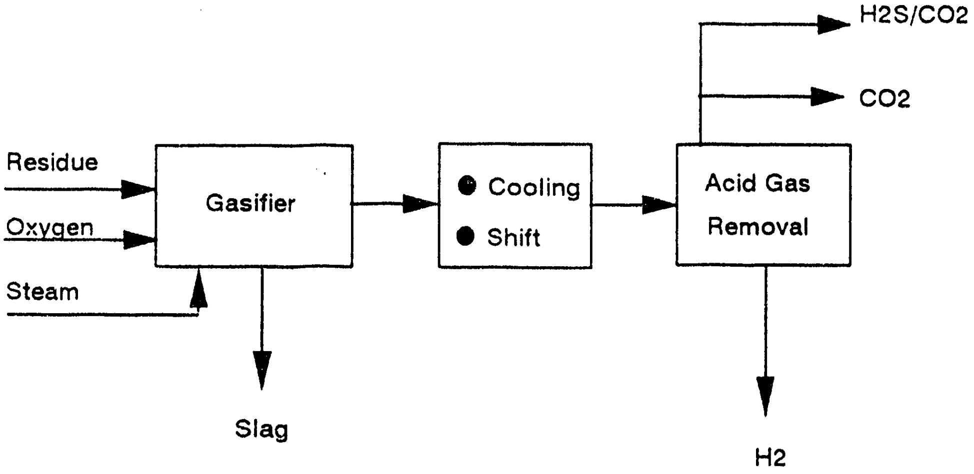
Cheaper acid gas removal systems are available (such as UOP's UCARSOL amine-based and Benfield hot potassium carbonate-based systems) for removing $H_2S$ selectively, along with some $CO_2$. Generally such mixtures contain 2-8 vol% $H_2S$ in the total $H_2S/CO_2$ stream. This mixture cannot be processed in a normal Claus plant like the $H_2S$ rich mixture from Rectisol. However, this mixture can be processed in special sulfur recovery units consisting of Catalytic Claus and/or Wet Oxidation units (which use $O_2$ rather than air). As shown in Appendix C-2, Viewgraph 13, this special processing is considerably more expensive and complicated than sulfur recovery in a normal Claus plant, inhibiting refiners from using the cheaper $H_2S$ separation processes. In view of the continuing pressure on refiners to reduce $SO_x$ emissions, there is a reluctance to move to more expensive and complicated sulfur recovery processes in this sensitive area. If inorganic membranes can be used to enrich a dilute $H_2S$ stream (less than 10 vol%) to a level of 15 vol% or more, where the $H_2S$ can be processed in a normal Claus plant, the membranes open a major route to disposing of high sulfur liquids and producing cheaper hydrogen.

The general flow plan of partial oxidation to make hydrogen is shown in Figure 5-6. Petroleum residue is gasified with oxygen and some steam, to control temperatures to 2,500-2,800°F, to produce a mixture of $H_2$, CO, some $CO_2$, $H_2S$ and COS. The hot gas is cooled, usually with a water quench, and the CO is converted with the steam to make $CO_2$ and $H_2$. The acid gases, $H_2S$, COS and $CO_2$, are removed for further processing, and the pure $H_2$ is recovered for further use.

As noted earlier, Rectisol is normally used for acid gas removal, providing an $H_2S$ concentration (in $CO_2$) of over 70 vol%. Other acid gas removal processes such as the new UOP amine-based or hot potassium carbonate *Hot Pot* processes can be used, but produce $H_2S$ levels of only 2-8 vol%. These processes are much cheaper as shown in Table 5-2 [1].

**Figure 5-6**

**Acid Gas Removal Is Key Element In Partial Oxidation Process**



Source: SFA Pacific, Inc.

## Table 5-2

## *Hot Pot* Is The Cheapest Investment For Acid Gas Removal

| | Investment for 100 MMscf/sd $H_2$, \$ MM | | |
|---|---|---|---|
| | Rectisol | UOP Amine | Hot Pot |
| Investments: \$MM | | | |
| Gasifier | 29.6 | 29.6 | 29.6 |
| Cooling | 13.6 | 13.6 | 13.6 |
| Acid gas removal | 46.5 | 15.8 | 9.4 |
| Utilities | 7.6 | 1.8 | 1.8 |
| Sulfur plant (1) | - | - | - |
| Contingency | 9.7 | 6.1 | 5.4 |
| Offsites | 37.5 | 23.4 | 20.9 |
| Facilities | 144.5 | 90.3 | 80.7 |
| Engineering | 11.0 | 6.7 | 6.0 |
| Startup | 5.5 | 3.3 | 3.0 |
| Working Capital | 1.1 | 0.7 | 0.6 |
| Royalties | 2.2 | 1.4 | 1.2 |
| Total plant cost | 164.3 | 102.4 | 91.5 |

---

(1) The sulfur plant investment is not included, but is accounted for in the economics for $H_2$ cost in Table 5-3.

Source: SFA Pacific, Inc.

Table 5-3 illustrates that the cost of producing hydrogen via partial oxidation is greatly reduced by using the new acid gas removal processes--even allowing for the increased cost of handling the dilute $H_2S$ streams in the more expensive sulfur recovery units.

The potential savings of about \$0.50/Mscf are large--about 20% of the base price. Inorganic membrane technology can be helpful in insuring the refiner's confidence in using the cheaper acid gas removal systems. Assuming inorganic membranes would cost twice as much as organic membranes used for $H_2$ recovery, the associate cost of applying inorganic membranes would be \$0.13/Mscf. This extra cost would be offset by using a cheaper sulfur recovery system, with a savings of about \$0.12/Mscf. If inorganic membranes are applied to the case of hot potassium carbonate acid gas removal, the sulfur recovery cost of \$0.18/Mscf $H_2$ would be reduced to the same level as that for Rectisol (\$0.06/Mscf $H_2$), so that the total savings will be: \$0.54 - 0.13 + 0.12 = 0.53/Mscf $H_2$.

## Table 5-3

## Better Acid Gas Removal Reduces $H_2$ Cost

| | $H_2$ Cost, \$/Mscf | | |
|---|---|---|---|
| | Rectisol | UOP Amine | Hot Pot |
| Vacuum residue @ \$10/b | 0.63 | 0.63 | 0.63 |
| Oxygen @ \$40/ton | 0.47 | 0.47 | 0.47 |
| Steam @ \$5.00/Mlbs | 0.04 | 0.10 | 0.10 |
| Power @ \$0.05/kWh | 0.15 | 0.05 | 0.05 |
| Other operating costs | 0.40 | 0.25 | 0.22 |
| Capital charge @ 20%/year | 0.99 | 0.62 | 0.55 |
| Compression credit | (0.18) | (0.18) | (0.18) |
| Subtotal | 2.50 | 1.94 | 1.84 |
| Sulfur recovery cost (1) | 0.06 | 0.15 | 0.18 |
| Sulfur credit @ \$120/lt | (0.07) | (0.07) | (0.07) |
| Total $H_2$ Cost | 2.49 | 2.02 | 1.95 |
| Savings | Base | 0.47 | 0.54 |

---

(1) This includes the appropriate capital charges for operating cost and return on investment.

Source: SFA Pacific, Inc.

The main key to keeping the cost under control is to minimize the cost of compressing the $H_2S/CO_2$ mixture for feed to the membrane system. For example, compressing the $H_2S/CO_2$ mixture from, say 6 psig from the acid gas removal step to 300 psig would add \$0.37/Mscf to the cost of the final $H_2$ product. This final $H_2$ cost is \$2.33/Mscf = 1.84 + 0.06 - 0.07 + 0.13 + 0.37. This would still make the inorganic membrane approach attractive but reduce the savings significantly (from \$0.54/Mscf to \$0.16/Mscf). Thus, experimental data are critical to establishing the merit of the inorganic membranes for this application. It should be remembered that no application of *organic* membranes have been made for this separation.

## Using Membranes To Remove Sulfur And Aromatics Is A Useful Way To Upgrade Diesel Fuel

New environmental standards are being implemented to upgrade diesel fuel--along with others. Generally, the U.S. standards for diesel have focused only on sulfur content. Before 1990, the sulfur standard was 0.4 wt% maximum. The aromatic content was generally 40-60 vol%, depending on how much aromatic light cat cycle oil was blended with the virgin paraffinic/naphthenic stocks.

The Federal 1990 Clean Air Act (CAA) Amendments set stricter standards for diesel. The maximum sulfur is set at 0.05 wt% and the cetane index (analogous to octane rating for gasoline) is to be at least 40. This cetane index effectively limits the aromatics to about 35-40 vol%. California has set even stricter standards, which begin in October 1993: sulfur is to be less than 0.05 wt% and aromatics are to be 10-20 vol%. Both standards will require substantial increases in hydrogen manufacturing and hydrotreating severity (reactor pressure, temperature, and volume) to bring the diesel production, about 2 million barrels per day, into compliance. The Federal standards may also tighten if California finds its standards significantly reduce pollution.

The increase in hydrogen required and reactor pressure are typically severe, as illustrated in Table 5-4 [5].

### Table 5-4

### New Diesel Standards Require Severe Treating

| Standard | Old | 1990 CAA | Calif. High Aromatics Standard | Calif. Low Aromatics Standard |
|---|---|---|---|---|
| Sulfur, wt% | 0.4 | 0.05 | 0.01 | <0.01 |
| Aromatics, vol% | 60 | 35 | 20 | 10 |
| $H_2$ consumption, scf/b | 150 | 400 | 700 | 1,200 |
| Pressure, psig | 600 | 800 | 1,200 | 1,800 |

Source: SFA Pacific, Inc.

Both aspects increase the cost of hydrotreating diesel by over $3/b, as illustrated in Table 5-5.

### Table 5-5
### New Diesel Standards Increase Upgrading Costs

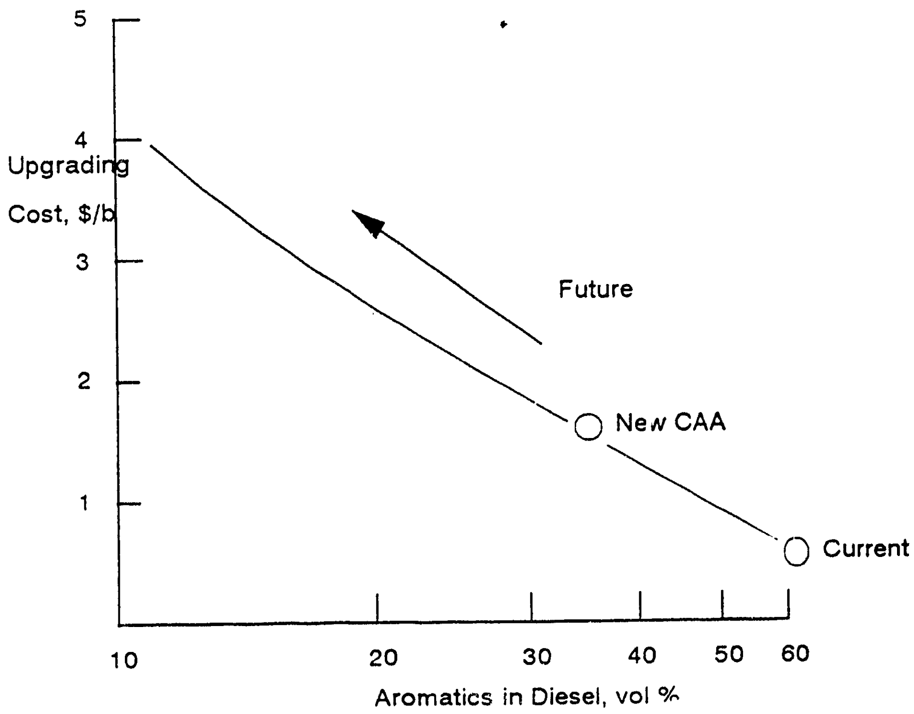
| Standard | Old | 1990 CAA | Calif. High Aromatics Standard | Calif. Low Aromatics Standard |
|---|---|---|---|---|
| Sulfur, wt% | 0.4 | 0.05 | 0.01 | <0.01 |
| Aromatics, vol% | 60 | 35 | 20 | 10 |
| $H_2$ cons., scf/b | 150 | 400 | 700 | 1,200 |
| Pressure, psig | 600 | 800 | 1,200 | 1,800 |
| Base: 20 Mb/sd | | | | |
| Investment, $MM | 6.7 | 13.0 | 24.4 | 26.6 |
| Upgrading Costs, $/b | | | | |
| Operating costs | 0.08 | 0.16 | 0.23 | 0.32 |
| Capital charges | 0.20 | 0.39 | 0.57 | 0.81 |
| $H_2$ @ $2.50/Mscf | 0.38 | 1.00 | 1.75 | 3.00 |
| Total | 0.66 | 1.55 | 1.75 | 4.13 |
| | Base | 0.89 | 1.89 | 3.48 |

Source: SFA Pacific, Inc.

Thus, the refiner is faced with a potentially changing standard for diesel, along with an increasing upgrading cost, as shown in Figure 5-7.

**Figure 5-7**

**Hydrogenating Aromatics And Sulfur Is Expensive**



Source: SFA Pacific, Inc.

Inorganic membrane technology could provide a simple and effective technique that the refiner can use to adapt to a changing target. If the refiner takes steps to meet the Federal standards (marked as *New CAA* on Figure 5-7), inorganic membrane systems may be added to treat diesel to remove extra increments of aromatics and sulfur compounds as the regulations change.

Sulfur occurs primarily in aromatic structures. The aromatic compounds are generally planar in shape--being alkyl benzenes and naphthalene-type structures. The paraffin compounds, the best components in diesel, are more linear in nature. Thus, inorganic membranes might be able to filter out the poorer aromatic type materials.

This presents an unique opportunity for inorganic membranes over organic membranes: the performance of organic membranes suffers since they are mechanically weakened by liquid hydrocarbons.

The removal of sulfur and aromatic compounds is also useful in treating many other refinery feedstocks and products, such as cat naphthas, jet fuels, lube oil stocks, and higher boiling gas oils (650-1,000°F). These materials are of higher value and more abundant than diesel fuel.

### Summing Up...

There are several key applications of inorganic membrane technology in the refining industry where they can significantly reduce costs:

- $H_2$ recovery from hydrotreater purge streams
- Enrichment of $H_2S$ from $CO_2$ in partial oxidation processes
- Improvement of diesel quality by removal of sulfur and aromatics

Wider applications are also possible if the experimental results are good:

- Use in hydrogen manufacture via steam methane reforming to separate $CO_2$ from the hydrogen product
- Use in partial oxidation of refinery gases for hydrogen manufacture, also by separating the $CO_2$ from the hydrogen
- Separation of sulfur and aromatics from gas oils and other liquid refinery streams

The incentives for application of inorganic membrane technology to the following areas are also potentially large:

- Catalytic membrane reactors--Combining reaction and separation processes that are normally conducted separately potentially permits higher conversion per pass, operation at less severe reaction conditions, less recycle (decreasing required downstream product separation), and lower capital investment for equipment. This capability will probably be largely unique to inorganic membranes.

- Wastewater treating--Separation of benzene from wastewater is crucial for refinery compliance with U.S. Clean Air Act National Emissions Standards for Hazardous Air Pollutants. Facilities which annually generate more than 10 tons of benzene in wastewater streams must identify all wastewater streams containing greater than 10 ppm benzene, and direct such streams to units that will reduce the benzene below that level.

As stated earlier, incentives for these later applications were not evaluated since a frame basis for the base case and/or reliability of the technical concept and performance were lacking.

## References

1. N. Korens, B.L. Schulman, H.E. Johnson (SFA Pacific, Inc.), "Hydrogen: Manufacture and Management," private multisponsored analysis, published December 1991.

2. Jerome Heyd (Conoco), "Hydrogen Recovery Using Membranes in Refining applications," 1986 NPRA Annual Meeting, Los Angeles, California, March 23-25, 1986.

3. P. Albulescu and G. Mazzella, "Conceptual Design of Commercial Oil Shale Plants--Fluidized Bed Retorting of Colorado Oil Shale-Alternate Design Study," DOE/MC/22134-2, November 1987.

4. R.J. Gaire and G. Mazzella, "Conceptual Design of Commercial Oil Shale Plants--Fluidized Bed Retorting of Eastern Oil Shale," DOE/MC/22134-2, March 1989.

5. B.L. Schulman, F.E. Biasca, et al. (SFA Pacific, Inc.), "Upgrading Heavy Crude Oils and Residues to Transportation Fuels: Technology, Economics and Outlook, Phase III," private multisponsored analysis, published July 1990.

# SECTION 6

# MARKET BENEFITS AND IMPACTS OF INORGANIC MEMBRANE TECHNOLOGY

# Section 6

## Market Benefits and Impacts of Inorganic Membrane Technology

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### Introduction

As shown in Section 5, there are significant incentives to use inorganic membrane technology in several separation applications important to the refining industry. The overall impact of these applications can be assessed by projecting the growth of the use of these membranes and the economic advantage achieved in each specific application.

Basically, the market benefit and impact relies on three assumptions:

- Growth of the general field
- Penetration of the field by inorganic membranes in competition with other methods
- Specific economic advantage of inorganic membranes over other conventional processing methods

SFA Pacific has used its prior studies and judgements to calculate the overall benefits and impacts of inorganic membranes to the U.S. refining industry. In addition, using historical data, the results can be applied to a broader range of applications (e.g. petrochemicals) and geography (e.g. worldwide). The market benefits and impacts of inorganic membrane technology were presented at the Mid-Course Review meeting on September 1, 1992. Viewgraphs from this presentation are attached in Appendix C-3.

### Hydrogen Recovery from Purge Gases

The growth of hydrogen manufacture in the United States has been substantial since 1980, increasing from about 1,800 MMscf/d in 1981 to almost 3,000 MMscf/d in 1990. The increase in growth depends on how much processing is needed to conform to the new fuel standards for gasoline and diesel. SFA Pacific has carefully analyzed the hydrogen demands for the steps involved in improving the U.S. fuel supply, as shown in Table 6-1 [1].

### Table 6-1

### Hydrogen Demands For Improving U.S. Fuel Supply

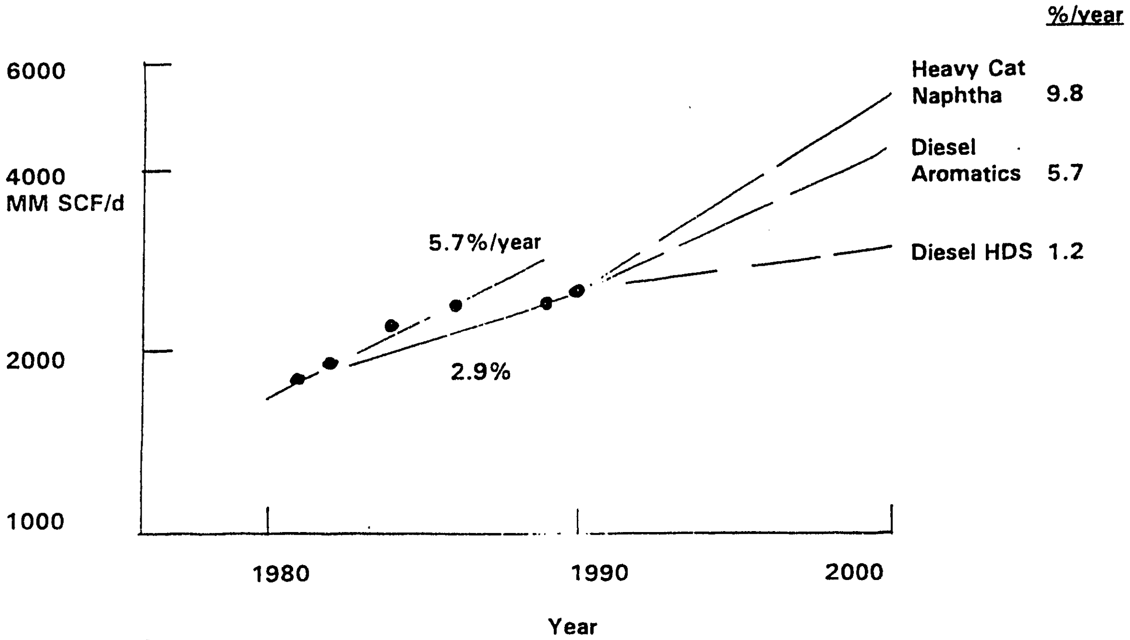
| | $H_2$: MMscf/d | |
|---|---|---|
| | Step | Total |
| ● Reduce diesel sulfur | 350 | 350 |
| ● Reduce diesel aromatics | 1,510 | 1,860 |
| ● Hydrotreat heavy cat naphtha to diesel | 840 | 2,900 |

Source: SFA Pacific, Inc.

SFA judges these steps might occur over the next 8 years, being achieved in about the year 2000, as illustrated in Figure 6-1.

### Figure 6-1

### Hydrogen Growth Can Be Very Large



Source: SFA Pacific, Inc.

If only diesel desulfurization were needed, the growth rate would be a small amount--1.2% per year. Adding diesel aromatic saturation and heavy cat naphtha treating would greatly increase the growth rate to the range of about 6-10% per year. In the early 1980s, the growth was almost 6% per year, and then decreased to 1-2% per year later in the decade.

A simple model for estimating the market value of inorganic membrane technology on $H_2$ recovery is as follows:

- Purge gas rate = 20% of production
- Beginning in 1996, inorganic membranes are applied to 20% of the purges
- Inorganic membranes achieve a permeate pressure of 700 psig, as compared to 350 psig on organic membranes, from a feed pressure of 800 psig
- Value of this pressure advantage is $0.15/Mscf

The above model assumes that *advanced* inorganic membranes are available with suitably high hydrogen separation factors and acceptable recoveries are obtainable at high permeate pressures. Applying this model to the potential growth in the year 2001 shows a high incentive, as shown in Table 6-2.

**Table 6-2**

**Inorganic Membranes Show High Value In Recovering $H_2$ From Purges**

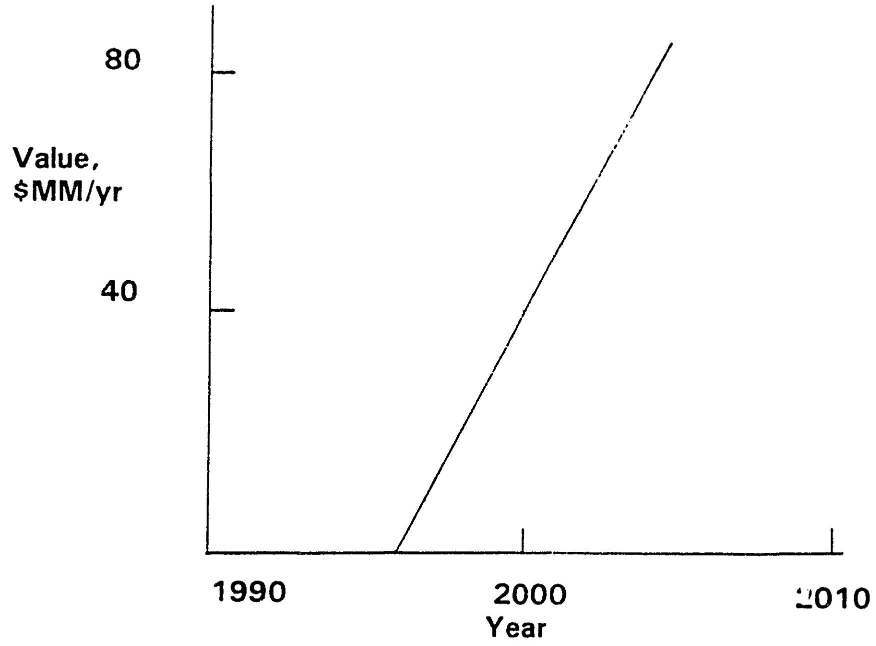
| Treating Step | Additional $H_2$ Manufacture, MMscf/d | Membrane Savings, $MM in 2001 |
|---|---|---|
| ● Diesel | | |
| - Sulfur removal | 350 | 5 |
| - Aromatic saturation | 1,860 | 20 |
| ● Heavy cat naphtha | 2,900 | 40 |

Source: SFA Pacific, Inc.

This amount for all the three steps may continue to grow, as illustrated in Figure 6-2. We have arbitrarily stopped the year at 2005, in view of the uncertainties of such growth of transportation fuels.

**Figure 6-2**

**$H_2$ Recovery By Membranes Is Valuable**



Source: SFA Pacific, Inc.

### $H_2S$ Enrichment From $CO_2$ Shows High Values

Hydrogen production via partial oxidation, combined with hot potassium carbonate acid gas removal can be very attractive (potential savings of $0.50/Mscf $H_2$)relative to the conventional route utilizing steam methane reforming if inorganic membrane technology can be shown to enrich $H_2S$ from dilute mixtures with $CO_2$.

For this market evaluation, the following three assumptions are made:

- Partial oxidation will pick up 20% of new hydrogen manufacture

- Use of inorganic membranes and *Hot Pot* will achieve 50% of the $0.50 credit = $0.25/Mscf
- Plants come on-stream beginning in 1996

The advantages for this application are large, as shown in Table 6-3.

**Table 6-3**

**Membranes Used With Partial Oxidation Provides Large Savings**

| Treating Step | Additional $H_2$ MMscf/d | Value, $MM 2001 | Value, $MM 1996-2001 |
|---|---|---|---|
| ● Diesel | | | |
| - Sulfur removal | 350 | 6 | 29 |
| - Aromatic saturation | 1,850 | 31 | 139 |
| ● Heavy cat naphtha | 2,900 | 48 | 201 |

Source: SFA Pacific, Inc.

The larger credits for this application reflect the value of using inorganic membranes in the manufacturing step, together with the high incentive on the separation.

## Diesel Quality Improvement Is A Good Use For Membranes

Refiners are currently undertaking the task of complying with the requirement of lowering the diesel sulfur to 0.05 wt%. This will be done by adding hydrotreating severity and hydrogen capacity. Inorganic membranes can make an important contribution in the future as the demand for higher quality fuels increases.

An estimate of the value of inorganic membranes is made, assuming a refiner can add membranes to treat the improved diesel fuel. SFA has used the following model:

- Diesel production rate in the U.S. = 2 MM bbl/d
- Reduce aromatics from 35 to 20 vol% and sulfur from 0.05 to 0.01 wt%
- 20% of the diesel treated
- Savings = $1.00/bbl

The savings for this model is $132 MM/year, reflecting both the large amount of diesel produced and the high saving in processing.

### Long Range "Market Growth" Can Be Large

The previous examples of market value have focused on examples where inorganic membranes have a known or probable application. Once experimental data on *advanced* inorganic membranes becomes available for these applications demonstrating positive results, a wider range of applications can be considered as follows:

- Use inorganic membranes to separate $H_2$ from $CO_2$ in hydrogen manufacture. Hydrogen manufacture is about 5 times the amount from purge streams used in the previous calculations.

- Apply inorganic membrane technology to ammonia and methanol manufacture. These applications are equal to about 50% of the hydrogen that is produced in refining.

- Use inorganic membranes to remove sulfur and aromatics in treating gas oils in fluid catalytic cracking, lube oil manufacture, and jet fuel production. The volume of these liquids is potentially about 20 times that of diesel.

- Expand use of inorganic membrane technology to worldwide operations
  - Foreign hydrogen usage is about equal to that of the U.S.
  - Foreign diesel consumption is about twice that of the U.S.

Several issues relating to the potential application of inorganic membrane technology in the refining industry remain to be addressed. These issues include the following:

- Commercial availability -- The availability of the technology necessary to design, manufacture, and market inorganic membranes commercially with no significant use restrictions is needed.
- Competitive commercial cost -- The appropriate cost information for inorganic membranes relative to that for organic membranes producing the same separation is needed.
- Other commercial uses -- The availability of inorganic membranes to the open market at competitive costs may foster a great number of commercial applications not foreseen in this screening analysis.

## References

1. N. Korens, B.L. Schulman, H.E. Johnson (SFA Pacific, Inc.), "Hydrogen: Manufacture and Management," private multisponsored analysis, published December 1991.

# APPENDIX A

## Viewgraphs from Kick-Off Meeting

# ASSESSMENT OF THE POTENTIAL FOR REFINERY APPLICATIONS OF INORGANIC MEMBRANE TECHNOLOGY--AN IDENTIFICATION AND SCREENING ANALYSIS

## KICK-OFF MEETING

June 23-24, 1992

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Harry E. Johnson

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Mountain View, CA

Tel (415) 969-8876
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SFA/VG1

# ASSESSMENT OF THE POTENTIAL FOR REFINERY APPLICATIONS OF INORGANIC MEMBRANE TECHNOLOGY--AN IDENTIFICATION AND SCREENING ANALYSIS

- Key Competitive Separation Technologies
- Application of Separation Technology in the Refining Industry
- "Market Entry" and "Market Growth" Applications for Inorganic Membranes
- Key Systems for Initial DOE Testing
- Future Work Joint Discussion

SFA/VG2

## KEY SEPARATION TECHNOLOGY--STRENGTHS AND WEAKNESSES

- Organic Membranes
- Pressure Swing Adsorption
- Cryogenics
- Liquid Scrubbing
- Distillation

SFA/VG3

# KEY SEPARATION TECHNOLOGY--ORGANIC MEMBRANES

- **Principles of Separation**
  - Difference in Permeation Rates Relative to Membrane Material
  - Gas Solubility/Membrane Chemical Composition
  - Diffusivity/Membrane Physical Structure
  - Pressure Differential Driving Force

- **Organic Membrane System Design**
  - High Permeate Recovery at Lower Pressure
  - Polymeric Materials
  - Hollow-Fiber and Spiral-Wound
  - Multiple Stages

- **Performance of Organic Membranes**
  - Feed/Permeate Pressure, Feed Flow Rate, Product Recovery/Purity, Membrane Area
  - Selectivity, Permeability, Membrane Life

SFA/VG4

# KEY SEPARATION TECHNOLOGY--ORGANIC MEMBRANES

- Strengths
  - Best for Small Streams (< 5 MM SCF/D)
  - Modular Construction
  - Low Capital and O&M Charges
  - Compatibility with Other Systems
  - Increasing Commercial Applications

- Weaknesses
  - Lower Pressure Permeate
  - Liquid Removal Required
  - Sensitive to Feed Composition Variations

SFA/VG5

# KEY SEPARATION TECHNOLOGY--ORGANIC MEMBRANES

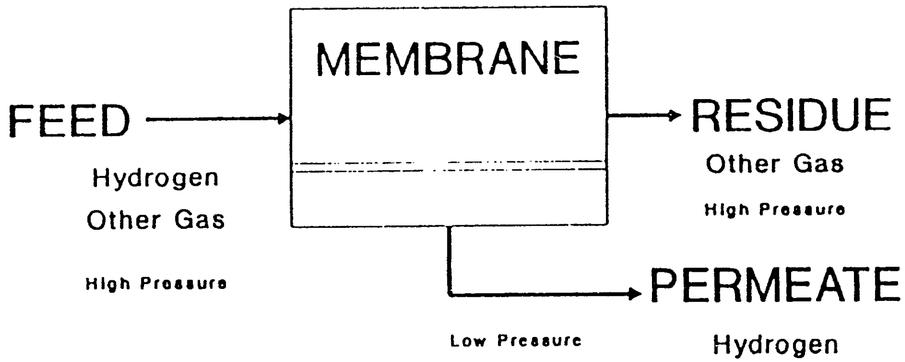
## Relative Permeabilities of Various Gases for Several Organic Membranes

Fast------------------------------------------------------------------------>Slow

| Membrane | $H_2O$ | $H_2$ | He | $H_2S$ | $CO_2$ | $O_2$ | Ar | CO | $CH_4$ | $N_2$ | $C_2H$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Polysulfone | - | 13 | - | - | 6 | 1 | - | - | 0.22 | 0.2 | - |
| Cellulose Acetate | 120 | 12 | - | 10 | 6 | 1 | - | 0.30 | 0.20 | 0.17 | 0.10 |
| Polyamide | - | 9 | - | - | - | 0.5 | - | - | 0.05 | 0.05 | - |
| Dow Product | - | 136 | - | - | 93 | 32 | - | - | - | 8 | - |
| Permea Product | - | 22 | - | - | 9 | 2.3 | - | - | 0.4 | 0.4 | - |
| Polydimethylsiloxan | - | 649 | - | - | 1070 | 604 | - | - | 3230 | 281 | - |

## KEY SEPARATION TECHNOLOGY--ORGANIC MEMBRANES

### Idealized Separation of Two Gases by an Organic Membrane



FEED

Hydrogen
Other Gas

High Pressure

MEMBRANE

RESIDUE

Other Gas

High Pressure

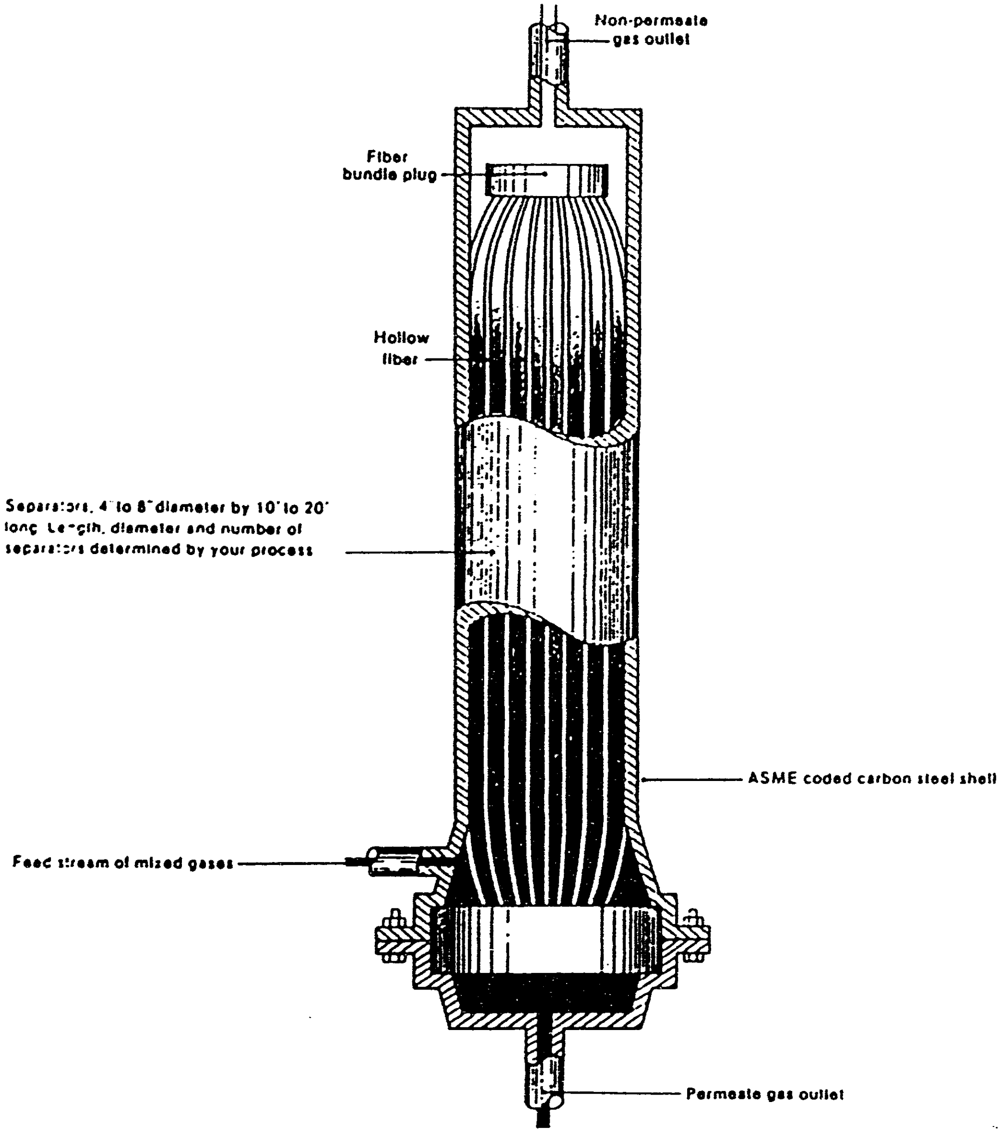
PERMEATE

Low Pressure

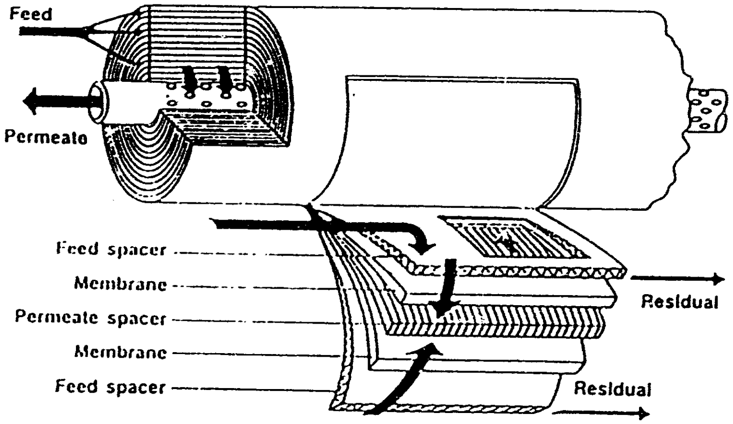
Hydrogen

# KEY SEPARATION TECHNOLOGY--ORGANIC MEMBRANES

### HOLLOW-FIBER MEMBRANE SEPARATOR



### SPIRAL-WOUND MEMBRANE SEPARATOR



## KEY SEPARATION TECHNOLOGY--ORGANIC MEMBRANES

### Commercial-Scale Organic Membrane Suppliers

|  |  |  | Air |  |  |
|---|---|---|---|---|---|
| Company. | $CO_2$ | $H_2$ | $O_2$ | $N_2$ | Other* |
| A/G Technology (AVIR) | X |  | X | X |  |
| Air Products (PRISM) | X | X | X | X | X |
| Asahi Glass (HISEP) |  |  | X | X |  |
| Cynara (Dow) | X |  |  |  |  |
| Dow (Generon) |  |  | X | X |  |
| DuPont |  | X |  |  |  |
| Grace Membrane Systems | X | X |  |  | X |
| Hoechst Celanese (Separex) | X | X |  |  | X |
| International Permeation | X |  |  |  | X |
| Membrane Technology & Research |  |  |  |  | X |
| Nippon Kokan K.K. |  |  |  |  | X |
| Osaka Gas |  |  | X |  |  |
| Oxygen Enrichment Co. |  |  | X |  |  |
| Perma Pure |  |  |  |  | X |
| Techmashexport (USSR) |  |  | X |  |  |
| Teijin Ltd. |  |  | X |  |  |
| Toyobo |  |  | X |  |  |
| Ube Industries |  | X |  |  | X |
| Union Carbide (Linde) |  | X | X | X |  |
| UOP/Union Carbide |  | X |  |  |  |

*Includes solvent vapor recovery, dehumidification and/or helium recovery membranes.

# KEY SEPARATION TECHNOLOGY--PRESSURE SWING ADSORPTION

- Principles of Separation
  - Physical Separation
  - Adsorption on Molecular Sieves

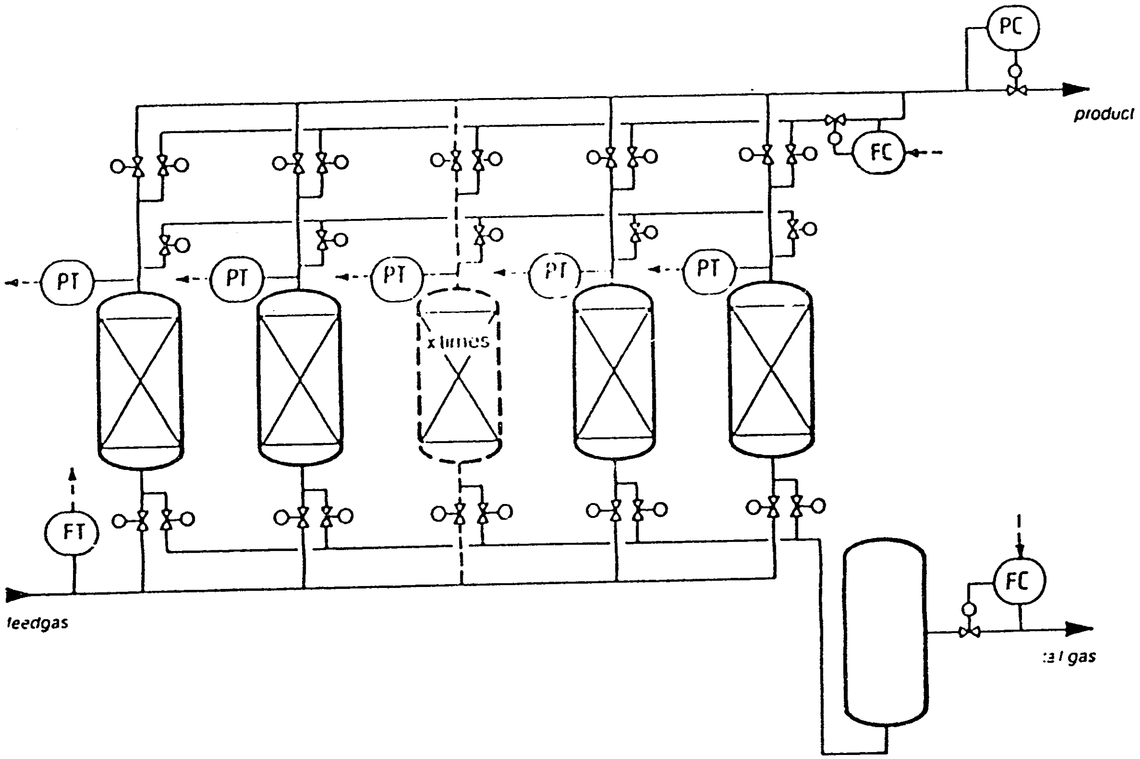
- PSA System Design
  - Pressurized Vessels
  - Cycling Multi-Bed System

- Strengths
  - High Product Purity
  - Insensitive to Feed Composition Variations
  - Little Pretreatment Required
  - Good for Large Scale Operations
  - Low Capital and O&M Charges
  - Compatible with Other Systems

- Weaknesses
  - High Product Loses at Low Inlet Pressue

# KEY SEPARATION TECHNOLOGY--PRESSURE SWING ADSORPTION

## Simplified Multi-Bed PSA Schematic



## KEY SEPARATION TECHNOLOGY--CRYOGENICS

- Principles of Separation
    - Extreme Low Temperature Phase Separation
    - Difference in Relative Volatilities

- Strengths
    - Best for Relatively Large Streams (> 20 MM SCF/D)
    - More Efficient than PSA and Membranes
    - High Pressure Product
    - Recovery of Multiple Streams in High Purity
    - Good Economies of Scale
    - Compatible with Other Systems

- Weaknesses
    - High Capital Costs
    - Pretreatment Required
    - Need High By-Product Value to Justify

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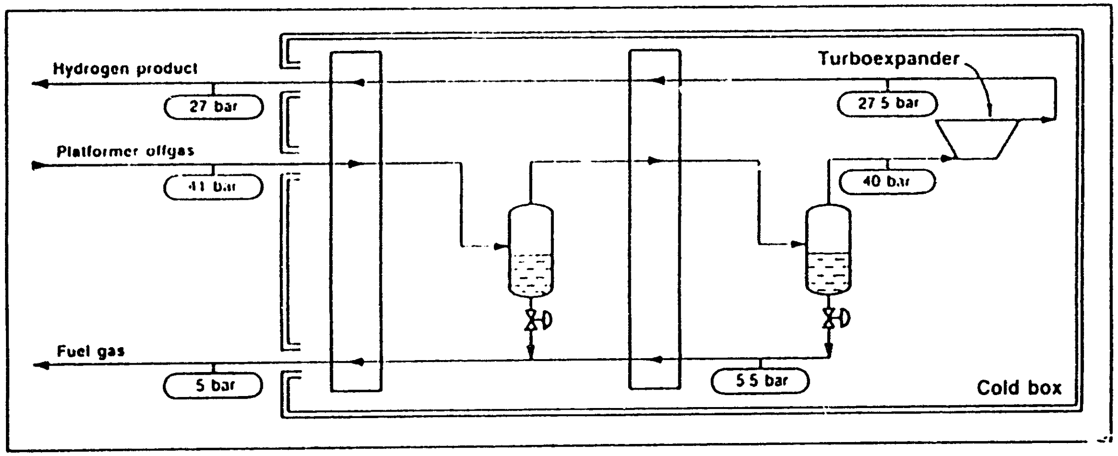
# KEY SEPARATION TECHNOLOGY--CRYOGENICS

## Simplified Two-Stage Cryogenic Recovery Schematic



# KEY SEPARATION TECHNOLOGY--LIQUID SCRUBBING

- Chemical Solvents
- Physical Solvents
- Hybrid Solvents (Physical and Chemical)

# KEY SEPARATION TECHNOLOGY--LIQUID SCRUBBING

## Chemical Solvents

- Amine-Based Systems
  - MEA
  - DEA
  - DIPA
  - MDEA (Gas/Spec, FLEXSORB)

- Promoted Hot Potassium Carbonate
  - Benfield
  - CATACARB
  - FLEXSORB HP

## Physical Solvents

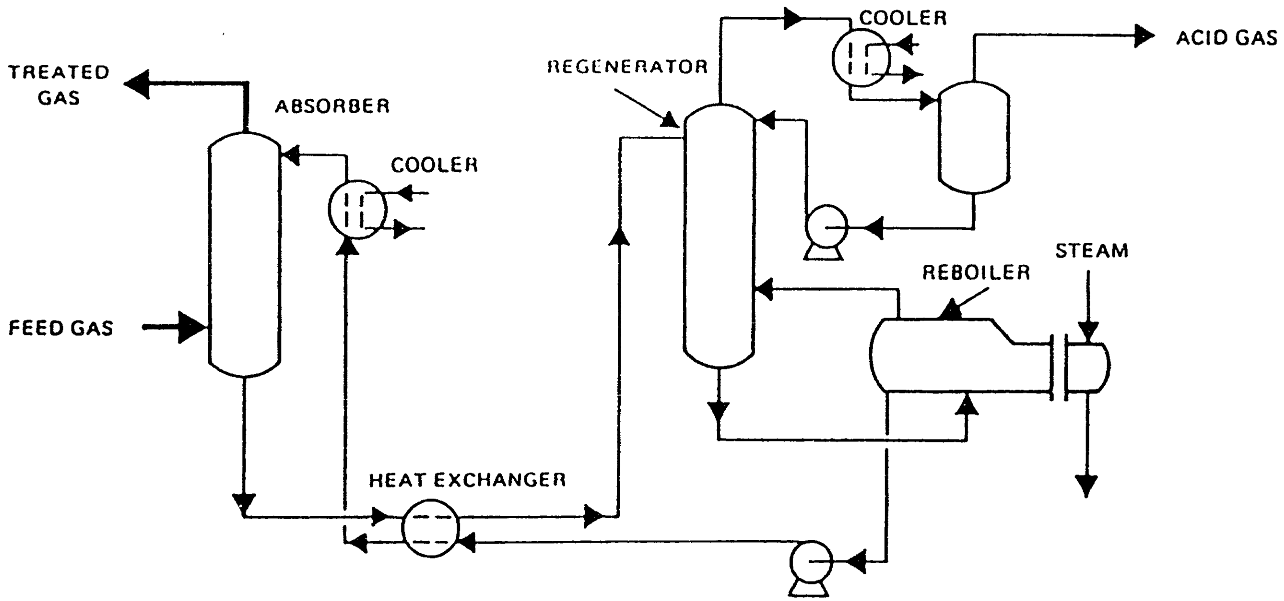
- Rectisol
- Selexol
- Purisol

## Hybrid Solvents

- Physical and Chemical
  - Sulfinol
  - Amisol
  - FLEXSORB PS
  - Selefining
  - Ucarsol LE-701

## KEY SEPARATION TECHNOLOGY--LIQUID SCRUBBING

### Simplified Aqueous Amine-Based Solvent Process Schematic

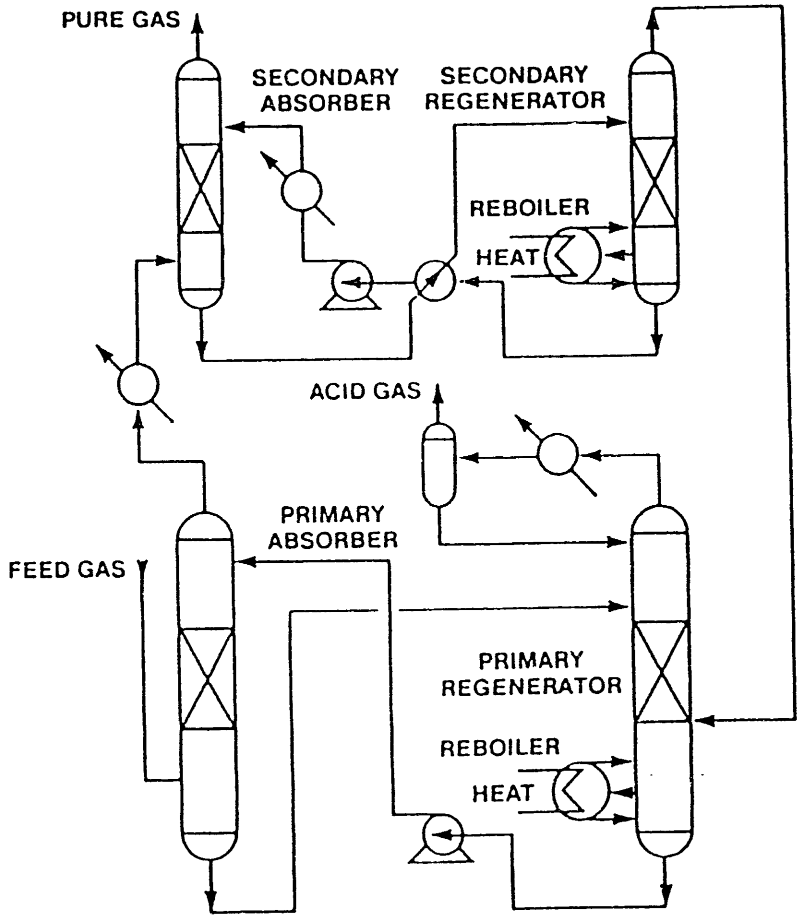


Source: Shell

SFA/VG16

# KEY SEPARATION TECHNOLOGY--LIQUID SCRUBBING

## Simplified Benfield HiPure Process Schematic



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# KEY SEPARATION TECHNOLOGY--DISTILLATION

- Utilizes Heat/Condensation to Separation Fractions
- Fractionation in Series of Distillation Columns
- Recover Valuable Components from Mixed Streams

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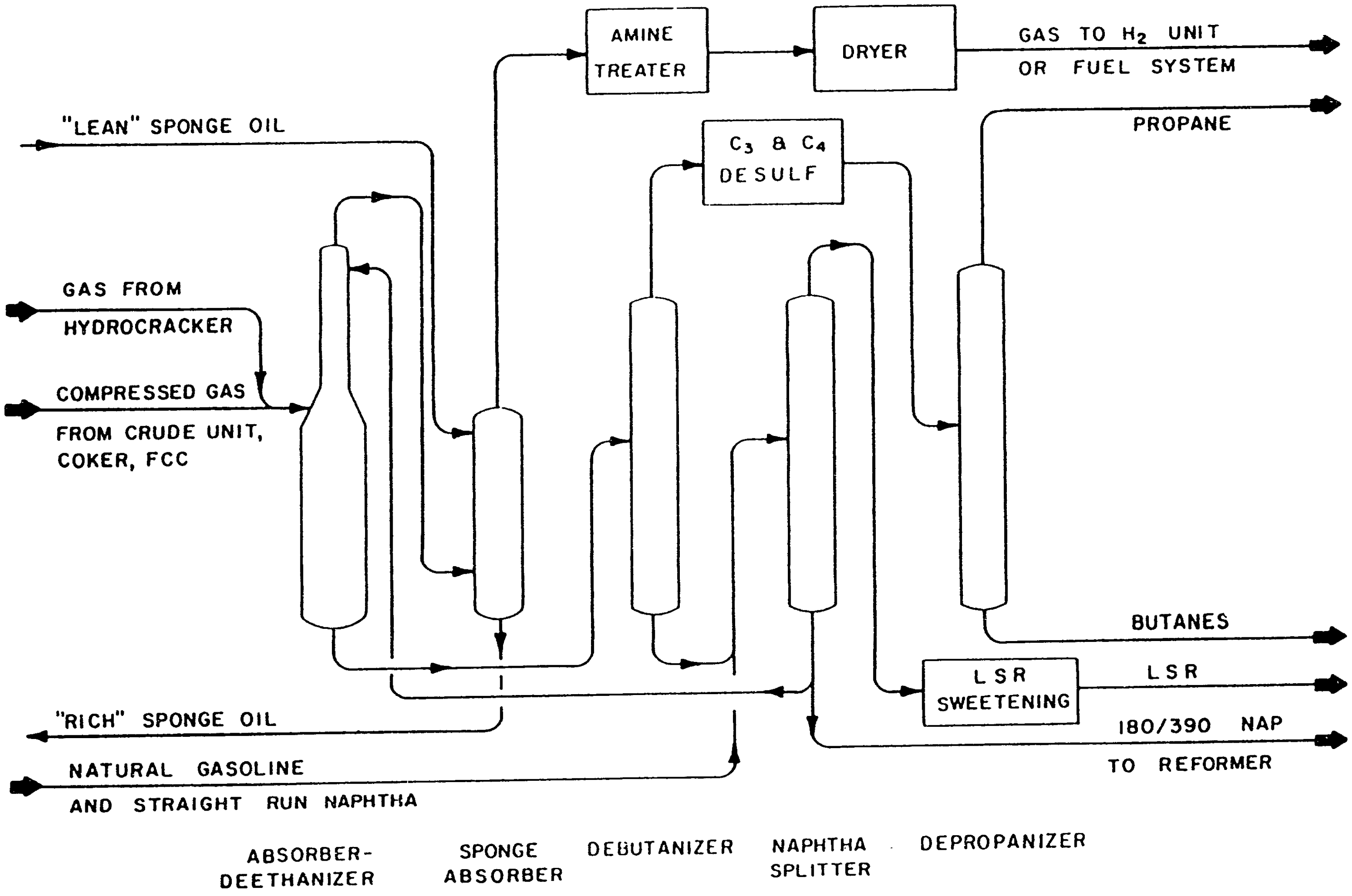
# KEY SEPARATION TECHNOLOGY--DISTILLATION

## Simplified Gas Processing Schematic



# APPLICATION OF SEPARATION TECHNOLOGY IN THE PETROLEUM REFINING INDUSTRY

- **Refinery Applications**
    - $H_2$ Production and Recovery
    - Acid Gas Removal and Purification
    - $O_2/N_2$ Separation
    - Other Refinery Streams

- **Technology Selection is Dependant On:**
    - Stream Composition
    - Pressure
    - Flow Rate
    - Product Requirements
    - Capital Investment

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# $H_2$ PRODUCTION

**Catalytic Reforming of Naphtha**

- Primary source of hydrogen in refineries (61% of total $H_2$ mfr in U.S.)
- Increased yields due to technology and catalyst improvements
- New $H_2$ demand will need to come from supplemental facilities

**Steam Methane Reforming**

- PSA is now the default standard for SMR $H_2$ purification
- PSA/SMR combination generates substantial export steam
- When steam is not needed, can use amine or hot carbonate processes
- New reformer designs are integrated for high-level heat recovery; examples include: EHTR (Air Products), HER (Haldor-Topsoe), GHR (ICI)

**Partial Oxidation**

- Mature technology with more than 200 reactors worldwide
- Shell and Texaco are the primary licensors offering similar systems
- Most important improvement is the use of new amine systems--various formulated MDEA processes

# $H_2$ RECOVERY FROM REFINERY STREAMS

- Viable Candidate Streams
  - Naphtha Cat Reforming Off-Gas
  - Hydrotreating/Hydrocracking Purge
  - FCC Off-Gas
  - Ammonia/Methanol Purge
  - Alkane Dehydrogenation Off-Gas

- Commercially Available Upgrading Technologies
  - PSA
  - Organic Membranes
  - Cryogenic Separation

- Application of Separation Technologies is Attractive
  - Recovery is Economic Alternative to Manufactured $H_2$
  - PSA & Membranes are Inexpensive
  - Economics of PSA/Membranes are Excellant
  - Compression credit favors PSA
  - Process Flexibility is Increased

# ACID GAS REMOVAL AND PURIFICATION

- $H_2S/COS/CO_2$ Resulting from Processing
  - Also Occurs in Some Natural Gas
- Acid Gas Removal and Purification Necessary for Environmental and Economics Purposes
- Acid Gas Removal Large Part of $H_2$ Manufacturing Costs
- Principal Processes for Removal and Purification
  - Amines
  - Hot Potassium Carbonate
  - Rectisol
  - PSA
  - Organic Membranes
  - Dry adsorbents
- Most Recent Developments are in:
  - Newly Formulated Amines
  - Organic Membranes

# ACID GAS REMOVAL AND PURIFICATION

- Newly Formulated Amines (MDEA) are Offered for a Variety of Applications
  - Bulk $CO_2$ Removal
  - Selective Removal of $H_2S$ and CO2
  - Deep $CO_2$ Removal
  - Low Solvent Circulation Rates and Regeneration Heat Requirement
  - Can be Used in Combination with PSA

# ACID GAS REMOVAL AND PURIFICATION

- Hot Potassium Carbonate is Still the Process of Choice for Some Cases
  - High Partial Pressures of CO2 with Little or No H2S in the Feed Gas
  - Primary Application is for Steam Reformed Syngas for Ammonia Manufacture
  - Removes COS but Not Mercaptans

## ACID GAS REMOVAL AND PURIFICATION

- PSA is Prominent Among All the Purification Processes Used in $H_2$ Manufacture
  - Major Advantages are High $H_2$ Purities, No Regenerative Heat Requirement, Insensitivity to Gas Composition Variations, and Low Capital and O&M Charges
  - Disadvantages are Incomplete $H_2$ Recovery and Low-Btu Purge Gas (results in high steam production in reformer)

# $O_2/N_2$ SEPARATION

- Air Separation is Relatively Straightforward
    - Fixed Feed Composition
    - Minimal Pretreatment (essentially no impurities)
- Separation Goals
    - Oxygen-Enriched Air
    - Nitrogen-Enriched Air
- Separation Processes Used
    - Cryogenics (extremely well engineered)
    - Membranes
    - PSA

# OTHER REFINERY STREAMS

- Hydrocarbon Recovery
    - $C_2$ - $C_6$ Separation from Various Gas Streams
    - FCC Feed Pretreatment
    - Paraffin/Olefin Separation
    - Normal/Iso-Paraffin Separation
    - High-Purity Aromatics
    - Catalyst Particle Removal
    - Gas Desulfurization

- Refinery Waste
    - Oily Wastewater Treating
    - Solvent Recovery
    - Caustic Recovery

# "MARKET ENTRY" APPLICATIONS FOR INORGANIC MEMBRANES

- $H_2$ Recovery from Hydrocarbon Gases
- $H_2$ Recovery from Syngas ($H_2$ and Methanol mfr)
- $H_2S/CO_2$ Separation
- Aromatic Removal from Diesel Fuel
  - Also useful for jet fuel, gas oils

# $H_2$ RECOVERY FROM HYDROCARBON GASES

- Purification of HiP recycle gas
    - Hydrocarbons are $C_1$ - $C_4$
    - Boost purity to $> 98\%$ $H_2$ from 80-90%
    - Minimum gas loss and $\Delta P$
    - Replaces PSA pressure letdown

- Recovery from low $H_2$ purge gas
    - Contains $C_1$ - $C_4$ saturates, olefins and some $N_2$, $CO_2$
    - Boost to $> 75\%$ from $< 50\%$
    - Can use $> 95\%$ $H_2$ directly
    - Can use $75\%^+$ as fuel to PSA
    - Replaces PSA (high purity) or cryogenics

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# $H_2$ RECOVERY FROM SYNGAS

- Gas is typically 60-80% $H_2$
    - Balance is $CO_2$ (methane reforming) and CO (methanol)
    - Some $H_2S$, $N_2$ if partial oxidation of residues used

- Goal is to achieve $H_2$ purity of > 99%
    - Minimum loss of $H_2$ and product pressure
    - PSA gives 7-10% loss of $H_2$
    - Membranes give high pressure loss and modest purity gain

SFA/VG31

## $H_2S/CO_2$ SEPARATION IMPORTANT
## IF PARTIAL OXIDATION USED FOR $H_2$

$CH_2\,S_{0.05} \rightarrow CO_2 + 2H_2 + 0.05\,H_2S$ (not balanced)

- If remove $H_2S + CO_2$ non-selectively, the cost is very low

- But S recovery from dilute $H_2S$ (5-10%) is quite costly
  3-4 times that of standard Claus process

- Need concentration to at least 15-25% $H_2S$ to use regular Claus process
  - $CO_2$ discharge should be less than 1.0 vol% $H_2S$
    - + Can use wet oxidiation to remove $H_2S$

SFA/VG32

## AROMATIC REMOVAL FROM DIESEL FUEL

- New Federal specifications about 25 vol% in 460/650°F cut
  - Also 0.05 wt% sulfur (in aromatic molecules)

- Current specifications:
  - 40-60 vol% aromatics
  - 0.4 wt% sulfur

- Specifications may become more stringent
  - < 10 vol% aromatics in California in 1993
  - Federal rules usually follow California

- Would also be useful for
  - Naphtha isomerization
  - Improving Fluid Cat Cracking feedstocks
    - + Multi-ring aromatics make high coke
    - + Single ring aromatics okay

# "MARKET GROWTH" APPLICATIONS FOR INORGANIC MEMBRANES

- $H_2$ Recovery
- $CO_2/H_2S$ Separation
- $O_2/N_2$ Separation
- Liquid Phase Separation
    - Aromatics
    - Sulfur
    - Nitrogen

SFA/VG34

# KEY SYSTEMS FOR INITIAL TESTING

- $H_2/C_1$ - $C_4$ Hydrocarbons
- $CO_2/H_2S$
- $O_2/N_2$
- Normal-Hexane/Cyclo-Hexane Liquids
- Kerosene Sulfur

SFA/VG35

# APPENDIX B

## Memorandum (July 10, 1992)

## Performance targets on key separation candidate streams

**SFA Pacific, Inc.**
**Engineers**

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Telephone: (415) 969-8876
FAX: 415-969-1317

July 10, 1992

First, let me say how much Harry Johnson and I enjoyed our visit to DOE. I just regret that you could not have been available for both days.

As we discussed (on both days), I wanted to send you some basic information on the targets for performance on several key separations SFA Pacific had suggested as candidate systems. These suggestions can be used in your formulation for your future program testing -- beyond making suitable small pore-size membranes for experimental testing.

The attached memorandum covers my suggestions, as well as some background information, for the key areas agreed on at the meeting:

- $H_2/CH_4$ separation
- $H_2S$ enrichment in dilute $H_2S/CO_2$ gases
- Separation of normal hexane from cyclohexane (or benzene)
- Removal of sulfur compounds and aromatics from kerosene/diesel
- Removal of benzene from water

During the meeting, a DOE representative volunteered to make up the spatial molecular models (I still call them "tinkertoys") for normal hexane and cyclohexane for your examination of the relative dimensions.

I have not put together the economic picture of the full incentives for achievement of the targets. That's still to be done to complete this part of our task.

Subsequent to the meeting, a DOE representative suggested adding the concept of "Catalytic Membrane Reactors" to the list of possible applications. A DOE representative, in his FAX of June 26, had suggested several types of reaction systems for which this concept would be applicable. I have not included these systems in this discussion primarily because SFA has not studied them, and some further engineering considerations need to be made, such as how to insure good heat addition, or removal, can be achieved when the walls are made of ceramic materials. There is enough good "red meat" on the platter for your program.

If you have any questions on the memorandum, please call me. I would be happy to help you in any way to assess the size of the various program steps. There are many details not discussed in the meeting that we may want to resolve.

My best regards to all your associates.

Yours very truly,

Bernard

Bernard L. Schulman
Manager Petroleum Processes

## Performance Targets for Testing Inorganic Membranes on Selected Systems

### Introduction

SFA Pacific (SFA) has undertaken a task for the U. S. Department of Energy (DOE) entitled "Assessment of the Potential for Refinery Applications of Inorganic Membrane Technology -- An Identification and Screening Analysis". The initial part of this effort began with a "kickoff" meeting at DOE on June 23-24, 1992.

As part of the overall presentation, SFA identified several systems which would be of interest to refiners:

- Recovery of $H_2$ from $CH_4$
- Enrichment of $H_2S$ in dilute $H_2S/CO_2$ streams
- Liquid phase separation of normal hexane from cyclohexane (or benzene)
- Removal of sulfur and aromatics from kerosene or diesel

During the discussions on water purification, the separation of small amounts of benzene from water was added to the list.

SFA was asked to suggest some specific performance targets for experiments on these systems.

This memorandum discusses the basic suggested experimental conditions, performance targets, and the general rationale for the refinery interest. The detailed analysis of the economic driving forces will be developed separately by SFA, as part of the general study. The recommendations reflect our judgments on keeping the experiments as simple as possible, while still providing the key valuable insights and quantitative data for evaluating the inorganic membranes' performance.

The goals are to provide information on a wide range of initial applications so as to compare inorganic membranes with methods currently practiced -- using organic membranes to separate $H_2$ from $CH_4$ -- or severe hydroprocessing to reduce sulfur and aromatics in diesel, kerosene and gas oils.

### Membranes do a Good Job on Separating $H_2$ from Hydrocarbon Gases

Refiners have found that organic membranes are a reliable and inexpensive way to recover hydrogen from refinery gases. Pressure Swing

Absorption units (PSA) are also popular for this application. Generally, most refineries today use high-pressure hydrogenation processes to remove sulfur and reduce aromatic content of products and process feedstocks. About 20% of the hydrogen generated must be purged from these processes to keep hydrocarbons from building up to excessive levels. Usually, these purge gases, which may contain 75 vol% $H_2$, are used as refinery fuel.

Commercial organic membranes can do an excellent job of recovering a high purity $H_2$ (> 90 vol%) at high yields ( > 90 wt%), as illustrated in Figure 8-11 below, taken from SFA Pacific's Phase III Study on Heavy Oil Upgrading. More details on this aspect are given in Attachment 1, which is excerpted from the same report.

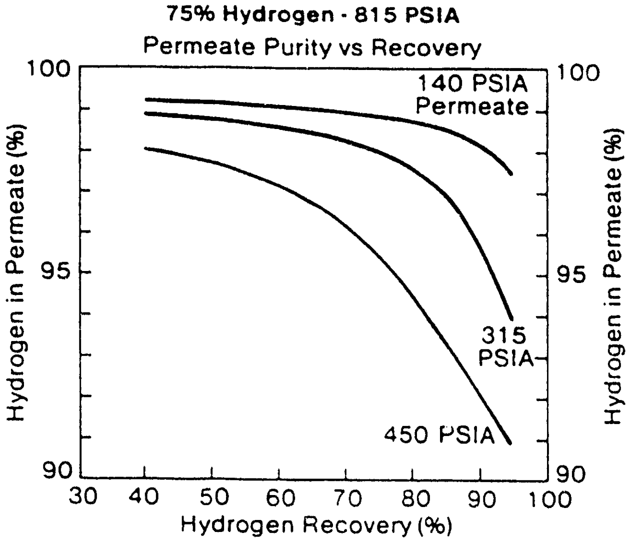


Figure 8-11

<u>Recovery of Hydrogen from Hydrotreater Purge Gases</u>

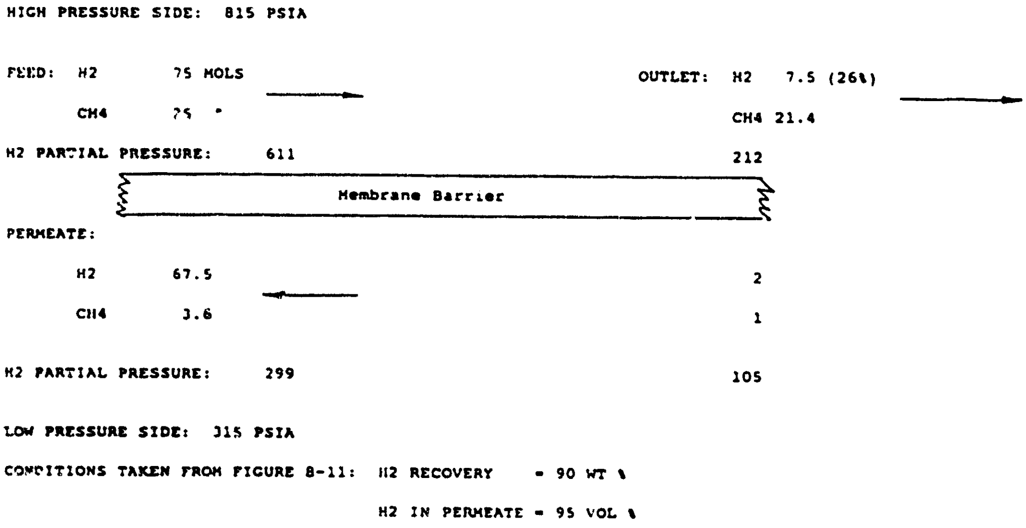
Source: Conoco

Lowering the permeate pressure greatly increases the hydrogen recovery and purity. However, there is a substantial penalty for dropping the pressure too low. For instance, the debit for a pressure of 140 psia relative to 315 psia is about $0.15 /Mscf $H_2$. This cost is essentially equal to the total cost of the membranes (see Attachment 1). As a result, there is a good driving force to having a membrane with both good selectivity and high permeability. This can provide high yield and purity with a high permeate pressure.

Using an inorganic membrane with countercurrent flow of high pressure feed gas and lower pressure permeate can give a good hydrogen partial pressure driving force, as illustrated in Figure 1, which uses the general conditions in Figure 8-11 as a basis.

Figure 1

COUNTERCURRENT MEMBRANE OPERATION GIVES GOOD DRIVING FORCE FOR HYDROGEN SEPARATION



SOURCE: SFA PACIFIC, INC.

The countercurrent flow provides a pressure gradient of 312 psia at the feed inlet end, with a smaller (unknown) gradient at the feed outlet end. Using two or more stages of membranes should provide a higher permeate pressure.

These calculations suggest that the preferred experimental conditions be about:

| | |
|---|---|
| · Pressure, psig | 700 - 800 |
| · $H_2$ in feed gas, vol% | 60 - 75 |
| · Permeate pressure, psig | 100 - 400 |
| · Temperature, °F | 100 - 200 |

The overall yield and quality of the permeate should be determined at the various permeate pressures. Temperature can be varied to see how it can best be used to enhance the $H_2$ selectivity and permeability rates.

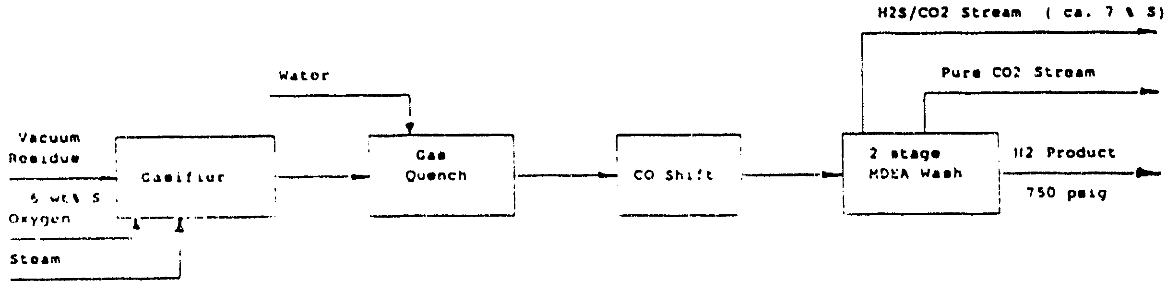
The target is to obtain yield curves at least as good as shown in Figure 8-11 at 145 and 315 psia, but at higher permeate pressures. Being able to achieve the same levels about 150 - 200 psia greater would give a large economic edge over organic membranes and provide strong competition for the high investment PSA process.

Enrichment of $H_2S$ in dilute $CO_2$ Streams will
Greatly Enhance Partial Oxidation for $H_2$

SFA Pacific recently complete an extensive study on the improvements made in the technologies and economics of making hydrogen. One particular improvement -- that of the new amine systems -- greatly enhanced the role of partial oxidation of heavy, high-sulfur liquids in making hydrogen. There are two processes widely used abroad, though only 2 plants in the United States, which are licensed by Shell and Texaco. These are described in detail in Attachment 2, taken from the SFA Phase III Heavy Oil Study. The major improvement in the Acid Gas Removal step is discussed in Attachment 3, taken from the SFA Hydrogen Study. A simplified flow diagram of the partial oxidation process is shown in Figure 2, below.

Figure 2

NEW PARTIAL OXIDATION DESIGN REDUCES COST
BUT PRODUCES LOW H2S STREAM FOR SULFUR RECOVERY



Source: SFA Pacific, Inc.

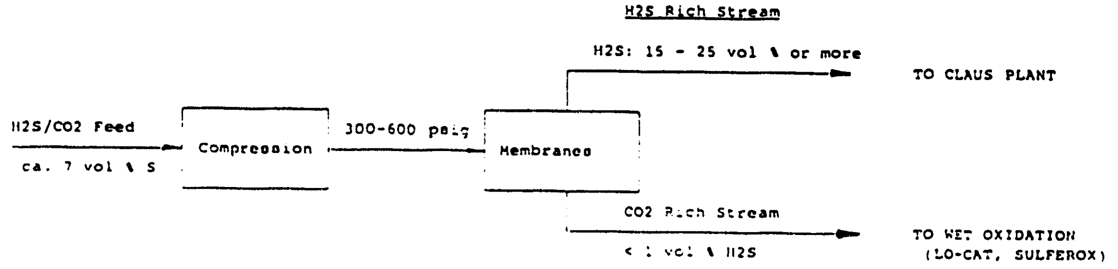
The vacuum residue is fed to a high pressure reactor, at 400 - 800 psig, typically, and reacted with oxygen and some steam to decompose the hydrocarbons to CO, $H_2$, and $H_2S$, primarily. The temperature is about 2500 - 2700°F. The hot gases are quenched with water, usually, and cooled to 400 - 500°F. The water-laden gases then are reacted over a sulfur-tolerant shift catalyst to convert the CO to $CO_2$ and $H_2$. The gases are then washed with a special MDEA(methydiethanolamine) solution to produce one stream of $H_2S/CO_2$ and a second $CO_2$ stream free of $H_2S$. The resulting $H_2$ is about 99 vol% purity and delivered at high pressure. The $H_2S/CO_2$ stream is generally only 7 vol% $H_2S$ and must be specially processed to convert it to elemental sulfur.

Traditionally, the Rectisol process (which uses refrigerated methanol) has been used to do the acid gas removal step, since it produces an $H_2S$ stream of at least 75 vol%. This allows the $H_2S$ to be sent to a normal Claus plant for conversion to sulfur. However, the Rectisol process is extremely expensive. It is far cheaper overall to use the MDEA wash and use a special oxygen-blown catalytic Claus to process the lean $H_2S$ stream.

Membranes can play an important role in further reducing the costs if they can achieve even a mild separation of $H_2S$ from $CO_2$. The general scheme is illustrated in Figure 3:

Figure 3

USE MEMBRANES TO CONCENTRATE H2S IN CO2
TO MAKE CLAUS PLANT FEED



Note: Final pressure on permeate stream from membrane can be 15 psig or less.

Source: SFA Pacific, Inc.

The $H_2S/CO_2$ stream is compressed and fed to the membrane where the stream is split into 2 parts:

- An $H_2S$-rich stream containing more that 15 vol% $H_2S$
- A $CO_2$ stream containing less that 1 vol% $H_2S$

The $H_2S$-rich stream can be fed to a regular Claus unit, along with the other $H_2S$ made in the refinery (which might be 10 times the amount from the partial oxidation unit). The $CO_2$ can be sent to a small wet-oxidation unit, such as Lo-Cat or Sulferox, which oxidizes the $H_2S$ completely to sulfur, leaving a $CO_2$ which can be sold or vented to the atmosphere. This arrangement of the recovery technique provides a cheap and environmentally excellent way to convert the $H_2S$ to sulfur.

For the experimental program, a feed stream of 5 -7 vol% $H_2S$ should be used. The membrane should be tested at various feed pressures, with the permeate being at essentially atmospheric pressure. The Claus and wet-oxidation processes generally operated at low pressure. The pressure and temperature should be adjusted to give the following targets:

| | |
|---|---|
| · $H_2S$ in the $H_2S$-rich stream | > 15 vol% |
| · $H_2S$ in the $H_2S$-lean stream | < 1 vol% |

APPROPRIATE SAFETY PRECAUTIONS MUST BE TAKEN: $H_2S$ IS EXTREMELY TOXIC!

## Liquid Separations Are a Good Test for Inorganic Membranes

Generally, in refineries is often necessary to reduce troublesome components in liquid streams to low levels, either to meet product specifications, pollution regulations or to improve the further processability of feedstocks. Organic membranes have not been used for this type of application. Hydrocarbons can dissolve in the organic membranes and interfere with their performance and, perhaps, physical strength. Inorganic membranes should not be affected by hydrocarbon liquids. Thus, if inorganic membranes can show desirable separations in the liquid phase, they will have an "open door" to many applications in refining.

Several possible applications have been suggested:

- Removal of benzene from naphtha
- Removal of sulfur and aromatics from diesel fuel and gas oils
- Removal of benzene (and other organics) from waste water
- Use membranes as "catalytic reactors" to remove reaction products where equilibrium limits feed conversion

The first two applications can be done currently for refinery processes but require severe processing. The cleanup of benzene from waste water is going to be a major challenge to meet the ever-increasing severe environmental restrictions.

Some simplified experiments are suggested to test the first 3 applications. The use of "catalytic reactors" requires some further study of the engineering of special features, such as how to get good heat input, and is not on the current agenda for detailed consideration. This concept can be pursued once the experimental data show the essential value of the membranes for various applications.

## Normal Hexane/Cyclohexane Is a Good Candidate System

Normal hexane and cyclohexane are close in molecular weight but have much different spatial arrangement of the atoms in the molecule. Each compound has six carbon atoms. Normal hexane has its six atoms in an approximately straight line -- somewhat like a pencil. Cyclohexane has its carbon atoms arranged in a ring (as does benzene). Hence, cyclohexane should have more difficulty in passing through a given membrane than normal hexane.

SFA suggests that a set of experiments be made to check this aspect -- as a precursor to the more critical tests on sulfur removal from diesel and benzene removal from water. The tests would use a mixture of, say, 20 vol% cyclohexane in normal hexane as a feedstock. The feed would be put through membranes at various pressures and temperatures to define what degree of separation is achieved. A typical range of conditions would be:

| | |
|---|---|
| • Pressure, psig | Up to 600 |
| • Temperature, °F | 100 - 200 |

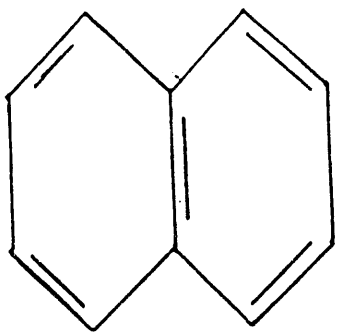
The goal would be to recover a normal hexane permeate with less than 5 vol% cyclohexane in it, in a yield of 85 vol% or more. If this operation looks feasible, then the experiments can proceed to the next, more difficult steps, as described below.

## Sulfur And Aromatics Removal From Diesel Is a Major Refining Problem

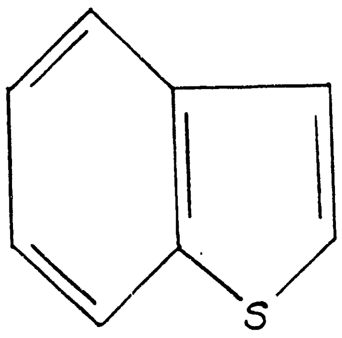
One of the leading problems facing the refiner today is that of achieving the higher diesel quality mandated by the 1991 Clean Air Act Amendments. The new Federal standards call for reducing sulfur to 0.05 wt% (from about 0.4 wt%) and to have a cetane number corresponding to about 25 -35 vol% aromatics. California has a much more stringent specification -- requiring aromatics to be no more that 10 vol% by October 1993. This specification will produce a sulfur well below 0.05 wt%. It may well be that the EPA will adopt the California regulations for all the United States once it is shown that the specifications significantly reduce emissions relative to the new Federal standards.

For diesel fuel, the typical "bad actors" are two-ring structures: such as naphthalene and benzothiophene, as illustrated below.

Naphthalene



Benzothiophene



Both types of structures are aromatic in nature and potentially can be separated from the more desirable normal and isoparaffin molecules by membranes -- particularly if the above experiments are successful.

The experiments are relatively straightforward. A commercial diesel fuel should be analyzed for sulfur and aromatics (as well as aromatic type) and used as the standard feed. The tests would be run at various pressures and temperatures, as in the normal hexane and cyclohexane tests. The overall conditions would be essentially the same as before. The target would be to reduce the sulfur to 0.05 wt% or less. The aromatic content is less critical but 10 - 25 vol% is an excellent level to achieve, if possible. The yield of permeate is not so critical, as long as it is about 60 vol% of the feed -- the high-sulfur reject can be recovered and recycled to hydrogenation units for either reuse of feed to other refinery processing units.

## Water Cleanup Is a Good Challenge For Membranes

During the presentations at **DOE** one of the achievements discussed was the use of the inorganic membranes to desalinate water, using reverse osmosis. **DOE personnel** suggested that this technique be tried on removing benzene from refinery waste water. Currently, standards are being proposed to have a maximum specification of 0.5 ppm by weight of benzene in water. This is a crucial specification, if adopted. It is not clear that even activated carbon treatment can reach this level. If membranes can allow water to permeate the pores, which retaining the benzene, the membranes would have a most valuable application here. It should be remembered that several stages of membranes can be used, if needed, to achieve high water purity.

A simple first test would be to use a water feed which is saturated with benzene. Benzene has a solubility in water of about 700 ppm by weight. The experiments should be run at a wide range of pressures and temperatures to see just how much benzene can be removed. The results from one stage operation can be extrapolated to multiple stages. Any set of conditions which would give more than 50 wt% removal in one stage would be very encouraging.
It would be best to see the results of this first phase in order to define a further set of tests.

## Summing Up....

Overall, inorganic membranes have the potential for several major applications in refineries, assuming their essential performance can be verified.

- Several gaseous systems offer good applications
  - Hydrogen recovery and purification
  - Improved sulfur recovery from dilute $H_2S/CO_2$ mixtures
- Liquid separations present a good challenge to larger pore membranes -- there is no corresponding application for organic

membranes, as in the case of hydrogen recovery. Some simple systems have been suggested to explore this "wide open" area:

- Separation of normal hexane and cyclohexane
- Removal of sulfur and aromatics from diesel fuel
- Removal of benzene from water

- The essential values of the membranes in these applications can be verified in simple experiments. The range of operating conditions, together with the target results have been summarized for each case as a guide so that a "report card" can be given on the technical success.

- SFA Pacific will continue to develop the economic incentives for typical refining situations to aid in assessing the results of this experimental work. SFA will be happy to consult further with DOE on any aspects of this program.

# ATTACHMENT 1

## DESCRIPTION OF COMMERCIAL MEMBRANES FOR HYDROGEN RECOVERY (TAKEN FROM SFA PACIFIC'S "HEAVY OIL UPGRADING: PHASE III")

There are many suppliers for these systems, which incidentally also cover applications other than hydrogen recovery, though hydrogen recovery is the most prevalent application. A list of the range of applications and vendors is shown in Table 8-10 [8]. For example, Permea (a subsidiary of Monsanto) has supplied more than 120 companies with its Prism systems.

Table 8-10

Commercial-Scale Membrane Suppliers

| Company | $CO_2$ | $H_2$ | Air | | Other* |
|---|---|---|---|---|---|
| | | | $O_2$ | $N_2$ | |
| A/G Technology (AVIR) | X | | X | X | |
| Air Products (Separex) | X | X | | | X |
| Asahi Glass (HISEP) | | | X | X | |
| Cynara (Dow) | X | | | | |
| Dow (Generon) | | | X | X | |
| DuPont | | X | | | |
| Grace Membrane Systems | X | X | | | X |
| International Permeation | X | | | | X |
| Membrane Technology & Research | | | | | X |
| Monsanto | X | X | X | X | X |
| Nippon Kokan K.K. | | | | | X |
| Osaka Gas | | | X | | |
| Oxygen Enrichment Co. | | | X | | |
| Perma Pure | | | | | X |
| Techmashexport (USSR) | | | X | | |
| Teijin Ltd. | | | X | | |
| Toyobo | | | X | | |
| Ube Industries | | X | | | X |
| Union Carbide (Linde) | | X | X | X | |
| UOP/Union Carbide | | X | | | |

*Includes solvent vapor recovery, dehumidification and/or helium recovery membranes.

Source: W.R. Grace

Membranes perform very effectively on high-pressure hydrogen streams. The yield of hydrogen and the purity of the product hydrogen can be adjusted by changing the product pressure. This is illustrated in Figure 8-11 [9]. For hydrotreater offgas of 70-75 vol% hydrogen, 95 vol% recovery is easily achievable at purities of 95 vol% or more.

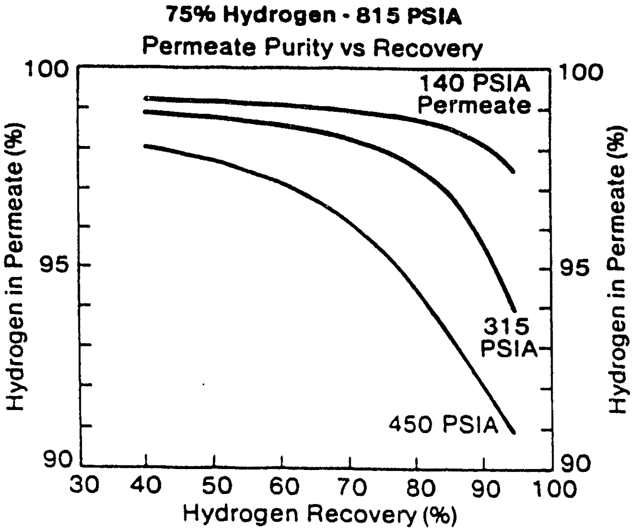
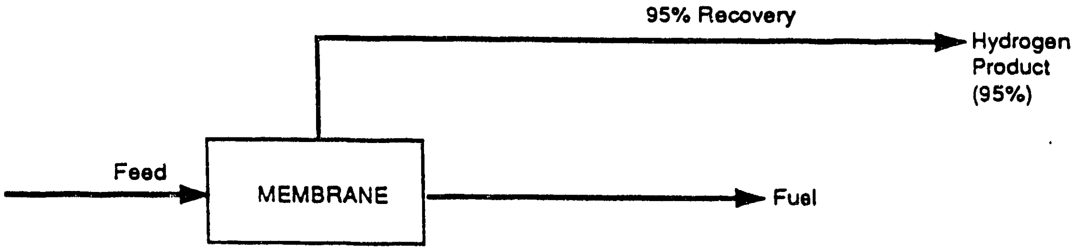


Figure 8-11
Recovery of Hydrogen from Hydrotreater Purge Gases

Source: Conoco

Under these conditions, the economics for using membranes are attractive. SFA Pacific received investments from three licensors (UOP, Separex, and Permea) for systems recovering hydrogen from purge gases [10, 11, 12]. These investments were provided for processing 10 MMscf/sd of gas containing 70 vol% $H_2$, 20 vol% $CH_4$, and 10 vol% $C_2H_6$. The investments provided ranged from $450M to $700M. The typical material balance is illustrated in Figure 8-12, where 95 vol% recovery is achieved and the product contains 95 vol% hydrogen.



| | | | |
|---|---|---|---|
| psig: | 650-1000 | 650-1000 | 250 |
| MM scf/d: | | | |
| $H_2$ | 7 | 0.35 | 6.65 |
| $C_1$ | 2 | 1.65 | 0.35 |
| $C_2$ | 1 | 1.00 | 0.00 |
| Total | 10 | 3.00 | 7.00 |

SOURCE: SFA Pacific, Inc.

FIGURE 8–12 A TYPICAL BALANCE FOR HYDROGEN RECOVERY BY MEMBRANES

The estimated cost of recovering hydrogen, based on the capital and operating costs provided by vendors, is illustrated in Table 8-11 using a membrane cost of $700M, combined with the associated offsite and engineering charges, etc. If the hydrogen stream is valued only at fuel value, there is a significant incentive to apply membranes, since the capital charges and operating cost are relatively low. The recovered hydrogen (at 250 psig, in this case) would cost only $1.00/Mscf, compared to $2.44/Mscf if it were manufactured in a large unit.

**Table 8-11**

**Typical Estimated Costs for**
**Recovering Hydrogen by Membranes**

| | $/Day | $/Mscf |
|---|---|---|
| Feed fuel value @ $2.50/MMBtu | 14,900 | 2.14 |
| Capital charges @ 20%/yr | 680 | 0.10 |
| Operating costs | 270 | 0.04 |
| Fuel product credit @ $2.50/MMBtu | (8,880) | (1.28) |
| Net charge for $H_2$ recovered | 6,970 | 1.00 |

Basis: Flows given in Figure 8-12

Source: SFA Pacific, Inc.

This is a very minor cost, and this technology would probably be a good route even for smaller capacities. From our discussions with vendors, the units are all available in a skid-mounted form, an advantage when considering lower flow rates.

### Hydrogen Recovery by Pressure Swing Adsorption (PSA)

Pressure swing adsorption has also been widely used in many applications, beginning in the early 60s. The first and most numerous applications were in gasoline filling stations to dry compressed air for filling tires. PSA has become extremely popular in recent years for hydrogen purification two reasons:

- The development of reliable flow-control valves
- The use of microcomputers to control the actuation sequence of the flow-control valves

The process uses a series of fixed beds filled with an appropriate molecular sieve for adsorbing heavy components other than hydrogen. The general scheme is illustrated in Figure 8-13 [13].

# Attachment 2

## Partial Oxidation Processes For Making Hydrogen
## (TAKEN FROM SFA PACIFIC'S "HEAVY OIL UPGRADING: PHASE III")

## Partial Oxidation is a Well-Established Route to Hydrogen

Partial oxidation is an old and well-proven process for making synthesis gas from petroleum residues. Other feedstocks can be used--for example, thermally cracked tars, visbreaker bottoms and asphaltenes. There have been many recent developments in applying the technique to make synthesis gas from coal. These processes can be used for petroleum coke as well. Most of the applications on solid fuels have been for making chemicals or for power generation, using coal gasification with combined-cycle power generation technology. The main emphasis for our consideration is for making hydrogen from liquid residues. There are two major processes for producing hydrogen by partial oxidation:

- Shell Gasification Process (SGP)
- Texaco Synthesis Gas Generating Process (SGGP)

Both processes have been widely used commercially. Lurgi, the licensor for SGP, lists more than 140 plants worldwide for the Shell technology. Texaco has about 100 plants in operation. As noted earlier, most of these applications have to do with manufacturing CO and $H_2$ for conversion to chemicals, but the technique is also used for hydrogen manufacture. The two technologies are similar in the nature of the gasification reactions and high-temperature reactors. However, the downstream configurations can vary significantly: radiant heat boilers or water quenching, acid gas removal, soot recycle, and/or final purification. The specific configurations given us by Lurgi (for the Shell process) and Texaco reflect their judgments as to the best choices for hydrogen. Most of the designs were originally used for ammonia and $CO/H_2$ synthesis gas manufacture, and this may account for some of the differences in the specific choices made.

### Shell Gasification Process

The heart of the SGP process is the gasification reactor, waste heat boiler, and soot recovery to make a solids-free synthesis gas. This is illustrated in Figure 8-4.

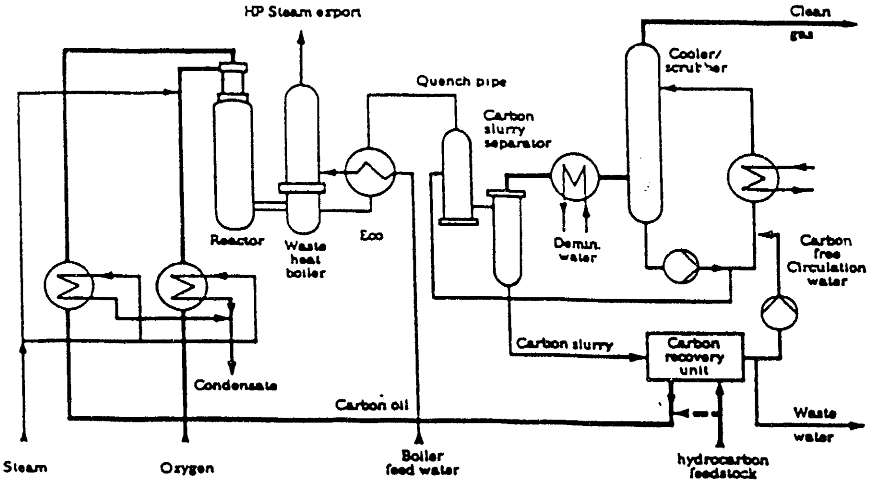
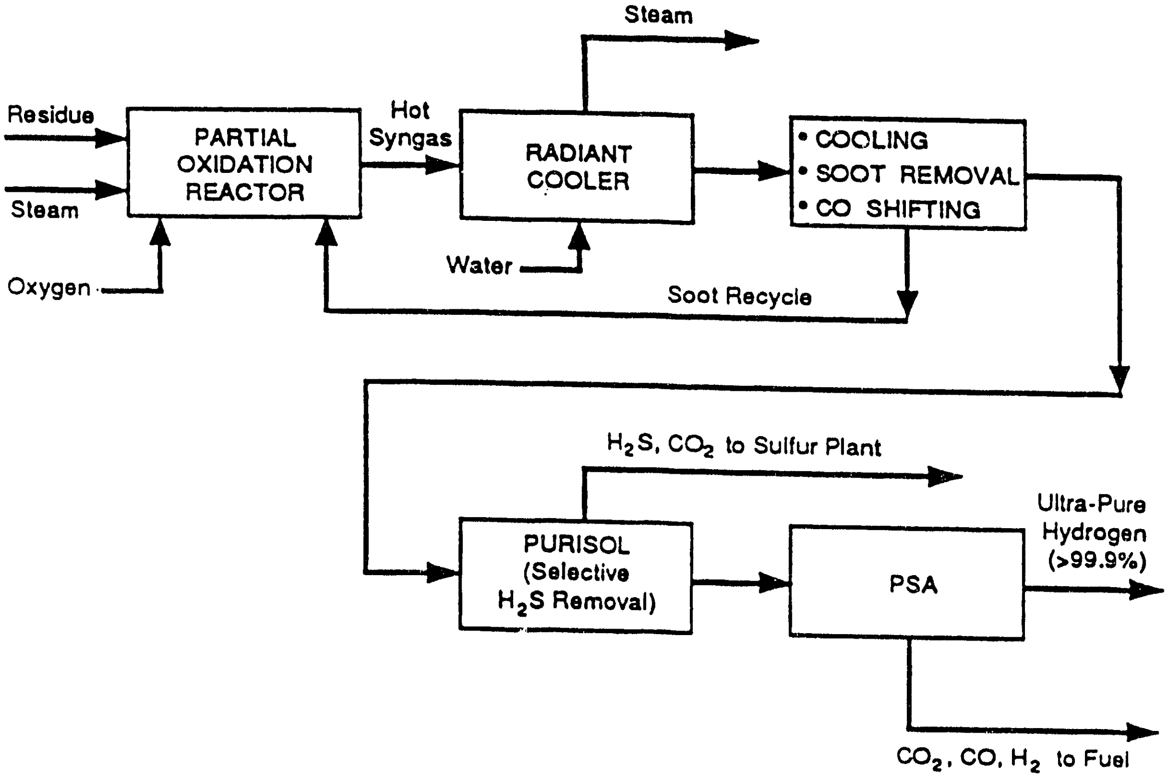


Figure 8-4

Shell Gasification Process: SynGas Generation

Source: Lurgi

Lurgi's recommended scheme for conversion to hydrogen is illustrated in Figure 8-5 [4].



SOURCE: SFA Pacific, Inc.

FIGURE 8-5 HYDROGEN BY SHELL GASIFICATION PROCESS — SIMPLIFIED FLOW DIAGRAM

The synthesis gas, following soot recovery, is shifted and the $H_2$ removed by washing with a physical solvent. Lurgi prefers its Purisol process, which makes a suitable gas for a Claus sulfur plant. The sulfur-free synthesis gas still contains a substantial amount of CO and $CO_2$. This goes to a PSA unit to provide the enriched hydrogen product.

Lurgi provided SFA Pacific with its estimated investment and utilities for producing 100 MMscf/sd of hydrogen using SGP [5]. The investment was $88 million for the SGP. The basic utilities are given in Table 8-6. There is a substantial export of energy in the process as configured here--both from the steam produced and the fuel gas purged from the PSA unit.

### Table 8-6

### Hydrogen Manufacture by Shell Gasification Process: Major Requirements

| | Units/Mscf $H_2$ |
|---|---|
| Vacuum residue (4.2 wt% S) | |
| -lb | 28.7 |
| -MBtu (HHV) | 525 |
| Oxygen, Mscf | 0.323 |
| Net steam export, lbs | 13.8 |
| Fuel gas export, MBtu | 89.3 |
| $H_2$ product pressure, psig | 355 |

Source: Lurgi

The cost of hydrogen using our base case costs is shown in Table 8-7. We have assigned an arbitrary level of $10/bbl to the vacuum residue, together with $50/t for the oxygen. The base case cost of hydrogen for these values would be $2.55/Mscf. The breakeven value for the residue, to provide hydrogen from steam reforming natural gas (at $2.50/MMBtu) at $2.44/Mscf (Table 8-3), is $8.70/bbl. This is an attractive value, particularly if a cracked stock is used. The byproduct credits for steam and fuel gas are significant. Therefore, it is important to make sure there is an effective way to use these streams.

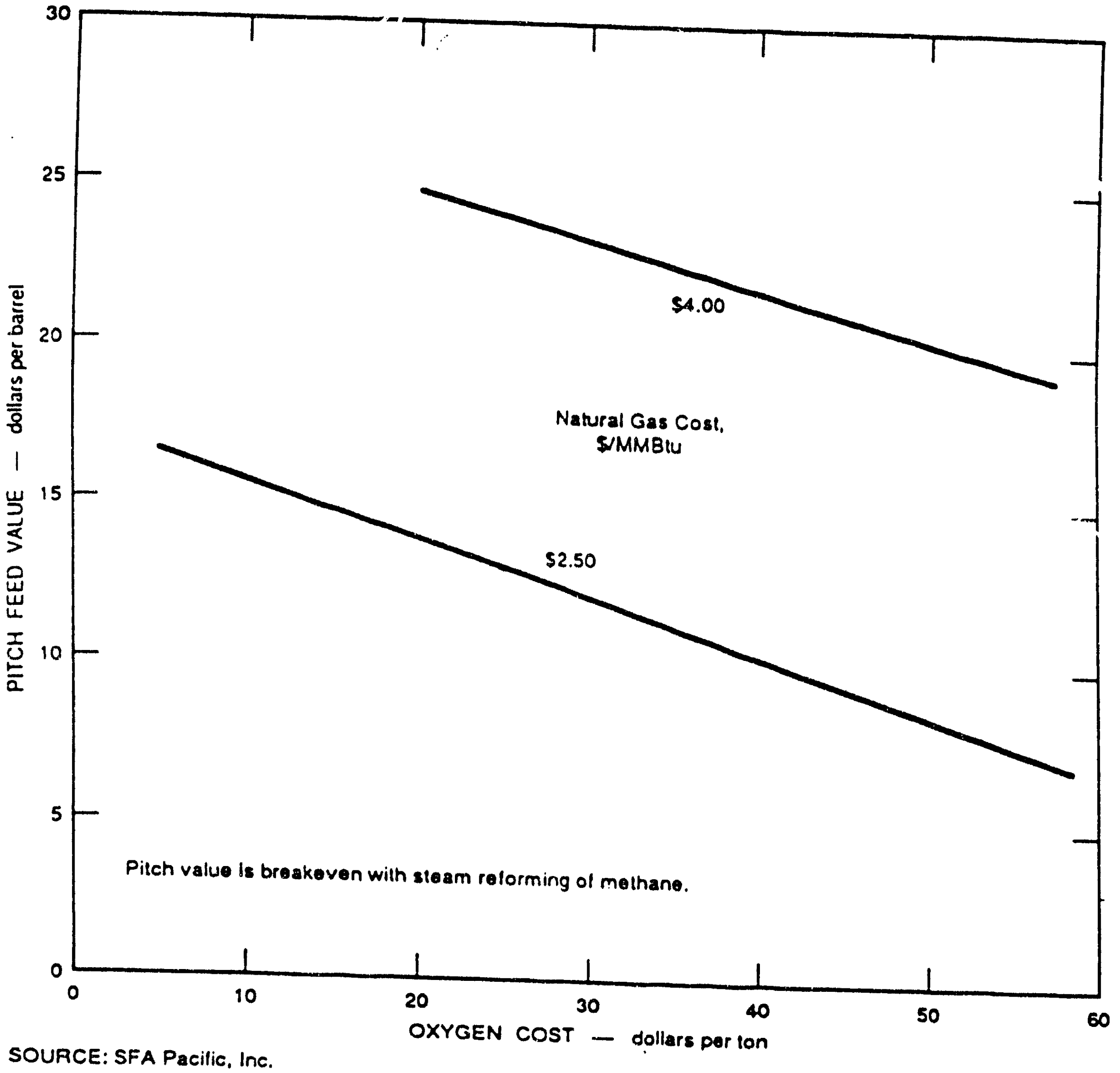
### Table 8-7

### Cost of Hydrogen by the Shell Gasification Process: Base Illustrative Case

| | $/Mscf $H_2$ |
|---|---|
| Capital charges @ 20%/yr | 0.95 |
| Operating costs (labor, maintenance, etc.) | 0.38 |
| Vacuum residue @ $10/bbl | 0.83 |
| Oxygen @ $50/t | 0.73 |
| Power @ $.05/Kwh | 0.03 |
| Steam credit @ $5/Mlbs | (0.07) |
| Fuel gas credit @ $2.50/MMBtu | (0.24) |
| Net sulfur recovery cost | 0.04 |
| Compression credit | (0.10) |
| Total | 2.55 |
| Residue breakeven value for $H_2$ cost of $2.44/Mscf | 8.70 |

Source: SFA Pacific, Inc.

The impact of oxygen cost, together with natural gas cost, is illustrated in Figure 8-6. For the range of gas costs that we think are applicable, above $2.50/MMBtu, the residue value rises well above $10/bbl. Since the oxygen demand for partial oxidation is almost twice that for the ICI design, the cost for oxygen would be expected to be less for the larger oxygen plant.



SOURCE: SFA Pacific, Inc.

FIGURE 8-6 HYDROGEN MANUFACTURING COSTS BY SHELL GASIFICATION PROCESS

## Texaco Synthesis Gas Generating Process (SGGP)

The gasification portion of Texaco's SGGP is shown in Figure 8-7 [6]. The oxygen, oil, and some steam flow to the gasifier, where high-temperature reactions take place. The hot synthesis gas is immediately quenched with water, with the resulting cooled gas containing a large amount of steam. Texaco has commercial experience with a radiant waste heat boiler. However, for hydrogen, it often chooses the water quench method, which lowers plant investment. The soot formed during the reaction is withdrawn with the water stream, and the soot subsequently recovered and recycled. The soot-free synthesis gas is then sent to further processing. The conversion to hydrogen is illustrated in Figure 8-8. Several stages of shifting are required to reduce the CO to a low level (generally less than 1 wt%). The gas then flows to a Rectisol unit, where a concentrated $H_2S$ stream is produced, and the balance of the $CO_2$ removed and vented. Generally, the synthesis gas is then methanated to remove the traces of CO, and a product purity of 98-99 vol% is obtained. As noted in Section 6, Texaco has found that it is not necessary to methanate the CO.

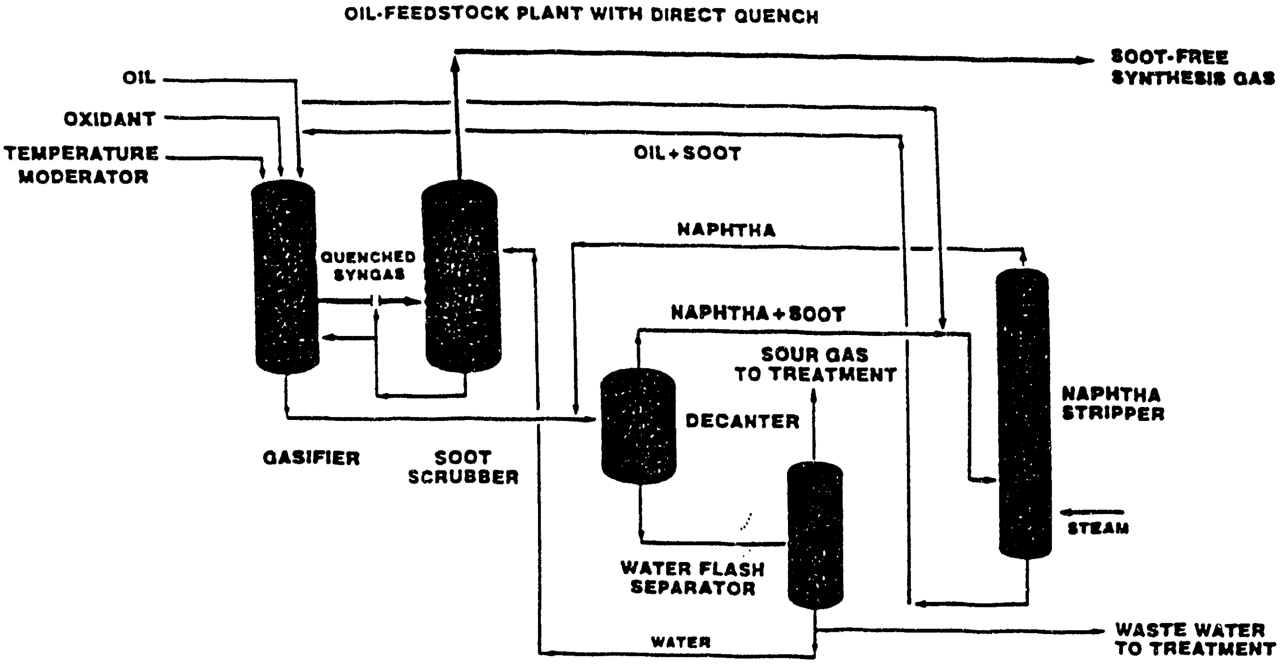
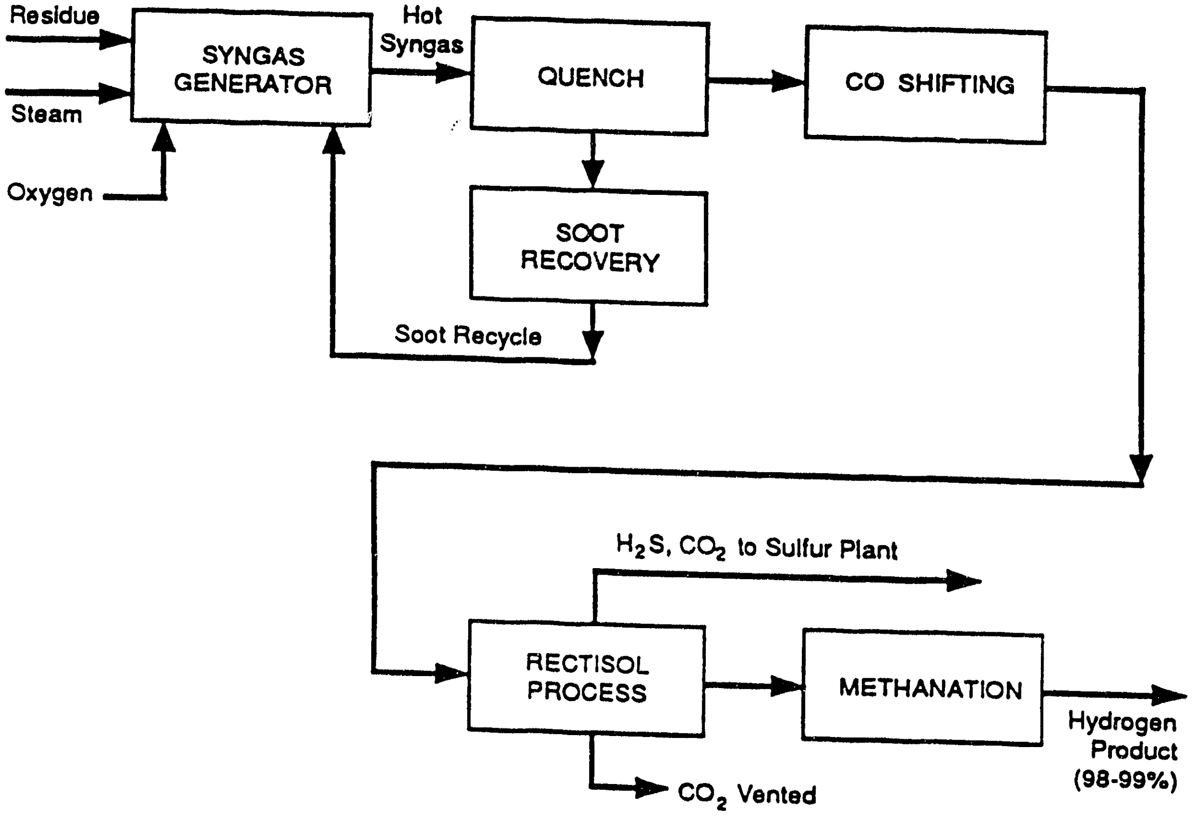


Figure 8-7
Texaco Synthesis Gas Generation Process

Source: Texaco, Inc.



SOURCE: SFA Pacific, Inc.

FIGURE 8–8 HYDROGEN BY TEXACO SYNTHESIS GAS GENERATION PROCESS — SIMPLIFIED FLOW DIAGRAM

Texaco provided SFA Pacific with an estimate for a plant using this arrangement of processes to produce 100 MMscf/sd [7] at an investment of $107 million. The utility requirements are given in simplified form in Table 8-8. The Texaco design uses less feed and oxygen but consumes more steam than the Lurgi design for Shell's SGP. This is the result of Texaco's design using the water quench cooling technique and the Rectisol process. The cost of making hydrogen by Texaco's SGGP is illustrated in Table 8-9, and is essentially the same as for the Shell example. The lower oxygen and residue use are offset partially by loss of the fuel credit.

Table 8-8
Hydrogen Manufacture by
Texaco Syngas Process: Major Requirements

| | Units/Mscf $H_2$ |
|---|---|
| Vacuum residue, | |
| -lb | 23.1 |
| -MBtu (HHV) | 423 |
| Oxygen, Mscf | 0.294 |
| Steam consumption, lb | 10.6 |
| $H_2$ product pressure, psig | 500 |

Source: Texaco

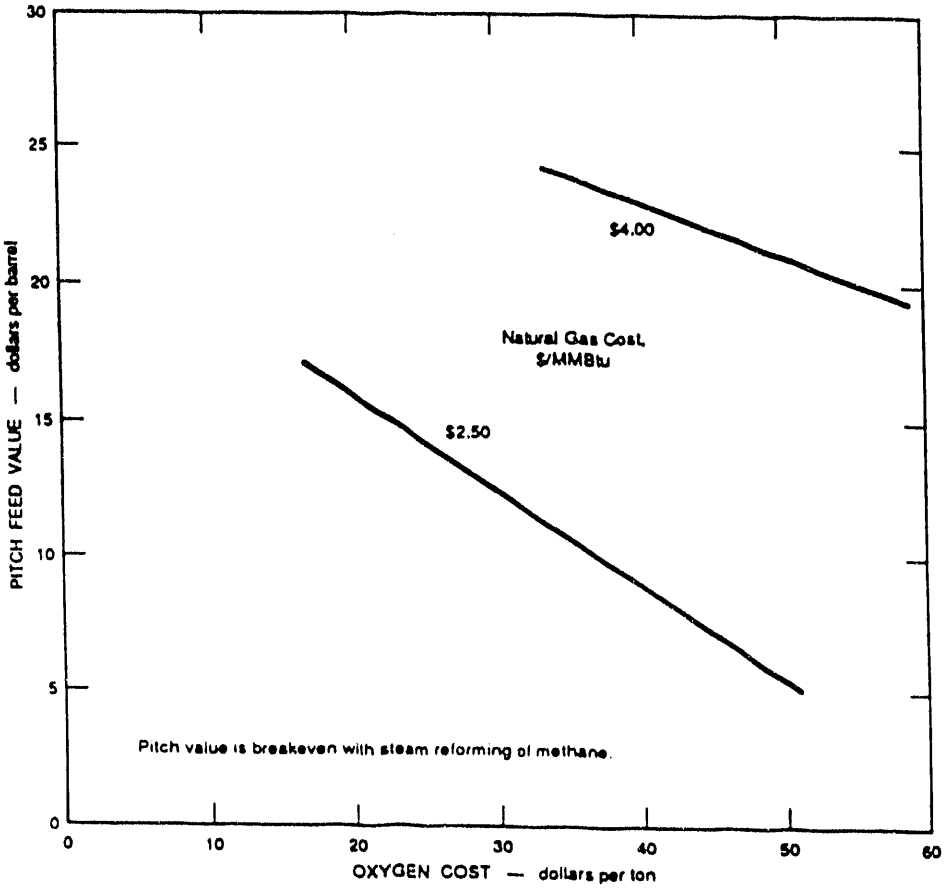
Table 8-9
Cost of Hydrogen by the Texaco Syngas Process:
Base Illustrative Case

| | \$/Mscf $H_2$ |
|---|---|
| Capital charges @ 20%/yr | 1.03 |
| Operating costs (labor, maint., etc.) | 0.41 |
| Vacuum residue @ \$10/bbl | 0.60 |
| Oxygen @ \$50/t | 0.62 |
| Steam consumed @ \$5/Mlb | 0.04 |
| Sulfur recovery | 0.03 |
| Compression credit | (0.15) |
| Total | 2.60 |
| Residue breakeven value for $H_2$ cost of \$2.44/Mscf | 8.20 |

Excludes contingency, engineering & certain items. See Appendix A for how items were added to arrive at final plant cost.

Source: SFA Pacific, Inc.

The impact of various oxygen and natural gas costs is shown in Figure 8-9.



SOURCE: SFA Pacific, Inc.

FIGURE 8-9 HYDROGEN MANUFACTURING COSTS BY TEXACO SYNTHESIS GAS GENERATION PROCESS

## Some Process Variations Can Make Partial Oxidation More Attractive

For this analysis, both Lurgi and Texaco provided us with process arrangements that they judged were adequate for our screening purposes. It is quite possible that the specific process configurations could be modified to improve the economics still further. Some of these variations are described below. Readers wishing to consider these in more detail should discuss them with the licensors or appropriate contractors for each technology.

The simplest modification is to use feedstocks that are even more carbonaceous than a normal vacuum residue. Some examples are visbreaker bottoms, asphaltenes from de-asphalting processes, and petroleum coke. Visbreaker bottoms are routinely used as feed to SGP units in Europe [14].

This use can have a significant impact on economics. For example, in Section 9, we use a base value of $5/bbl for high-sulfur pitch and $20/ton for coke and asphaltenes. If these materials have a value of $10/bbl as partial oxidation feed, the equivalent values of coke (in a slurry with vacuum residue) and molten asphaltenes rise to almost $60 per ton. These higher values can add appreciably to the net realizations for the delayed coking, thermal hydrocracking and deasphalting cases: about $0.20 to $0.40/bbl of crude for Maya. If coke or asphaltenes are fed as solids slurried with water, the oxygen requirements would be about 25% higher than for a hydrocarbon liquid feed, which would diminish the economic attractiveness. One must watch the hydrogen balance closely to see if all the byproduct can be consumed. In particular, the asphaltene and pitch yields at 85% conversion (or more) are low enough that they are totally consumed in making hydrogen.

Several alternative methods for $H_2S$ and $CO_2$ removal are available, some of which might reduce costs substantially, including the use of physical solvents (such as Selexol) or mixed physical solvent/amines (such as Sulfinol). These could be substantially cheaper than Rectisol. While Rectisol is a highly effective process for completely removing many contaminants from the synthesis gas, such high purification may not be necessary for hydrogen manufacture. For the case provided us by Texaco, the Rectisol section represents more than half the investment. In addition, the final PSA purification step can be optimized by using higher operating pressures, reducing fuel loss to purge.

Alternate financing arrangements could substantially improve economics as well. It might be possible to have industrial gas suppliers provide hydrogen from a pipeline, as is done in parts of the United States and Europe, or provide hydrogen generation facilities on some form of lease-back basis. Some alternate joint agreements are possible. For example, the refiner might supply the residue feed and high-pressure steam (or power) for a separate partial oxidation and oxygen plant to make hydrogen for the refiner, with the excess going into a pipeline for other users.

## Hydrogen Recovery from Purge Gases is Very Attractive

There are three routes to recovering hydrogen from hydrotreater purge gases:

- PSA
- Membranes
- Cryogenics

These purge gases contain more than 50 vol% hydrogen, and may be sent to the refinery fuel system. When hydrogen purity is above 50 vol%, both membrane systems and PSA can be used effectively to recover most of the hydrogen. These approaches have been taken in many applications. Below 50 vol%, cryogenic techniques are preferred.

### Hydrogen Recovery by Membranes

Membranes have become well established as a method for recovering hydrogen from high-pressure gases. The membrane is made from various polymers permeable to diffusion of gases. Diffusion rates of gases differ substantially depending

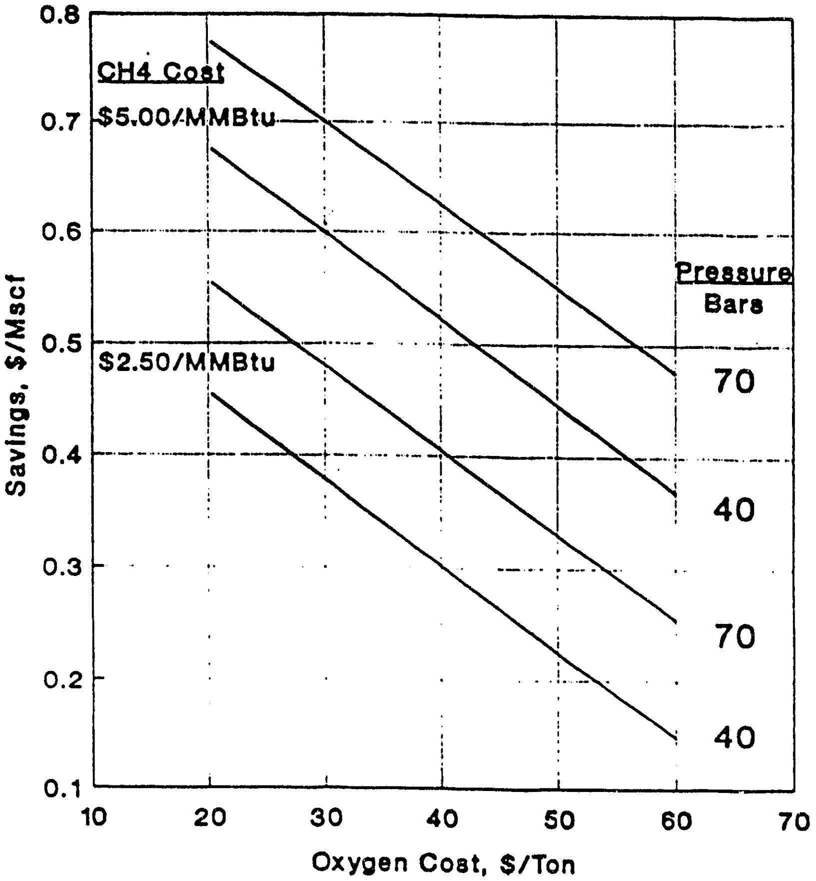
Attachment 3

# Using New Acid Gas Removal Systems Improves Attractiveness of Partial Oxidation

(TAKEN FROM SFA PACIFIC'S "HYDROGEN: MANUFACTURE AND MANAGEMENT")

Figure 7-2

ICI GHR DESIGN SAVINGS OVER CONVENTIONAL REFORMERS



Source: SFA Pacific, Inc.

## Partial Oxidation Process

As part of its Phase III study on heavy oil upgrading, SFA Pacific asked both Texaco and Lurgi to provide estimates for making hydrogen by the partial oxidation of residues.

Texaco patterned its flow diagram after its Convent, Louisiana unit [4], using a prior design on an aromatic, medium-sulfur H-Oil vacuum bottoms feed as the basis. It used three stages of CO shifting after a water quench of the hot gas. It also used the Rectisol process to remove $H_2S$ and $CO_2$ selectively prior to methanation. At our request, Texaco provided some basic flow rates and compositions, along with an investment breakdown for the various component sections.

Lurgi provided an overall investment for the Shell partial oxidation process combined with the use of a physical solvent wash (Purisol) to remove $H_2S$ and a PSA to remove other impurities and provide high-purity hydrogen. Lurgi also included a waste heat boiler, rather than using a water quench. Lurgi did not provide any details on the source or composition of the residual feedstock.

The major requirements of the two processes are summarized in Table 7-4. The Shell process has a slightly lower investment than the Texaco due to the Shell design's use of a cheaper $H_2S/CO_2$ removal system. The Shell design also uses more residue feed and oxygen, while producing a large amount of fuel gas for export (the PSA purge). This fuel gas is about 20% of the feed heating value, and equal to about 31% of the product hydrogen heating value.

Table 7-4

PROCESS REQUIREMENTS FOR PARTIAL OXIDATION OF VACUUM RESIDUES

(Plant size: 100 MMscf/sd of hydrogen)

| | Units/Mscf $H_2$ | |
|---|---|---|
| | Texaco | Shell |
| Vacuum Residue | | |
| - lb | 23.1 | 28.7 |
| - MBtu | 423 | 525 |
| Oxygen, Mscf | 0.294 | 0.323 |
| Net steam export, lb | (10.6) | 13.8 |
| Fuel gas export, MBtu | -- | 89.3 |
| $H_2$ product pressure, psig | 500 | 355 |
| Investment (no contingencies), $ million | 107 | 88 |

Source: References 4,5

Overall, the economics of the two processes are similar, as shown in Table 7-5. In addition, the costs are close to those for the base case of methane reforming. The breakeven costs for the residues (to make hydrogen at $2.49/Mscf) are in the range of $12-14/bbl.

Table 7-5

COST COMPARISONS BETWEEN TWO PARTIAL OXIDATION PROCESSES

| | $/Mscf $H_2$ | |
|---|---|---|
| | Texaco | Shell |
| Vacuum residue @ $10/bbl | 0.60 | 0.74 |
| Oxygen @ $40/ton | 0.45 | 0.55 |
| Steam @ $5/Mlb | 0.04 | (0.07) |
| Power @ 5¢/kWh | 0.01 | 0.03 |
| Fuel credit @ $2.50/MM Btu | -- | (0.24) |
| Compression credit | (0.11) | (0.04) |
| Operating costs | 0.39 | 0.35 |
| Capital charges @ 20%/yr | 0.98 | 0.88 |
| Total | 2.36 | 2.20 |
| • Breakeven residue cost to make $H_2$ @ $2.49/Mscf (in $/bbl) | 12.17 | 13.92 |
| • Effect of 15% extra investment, $/Mscf $H_2$ | +0.21 | +0.18 |

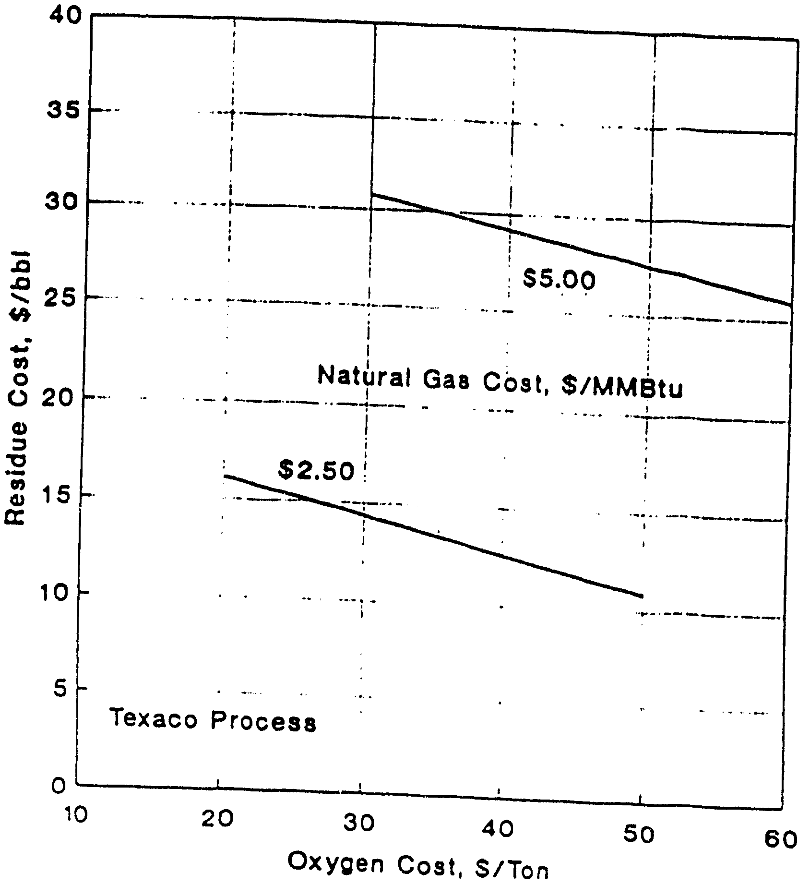
Source: SFA Pacific, Inc.

Partial oxidation becomes very attractive if the price of methane rises above $2.50/MMBtu, or if oxygen costs drop below $40/ton. This is shown in Figure 7-3, where the breakeven residue cost is shown for the Texaco design.

When low-value feeds (such as visbreaker bottoms or asphaltenes) are available, partial oxidation using these feeds can become more attractive than when using residues. Partial oxidation thus becomes an environmentally and economically effective way to make hydrogen.

Figure 7-3

BREAKEVEN RESIDUE COST VIA PARTIAL OXIDATION WITH STEAM METHANE REFORMING



Source: SFA Pacific, Inc.

<u>Enhanced Economics with New Amine Scrubbing Systems</u>

Lurgi was asked to provide a breakdown of the investments and flow rates for its Shell design, to enable us to define the merits of alternate $H_2S/CO_2$ removal steps. Lurgi declined, citing its very heavy workload and acknowledging the design to be an old one. As a result, we have used the Texaco design as the basis for this sub-section. Both processes are amenable to these improvements.

In the Texaco design, use of the Rectisol process, though it is an excellent and well-proven system, turned out to be very expensive. The combined Rectisol/refrigeration system amounted to 50% of the total investment. Normally, this system is used to ensure removal of all sulfur to levels less than 1 ppmv to protect the nickel catalyst in the final methanation step. Texaco has found that this step is not really needed--the presence of less than 0.6 vol% CO is acceptable in the H-Oil unit at its Convent refinery.

SFA Pacific discussed the possibility of using the new amine systems instead of Rectisol with several developers of these systems, including BASF, UOP, Dow Chemical, and Shell Oil, U.S.A. All agreed that their systems could remove $H_2S$ and COS to less than 1 ppmv and $CO_2$ to less than 1,000 ppmv. BASF has incorporated its activated MDEA process into its Texaco partial oxidation plant in Germany with excellent results: total sulfur is well below 1 ppmv, and $CO_2$ is below 50 ppmv.

We provided the developers with the flow rates and composition of the wet synthesis gas after 3 stages of CO shifting. In addition, we changed the feed from medium-sulfur H-Oil bottoms to Arabian Heavy vacuum residue. We asked the developers to give us investments and utilities needed for their preferred process. Only UOP responded early enough to allow us to meet our schedule, so these are the costs used. In general, the other processes should be competitive.

UOP provided two basic schemes [6]:

- A non-selective hot carbonate (Benfield)
- A selective UCARSOL amine

SFA Pacific revised the flow diagram to use the UCARSOL amine with the residue partial oxidation case. We calculated the new heat balance and investments. Even using the selective amine, the $H_2S$ concentration in the acid gas stream for the sulfur plant is only 7 vol%, too lean for a regular Claus unit. In addition, it should not be mixed with the regular refinery $H_2S$ stream, since the $CO_2$ would interfere with the amine scrubber in the Claus tailgas unit. As a result, we have used a catalytic oxidation process (oxygen-blown) as the primary converter for this stream. The tailgas recovery section reduces the $SO_2$ back to $H_2S$, and a wet oxidation process (such as Lo-Cat or Sulferox) removes the residual $H_2S$.

The cost of amine scrubbing is well below that of Rectisol/ refrigeration: about $16 MM compared to $46 MM. The impact on total investments is substantial, as shown in Table 7-6.

This reduction in investment carries over to the economics, as shown in Table 7-7. The difference in hydrogen cost shown for the Rectisol-based Texaco system in Table 7-7 and that shown in Table 7-5 is due primarily to the lower costs of the gas treating and sulfur plants, resulting from the lower sulfur content of the pitch used in the case shown in Table 7-5.

## Table 7-6

## LOWER INVESTMENTS WITH NEW AMINE SYSTEMS

| | Investment (mid-1991), $MM for 100 MMscf/sd $H_2$ | |
|---|---|---|
| | Rectisol | UOP Amine |
| Syngas generation | 29.6 | 29.6 |
| CO shifting | 13.6 | 13.6 |
| Acid gas removal | 41.2 | 15.8 |
| Refrigeration | 5.3 | -- |
| Sulfur plant | 5.1 | 8.4 |
| Utilities | 7.6 | 1.8 |
| Contingency | 13.5 | 9.0 |
| Offsites | 34.9 | 23.5 |
| | 148.1 | 99.0 |
| Engineering | 14.8 | 9.9 |
| Startup | 7.4 | 5.0 |
| Working capital | 1.5 | 1.1 |
| Royalties | 3.0 | 2.0 |
| Total | 174.8 | 116.9 |

Source: SFA Pacific, Inc.

## Table 7-7

## AMINE SYSTEM IMPROVES PARTIAL OXIDATION ECONOMICS

| | $H_2$ Cost: $/Mscf | |
|---|---|---|
| | Rectisol | UOP Amine |
| Vacuum residue @ $10/bbl | 0.63 | 0.63 |
| Oxygen @ $40/ton | 0.47 | 0.47 |
| Steam @ $5/M lb | 0.04 | 0.10 |
| Power @ $0.05/kWh | 0.15 | 0.05 |
| Other operating costs | 0.47 | 0.31 |
| Capital charges @ 20%/yr | 1.07 | 0.71 |
| Sulfur credit @ $120/lt | (0.12) | (0.12) |
| Compression credit | (0.18) | (0.18) |
| | 2.53 | 1.97 |
| Breakeven residue value, $/bbl | 7.80 | 17.50 |
| Impact of +15% investment on hydrogen cost | +0.25 | +0.16 |

Source: SFA Pacific, Inc.

The cost of hydrogen is well below that from methane reforming. Even with an extra 15% contingency added to the investment, the new amine route remains quite attractive.

## Hot Carbonate Scrubbing

Texaco recently announced its "HyTEX" process for partial oxidation of refinery fuel gas to make hydrogen [7]. The NPRA paper on the process was very general, giving no specific economics. At our request, Texaco gave us an estimate for the synthesis gas generation section using natural gas as the feedstock [8]. We then calculated the heat and material balances to produce 100 MMscf/sd. The various sections were prorated from Texaco's residue case.

For the $CO_2$ removal step, we used UOP's data on the Benfield hot potassium carbonate process. Since there is no sulfur present, this process is less costly than the selective amine system.

For this higher hydrogen-content feed, investment costs drop markedly relative to using residues. The sulfur plant is eliminated, and there is less CO shifting and $CO_2$ removal. The total investment is about $80 MM, as shown in Table 7-8.

### Table 7-8

### INVESTMENTS FOR PARTIAL OXIDATION OF METHANE

| | Investment (mid-1991), $MM for 100 MMscf/sd $H_2$ |
|---|---|
| Syngas generation | 23.8 |
| CO shifting | 10.8 |
| Cooling | 2.6 |
| $CO_2$ removal (Benfield) | 7.1 |
| Utilities | 1.2 |
| Offsites | 15.8 |
| Contingency | 6.1 |
| Subtotal | 67.4 |
| Engineering | 6.7 |
| Startup | 3.3 |
| Working capital | 0.7 |
| Royalties | 1.4 |
| Total | 79.5 |

Source: SFA Pacific, Inc.

The principal costs of hydrogen center on the methane and oxygen costs, as shown in Table 7-9.

Table 7-9

HYDROGEN COST FOR PARTIAL OXIDATION OF METHANE

| | $H_2$ Cost: $/Mscf |
|---|---|
| Natural gas @ $2.50/MMBtu | 0.92 |
| Oxygen @ $40/ton | 0.43 |
| Operating costs | 0.18 |
| Capital @ 20%/yr | 0.46 |
| Steam credit @ $5/M lb | (0.10) |
| Compression credit | (0.18) |
| Total | 1.71 |
| • Impact of +15% on investment | +0.08 |
| • Impact of adding methanation | +0.04 |

Source: SFA Pacific, Inc.

This cost of $1.71/Mscf is well below the base case for steam reforming. The investment is lower, and there is no combustion of hydrogen and CO (from the PSA) in the reformer furnace.

Adding a methanation step or increasing contingencies has only a minor effect. It should be remembered that the use of refinery fuel gas would add to the costs because of the presence of sulfur and the need to compress to 700-800 psig.

## Partial Oxidation of Petroleum Coke

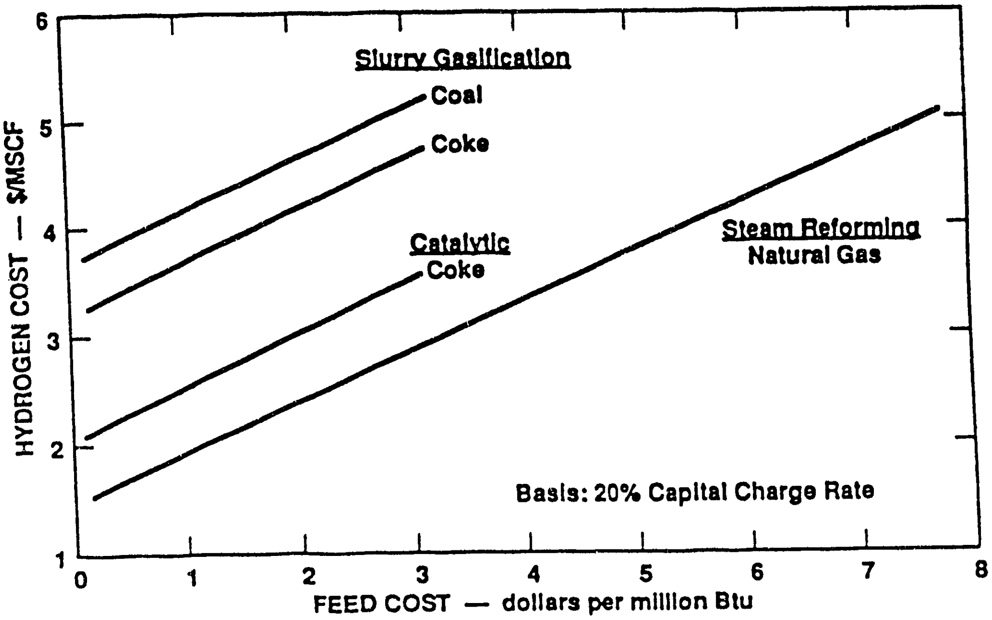
High-carbon solids, such as petroleum coke and coal, are well-suited technically for making hydrogen by partial oxidation. Texaco has tested a wide range of such feeds in its pilot units. In addition, several commercial plants operate partial oxidation units with coal as a feedstock, as a slurry with water. Texaco did not provide us with any current estimates for using petroleum coke to make hydrogen.

As part of our 1983 multisponsored report on synthesis gas [9], SFA Pacific studied making a mixture of CO and $H_2$, using a much different basis than this study. A self-contained plant, using internally generated power for an on-site oxygen plant, was the base case. In addition, a lower coke slurry was used compared to what Texaco now says is practical.

These data were used to estimate the costs of hydrogen for our report to the National Research Council on Liquid Transportation Fuels in 1989 [10]. The costs of hydrogen from methane, coal, and petroleum coke are shown in Figure 7-4.

Figure 7-4

HYDROGEN MANUFACTURING COSTS



Source: SFA Pacific, Inc.

Even for zero-value coke, the hydrogen cost is about \$3.20/Mscf--equivalent to methane at \$4/MMBtu. A more careful, updated study might reduce the costs somewhat.

It should be remembered that for this case, coke is slurried with water. If the coke were slurried with residue, the cost of gasification would be similar to that of the residues. Since coke is normally valued at about \$0.75/MMBtu, and residue at about \$1.50/MMBtu, the lower feed cost could partially offset the higher oxygen costs.

## Methanol Economics

### New ICI GHR

To evaluate the application of the ICI GHR to methanol production, we gave ICI our estimates based on conventional methanol technology. We asked for ICI's comments on that cost and the relative savings for using its GHR design. ICI said it agreed with our investments [11], and provided a paper on the application of the GHR to production of methanol [12].

SFA Pacific presented the costs of making methanol via the conventional route to the National Research Council in 1988 [10]. The investments have been updated to 1991, and are shown in Table 7-10.

# APPENDIX C

## Viewgraphs from Midcourse Review

| | |
|---|---|
| C-1 | Industry Trends and Markets |
| C-2 | Screening Analysis of Incentives for Inorganic Membranes |
| C-3 | Market Benefits/Impacts |

# C-1 Industry Trends and Markets

# ASSESSMENT OF THE POTENTIAL FOR REFINERY APPLICATIONS OF INORGANIC MEMBRANE TECHNOLOGY--AN IDENTIFICATION AND SCREENING ANALYSIS

## MIDCOURSE REVIEW MEETING

September 1, 1992

Bernard L. Schulman
Harry E. Johnson

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VG-1

## ASSESSMENT OF THE POTENTIAL FOR REFINERY APPLICATIONS OF INORGANIC MEMBRANE TECHNOLOGY--AN IDENTIFICATION AND SCREENING ANALYSIS

- Industry trends and markets (HEJ)
- Screening analysis of market entry/market growth applications (BLS)
- Market impacts/benefits of inorganic membrane technology (BLS)
- Future work discussion (SFA/DOE)

## ASSESSMENT OF THE POTENTIAL FOR REFINERY APPLICATIONS OF INORGANIC MEMBRANE TECHNOLOGY--AN IDENTIFICATION AND SCREENING ANALYSIS

### Task 2: Identification of Industry Trends and Potential Markets

- Current commercial trends/markets for organic membranes technology
- Current commercial trends/markets for PSA technology

# COMMERCIAL TRENDS/MARKETS IN ORGANIC MEMBRANE SEPARATION TECHNOLOGY

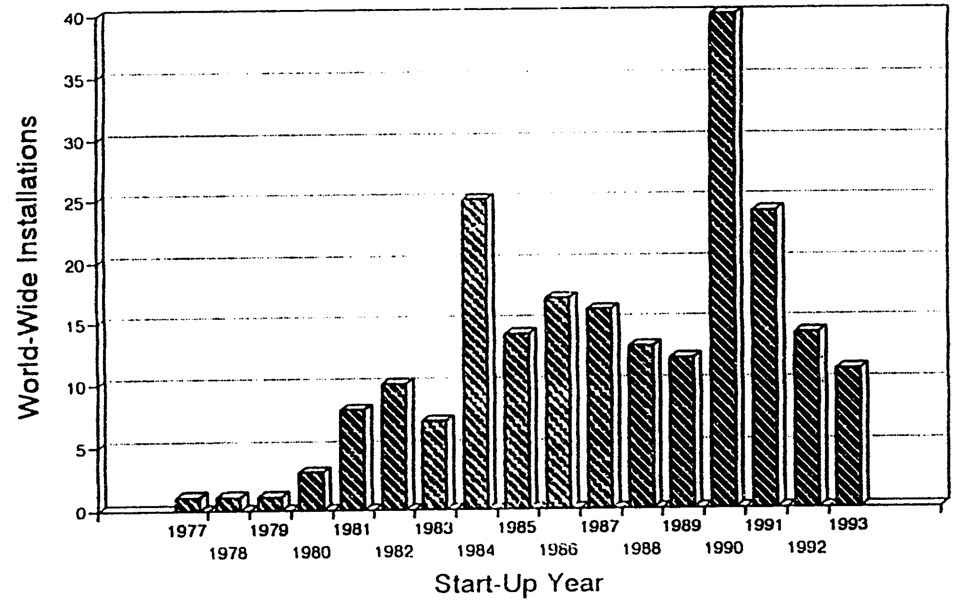
- Relatively new technology for gas separations in refinery applications
    - First used in 1977 for $H_2$/CO ratio adjustment
- Number of installations gradually increased in past 15 years
    - Material developments and improvements
    - Increased number of suppliers/competition
    - Reduced capital investment
- Technology gaining industry approval
    - On-site demonstrated technology/satisfied customers
    - Desperate need for $H_2$
    - Relatively easy to justify investment
    - Easy to install/operate

# ORGANIC MEMBRANE SEPARATION TECHNOLOGY IN THE REFINING INDUSTRY

- Technology Vendors
  - Airco Industries/Dow Chemical--*Generon*
  - Air Products/Akzo/Permea--*PRISM*
  - Du Pont/L'Air Liquide--*MEDAL*
  - UOP/Union Carbide/Innovative Membrane Systems--*Advanced Membrane Systems*
  - Hoechst Celanese--*Separex*
  - UBE Membrane Systems
  - Grace Membrane Systems
- Chemical/Gas Company Joint Ventures
  - Polymer/membrane technology expertise
  - Established customer network and known customer technology needs
  - Product synergy
  - Competition tightening

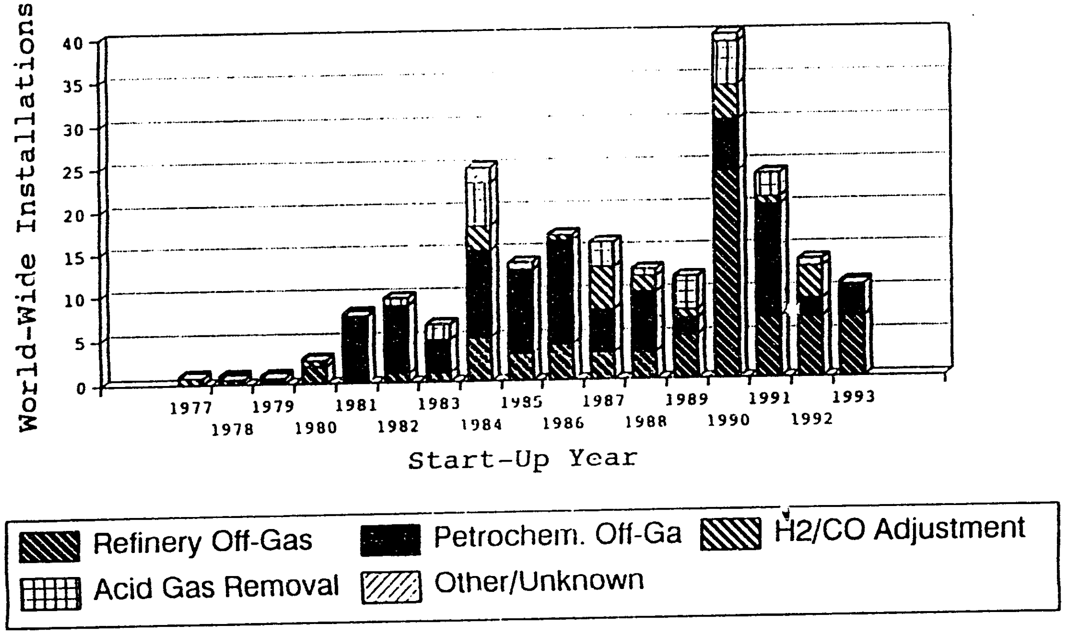
# ORGANIC MEMBRANE INSTALLATIONS

(217 Installations World-Wide)



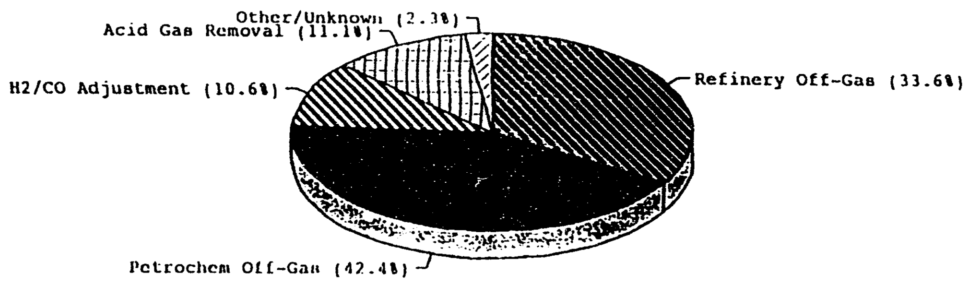
# ORGANIC MEMBRANE INSTALLATIONS

(by application)



## ORGANIC MEMBRANE SEPARATION TECHNOLOGY IN THE REFINING INDUSTRY

### ORGANIC MEMBRANE APPLICATIONS
(1977-1993)



## ORGANIC MEMBRANE SEPARATION TECHNOLOGY IN THE REFINING INDUSTRY

- Commercial Experience
    - ARCO Los Angeles Refinery--*PRISM*
    - Conoco Ponca City Refinery--*MEDAL*
    - Shell Dutch Refinery--UBE Membrane Systems
- Technology Comfort
    - Demonstrated value
    - Easy to operate
- Disadvantages
    - Pressure drop/compression costs
    - Durability/life
    - Refiners are extremely conservation

# ORGANIC MEMBRANE SEPARATION TRENDS

- Expected market improvement (U.S)
  - $44 million (1991)
  - $95 million (1996)
  - $200 million (2001)
- Improved membrane materials
  - Coated polymers
  - Separator fabrication
  - Hybrid systems
- Technology will continue to develop
  - More R&D activity
  - Organic membrane industry becoming more aggressive

# COMMERCIAL TRENDS IN PSA SEPARATION TECHNOLOGY

- Relatively mature technology for gas separation in the refinery applications
    - Used since the mid-1960s
- Number of installations steadily increased in past 25 years
    - Material developments and improvement
    - Improved automated control systems
- Technology has industry approval

# COMMERCIAL TRENDS IN PSA SEPARATION TECHNOLOGY

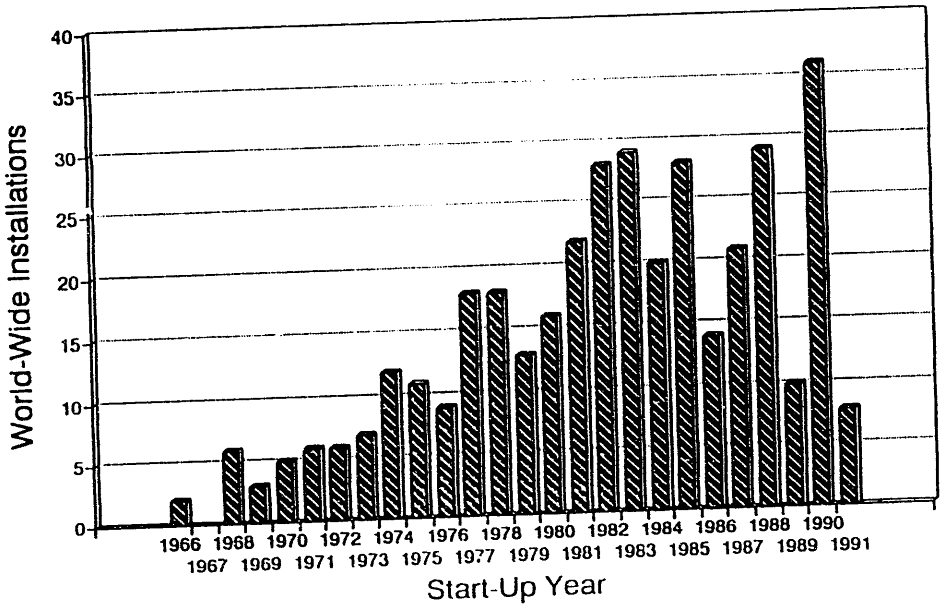
- Technology Vendors
  - Air Products--*Gemini*
  - Dow Chemical--*Generon*
  - Linde AG
  - Mitsubishi Heavy Industries
  - Nippon Kokan K.K.--*Co-PSA*
  - Toyo Engineering Corp.--*Lo-Fin PSA*
  - Union Carbide/UOP--*Polybed PSA*

- Dominated by UOP Polybed PSA technology
  - Over 350 refinery-related applications
  - Praxair $H_2$ Texas pipeline

## COMMERCIAL TRENDS IN PSA SEPARATION TECHNOLOGY

# UOP POLYBED PSA INSTALLATIONS

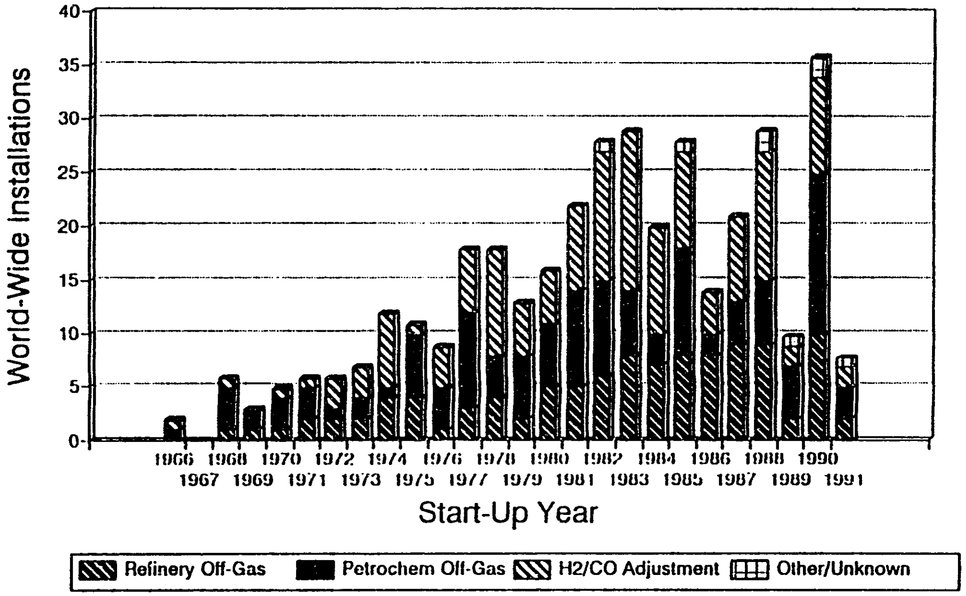
(377 Installations World-Wide)



## COMMERCIAL TRENDS IN PSA SEPARATION TECHNOLOGY

# UOP POLYBED PSA INSTALLATIONS

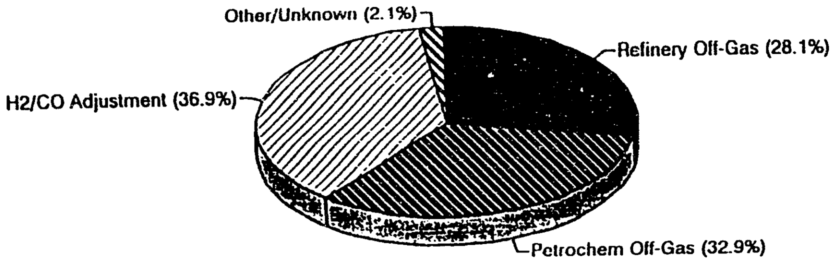
(by application)



## COMMERCIAL TRENDS IN PSA SEPARATION TECHNOLOGY

# UOP POLYBED PSA APPLICATIONS

(1966-1991)



## COMMERCIAL TRENDS/MARKETS IN PSA SEPARATION TECHNOLOGY

- Significant commercial experience
    - Standard for steam methane reforming $H_2$ plants
    - Adsorbents routinely changed-out
- Demonstrated value
    - Use in high-purity $H_2$ recovery
    - Use in air separation
- Disadvantages
    - Valve failures
    - More complicated than membranes
    - Refiners are extremely conservative

# C-2 Screening Analysis of Incentives for Inorganic Membranes

# Assessment of the Potential for Refinery Applications of

# Inorganic Membrane Technology -

## A Screening Analysis

Midcourse Review Meeting

September 1, 1992

Bernard L. Schulman

SFA Pacific, Inc.
Mountain View, CA

# Screening Analysis Covers Several Areas .... Others Need Data First

| | Market Entry | Market Growth |
|---|---|---|
| Hydrogen Recovery | ● $H_2/CH_4$ | |
| Hydrogen Manufacture | | |
| - Partial Oxidation | | |
| + Liquids | ● $CO_2/H_2S$ | |
| + Gases | $H_2/CO_2$ | |
| - Steam-Methane Refg | | $H_2/CO_2$ |
| Fuel Upgrading | | |
| - Diesel | ● S/aromatic removal | |
| Other | | |
| - Waster Water Cleanup | Benzene/$H_2O$ | |
| - Gas Generation | | .$O_2/N_2$ |

● = Case screened

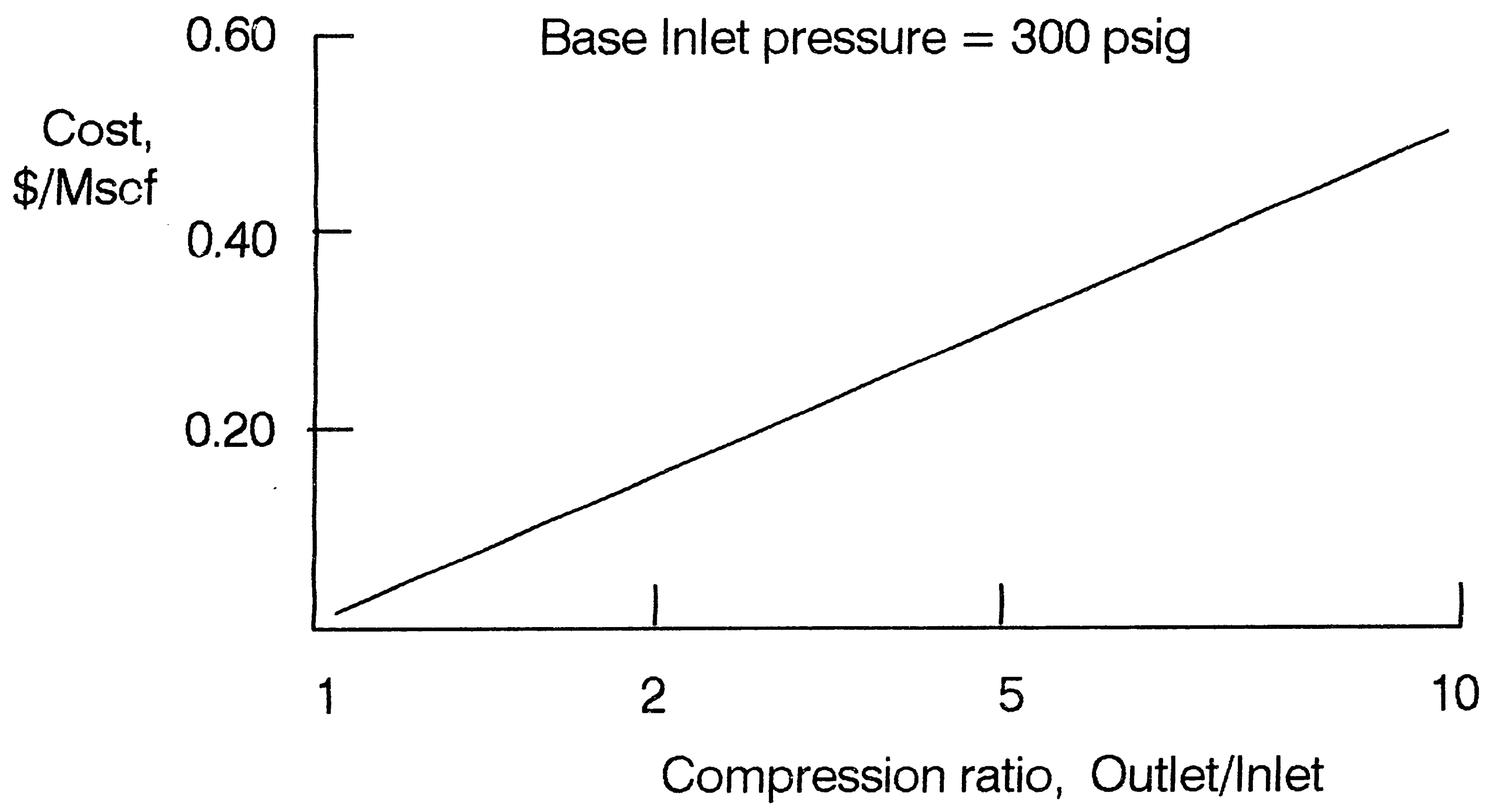
## H2 Compression Cost is a Key Factor for Membranes

Basis: Foster Wheeler Study on Oil Shale Retorting

| | |
|---|---|
| Compressor capacity, MM scf/sd | 108 |
| Pressure, psig | |
| - Suction | 300 |
| - Discharge | 3000 |
| Base Cost, $MM | 21.4 |
| Total Cost, $MM | 37.5 |

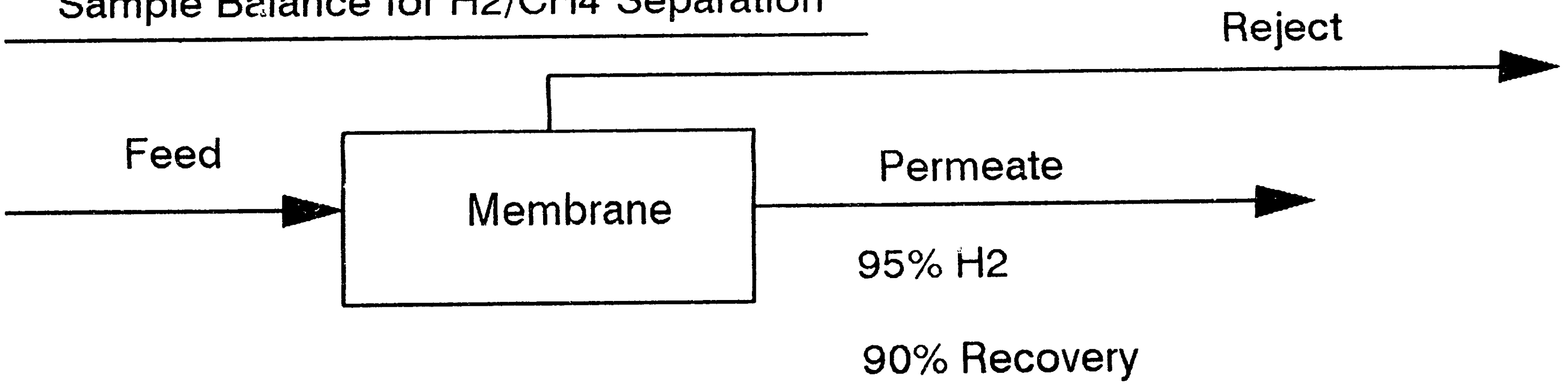
| | H2 Compression Cost, $/Mscf |
|---|---|
| Power @ $0.05/kwh | 0.21 |
| Operation Costs | 0.08 |
| Capital charge @ 20% | 0.21 |
| Total | 0.50 |

## Compression Costs Can Be High



VG- 4

# Sample Balance for H2/CH4 Separation



Feed

Membrane

Permeate

95% H2

90% Recovery

Reject

| | | | |
|---|---|---|---|
| **Scf** | | | |
| H2 | 75 | 67.50 | 7.50 |
| CH4 | 25 | 3.55 | 21.45 |
| | 100 | 71.05 | 28.95 |
| **Btu** | | | |
| H2 | 23,250 | 20,925 | 2,325 |
| CH4 | 25,250 | 3,585 | 21,665 |
| | 48,500 | 24,510 | 23,990 |

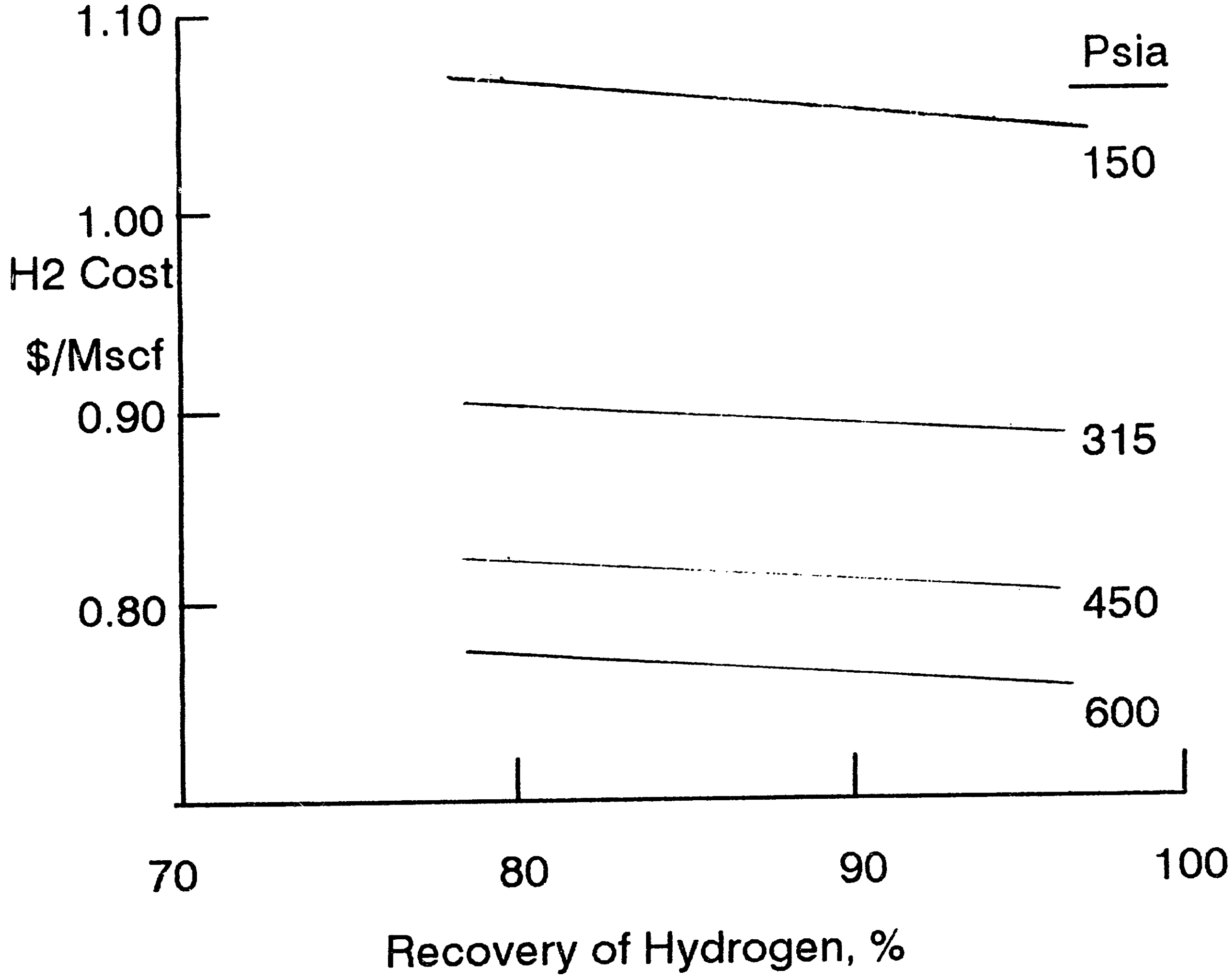
## Sample Economics for Membranes

Basis:

| | |
|---|---|
| Feed rate, MMscf/sd | 10 |
| H2 in feed, % | 75 |
| H2 in Permeate,% | 95 |
| H2 recovery, % | 90 |
| Permeate pressure, psig | 300 |
| Total Investment, $MM | 1.2 |

| | $/Mscf H2(100%) |
|---|---|
| Fuel value @ $2.50/ MMbtu | |
| - Feed | 1.80 |
| - Reject | (0.89) |
| - CH4 in permeate | (0.13) |
| Subtotal | 0.78 |
| Operating Costs | 0.03 |
| Capital Cost @ 20%/year | 0.08 |
| Total Cost | 0.89 |

# High Permeate Pressure is Main Goal



# Sample of Performance of Membranes

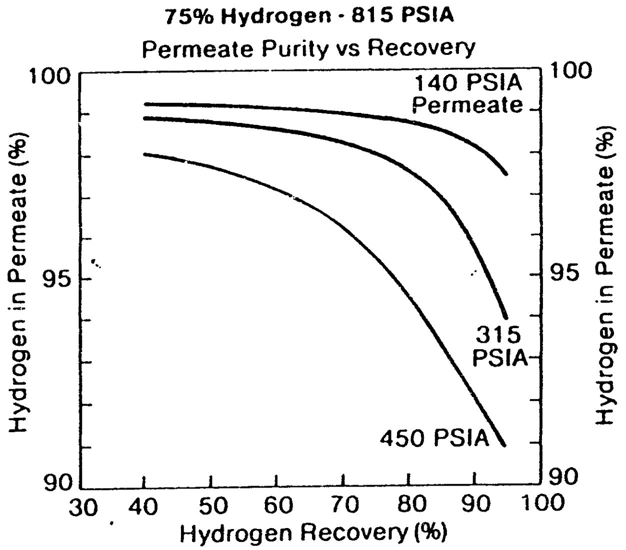
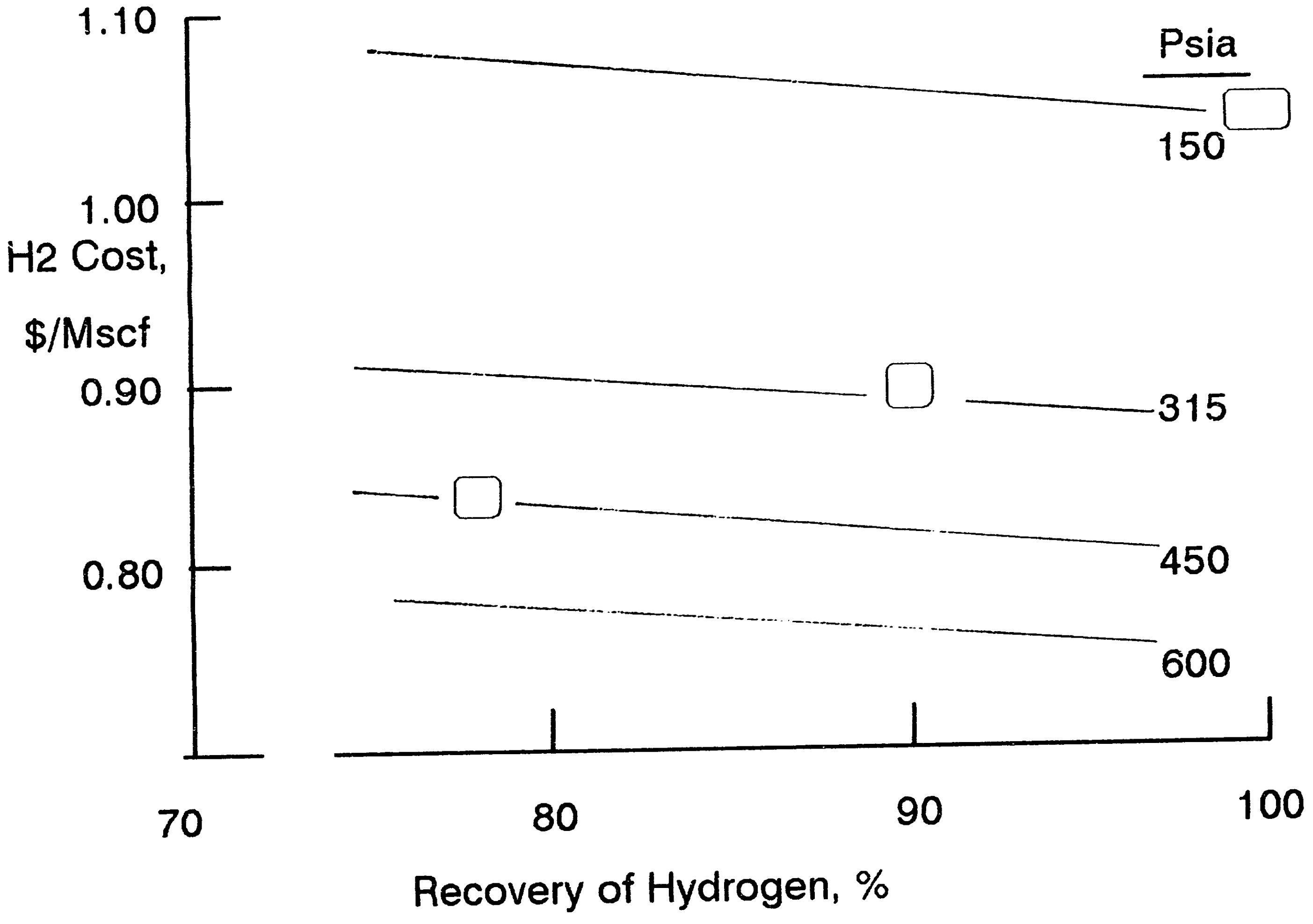


Figure 8-11

Recovery of Hydrogen from Hydrotreater Purge Gases

Source: Conoco

## Actual Performance Shows Value of High Pressure

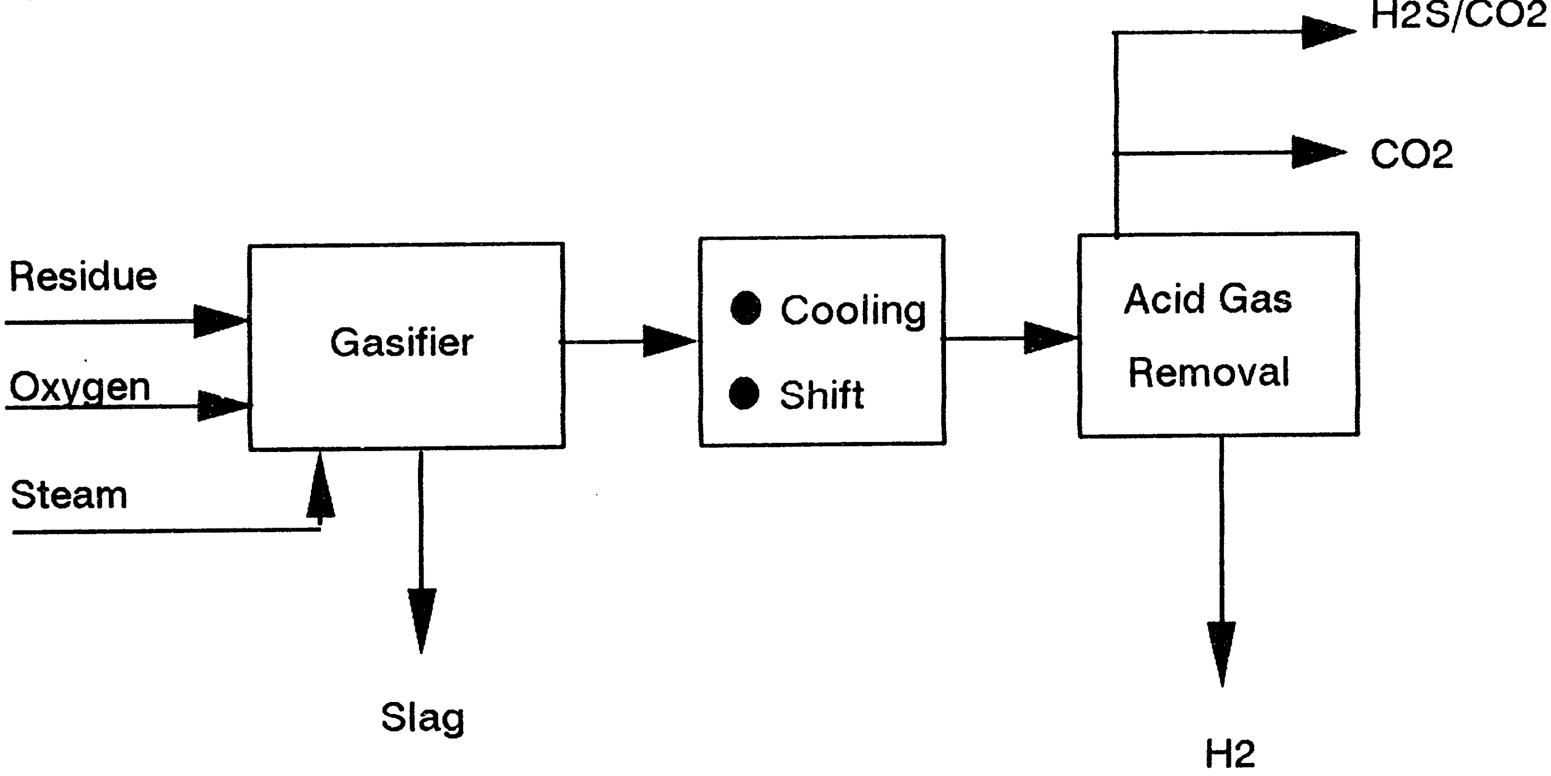


## $H_2S$ Enrichment From $CO_2$ Enchances

## Partial Oxidation of High Sulfur Liquids

- Partial oxidaton is well proven
  - More than 200 units worldwide
- Environmentally excellent
  - No $NO_x$
  - Good Control of $H_2S$
  - Ni/V slag is vitreous, not soluble in water
- Main problem is the high cost of using Rectisol for $H_2S$/ $CO_2$ removal
  - Standard process with Texaco and Shell processes
- Membranes can provide enrichment when using cheaper systems

# Acid Gas Removal is Key Element in Partial Oxidation Process



H2S/CO2

CO2

Residue

Oxygen

Steam

Gasifier

- Cooling
- Shift

Acid Gas Removal

Slag

H2

# Acid Gas Removal Process Vary Widely in Selectivity

| AGR Process | $H_2S$ in $CO_2$, % | Sulfur Recovery |
|---|---|---|
| Rectisol | 75 | Claus + SCOT |
| UOP amine | 7 | Cat Claus + Wet Ox |
| Hot Pot Carbonate | 2 | Wet Oxidation |

# Sulfur Plants are Vital .... and Expensive

Basis: 60 lt/sd (100 MMscf/sd H2)

| AGR Process | Primary | Tail Gas | Investment, $MM | Sulfur Cost, $/lt |
|---|---|---|---|---|
| Rectisol | Claus | SCOT | 7.4 | 105 |
| UOP Amine | Cat Claus | Wet Ox | 14.3 | 243 |
| Hot Pot | Wet Ox | - | 14.0 | 295 |

## "Hot Pot" Is The Cheapest Investment For AGR

Basis:  100 MMscf/sd H2

| | Rectisol | UOP Amine | Hot Pot |
|---|---|---|---|
| Investments: $MM | | | |
| Gasifier | 29.6 | 29.6 | 29.6 |
| Cooling | 13.6 | 13.6 | 13.6 |
| Acid Gas Removal | 46.5 | 15.8 | 9.4 |
| Utilities | 7.6 | 1.8 | 1.8 |
| Sulfur plant | --- Included in Economics as Cost --- | | |
| Contingency | 9.7 | 6.1 | 5.4 |
| Offsites | 37.5 | 23.4 | 20.9 |
| Facilities | 144.5 | 90.3 | 80.7 |
| | | | |
| Engineering | 11.0 | 6.7 | 6.0 |
| Startup | 5.5 | 3.3 | 3.0 |
| Working Capital | 1.1 | 0.7 | 0.6 |
| Royalties | 2.2 | 1.4 | 1.2 |
| Total plant cost | 164.3 | 102.4 | 91.5 |

## Better Acid Gas Removal Reduces H2 Cost

|  | Rectisol | UOP Amine | Hot Pot |
|---|---|---|---|
|  |  | $/Mscf H2 |  |
| Vacuum Residue @ $10/b | 0.63 | 0.63 | 0.63 |
| Oxygen @ $40/ton | 0.47 | 0.47 | 0.47 |
| Steam @ $5.00/Mlbs | 0.04 | 0.10 | 0.10 |
| Power @ $0.05/kwh | 0.15 | 0.05 | 0.05 |
| Other op. costs | 0.40 | 0.25 | 0.22 |
| Capital Charge @ 20%/year | 0.99 | 0.62 | 0.55 |
| Compression credit | (0.18) | (0.18) | (0.18) |
| Subtotal | 2.50 | 1.94 | 1.84 |
|  |  |  |  |
| Sulfur recovery cost | 0.06 | 0.15 | 0.18 |
| Sulfur credit @ $120/lt | (0.07) | (0.07) | (0.07) |
| Total H2 Cost | 2.49 | 2.02 | 1.95 |
|  |  |  |  |
| Savings | Base | 0.47 | 0.54 |

## Main Incentive For Membranes Is To Provide Claus Plant Feed From Hot Pot System

- Wet Oxidation not yet practiced well at sizes above 10 t/d
- Would need 4-6 on 100 MMscf/sd H2 plants
- Good membranes would help acceptance of partial oxidation to insure reliability of critical sulfur control
- If inorganic membranes on H2S/CO2 cost twice as much as organics on H2
  - Adds $0.13/Mscf to H2 cost
- Compression is still key to cost
  - Compression from 6 psig to 300 psig adds $0.37/Mscf

## Diesel Upgrading Can Be interesting Application
## If Membranes Can Remove Aromatics and Sulfur

- In the past, diesel was about 0.4 wt % S and 40 - 60 vol % aromatics
- New Clean Air Act sets sulfur at 0.05 wt % and aromatics will be about 35 - 40 vol %
- California has set 1993 aromatics at 10 - 20 vol %
  - S max will be 0.05 wt %
- Current diesel production is about 2 MM b/sd

# New Diesel Standards Require Severe Treating

| | | | | |
|---|---|---|---|---|
| Sulfur, wt % | 0.4 | 0.05 | 0.01 | <0.01 |
| Aromatics, Vol % | 60 | 35 | 20 | 10 |
| H2 cons., scf/b | 150 | 400 | 700 | 1200 |
| Pressure, psig | 600 | 800 | 1200 | 1800 |

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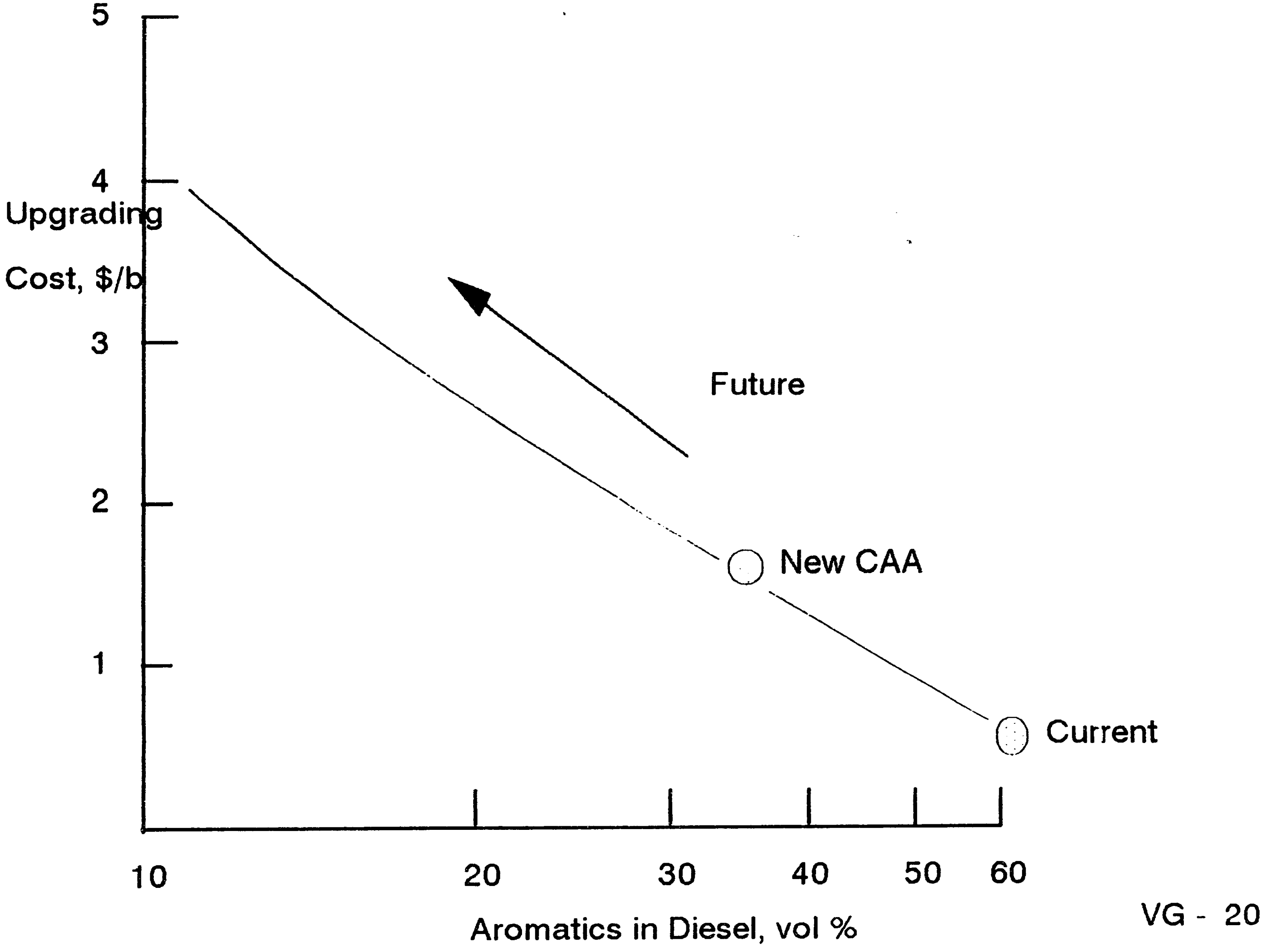
| Pressure, psig | 600 | 800 | 1200 | 1800 |
| Basis: 20 Mb/sd | | | | |
| Investment, $MM | 6.7 | 13.0 | 24.4 | 26.6 |
| Upgrading Costs, $/b | | | | |
| Operating costs | 0.08 | 0.16 | 0.23 | 0.32 |
| Capital Charges | 0.20 | 0.39 | 0.57 | 0.81 |
| H2 @ $2.50/ Mscf | 0.38 | 1.00 | 1.75 | 3.00 |
| Total | 0.66 | 1.55 | 1.75 | 4.13 |
| | Base | 0.89 | 1.89 | 3.48 |

# Hydrogenating Aromatics and Sulfur is Expensive



VG - 20

## Summing Up ....

- Incentives show good potential for inorganic membranes in key refinery applications
    - $H_2$ recovery from high pressure purge streams
    - $H_2S$ enrichment from $CO_2$ produced in partial oxidation of liquids
    - Sulfur/aromatics from diesel fuels
- If experimental data show good results, other areas can use also
    - $H_2$ purification in partial oxidation of oils and gases
    - Sulfur/aromatic separation from gas oils

# C-3 Market Benefits/Impacts

# Assessment of the Potential for Refinery Applications of Inorganic Membrane Technology -- Market Benefits / Impacts

## Midcourse Review Meeting

September 1, 1992

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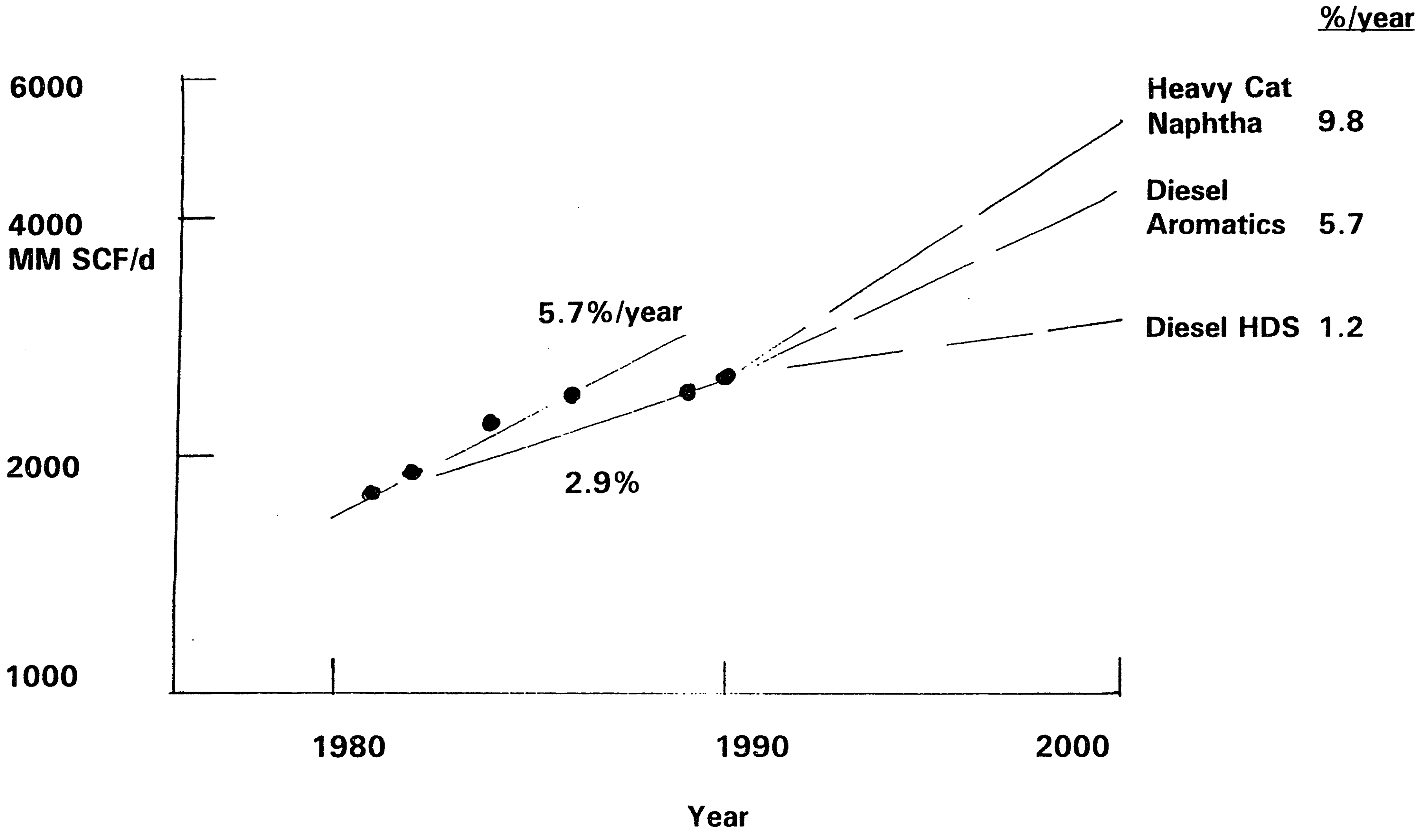
# Hydrogen Growth Can Be Very Large



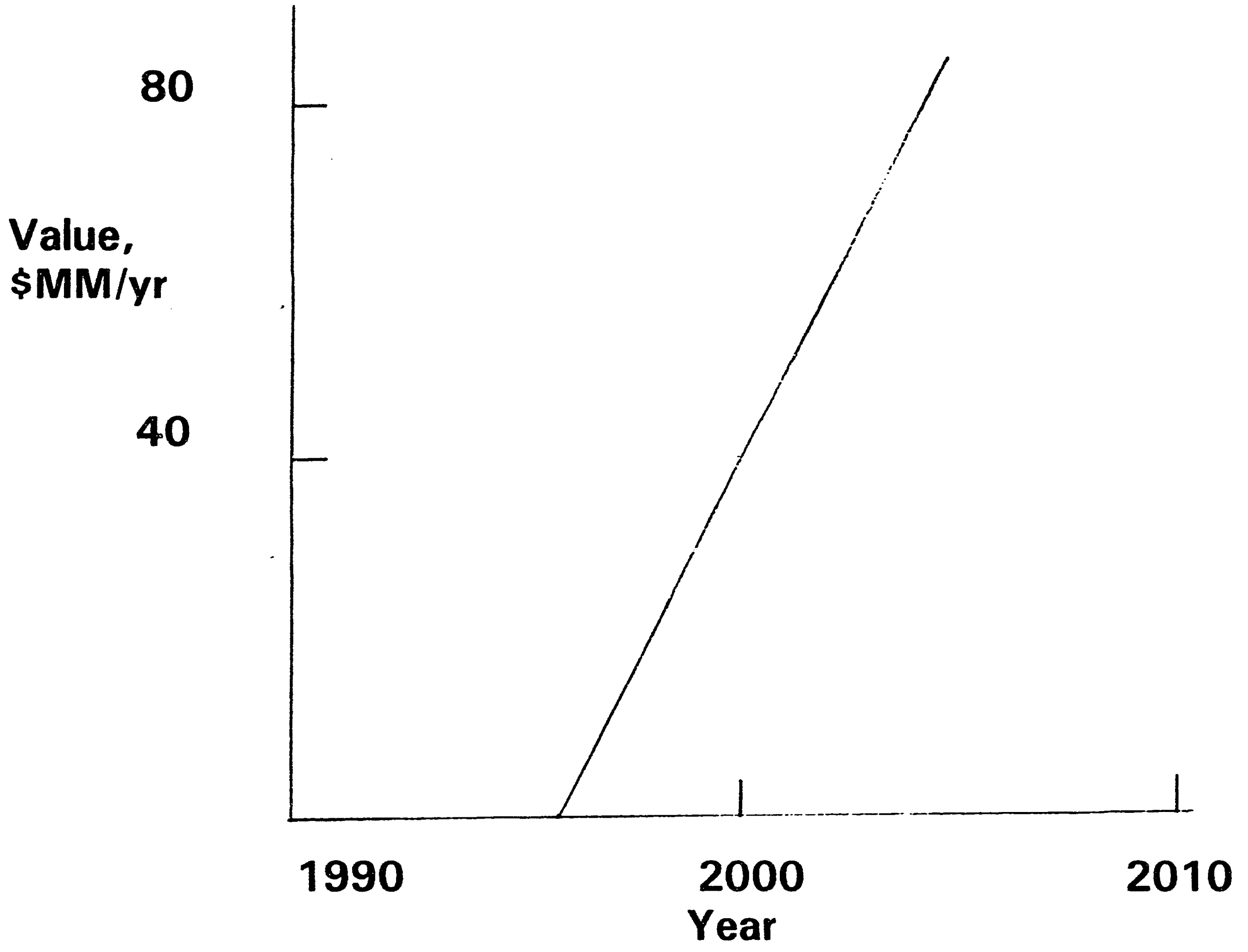
# $H_2$ Recovery

## Assume:

- Purges = 20% of production
- Inorganic membranes get 20% of market in 1996
- Provide advantage of 700 psig vs 350 psig on permeate
- Value of higher pressure = $0.15/Mscf

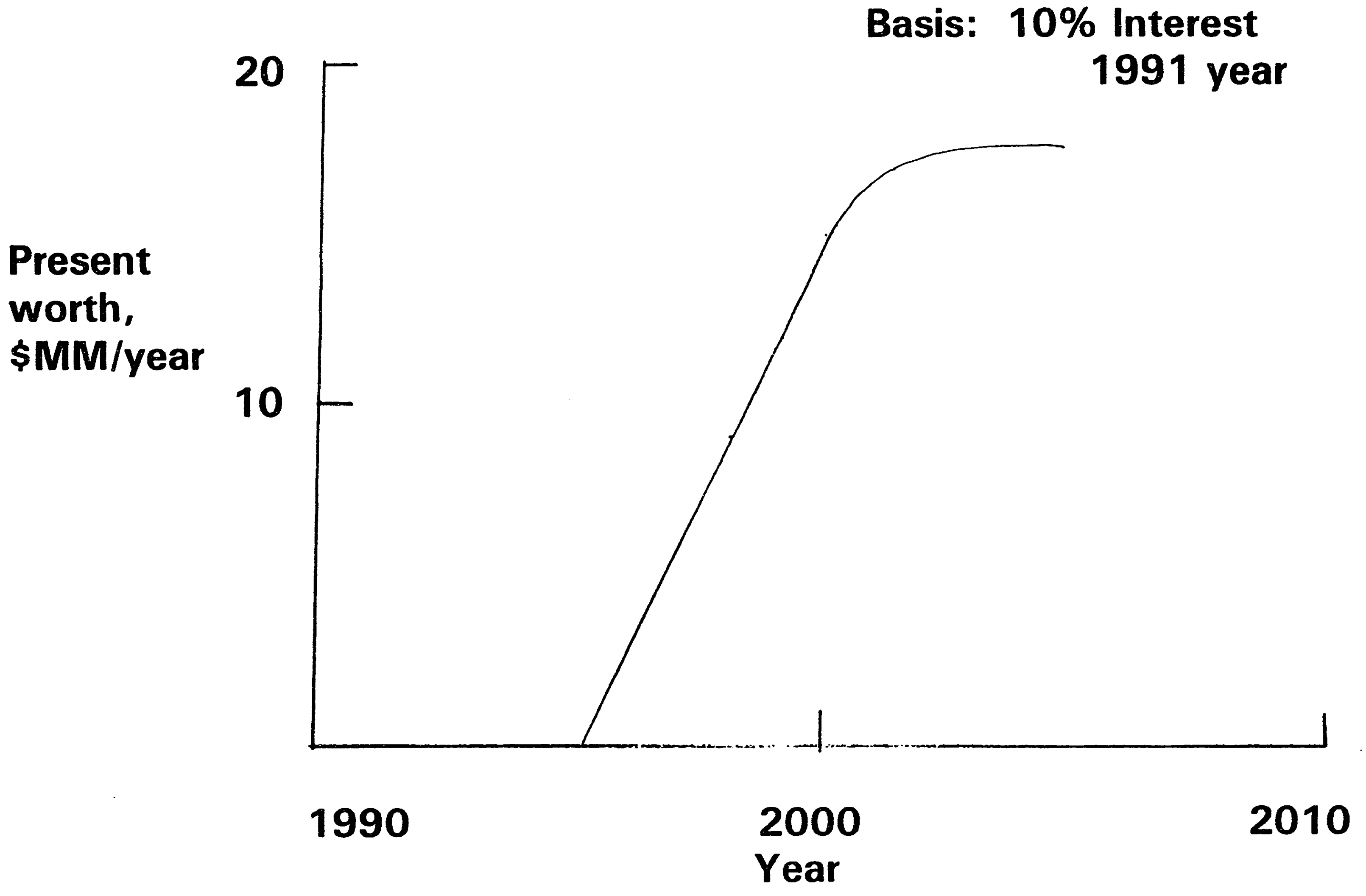
| Step | Total $H_2$: MMscf/d | Value in 2001, $MM |
|---|---|---|
| Diesel | | |
| - HDS | 350 | 5 |
| - Aromatics | 1860 | 20 |
| Add HCN treating | 2900 | 40 |

# $H_2$ Recovery By Membranes Is Valuable



VG-4

# Present Worth on $H_2$ Recovery Still Shows Good Value



Basis: 10% Interest
1991 year

# $H_2S$ Enrichment From $CO_2$

## Assume:

- Partial oxidation picks up 20% of $H_2$ manufacture
- Membrane used in connection with Hot Pot
  - Take 50% of \$0.50 credit = \$0.25/Mscf

| Step | Total $H_2$: MMscf/d | Value, \$MM 2001 | Value, \$MM 1996-2001 |
|---|---|---|---|
| Diesel | | | |
| - HDS | 350 | 6 | 29 |
| - Aromatics | 1850 | 31 | 139 |
| Add HCN treating | 2900 | 48 | 201 |

# Membranes for Treating Diesel

Assume:

- 20% of diesel treated by membranes
- Used to reduce aromatics from 35 to 20% on 0.05% S material
- Savings = $1/barrel
- Total diesel = 2 million barrels per day

Value = $132 MM/year

# Longer Range "Market Growth" Can Be Large

- $H_2$ purification on $H_2$ manufacture = 4 times that used for $H_2$ recovery
- Application to ammonia and methanol is about 50% of hydrogen usage
- Sulfur and aromatics removal from gas oils potentially about 20 times that of diesel

# Worldwide Usage Enlarges Market Value

- Worldwide $H_2$ usage about equal to U.S.
- Worldwide diesel about twice U.S.

## Summing up - - -

- Excellent market potential for membranes in several areas
- Need experimental data to define actual value

DATE
FILMED
10/25/93