

Optimization of the hydrogen separation membrane unit of an autothermal reforming plant

OA Agbabiaka BSc Hons
Student no: 20510306

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Supervisor: Prof PW Stoker

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DEDICATION

This dissertation is dedicated to the Almighty God, who in His steadfast love, unstinting mercies and loving kindness has kept me till this day.

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ABSTRACT

This research work has been carried out to enhance the performance of the membrane unit of an Autothermal Reforming (ATR) plant. The plant in question refers to the ATR plant of one of the leading petrochemical industries in South Africa.

The membrane is used to separate hydrogen from a feed of hydrogen-carbon monoxide mixture (reformed gas) containing gases such as carbon dioxide and small amounts of methane, nitrogen, oxygen, argon, water, ammonia and hydrogen cyanide. The exit streams from the membrane are permeate (hydrogen gas) and non-permeate (synthesis gas, a mixture of hydrogen and carbon monoxide) with trace quantities of the other aforementioned gases.

This dissertation investigated into the causes of decreasing membrane hydrogen (permeate) purity and insufficient membrane capacity to achieve the required synthesis gas (non-permeate) ratio.

High differential pressure across the membranes as well the presence of ammonia and water in the feed gas to the membrane fibres were some of the causes of the membranes' low performance. Others include high speed of the membrane feed gas, the presence of strongly adsorbed gas - methane and insufficient heating of the feed gas by the preheaters. These led to broken and twisted membrane fibres. As a result, carbon monoxide and other constituents of the feed slipped into the permeate stream.

From the research work, ways of enhancing the performance of the membrane unit were proffered. They include integrating a Pressure Swing Adsorption unit (upstream) with the membrane unit, recycling the permeate back to the feed stream, increasing the temperature of the feed gas and lowering the differential pressure across the membranes.

Furthermore, the condensate should be prevented from getting to the membrane fibres by installing a drying unit, a demister unit or drains in the membrane feed gas header. In addition, periodic maintenance and backwashing should be carried out on the membranes.

However, recommendations were made on further study regarding the cost impacts of implementing the ways of optimizing the membrane unit and simulation of the membrane unit's operation. The latter was suggested in order to obtain the process variables and parameters for improving the performance of the unit in question.

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LIST OF ABBREVIATIONS

Abbreviation	Definition
ATR	Autothermal Reforming
CVI/CVD	Chemical Vapour Infiltration/Deposition
DCS	Distributed Control System
FCC	Fluid Bed Catalytic Cracker
F-T	Fischer-Tropsch
GTL	Gas-To-Liquids
OP	Operators' Questionnaire
PLC	Programmable Logic Control
PSA	Pressure Swing Adsorption
SP	Senior Personnel's Questionnaire
TCF	Trillion Cubic Feet

LIST OF NOTATIONS AND SYMBOLS

Notation or Symbol	Definition
$\text{\AA}$	Angstrom
abs	absolute
Ar	Argon
bar	unit of pressure
CH_4	methane
cm	centimeter
$\text{cm}^3 \cdot \text{cm}/\text{sec} \cdot \text{cm}^2 \cdot \text{cmHg}$	cubic centimeters per second square centimeters centimeter of mercury
cm^3/min	cubic centimeters per minute
CO	carbon monoxide
CO_2	carbon dioxide
C1	carbon-1 compound
C2	carbon-2 compound
C_2H_2	ethyne
C_2H_4	ethene
C_2H_6	ethane
C3	carbon-3 compound
C_3H_4	propyne
C_3H_6	propene
C_3H_8	propane
g	gauge
HCN	hydrogen cyanide
H_2	hydrogen
H_2O	water
H_2S	hydrogen sulphide
kNm^3/hr	kilo normal cubic meters per hour
kPa	kilo Pascal (unit of pressure)
m	meter
MMBtu	Million British Thermal Units
mol%	mole percent
MPa	Mega Pascal
m^2/m^3	square meters per cubic meters

Notation or Symbol	Definition
NH ₃	ammonia
nm	nanometer
Nm ³ /hr	normal cubic meters per hour
N ₂	nitrogen
n-C ₄ H ₁₀	n-butane
O ₂	oxygen
ppm	parts per million
SiO ₂	silica oxide
Si(OEt) ₄	tetraethoxysilane
SO ₂	sulphur dioxide
t/a	tonnes per annum
wt%	weight percent
w/w	weight by weight
μm	micron
°C	degrees Celsius (unit of temperature)
α	alpha
γ	gamma

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND

Proven world natural gas reserves, which currently exceed 5,000trillion cubic feet (TCF), have been growing at a faster rate than proven oil reserves. In some remote locations, wellhead costs of natural gas have been estimated to be below \$0.25/MMBtu (Million British Thermal Units), while the cost of reinjecting “associated” gas from crude oil production as an alternative to flaring may greatly exceed its value. About 3,000TCF of such gas reserves is considered to be “stranded”; i.e. accessible by drilling but located too far from potential markets for economical transportation to those markets. Apanel (2002:1)

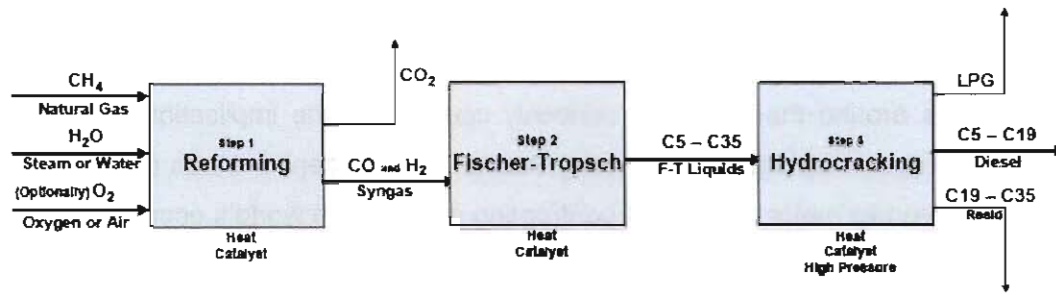
The chemical conversion of natural gas (methane) to liquid fuels which may be more cost effective to transport long distances from remote gas sources, has therefore attracted renewed interest. Apanel (2002:1). Examples of these liquid fuels are diesel and gasoline. The technology by which this process is carried out is the gas-to-liquids (GTL) technology.

Conversion of natural gas to liquid fuels, particularly liquid fuels that would be useful as transportation fuel has generated a lot of interest by many companies throughout the world. Amongst such companies are ConocoPhillips, Sasol, ExxonMobil, Shell, Syntroleum and British Petroleum.

Apanel (2002:12) wrote that GTL technology converts natural gas to clean liquid fuels in a three-step process which involves conversion of natural gas to synthesis gas (also called “syngas”), followed by the synthesis of the syngas to produce a range of liquid hydrocarbons. The final step is the upgrading and refining of the subsequent syngas-derived liquid hydrocarbons into a specific state of liquid fuels and/or petrochemical products or intermediates.

The figure below shows a block diagram of the general gas-to-liquids process.

Fig 1.1: General GTL Processing Scheme



Source: Apanel (2002:12); Retrieved on August 15, 2006

The initial conversion of natural gas to synthesis gas occurs through a process known as reforming. There are various reforming technologies. Amongst them are Partial Oxidation (catalytic or non-catalytic), Steam Reforming (Steam Methane Reforming), Autothermal Reforming, Combined Reforming and Compact Reforming. The subsequent conversion of synthesis gas to liquid fuels is made possible by the *Fischer-Tropsch* (F-T) process. Petroleum Economist Journal (2003:16, 17); Vosloo (2004:1)

The companies with GTL technologies at present and their reforming processes include:

1. ConocoPhillips: Catalytic Partial Oxidation
2. Shell: Non-Catalytic Partial Oxidation and Steam Reforming
3. ExxonMobil: simultaneous Catalytic Partial Oxidation and Steam Reforming
4. BP: Compact Reforming
5. Syntroleum: Combined Partial Oxidation and Steam Methane Reforming
6. Sasol: Autothermal Reforming. Petroleum Economist Journal (2003:5, 6, 7)

The natural gas conversion process of concern in this dissertation is the Autothermal Reforming (ATR) technology. In the first step, natural gas is converted to reformed gas (a mixture of hydrogen, H₂ and carbon monoxide, CO) with a molar ratio of 2.24:1. However, the downstream process (*Fischer-Tropsch synthesis*) requires synthesis gas with a ratio of 1.89:1.

Therefore, the reformed gas is converted to synthesis gas by hydrogen separation in a membrane. In effect, the membrane system is used to adjust a non-permeate stream H₂/CO molar ratio to a predetermined value for the Fischer-Tropsch synthesis downstream, by withdrawing some of the hydrogen in the feedstream. In some other

processes, the ratio is adjusted by removing hydrogen with the aid of the pressure swing adsorption system (PSA). U.S. Department of Energy (2006:1)

Many countries around the world are seriously considering the implications of a shift towards a hydrogen economy. The growing interest in hydrogen is driven mainly by its potential to solve two major challenges confronting many of the world's economies, how to achieve energy independence while minimizing the environmental impact of economic activity.

There are four critical technologies that need to be developed before a hydrogen economy could be realized:

- (1) Cost-effective production of hydrogen in a carbon constrained global energy system. The challenges in this area include the production of H_2 from fossil fuels with carbon sequestration taken into account, and increasing utilization of renewable sources.
- (2) Hydrogen purification and storage technologies that will be able to separate, and purify the hydrogen streams to the requirements of the subsequent storage and utilization systems. Efficient and practical storage devices for hydrogen will have to reach the United States Department of Energy's target of 6.5 wt% (weight percent).
- (3) An efficient, widely available and well-managed hydrogen delivery and distribution infrastructure.
- (4) Efficient fuel cells and other energy conversion technologies that utilize hydrogen.

Lu *et al.* (2007:1, 2)

In thermo-chemical processes for hydrogen production from fossil fuels, separation and purification is a critical technology. Where water–gas shift reaction is involved for converting the carbon monoxide to hydrogen, membrane reactors show great promises for shifting the equilibrium. Membranes are also important to the subsequent purification of hydrogen.

Membrane gas separation is based on the difference in the rate of permeation through a membrane. It is a pressure-driven process. The typical performance of membrane modules for hydrogen recovery is such that there is a trade-off between product recovery and purity. Product recovery and purity are terms related to *permeability* and

selectivity respectively, the most critical properties of membranes. Either a high recovery can be obtained or a high purity, but seldom both. Feng *et al.* (1998:1689)

Lu *et al.* (2007:5) stated that in addition to these two properties, a practical membrane system must be able to achieve certain upstream or downstream gas (hydrogen) compositions. The *permselectivity*, i.e., the ratio of the intrinsic permeabilities of the two permeates, should be as high as possible to allow flexibility in setting transmembrane pressure differences, while still meeting gas purity requirements.

For hydrogen production and purification, there are generally two classes of membranes both being inorganic: dense phase metal and metal alloys, and porous ceramic membranes. Porous ceramic membranes are normally prepared by sol-gel or hydrothermal methods, and have high stability and durability in high temperature, harsh impurity and hydrothermal environments. In particular, microporous membranes show promises in water gas shift reaction at higher temperatures. Lu *et al.* (2007:1)

Membrane technologies possess a high potential to separate hydrogen with high effectiveness and selectivity. Especially if process streams with high temperatures are involved, inorganic membranes are the only alternative. Kilgusa *et al.* (2006:95)

Membranes are used to separate a wide variety of gases, and separation of carbon dioxide (CO₂) from natural gas is one of the most important emerging applications of this technology.

Most membrane-based gas separations are accomplished with asymmetric hollow fiber or spiral-wound modules, which provide a large amount of separation area per unit volume. Asymmetric fibers are comprised of a thin 500–2000Å (Å = Angstrom = 10⁻¹⁰m) separating skin layer, which is supported on a second porous layer that is usually 50–200µm thick. Ideally, the porous support has no effect on the permeation properties of the membrane. Al-Juaied & Koros (2005:227)

The development in the last few decades has been mainly directed to the fabrication of membranes as thin as possible to reduce the material cost and to achieve a higher permeability but without compromising the permselectivity. At the same time, the limited

ratio of effective separation area to volume of available membranes or modules is also recognized as one of the limitations to the industrial applications, compared with polymer membranes in the configuration of hollow fiber.

Natural gas streams contain numerous trace heavy hydrocarbons. A topic of concern in designing a reliable membrane system for natural gas purification involves the impact of such heavy hydrocarbon on the membranes. Very heavy hydrocarbon contamination is believed to be the cause of some membrane failures and loss in performance even at low mass fractions. Due to this, it is very important to carefully consider the required pretreatment requirements for membrane systems. Al-Juaied & Koros (2005:227)

The impact of these hydrocarbons on the membrane system has remained poorly understood due to the complexity of the components present and the difficulty in characterizing their effects experimentally. Previous work on membrane formation has led to reliable membrane structures for CO₂ removal from natural gas feeds; however, most of the tests performed in the laboratory on these membranes were contaminant-free. In actual field tests, membranes often exhibit poorer performance. Al-Juaied & Koros (2005:227)

When a mixture is brought to a membrane surface by any driving force, there is an accumulation of the less permeable species and a depletion of the more permeable components in the boundary layer adjacent to the membrane and this causes a concentration gradient building up in the boundary layer. This phenomenon is referred to as concentration polarization. He *et al.* (1999:243)

Furthermore, He *et al.* (1999:243) wrote that, theoretically speaking, concentration polarization exists in all membrane separation processes because of the selective permeability of membrane. It has serious adverse effects in membrane separation processes. It leads to a decrease in the available driving force for the more permeable species across the membrane and an increase for the less permeable species. This reduces the overall efficiency of separation and raises the costs of capital and operation.

Membrane life is affected by the operating conditions of the total process. Depending on the feed gas, certain chemicals present in the feed stream damage membrane fibres and therefore affect the efficiency of the membrane unit. High speed of the feed gas also affects the orientation and arrangement of the fibres in the membrane bundles.

The presence of water is another factor that affects the mechanical properties of certain membrane fibres. The carbon membrane is strongly affected by water content and organic contaminants. Luque & Alvarez (2001:474)

Other important membrane considerations are the mechanical design, including the mechanical integrity of the membranes and the necessary membrane-to-metal junctions. Asymmetric structure of membranes is a mechanical property that enhances permeability for certain type of membranes. Luque & Alvarez (2001:381)

1.2 DEFINITION OF TERMINOLOGIES

Cryogenic Separation: This technology makes use of a large plant to cool a gaseous mixture to several hundred degrees below zero in order to separate the component gases. Cryogenic processes are also used for the recovery of pure carbon monoxide and pure hydrogen from gases resulting from partial oxidation or catalytic reforming processes.

Hydrogen Skimming: It is a hydrogen recovery process that involves separation of hydrogen from feedstreams containing hydrogen gas. The feedstream is usually a hydrogen-rich feed gas in order to ensure a reasonable recovery of the gas (hydrogen).

Membrane: A membrane is a thin physical barrier that allows selective transport of mass species by allowing some compounds or liquids to pass through, and prevents others. It is a semi-permeable skin of which, the pass-through is determined by size or special nature of the particles. Lu *et al.* (2007:3)

Non-Permeate (also known as **Retentate**): see **Permeate**

Non-Porous Membrane: This is a membrane type referred to as polymer membrane. Gas components pass through polymer membranes by the solution of gas molecules into the polymer material and by diffusion through the membrane material. SRI International (1990:4-1)

Permeability (also called **flux**): A property used to characterize a membrane material; it is the molar flux rate of the desired component (to be separated and purified) onto the surface and then through the thin film membrane. It is independent of membrane thickness and its unit is $\text{cm}^3\cdot\text{cm}/\text{sec}\cdot\text{cm}^2\cdot\text{cmHg}$. It is related to productivity. SRI International (1990:4-1, 4-2)

Permeance: Another useful parameter in thin film membranes; it is the ratio of the permeability to the membrane thickness. SRI Consulting (2001:3-5)

Permeate: In a membrane separation process for recovering hydrogen from a feed gas mixture comprising hydrogen and at least one other component, the feed gas mixture is separated in a membrane separation unit to produce a hydrogen-rich stream and a hydrogen-lean stream. The resulting hydrogen-rich stream is called the *Permeate* while the hydrogen-lean part is referred to as the *Non-Permeate*. Hopkins, DiMartino & Nicholas (2004:1)

Porous Membrane: This is a kind of membrane in which gases are separated on the basis of their molecular weight. It is typically made of ceramic, metallic, or carbon materials that do not possess high separation factors. SRI International (1990:4-1)

Pressure Swing Adsorption (PSA): This process is an energy efficient, non-cryogenic way of purifying gas. PSA is an adiabatic process and is applied for purification of gases by removing the accompanying impurities by adsorption through suitable adsorbents in fixed beds contained in pressure vessels under high pressure. BOC (2002:1)

Selectivity: A membrane property that is the ability of a thin film membrane to preferentially allow a component to pass through it while rejecting another component. It has no unit. A high selectivity gives a more effective separation of key components. For example, a membrane with relatively high selectivity increases the recovery of fast

gases, which reduces feed flow requirements to obtain a given permeate flow rate of desired product purity. SRI Consulting (2001:3-5)

Synthesis gas: It is referred to as the **non-permeate** stream in this dissertation. Also called “syngas”, it is a mixture of hydrogen and carbon monoxide. The ratio of the two gases in the mixture is dependent on the upstream process through which the gas has been produced and the downstream process where the gas would be utilized. Apanel (2002:12)

1.3 PROBLEM STATEMENT

The ATR plant under consideration produces reformed gas, synthesis gas (for diesel production) and hydrogen from natural gas. The section to be considered in this research work is the membrane unit.

The membrane unit produces synthesis gas and hydrogen from the reformed gas by a separation process. The synthesis gas (a mixture of hydrogen and carbon monoxide with a ratio of 1.89) is produced from the membrane by stripping some hydrogen from the reformed gas (hydrogen-carbon monoxide ratio of 2.24).

The hydrogen stream (the permeate) has a maximum allowance of about 2.5mol% of carbon monoxide concentration. However, the unit is currently not performing at its optimum capacity. There has been an increased concentration of carbon monoxide in the permeate stream (about 6mol%), reducing the stream's purity. In addition, the slippage of more carbon monoxide into the permeate has caused an increase in the synthesis gas (non-permeate stream – also called retentate) ratio required by downstream plants.

This dissertation seeks to find the reasons for the non-optimal membrane performance, and the steps to be taken to rectify such.

1.4 OBJECTIVES OF WORK

The aims of this research work are the following:

1. To investigate the cause of decreasing membrane hydrogen purity (decreasing selectivity).
2. To investigate the cause of insufficient membrane capacity to achieve the required synthesis gas ratio.
3. To proffer solutions to the aforementioned membrane conditions with reference to the operation of the membrane system and its design.

1.5 SIGNIFICANCE OF WORK

The petrochemical industry under consideration aims to produce “green” diesel (sulphur-free diesel) through the gas-to-liquids (GTL) technology. This dissertation is poised to help achieve this goal.

The efficiency of the Fischer-Tropsch process and the subsequent product upgrading are to a great extent a function of the effectiveness of the membrane unit in ensuring the right syngas composition. The GTL technology is aimed at producing cleaner fuels that are environmentally friendly, environmental specification compliant and which increase the performance of automobiles under some of the toughest road conditions.

Furthermore, this research work is aimed at increasing economic value for the industry’s shareholders and other stakeholders. This would be accomplished by the increase in productivity and profitability, from the elimination of conditions that decrease the membrane’s reliability and subsequently the plant’s availability.

1.6 SCOPE AND LIMITATION OF WORK

The scope to be covered by this research work is the ATR plant. This scope in turn, would be limited to the membrane unit of the ATR plant. The attendant problems that reduce the efficiency of the membrane unit including how to optimize this unit are encompassed in the scope of this project work.

However, it is noteworthy that the economic implications of optimizing the membrane operations are not treated within the scope of this research work.

CHAPTER TWO

LITERATURE SURVEY

2.1 THE NEED FOR HYDROGEN GAS SEPARATION IN THE INDUSTRY

The concept of a hydrogen (H_2) economy, a situation where hydrogen is used as the major carrier of energy, has been popular for many decades among futurists and some policy makers. The potential of hydrogen has been known for almost two centuries. The first combustion engine, developed in 1805 by Isaac de Rivaz, was fuelled with hydrogen. However, it was steam, and later petroleum, that have powered the world's engines so far. Lu *et al.* (2007:1)

The need for hydrogen will increase dramatically in the coming years due to the increasing demand for it as a raw material for the chemical industry, and for clean fuels in cars and home heating. This recent development has been spurred by the depletion of fossil reserves and the friendly environment requirement. Over the next decade, the demand for hydrogen in refineries is expected to increase rapidly due to the growing demand for environmentally friendly fuels, and the deterioration of crude oil quality.

The ever-increasing demand for H_2 as a green energy carrier or chemical in a variety of industries has promoted intense research interests in H_2 production and purification. However, the problem with H_2 production is that it is generally produced along with other co-products or side products. For instance, methane reforming, which is an important route for H_2 production, simultaneously generates carbon monoxide as a co-product. Hence, the separation or purification of H_2 is an inevitable process for many applications where pure H_2 is needed such as in semi-conductor processing, fuel cell applications, etc. Sun, Hidagat & Kawi (2006:110)

The purification or separation of hydrogen from industrial gases by means of membrane technology serves several purposes, including the improvement of existing processes and cheaper production of pure hydrogen.

Depending on its purity, the separated hydrogen can then be used for several hydrogenation reactions. The surplus can be sold as clean fuel. Naphtha crackers produce raw materials for commonly used plastics such as ethylene, propylene, butadiene and styrene. The worldwide hydrogen production from ethane and naphtha

crackers is approximately 2,400,000 t/a (tonnes per annum). If 50% of the hydrogen can be separated using hydrogen-separating membranes, 1,200,000 t/a will be retrieved. Meinema et al. (2005:86)

2.2 IMPORTANT MEMBRANE PROPERTIES REQUIRED FOR EFFICIENT SEPARATION

The basic and most important membrane properties are *selectivity* and *permeability*.

In the absence of defects, selectivity is a function of the material properties at given operating conditions. The productivity is a function of the material properties as well as the thickness of the membrane film; the smaller the thickness, the higher the productivity. Permeability and selectivity depend on the microstructures of the membrane/support composites such as pore size and distribution, porosity and the affinity between permeating species and the pore walls.

There are two basic requirements for membrane gas separation systems, i.e., technical and practical requirements. The former refers to those characteristics that must be present for the system to even be considered for the application. The latter refers to the characteristics that are critical to making a technically acceptable system competitive with alternative technologies, such as cryogenic distillation or pressure-swing adsorption (PSA). Lu et al. (2007:4, 5)

The *technical requirements* for two main types of membranes of interest to hydrogen separation are as follows:

- (1) For solution-diffusion membranes (polymeric or metallic), it is critical to attain a perfect pin-hole free or crack-free selective layer that can last for the entire working life of the membrane, in the presence of system upsets and long term pressurization.
- (2) For molecular-sieve membranes, a similar standard of perfection must be ensured to have no continuous pores with sizes greater than a certain critical size existing between the upstream and downstream membrane faces. For hydrogen separation, the pore size limit is around 0.3nm–0.4nm. Adsorption on the pore walls may reduce the effective openings well below that of the “dry” substrate.

(3) Most gas streams in industry contain condensable and adsorptive or even reactive components, so it is often desirable to remove such components prior to the membrane separation stage. Such pretreatment is not a major problem and other competitive separation processes such as PSA also use feed pretreatments. However, the more robust the membrane system is in its ability to accept unconditioned feeds, the more attractive it is in terms of flexibility and ease of operation. Therefore, for any type of membrane, the chemical and/or thermal stability are significant with respect to its life and operation. Lu *et al.* (2007:4, 5)

Besides the technical requirements as mentioned above, *practical requirements* dictate that a membrane should provide commercially attractive throughputs (fluxes or permeabilities). Even for materials with relatively high intrinsic permeabilities, commercially viable fluxes require that the effective thickness of the membrane be made as small as possible without introducing defects that destroy the intrinsic selectivity of the material. In practice, even highly permeable membranes are not used in thick film form to minimize the total materials costs because of the enormous membrane areas required for large-scale gas separation. Lu *et al.* (2007:5)

Loffler, Taylor & Mason (2003:9) wrote that the permeation rate increases with the hydrogen partial pressure differential across the membrane, and it is inversely proportional to the membrane thickness. As the thickness of the membrane is reduced, the permeation rate increases, hence less surface area is needed for a given hydrogen production. The permeation rate is an indication of gas flow across the membrane.

To corroborate the claim made by Loffler *et al.* above, Fick's equation describes the passive diffusion of gas molecules across a membrane viz:

$$F = \frac{A \cdot P \cdot c}{D} \dots\dots\dots (1)$$

Where,

F = gas flow

A = membrane surface area

P = pressure difference on the two sides of the membrane

c = a mathematical constant

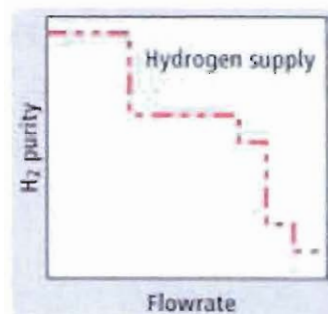
D = distance over which diffusion takes place (at the minimum, thickness of the membrane). National Oceanic and Atmospheric Administration (2001:3)

Therefore, increasing the membrane's surface area, reducing the membrane's thickness, and/or increasing the pressure difference across the membrane will increase gas flow across a membrane. "Pressure difference" is related to the difference in concentration of a gas on one side of the membrane compared to the other side. If there is no difference, then there will be no net flow of gas (according to Fick's equation, if $P = 0$ then $F = 0$). National Oceanic and Atmospheric Administration (2001:3)

Permselectivity (the *ideal separation factor* i.e., the ratio of the intrinsic permeabilities of the two permeates) also determines the energy used in compressing the feed gas, and if multistage system designs are needed. Unfortunately, high permselectivities often correlate with low intrinsic membrane permeabilities, and this presents a compromise between productivity and selectivity of the membrane. The trade-off between intrinsic membrane permeability and selectivity is a major issue amongst researchers who are constantly striving for better materials to optimize both properties. Lu *et al.* (2007:5)

Permeability is an indication of flow rate while selectivity is an indication of permeate purity. When permeability increases, it is usually accompanied by a decrease in permeate purity. Luque & Alvarez (2001:381). The figure below shows the relationship between the purity of hydrogen and its flowrate for a gas separation process.

Figure 2.1: Hydrogen composite curve



Source: Sentjens & Kerkhof (2003:1); Retrieved on October 15, 2006.

The higher the selectivity, the more efficient the process, the lower the driving force (pressure difference) required to achieve a given separation and thus the lower the operating cost of the separation system. The higher the flux, the smaller the membrane area that is required thus, the lower the capital cost of the system.

Gas permeance and selectivity are not the only criteria that determine suitability of membrane material for a given gas separation. High temperature resistance, high degree of strength, and reasonable resistance to a multitude of chemicals are also desired properties. SRI International (1990:4-5)

Another important property is the effective separation area to volume. Commercially available membranes are usually hundreds of microns thick. The development in the last few decades has been mainly directed to the fabrication of membranes as thin as possible – to reduce the material cost and to achieve a higher permeability, but without compromising the permselectivity. At the same time, the limited ratio of effective separation area to volume of available membranes or modules is also recognized as one of the limitations to the industrial applications, compared with polymer membranes in the configuration of hollow fiber. The best flat membranes provide a ratio of separation area/volume of $30 \text{ m}^2/\text{m}^3$ and tubular membranes of $250 \text{ m}^2/\text{m}^3$. Hollow fibers can be as high as $1000 \text{ m}^2/\text{m}^3$. Pan *et al.* (2003:265)

2.3 HYDROGEN SKIMMING METHODS

The commonly used hydrogen skimming methods include:

- Membrane separation
- Pressure swing adsorption
- Cryogenic separation

Heung & Congdon (2003:2) stated that all three processes are efficient for high hydrogen contents and high pressure feeds but not for low hydrogen contents and low pressure feeds.

2.3.1 MEMBRANE SEPARATION

2.3.1.1 HOW MEMBRANES EFFECT SEPARATION

Selective permeation is the general principle behind a membrane system. Each gas has a characteristic permeation rate that is a function of its ability to dissolve in, diffuse

through and dissolve out of the hollow-fibre polymer membrane. This characteristic allows "fast" gases such as oxygen to be separated from "slow" gases such as nitrogen. Air Products and Chemicals, Inc. (© 1996–2006:1)

The driving force of the separation process is the differential partial pressure that is created between the (compressed) feed side and the low-pressure side of the membranes.

A membrane filter consists of a bundle of hollow membrane microfibres. In the case of separating the components of air, the air is first compressed to the design pressure of the membrane. The compressed air is then passed through these hollow fibres, and the water vapour and/or carbon dioxide is removed by the principle of selective permeation through the membrane fibre wall. The relative permeation rates are as follows: water vapour (H₂O), carbon dioxide (CO₂), oxygen (O₂), argon (Ar), nitrogen (N₂).

In the case of syngas (a mixture of hydrogen and carbon monoxide), the permeation rate is the product of the solubility and diffusivity rates of the gases in the membrane. The membrane system utilizes these relative permeation rates to selectively separate hydrogen (a "fast" gas in this case) from carbon monoxide (the "slow" gas component) in the process gas stream. Air Products and Chemicals, Inc. (© 1996–2006:1)

2.3.1.2 TYPES OF HYDROGEN SEPARATION MEMBRANES

Basically, there are two major classifications for hydrogen separation membranes namely: *porous* and *non-porous*.

2.3.1.2.1 POROUS MEMBRANES

Under the classification of porous separation membranes, we have the following types:

- Ordered microporous inorganic membranes (IUPAC Recommendations 2001), e.g. zeolite membranes
- Microporous inorganic membranes e.g. carbon and amorphous silica. Bischoff, Judkins & Armstrong (2004:2)

2.3.1.2.1.1 ZEOLITE MEMBRANES

Zeolite membranes are generally formed on porous supports by hydrothermal synthesis. The pores in zeolite membranes are part of the crystal structure and, hence, have uniform dimensions. The size of the micropores, with molecular dimensions generally less than 1 nm, can be varied by the crystal structure.

Zeolites can separate molecules based on size, shape, polarity and degree of unsaturation, amongst other things. Many zeolites are thermally stable above 500°C. Some are stable in alkaline environments and some are stable in acidic media. Numerous available materials have been reported as support material, such as steel-wool sintered steel composites and porous alumina supports. Meinema *et al.* (2005:88)

In the production of zeolite membranes, the ability to prepare reproducibly very thin (less than 1.5 µm) and oriented zeolite layers with an almost complete absence of defects, as well as sufficient mechanical strength, has still to be reached.

Zeolite membranes offer good separation properties for gas molecules. At low temperatures the permeation rate increases with molecular weight, being essentially zero for hydrogen. At high temperatures (about 500°C), however, the trend is reversed, and permeation decreases with increasing molecular weight. At high temperatures the permeation rate for hydrogen is higher than for hydrocarbons, making the membrane particularly useful for hydrogen separation, e.g. in dehydrogenation reactions. Meinema *et al.* (2005:88)

2.3.1.2.1.2 AMORPHOUS SILICA MEMBRANES

Amorphous silica membranes are produced by sol-gel techniques. The micropore structure of the silica layers is determined by both the reactivity and the size of the precursors.

Microporous silica membranes have a high potential for gas separation and pervaporation at high-temperatures in chemically aggressive environments. Such membranes are of particular interest for high-temperature industrial hydrogen separation and purification. A major challenge is to increase the stability of the silica layer towards

hot steam. In this respect, the development of hydrophobic silica membranes is considered to be of interest. Preliminary studies have shown that hydrophobic membranes are much easier to handle and show less deactivation than hydrophilic materials. Alumina (3%), zirconia (10–70mol%) or titania may be added to silica to increase the stability of the composite in high humidity environments. Meinema *et al.* (2005:87)

2.3.1.2.1.3 CARBON MEMBRANES

Carbon membranes are produced by pyrolysis (carbonization at 500°C to 900°C) of polymeric precursor films (e.g. polyimide, polyfurfuryl alcohol, polyvinylidene chloride or phenolic resin) on a macroporous carbon substrate or an alumina support tube. Carbon polyimide membranes are the ones of major concern in this dissertation.

Carbon membranes prepared by the carbonization of a phenolic resin film have been transformed into adsorption-selective carbon membranes by an additional short time air oxidation prior to or after carbonization. In this way the separation properties of carbon membranes towards multi-component mixtures of hydrocarbons with and without nitrogen can be tailored. Meinema *et al.* (2005:87)

The predominant transport mechanism of most carbon membranes is molecular sieving. Hollow-fibre carbon molecular sieve membranes have been made via pyrolytic carbonization of organic polymers. Mixed carbon-silica membranes with excellent gas separation properties have been prepared by the pyrolysis of imide-siloxane copolymers at 600°C, 800°C and 1000°C. Meinema *et al.* (2005:87)

Microporous carbon membranes are classified into activated carbons with pore size 0.8nm–2nm and ultra microporous carbons or carbon molecular sieves with pores 0.3nm–0.6nm. The thermal stability of the carbon membrane depends on the nature of the contact gas. For helium gas, the maximum operating temperature of a carbon membrane is 700°C. For hydrogen, the temperature is greater than 500°C. For methane, 500°C is the maximum. For CO₂, the maximum operating temperature is 400°C while for oxygen it is less than 200°C. Meinema *et al.* (2005:87)

At present the most important large scale application of carbon membranes is in the production of low cost and high purity nitrogen from air, although they are also used for the separation of other mixtures, i.e. hydrogen from gasification gas, purification of methane, etc. Meinema *et al.* (2005:88). Due to the environmental concern of using coal for producing reformed gas through gasification, natural gas is currently being used in its place.

2.3.1.2.2 NON-POROUS MEMBRANES

Non-porous membranes are also referred to as dense inorganic membranes. The common types are:

- Dense perovskite membranes
- Dense palladium membranes
- Dense silica membranes

These membranes are prepared as unsupported ones as well as thin films on porous supports. They are made of polycrystalline ceramic material, in particular perovskites, or metal (palladium), which allows specific gas species to permeate the dense material.

Depending on the nature of the dense membrane material, hydrogen selectively permeates in atomic (palladium alloys), molecular (dense SiO_2 – silica oxide) or protonic (proton-conductive solid electrolytes) form. Meinema *et al.* (2005:87)

Both hydrogen and oxygen can permeate selectively through various types of dense membranes. Dense membranes are impermeable to all gases except for a very limited number of gases that can permeate the material (i.e. hydrogen through palladium) or can be incorporated into the structure of the membrane and transported through the material (i.e. oxygen through perovskites). Meinema *et al.* (2005:87)

Dense silica membranes are produced by CVI/CVD (chemical vapour infiltration/deposition) techniques. CVI/CVD silica membranes are produced by reaction of a gaseous silica precursor such as tetraethoxysilane, $\text{Si}(\text{OEt})_4$, with an oxidizing agent in the pores and/or on the surface of a macro-or mesoporous support such as an α -alumina layer or a γ -alumina layer deposited on an α -alumina support by a sol-gel process. Meinema *et al.* (2005:88)

CVI silica membranes have very high permselectivities towards hydrogen, however combined with a relatively low permeation rate. Higher hydrogen permeation can be achieved, though at the expense of selectivity. Silica membranes formed by CVD were both hydrogen and water selective depending on preparation procedure and post-treatment conditions. Meinema *et al.* (2005:88)

2.3.2 PRESSURE SWING ADSORPTION (PSA)

With respect to hydrogen, the PSA technology involves adsorbing impurities from a hydrogen-rich feed gas onto a fixed bed of adsorbents at high pressure. Subsequently, the impurities are desorbed into an offgas stream to produce an extremely pure hydrogen product. Product purities in excess of 99.999% can be achieved.

The process is semi-continuous in operation with a constant stream of hydrogen being produced by using multiple vessels. Each vessel adsorbs on-line in a predetermined sequence, controlled by a PLC (Programmable Logic Control) acting on a number of switch valves. Monitoring and proper control of process parameters ensures a stable operation. Stable operation means a pendulating swing in each particular location, in adsorber bed or piping, of values for all parameters, i.e. pressure, temperature, flow and composition of gaseous and adsorbed phase. NATCO (2006:1)

Certain porous materials (adsorbents), such as activated carbon, silica gel, activated alumina and zeolite, can preferentially adsorb gas molecules onto their surface. PSA uses this ability to separate hydrogen from syngas. The impurities in the feed gas are adsorbed into the carbon or zeolite packing leaving a pure stream of hydrogen to pass through.

Mostly, combinations of adsorbent beds are used on top of one another, so dividing the adsorber contents in a number of distinct zones. Waste gas molecules (carbon dioxide, carbon monoxide and water) in the gas stream are adsorbed onto the surface of the sieve particles, but the hydrogen passes up through the sieve bed to the top of the vessel. The bed gradually becomes saturated with the waste gases and if the process were allowed to continue, they would escape with the hydrogen. BOC (2002:1)

To ensure constant hydrogen purity, the bed is depressurized every few minutes allowing the adsorbed waste gas molecules to flow out of the bed. To obtain a continuous flow of product, a minimum of two adsorbers is needed, such that at least one adsorber is receiving feed gas and actually produces a product of desired purity. Simultaneously, the subsequent steps of depressurization, purging and repressurization back to the adsorption pressure are executed by the other adsorber(s). After such adsorbent regeneration and repressurization, the adsorber is switched onto adsorption duty, whereupon another adsorber is regenerated. BOC (2002:1)

2.3.3 CRYOGENIC SEPARATION

Cryogenic air separation is the traditional method of producing nitrogen and oxygen gases. However, cryogenic processes are also used for the recovery of pure carbon monoxide and pure hydrogen from gases resulting from partial oxidation or catalytic reforming processes.

Carbon monoxide is mainly used for the production of acetic acid, formic acid, polyurethane, polycarbonates and methylacrylates. The desired purity of carbon monoxide depends on the prevailing requirements and can be adjusted into the ppm (parts per million) range with respect to the residual contents of hydrogen and methane. Linde Engineering Division (2005:1)

To separate carbon monoxide from synthesis gas, there are basically two main cryogenic process types:

- Condensation process
- Methane scrubbing process

For both cases it is mandatory that the feed gas to the process is absolutely free from water, carbon dioxide and other components that could freeze at the low operation temperatures. Therefore process gas is initially purified in a molecular sieve adsorber station.

Feed gas from partial oxidation is normally supplied with high pressure, high carbon monoxide and low methane content. In this case, the condensation process is used. Alternatively, gases from steam reforming have lower pressure, lower carbon monoxide

and elevated methane content. In this case preferably methane wash is used and operated with methane supplied through the process gas. Linde Engineering Division (2005:1)

2.3.4 COMBINATIONS OF UPGRADING PROCESSES

Potential combinations of the three hydrogen separation processes under consideration have been receiving increased attention in recent years, particularly combinations involving the more recently developed membrane process. Integrations of the processes are designed to take advantage of the different process characteristics, e.g.:

- The ability of the PSA process to produce a high purity hydrogen product and to completely remove low boiling components.
- The ability of the membrane process to achieve high hydrogen recovery and to provide tail gas at feed pressure.
- The ability of the cryogenic process to efficiently separate the feedstream into multiple streams at high recovery. Miller & Stocker (1999:25)

There are still relatively few commercial applications involving combined processes. One reason for this is that the combined processes typically have significantly higher capital costs than any of the individual processes. High capital costs are sometimes unavoidable, because many applications require high hydrogen recovery from each process, and the capital costs of the membrane and PSA processes increase significantly with recovery. Miller & Stocker (1999:25)

2.3.4.1 PRESSURE SWING ADSORPTION/CRYOGENIC PROCESS

One of the more common integrations is the combined PSA/cryogenic process. The cryogenic process is used to make a bulk separation, usually with by-product production. The PSA process is used to further upgrade the product hydrogen from the cryogenic unit, either to increase hydrogen purity or to remove specific impurities. The tail gas may be recycled back to the cryogenic unit.

In this integration, the cryogenic unit can be made simple and less expensive (by avoiding for example, a methane wash column) and the PSA unit can be made smaller and achieve higher hydrogen recovery because of the reduced amount of impurities to

be adsorbed. This approach can be used for upgrading ethylene off-gas or low hydrogen content streams such as Fluid Catalytic Cracking off-gas. Miller & Stocker (1999:25)

2.3.4.2 MEMBRANE/PRESSURE SWING ADSORPTION PROCESS

A membrane unit can replace the cryogenic unit upstream of the PSA unit in some applications. The membrane unit is used to reject the bulk of the impurities at high hydrogen recovery, and the PSA unit upgrades the relatively low purity hydrogen produced by the membrane system. Hydrocarbons in the non-permeate from the membrane system can be recovered. The combined system achieves both high recovery and high hydrogen product purity, and low pressure tail gas is minimized. Feng *et al.* (1998:1689)

One example of using the combined technologies is the production of oxygen and nitrogen from air for aircraft on-board application where bulk separation by a membrane is followed by adsorption process for further purification. Several membrane/PSA combination schemes have been proposed in patent literature for various applications, including hydrogen purification, helium recovery, acid gas removal and nitrogen production. These hybrid schemes can be simply classified into two categories: one is membrane followed by PSA, the other is PSA followed by membrane. Feng *et al.* (1998:1689)

2.3.4.3 HYBRID MEMBRANE/CRYOGENIC PROCESS

The present invention involves a process for recovering hydrogen from a feed gas mixture comprising hydrogen and at least one other component. The feed gas mixture is initially separated in a membrane separation unit to produce a hydrogen-rich stream and a hydrogen-lean stream. The hydrogen-lean stream is subsequently treated in a cryogenic separation unit to remove a portion of the non-hydrogen components and produce a hydrogen-enriched stream. The hydrogen-enriched stream from the cryogenic separation unit is recycled and combined with the feed gas mixture to the membrane separation unit. Hopkins, Dimartino & Nicholas (2004:1)

Both the hydrogen-deficient stream from the cryogenic separation unit and the hydrogen-rich stream from the membrane separation unit are recovered as products from the system. In some instances, the hydrogen-rich stream recovered as product may

undergo post treatment for further purification and/or removal of undesirable components. For example, if the carbon monoxide (CO) concentration exceeds the CO product specification, the hydrogen-rich stream may be fed to a methanation reactor that reacts most of the remaining CO with some of the hydrogen to form methane and water. Chillers may also be used to remove the water if the hydrogen product dew point specification dictates. Hopkins, Dimartino & Nicholas (2004:1)

2.4 REVIEW OF STUDIES ON HYDROGEN SKIMMING

Hydrogen Separation in Gasification Gas Streams by Zeolite Filled Polyimide Membranes was a paper presented as a lecture at the "Engineering with Membranes" conference held in Granada, Spain. Luque & Alvarez (2001:379-384). It described the effect of microporous materials such as zeolites on the permeability and selectivity of polymer membranes.

Polyimide-zeolite composite membranes were described by permeation measurements using nitrogen (N₂), H₂ and carbon dioxide (CO₂). At high zeolite loadings, significant permeabilities and selectivities were observed while significant drops in permeate purity (selectivity) were observed due to penetration of other gases through cavity formations.

The membranes were prepared by dissolving polyimide and dispersing the zeolite powder in methylene chloride at three different percentages, 10%, 20% and 30% w/w (weight by weight). After thorough mixing to ensure homogeneity, the mixture was cast onto plates as film. Finally the membrane specimens were further dried at 100°C for 24hours.

For the measurement of permeability coefficients and the permeation fluxes of single gases and mixtures, a permeation cell was used. The high-pressure side was at 10bar to 30bar and the permeate side was at atmospheric pressure. A constant temperature water bath was used to obtain the desired temperature (25°C to 70°C), which was controlled within 0.5°C. A soap bubble meter connected to the low-pressure side was used for the measurement of the time dependent properties of the change in permeate volume. Gas chromatography was used for measuring the gaseous concentrations in the permeate and retentate streams.

From the experiment carried out, there was an increase in the permeabilities of all the gases that was almost linear with the increase in zeolite content. The enhancement of permeability could be linked directly to the asymmetric structure of the prepared membranes. It was noticed that an increase in the zeolite content led to a substantial decrease in the active membrane thickness.

Furthermore, two gaseous mixtures were chosen so as to look into the separation characteristics of the polyimide-zeolite membranes:

- i. 28.4% H_2 – 71.6% N_2 , simulating the composition of a stream produced by a Shell gasifier using bituminous coal, and
- ii. 43.4% H_2 , 10.2% CO_2 and 46.4% N_2 , simulating the composition of a stream produced by a Texaco gasifier using bituminous coal.

When permeability increases, it is usually accompanied by a decrease in permeate purity. However, the permeate purity almost remained constant for the membranes. In the membranes, the zeolite served as an extra sieving medium, which allowed the permeation of hydrogen while blocking the nitrogen molecules. In this way, the selectivity of the membranes was enhanced.

However, for the three component mixture (H_2 , CO_2 and N_2), a significant drop in permeate purity was observed due to cavity formation between the zeolite and polyimide structure through which gas could penetrate. The hydrogen concentration of the permeate stream decreased due to the permeation of carbon dioxide through the cavity. As carbon dioxide continually found its way through the cavity, the selectivity of the membrane was drastically affected. This counteracted the effect of the zeolite in enhancing the selectivity of the membrane.

The study carried out shows the effect of other components of the feed gas stream on the selectivity of hydrogen separation membranes leading to low purity of the permeate stream. This effect becomes more pronounced when the mechanical integrity of the membrane structure breaks down. Even when membranes are made with materials to improve the membrane properties (selectivity and permeability), gaseous contaminants could play a more damaging role to nullify the effect of these materials. The process

variables under consideration in this work are in conformity with those used in typical industrial scenarios.

Some of the gaseous components considered in this study with the hydrogen stream are synonymous to those obtained in autothermal reforming processes of natural gas to produce reformed gas as a substitute to coal gasification. In industrial processes of this kind, the gaseous contaminants exceed the ones used in this study.

Microporous Inorganic Membranes for Fluid Bed Catalytic Cracker (FCC) Off-Gas Recovery was another paper presented as a lecture at the “Engineering with Membranes” conference held in Granada. Luque & Alvarez (2001:450-455). With reference to investigating the effect of light hydrocarbons on the permeance of hydrogen through a hydrogen separation membrane, binary systems and quaternary systems were used. Substantial reduction in the hydrogen permeance through the membrane was observed between 15°C to 70°C and feed pressures from 100kPa to 1000kPa.

The gas mixtures studied included these four binary systems, hydrogen/methane (H_2/CH_4), hydrogen/ethane (H_2/C_2H_6), hydrogen/propane (H_2/C_3H_8), hydrogen/n-butane ($H_2/n-C_4H_{10}$) and a quaternary system, $H_2/CH_4/C_2H_6/C_3H_8$. The quaternary mixture, which was supplied by Air Products, consisted of 25% H_2 , 50% CH_4 , 20% C_2H_6 and 5% C_3H_8 .

Hydrothermal synthesis was used to prepare the membrane at a temperature of 170°C and afterwards calcination at 500°C was carried out. Adsorbed materials were removed before use, by pretreatment at 150°C in a flow of nitrogen. The apparatus used for this study was operated at feed pressures up to 900kPa. Back-pressure controllers were used for controlling the feed and permeate pressures. Measurements of gas flow rates were carried out using mass flow controllers.

Plots were drawn to show the effect of partial pressures on the membrane selectivity. For the results, there was a high recovery of hydrocarbons while a substantial rejection of hydrogen was noticed for the membrane. For the first binary mixture, the separation factor was moderate, having a value of 5. However, for the other hydrocarbons, there were higher separation factors over hydrogen ranging from 20 to 70. The observation

was that the presence of the strongly adsorbed components carbon-1 (C_1), carbon-2 (C_2) and carbon-3 (C_3) significantly reduced the hydrogen permeance.

On the other hand, for the quaternary mixture, the separation factors were observed to be lower than those of the binary mixtures due to the competitive adsorption of the hydrocarbons. The outcome of this was lower adsorption in the quantities of each of the hydrocarbons.

Furthermore, the effect of partial pressures of other components on the separation factors was noticed. The separation performance of hydrogen from the hydrocarbons was found to decrease as a result of an increase in the partial pressures of C_2H_6 and C_3H_8 in the permeate stream. The permeation of these hydrocarbons through the membrane was as a result of their concentration gradient in the adsorbed phase.

The study gives an explanation to how the partial pressures of hydrocarbons have an effect on the separation performance of hydrogen. Their partial pressures are a direct function of their mole fractions in the entire permeate stream. Wikipedia (2007). Therefore, as their number of moles increase, a corresponding increase would be noticed in their partial pressures, causing a reduction in that of hydrogen. As a result, the purity of hydrogen in the permeate stream is greatly affected.

Moreover, the study shows that the greater the types of hydrocarbons in the feed, the lesser their individual adsorption into the permeate stream. Nonetheless, the permeance of hydrogen is greatly reduced by the presence of strongly adsorbed components C_1 , C_2 and C_3 . However, in conditions whereby the hydrocarbons exist in the feed gas with other gaseous contaminants, their effects on each other should be studied. Certain gases tend to show lesser adsorption properties when co-existing with other gases, reducing their amounts in downstream sections of membrane separation.

Upgrading Biogas – Fuel Criteria was another paper presented as a lecture at the “Engineering with Membranes” conference held in Granada. It demonstrated the effect of water content and organic contaminants on the selectivity of microporous hydrogen separation carbon-membranes. Biogas containing CH_4 (methane), CO_2 , N_2 , O_2 (oxygen),

H₂, H₂S (hydrogen sulphide) and H₂O (water) was used for this experiment. The main components were methane (CH₄) and carbon dioxide (CO₂).

The carbon membrane used for this experiment was regenerated under vacuum at 200°C. For several feed compositions of CH₄ and CO₂, the permeability fluxes were measured at a temperature of 50°C while the feed pressure was decreased from 5bar (abs) to 1bar (abs) during the experiments. However, for these process variables, the compositions were kept constant.

It was observed that for the measurements of the methane permeation flux, it decreased with time (days). This loss of methane permeation was suggested to have been due to the adsorption of contaminants, including water, on the surface of the membrane and on the walls of its pores. Adsorbents could also have new sites on the surfaces and pore walls due to oxidation. As a result, the permeation of methane would continue to decrease. However, process solutions were suggested after the research work in order to reduce the loss of permeating methane. They are as follows:

1. It was suggested to recycle a fraction of the permeate stream to the feed (for the case of one membrane separator) or a second case is the cascade of two separators. Here, the permeate from the first module serves as feed for the second module.
2. The feed should be dried before it enters the membranes. This is a crucial step.

After the suggested process solutions, simulations of the above separation processes were carried out again and the results were impressive. The loss of methane through the permeate was drastically reduced.

There is no gainsaying the fact that an appreciable amount of work was carried out by Luque & Alvarez (2001:474-479). The major difference between this work and this dissertation is that, the main components here are methane and carbon dioxide, while hydrogen and carbon monoxide are the major components in my case. However, the components of the feed stream are similar, although not totally the same. Other membrane feed gas constituents in this dissertation (such as carbon monoxide, argon, ammonia and hydrogen cyanide) do not exist in this work.

Nonetheless, this research work has delved into the effects of water and other contaminants on permeation. The after-effect of its presence on the membrane surface and pore walls have been shown to be damaging.

A very commendable aspect of this work was the suggestion of solutions to the process in order to foster a better separation process. Also, the suggested solutions were simulated and the results were encouraging. However, the process of recycling the permeate would entail some re-design of the separation process which might not be cost-effective.

Feng *et al.* (1997:1689-1698) wrote a paper on a research carried out on Integrated membrane/adsorption process for gas separation. The research was aimed at improving the performance of gas separation by incorporating membrane permeation into the cyclic process of pressure swing adsorption (PSA).

The integrated process gives the opportunity for obtaining high permeability (product recovery) through the membrane process and high selectivity (product purity) through PSA. Noteworthy results were achieved especially for cases where the feed gas mixture contained unwanted contaminants that could not easily be removed by adsorption.

The combination of the two processes gave rise to a process with changing pressure as permeation proceeds with time. Therefore, the permeation process with varying pressure was studied to look into how feasible the integration of membrane into a PSA process would be. For the research work, two designs of the integrated process were investigated namely:

- i. Membrane-assisted feed gas pressurization (a membrane unit followed by two adsorbers)
- ii. Membrane-assisted co-current depressurization (two adsorbers followed by a membrane unit)

These two configurations were tested with hydrogen separation. Asymmetric hollow fibre membranes and 5A molecular sieve were used for permeation and adsorption, respectively.

For the measurement of permeability, an arrangement similar to a shell-and-tube exchanger was used for assembling 20 fibres of 15cm long in a U-loop configuration in a

small separation module. The feed gas was fed to the shell side of the module while the permeate exited through the lumen of the fibres. It was found out that as generally observed, the permeability (expressed by permeation flux) normalized by the transmembrane differential pressure was independent of pressure. From the results, there was a trade-off between product recovery and purity. Either a high recovery or a high purity was obtained, but seldom both.

In order to investigate how feasible the integration of membrane into a PSA process would be, permeation with changing permeate pressure was studied. In this case, a high-pressure feed gas was fed into the membrane unit, and the permeate was directed into a receiver (which would be an adsorber in the integrated membrane/adsorption system).

It was observed that the pressure in the permeate receiver increased as permeation proceeded with time. The permeation rate determined the rate of pressure buildup in the receiver, which in turn affected permeation rate. As expected, initially, there was a rapid permeate pressure build-up which later slowed down gradually. Since PSA normally operates under fast cycle conditions, fast permeate pressure build-up in the permeation period is specifically desired for incorporating a membrane into a PSA system.

At a point in time, the smaller the volume of the receiver, the greater would be the permeate pressure and the permeate concentration would become lower. This implied that a significant permeate pressure can be built up within a short period of time, making it possible to incorporate a membrane into a PSA process.

The feed gases separation tests were: (i) a 90% H_2 , 10% N_2 mixture (ii) a 60% H_2 , 20% N_2 , 10% CH_4 and 10%Ar (Argon) mixture. The feed gas pressure was 2170kPa and the cycle time was 18seconds.

For the membrane-assisted feed gas pressurization, the feed was introduced to the high-pressure side of the membrane unit before it entered two adsorbers. For the membrane-assisted co-current depressurization step of PSA, the permeator inlet was connected to the adsorber that was being depressurized and the outlet was connected to the adsorber that was being pressurized. Here, the pressure difference during pressure swing was used as the driving force of permeation to effect a separation. Thus,

the gas used for adsorber pressurization was purer than that gotten from the straight co-current depressurization process.

From the perspective of this dissertation, the results clearly showed improved separation performance of high selectivity and high permeability at the same time especially for the case where the feed gas contains impurities such as Argon that are difficult to remove by adsorption. Membrane-assisted co-current depressurization showed greater significance from an application point of view.

Furthermore, this novel process would help in solving problems of gas separation systems. Achieving high selectivity and high permeability concurrently, is a remarkable development in gas separation processes especially membrane applications. This study has shown that at a given feed throughput, the product purity can be enhanced significantly with a marginal reduction in the product recovery. For the case dealt with in this work, the adsorption process removes impurities from hydrogen while the permeation process extracts hydrogen from the impurities, which are much less permeable than hydrogen.

In a publication by Rautenbach *et al.* (1997:217-223), a study was carried out to investigate the effect of operating pressure on the permeability of gases in hollow fibre membranes. The gases used for the experiment were helium, oxygen and nitrogen.

The pure gas permeation experiments were performed in dead-end mode, i.e. the outlet on the high-pressure side and the inlet on the low-pressure side were closed. The feed pressure was automatically set with a pressure controller. The permeate flow rate was measured with thermal mass flow meters with different flow ranges. For temperature control, the entire set-up was placed in a thermostat that was set to 30°C.

All experimental data were continuously monitored. There were two fibres types taken from commercial air separation modules. A symmetric design of the module allows bore-side feed as well as shell-side feed. Each outlet was connected to a pressure gauge. Before any experiment, module and piping had been rinsed with the specific gas.

The permeance was calculated from permeate flow rate, pressure difference and the given geometry of the membrane. Pressure was varied in 2bar-steps from 2.8bar (abs) to 12.8bar (abs). At each level the pressure was held constant for 30minutes. The permeance varied instantaneously with the slightest change in pressure.

Only when the pressure was decreased in shell-side feed, some strange time-dependent behavior was observed. It was found out that a significant difference between bore-side feed and shell-side feed was observed: permeance of shell-side was always lower than in bore-side feed mode. But more interestingly, the difference even increased with increasing pressure.

Furthermore, the results showed that in both fibre types, the permeance of any gas increased with pressure in bore-side feed mode. In all cases, the increase of permeance for a pressure range from 2.8 to 12.8bar (abs) amounted to about $6\pm 12\%$ of the initial value.

With shell-side feed, a slight decrease of permeance was observed for oxygen and nitrogen (about $4\pm 8\%$ of the initial value) while the helium permeance seemed to be more or less constant. Since the effect was similar in relative numbers for all gases, no significant impact on the fibre selectivity was observed. Interestingly, both fibre types showed essentially the same behavior; although they were made from different material and have significant differences in morphology and geometry.

However, it was found out that in both fibres, the pressure changes caused changes in fibre dimensions. In principle, when the fibre diameter changes due to the applied pressure difference, the permeance will change in the same direction: bore-side feed will expand the fibre and increase permeance; shell-side feed will compress the fibre and decrease permeance. This mechanical deformation of the fibres was responsible for the change in permeabilities observed.

The question arose whether the permeance (ratio of permeability to membrane thickness) depended on the feed pressure or on the differential pressure across the membrane. Therefore, the results of an experiment with different permeate pressure were plotted. From the plot, it was obvious that the difference between bore and shell-side feed increased with increasing pressure difference and not with feed pressure.

The study has showed a good insight into some of the problems affecting hollow fibre membranes. It greatly shows the effect of transmembrane differential pressure on the properties of the membranes. Interestingly, from this research work, it can be seen that mechanical stress induced by the pressure difference across the membrane affects the permeance of the skin layer. This permeance is directly related to permeability of the membrane, as it is the ratio of permeability to the thickness of the selective skin layer i.e. the membrane.

Therefore, from this study, it can be seen that if the pressure difference across the membrane is not within the optimum range, the permeability would be greatly affected. Consequently, this would have an impact on the product recovery of the membrane. However, the results from this experiment stemmed from a pressure range of 2.8bar (abs) to 12.8bar (abs). From an industry perspective, the aforementioned pressure range might not be applicable due to high-pressure values that are encountered in real-life scenarios. Nonetheless, the pressure range in question gives a reasonable range for small-scale applications.

From a publication by Kluiters (2004:27), practical reasons on why membrane performance generally decreases with time were discussed. The effects of concentration polarization and fouling on the performance of hydrogen separation membranes were described.

In any membrane separation process, transport of the permeate (desired gas) through the membrane gradually reduces with time. This happens as a result of limited permeation of certain components of the feed gas stream. The author described this occurrence as the cause of concentration polarization. As a result of restriction in the permeation of these constituents, their concentration increases directly adjacent to the membrane. When this occurs, the desired gas would be hindered from permeating through. In order to reduce the effect of concentration polarization, the gas feed flow directly adjacent to the membrane is made turbulent. This would result in a better mix of the concentrated layer with the feed flow.

In another report by SRI Consulting (2001:3-6), increasing the cross-flow velocity well into the turbulent range can compensate for higher driving forces and flux rates that might otherwise foul a membrane through critical concentration polarization. This corroborates the publication by Kluiters on how to combat the effect of concentration polarization. However, a very important aspect of the report by SRI Consulting was the inclusion of periodic cleaning and backwashing as other effective means of removing the phase of high concentration formed by other constituents of the gas.

Kluiters described the adsorption of these gaseous components to the membrane surface (also inside the pores), limiting and even blocking permeation as fouling. H_2S and SO_2 (sulphur dioxide) were given as examples of gases that foul membranes. Suggestions given on how to alleviate the effects of fouling include:

- i. Cleaning the membranes by heating and purging with non-adsorbing gases.
- ii. Removing small particles from the feed flow using a filter.

A commendable aspect of this write-up on concentration polarization and fouling is the inclusion of ways in which their effects could be lessened in membrane separation processes. As a result, membrane operations can still be improved when performance has been hindered by the occurrence of these two phenomena.

“Microporous polypropylene hollow fibres can be coated with a $1.9\mu\text{m}$ layer of perfluorosulfonic acid polymer ('Nafion'), to give membranes selective for ammonia and hydrogen.” This statement was a result of study carried out on ammonia selective fibres by Vincenzo & Cussler (1995:19-26). The research work was aimed at the following:

- Developing membranes that are highly selective for ammonia.
- The membranes must be formed into a geometry capable of high fluxes per volume, probably in either a hollow-fiber or a spiral-wound module.
- Such membranes must be capable of functioning at the high pressures involved in this system.

In order to develop these membranes high flux capability, microporous hollow fibers were coated with $1.9\mu\text{m}$ skins of an ammonia selective membrane. The membranes used in this work were made of polyperfluorosulfonic acid ('Nafion'). Both flat sheets and coated microporous hollow fibers were made with this material. Both the flat membrane and the hollow fiber were mounted the same steady state flow apparatus. In this

apparatus, the feed gas was a mixture of ammonia and either nitrogen or hydrogen having several compositions.

The feed flow was at least $10^3 \text{cm}^3/\text{min}$. The feed pressure was 5kPa to 500kPa; its temperature was 25°C to 180°C . (Actual pressures for ammonia synthesis are often around 14MPa). The sweep gas was $10 \text{cm}^3/\text{min}$ helium except when hydrogen was in the feed; then it was $10 \text{cm}^3/\text{min}$ nitrogen. Gas concentrations in the retentate and the permeate were measured with a gas chromatograph which had been calibrated with gas mixtures of known concentration. In every case, the partial pressure of each gas in the permeate was less than 5% of its partial pressure in the feed.

The flux of ammonia across flat membranes, and the fluxes of ammonia, nitrogen, and hydrogen across coated hollow fibres were measured. The flux of ammonia across flat perfluorosulfonic acid membranes $18 \mu\text{m}$ thick was plotted as a function of temperature and pressure.

It was found out that the flux increased as the ammonia pressure difference across the membrane increased. This increase was linear with pressure at higher temperature, but it was more rapid than linear at lower temperature. The data at high temperature sometimes showed an apparent intercept, a zero flux at finite pressure, suggesting non-linear behavior at lower pressures than those measured. The ammonia fluxes across these membranes varied with temperature in a more complex fashion. The flux first dropped with temperature and then increased.

Furthermore, the ammonia fluxes across the coated hollow fibres also showed a flux at room temperature that increased more than linearly with ammonia pressure. Moreover, the ammonia flux was independent of the partial pressure of nitrogen in the feed, which in the experiments shown ranged from 0 to 300kPa. While the sets of data were in rough agreement, those on the flat membranes fell systematically below the results for coated hollow fibers. From this study, it was speculated that these systematic differences may have been due to uneven coating, to coating penetrating the pores, or to uncertain membrane areas.

In addition, hydrogen fluxes across the coated hollow fibers were measured using hydrogen-ammonia ($\text{H}_2\text{-NH}_3$) mixtures. The mixtures had different hydrogen

concentration, but the total pressure was always 1 atmosphere. The plots drawn showed that hydrogen fluxes increased linearly against hydrogen pressure at low hydrogen pressure, but more slowly against hydrogen pressure at higher hydrogen pressure. This implies a permeability that drops as the driving force increases.

Also, the flux of hydrogen increased with temperature. This simple behavior sharply contrasts with the more complex variation of ammonia flux with temperature. Such different variations implied that the membrane selectivity would be eroded by operation at high temperatures. Still, at 60°C, the perfluorosulfonic acid membrane was at least 50 times more selective for ammonia than for hydrogen.

From the study carried out, there is no gainsaying the fact that thorough work was done with respect to factors affecting the permeability and selectivity of the membrane in question.

The study shows that the perfluorosulfonic acid membranes possess a high ammonia permeability that varies relatively weakly with temperature. They show a high ammonia selectivity against nitrogen and hydrogen, but one that is reduced by increasing temperature. However, these experiments were not performed at the high pressures typical of ammonia synthesis. As a result, any effort to use these membranes at high pressures of industrial applications would need to consider not only membrane supports but also module seals and potting.

Furthermore, for this study, pure gaseous components were used which is in great contrast to typical practical situations. As a result, the effect of contaminants (unwanted gases) on the permeability and selectivity of the membrane materials need to be researched on.

With reference to minimizing the effect of deleterious chemicals on the performance of membrane fibres, the heat-resistant resin poly(etherimide) was selected as the polymer with the most outstanding properties for the separation of hydrogen from nitrogen and carbon monoxide. This formed the result of studies carried out by Membrane Technology and Research, Inc., Menlo Park, United States (1990:1).

Multilayer composite poly(ether-ester-amide) membranes were also developed. Their studies on these flat sheet and hollow fiber membranes were evaluated with pure gases and gas mixtures at elevated pressures and temperatures. The poly(etherimide) asymmetric membranes were evaluated with five different gases: hydrogen, carbon dioxide, carbon monoxide, methane and nitrogen. High-pressure permeability tests were carried out with flat-sheet membranes but the results were valid for the hollow-fiber poly(etherimide) membranes as well.

If the stream contains small quantities of hydrogen, the hydrogen-permeable poly(etherimide) membrane would be used to produce a hydrogen-enriched permeate. If the stream contains small quantities of carbon dioxide or hydrogen sulfide, the poly(ether-ester-amide) membrane would be used to produce a carbon dioxide/hydrogen sulfide-free, hydrogen-enriched residue stream.

The research carried out depicts a reasonable range of media for experimenting and testing the suitability and resistance of the multilayer composite membranes for use in hydrogen separation/skimming. Therefore, in the development of a material with better chemical resistant properties in order to decrease the susceptibility of membrane fibres (to damage by deleterious chemicals), the properties of poly(etherimide) and poly(ether-ester-amide) should be given consideration to.

Nonetheless, the specific process conditions under which the experiments were carried out were not included in this study. This is a crucial aspect in determining whether membrane materials under test conditions would be able to withstand the effect of deleterious chemicals in industrial applications such as the one for which this dissertation is written.

In this chapter, studies relating to the causes of low performance of hydrogen separation membranes were reviewed. Furthermore, some methods of improving the performance of these membranes as described in literature, were reviewed. The next chapter will give a brief description of the membrane operation and equations relating to the entire autothermal reforming process.

CHAPTER THREE

PROCESS DESCRIPTION

In this chapter, a brief description of the process according to design will be discussed. From the process description, the extent to which the membranes perform will be known in order to effectively proffer ways of improving their efficiency.

3.1 BRIEF PROCESS DESCRIPTION

The Autothermal Reforming plant is designed to convert natural gas (mainly methane) to reformed gas (a mixture of hydrogen, H_2 and carbon monoxide, CO). The processes/stages involved are natural gas desulphurization, natural gas pre-reforming, and reforming of the pre-reformed gas. The design ratio for the reformed gas is 2.24. After the reforming process, the hot reformed gas is cooled by several heat exchangers and the final condensate separator removes the condensate formed due to cooling. The cooled reformed gas is then sent to the membrane unit for hydrogen separation from carbon monoxide and other gaseous contaminants accompanying the gas from the upstream process.

The H_2/CO Membrane system is designed to produce a fixed ratio of H_2/CO mixture (synthesis gas). The feed gas (reformed gas) enters the system at a pressure of 2820kPa (g) and a temperature of 38°C.

The gas is heated in feed preheaters by heat exchange with high-pressure steam. Approximately 7% of the membrane feed gas enters the feed preheaters and is heated to around 149°C. The remaining 93% bypasses the heaters and mixes with the gas from the heaters. The mixed temperature is 47°C with an allowance within 38°C to 65°C. This is the final temperature of the feed gas entering the membranes. The purpose of heating is to drive the gas away from saturation and to give optimum performance of the membrane separators downstream of the feed heaters to maintain operating temperature in the downstream membrane separators.

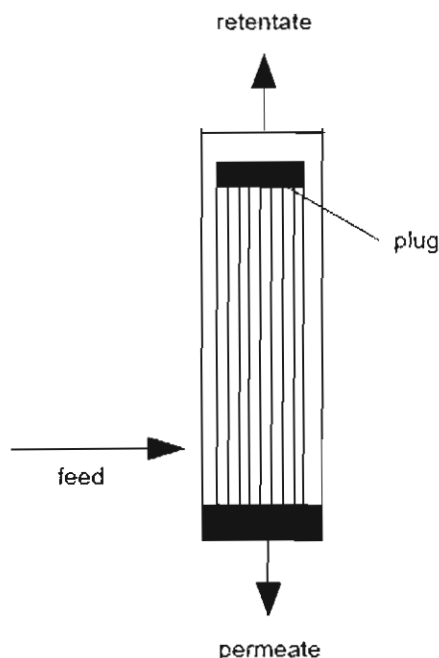
The membrane system consists of 36 membrane separators (or prisms) arranged in two parallel banks of 18 separators. Each bank contains three parallel groups of five, five and eight separators. Figure 3.1 shows the diagram of a membrane separator. Each separator is designed to handle a capacity of 10,000Nm³/hr of reformed gas. The

hydrogen-rich permeate stream flows through to the bore of the hollow fibres and leaves through the permeate gas nozzle. The remaining gas, which has a reduced hydrogen content, is the non-permeate product stream (synthesis gas) in which the H_2/CO ratio is required to be 1.89.

The membrane system has been designed to handle a future 125% case simply by the addition of additional membrane separators. Each bank of 18 membranes can be isolated for maintenance whilst the other bank remains online. Each group of separators can be manually turned off to maintain optimum membrane performance during turndown. The hydrogen and synthesis gas streams are then sent to downstream plants where they are utilized. The *Fischer-Tropsch* (F-T) process is one of the processes that utilize the synthesis gas. However, part of the hydrogen is sent back to the autothermal reforming process where it is also being used. (Air Products, 2002)

The figure below shows the schematic diagram of a membrane prism used for separating the feed gas into synthesis gas (retentate or non-permeate) and hydrogen (permeate)

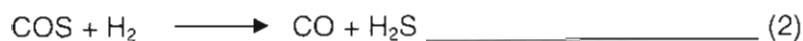
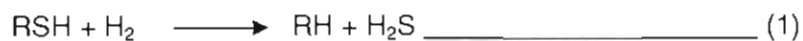
Figure 3.1: Membrane hollow-fibre configuration for gas separation



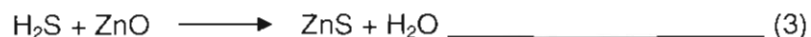
Source: Kluiters (2004:21); Retrieved on January 12, 2007.

3.2 EQUATIONS OF THE REACTIONS TAKING PLACE IN THE ATR PROCESS

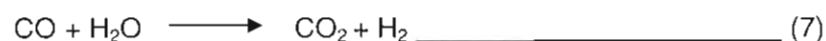
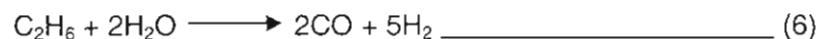
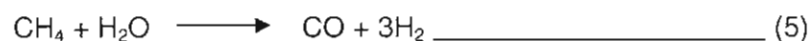
3.2.1 Hydrogenation:



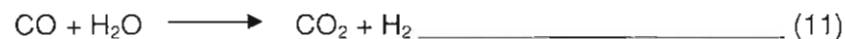
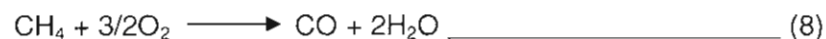
3.2.2 Desulphurization:



3.2.3 Pre-Reforming:



3.2.4 Reforming:



KEY:

RSH – Organic Sulphide

COS – Inorganic Sulphide

RH – Alkane

ZnO – Zinc Oxide

The next chapter will address the mode of data collection from the various data sources. The data to be obtained will give an insight to what obtains in practice regarding the causes of low membrane performance and how to optimize the membrane unit.

CHAPTER FOUR

EMPIRICAL INVESTIGATION

Chapter four addresses the collection of data from various available sources for the purpose of analysis and subsequent verification. The data obtained referred to the causes of low membrane performance and how to improve their efficiency from a practical point of view.

Data from the practical perspective (influenced by practical experience and human factors) obtained through questionnaires and personal interviews, will be compared with the literature review. In order to adequately optimize the membrane unit in question, disparities between theory and what is obtainable in practice will be discussed.

4.1 LITERATURE SURVEY AND EMPIRICAL INVESTIGATION – THE LINK

In chapter two, the literature sources that were used for the literature survey include:

- Journals containing recent developments on membrane separation
- Handbooks on membrane processes
- Papers and reports written by experts in the field of hydrogen membrane separation technology
- Scientific databases on conditions affecting membrane efficiency and causes of membrane failures
- The plant-specific operation manual of the Autothermal Reforming (ATR) plant of one of the leading petrochemical industries in South Africa

Afterwards, a review of the work done in literature was carried out. This involved a critical appraisal of the work reported in literature. Furthermore, principles involved in hydrogen separation and purification from various feed gas streams were explained in chapter two.

This section describes the link between the literature survey and the empirical investigation. The sources of data collection in this chapter include: the questionnaire, personal interviews and observation (see section 4.2).

The questions that formed the body of the questionnaire were a product of the review of studies in literature. However, some of the questions were completely plant-specific (the

ATR plant in question). Nonetheless, the possible operating conditions and factors limiting the performance of the membrane unit including the possible ways to improve its efficiency were obtained from the survey of work done in chapter two.

Thereafter, this link is aimed at comparing the results obtainable in practice with what is found in literature so as to make scientific judgments. However, should any disparity be found, explanations would be given where necessary.

4.2 COLLECTION AND GATHERING OF DATA

The methods of empirical investigation used for this research work include the following data sources:

1. Structured questionnaire (as compiled by the author of this dissertation)
2. Personal Interviews
3. Observations

4.2.1 THE QUESTIONNAIRE

The questionnaire was designed to understand the views of operators and senior personnel on the conditions affecting the performance of the membrane and ways of improving this performance. Their views are vital in order to be able to compare what is obtainable in practice with theory. Afterwards, these views would be synergized. The sample population for this survey includes the ATR plant operators, production foremen, managerial staff and engineers. This target population would be referred to as the *research community* in this research work.

The questionnaire consists of four (4) different parts namely:

- PART 1: RESPONDENT'S INFORMATION
- PART 2: PROCESS BACKGROUND
- PART 3: FACTORS MILITATING AGAINST MEMBRANE EFFICIENCY
- PART 4: OPTIMIZING THE MEMBRANE OPERATIONS

A total of 39 questions were drafted for both the operators' questionnaire and senior personnel's questionnaire. The designed questionnaires are displayed in Appendices A and B.

The questionnaires were distributed to the research community and results from the respondents are displayed in chapter five. Others are shown in Appendices D and G. The elements of the questionnaire are elaborated in the subsequent sub-sections.

4.2.1.1 DESIGN OF THE QUESTIONNAIRE

In order to design the questionnaire, existing and available 'measuring instruments' (questionnaires) from the scientific databases were sought for. However, some of the questionnaires published in open literature do not sufficiently cover the information intended to be extracted through the experimental design.

For the questionnaires published in open literature, the questions drafted with respect to the membrane units differ from the type of membrane unit at the ATR plant in this dissertation. The membrane units considered in open literature were those that were designed as a joint unit with the Autothermal Reforming reactor and not the type which involves the design of the unit as a complete and separate section downstream the Autothermal reforming reactor. Furthermore, the membrane types considered were the proton-conducting membranes, dense palladium and dense perovskites membranes as opposed to the hollow-fibre carbon membrane type for this study.

Following an interview with one of the plant engineers (*Personal Interview, November 2, 2006*), valuable inputs were obtained as to the design of the questions.

The format of the questionnaire and the questions were drafted to adequately cater for the current situation of the membrane unit of the plant under consideration. The progressive arrangement of questions was done in the following manner:

- i. Knowledge of the operational mode of the membrane unit
- ii. Acknowledgement of the conditions affecting the efficiency of the membranes
- iii. Causes of the factors militating against the efficiency of the unit
- iv. Solutions to optimize the performance of the membrane unit

4.2.1.2 OBJECTIVES OF THE QUESTIONNAIRE

The questionnaire was aimed at the following:

- To address the performance of the membrane unit of the ATR plant.
- To know the diverse views of the research community about the performance of the membrane unit.

- To test the awareness of the research community concerning what the operating conditions of the membrane unit should be and if they operate the plant at those conditions.
- To obtain different facets of the conditions affecting the membrane to include the practical (from the operators), technical (from the shift supervisors and managerial staff) and engineering (from the Research and Development personnel) perspectives.
- To gather the solutions proposed by these personnel on improving the membrane operations. Then make comparisons of these solutions with what obtains in literature and harmonize them in order to then get the plausible solutions to optimizing the membrane unit.

4.2.1.3 DATA COVERAGE

The questionnaire was distributed to all the operators for each of the production shifts of the ATR plant. Each shift consists of eight operators (both control panel operators and outside operators). Since there are four shifts, the total sample population for the production operators was 32.

The senior personnel consist of the shift supervisors, and personnel from the Research and Development Unit. There is a shift supervisor for each of the production shifts, making a total of four shift supervisors. Four managers of the plant formed part of the sample population. For the Research and Development Unit, a total of eight people were considered as the membrane section was not relevant to other personnel in this unit.

As a result, the total sample population for the questionnaire was a total of 48 people. However, out of the total sample population, 44 people (92%) filled and returned their questionnaires. This consists of 32 operators, the four shift supervisors, the four managers and four Research and Development engineers.

4.2.1.4 REASONS FOR TARGET POPULATION

The sample population considered for the questionnaire includes:

- The ATR plant operators
- The production shift supervisors

- The Research and Development personnel (engineers)
- Managers of the plant

The respondents were limited to this number owing to the fact that the ATR plant under consideration is the only Autothermal Reforming plant currently producing synthesis gas commercially within the jurisdiction of this work. Other companies such as ConocoPhillips, ExxonMobil, Shell, Energy International, Rentech, Syntroleum and British Petroleum make use of other reforming technologies like Partial Oxidation, Steam Reforming, Compact Reforming and Combined Reforming. Therefore, the sample population with some experience and knowledge on this reforming technology are the personnel in direct contact with the plant, as listed above.

4.2.1.5 VALIDATION OF THE QUESTIONNAIRE

The Production Manager and Training Manager of the ATR plant in question were formally used in validating the questionnaire. During the validation process, the questions were tailored to adequately cater for the conditions of the membrane unit in question. Afterwards, the cogency of the questions in producing the required results was confirmed.

4.2.2 PERSONAL INTERVIEWS

4.2.2.1 DESIGN OF THE INTERVIEW QUESTIONS

The questions for the personal interviews were drafted in order to give the research community opportunities to air their own views on the factors militating against the performance of the membrane unit and how to optimize the membrane operations. This was done in order to easily harmonize the views of the interviewees for both the plant and Research & Development unit on the issues concerning the membrane unit. This would also allow for ease of statistical analysis during the process of analyzing the results. The personal interview questions are displayed in Appendix C.

4.2.2.2 OBJECTIVES OF THE INTERVIEWS

The personal interviews were aimed at the following:

- To address the conditions facing the membrane unit from a perspective of the respondents. Do the views of the different set of interviewees differ from the each other? If it does, then a synergy of the views would be done

- To be able to get the true views of the interviewees on the issue at hand instead of restricting them to the limits of the questionnaire.
- To optimize the membrane operations by getting solutions from both the operators' perspective, senior personnel's standpoint and then comparing with what is obtainable in literature.

4.2.2.3 TARGET POPULATION

Some of the respondents of the questionnaire formed the target population for the personal interviews. However, every group that the research community consists of was represented amongst the interviewees.

4.2.2.4 REASONS FOR SIZE OF SAMPLE POPULATION

Owing to time constraints and difficulty in engaging the entire research community in interviews, the number of interviewees was limited to 12. This consists of six production operators, two shift supervisors, three managers and one engineer.

4.2.3 OBSERVATIONS

This data collection method involved participant observation on the field. I collected data from this mode from three different sources namely:

1. Field observation
2. Data collection from the control panel (DCS – Distributed Control System) of the plant
3. The plant's laboratory analysis

The **field observation** process is as follows:

- a) A critical examination of the physical conditions of two decommissioned membrane modules
- b) Recording of my findings

The **data collection from the control panel** involved the recording of the values of certain critical process parameters with respect to the operation of the membrane unit. The time frame for the collection of data from the control panel and laboratory analysis was three months.

The data obtained from observations are displayed in chapter five.

4.2.3.1 OBJECTIVES OF THE FIELD OBSERVATIONS

The observations that were carried out on the field were aimed at:

- Having a physical inspection and examination of the membrane prisms on the plant, with a view to documenting the conditions of the unit
- Comparing the actual conditions of the membrane unit on the field with the conditions acknowledged by the research community
- Subsequently harmonizing the observations of the actual conditions of the membrane unit with the ones obtained from the questionnaire and personal interviews.

4.2.3.2 OBJECTIVES OF COLLECTING RAW DATA FROM THE CONTROL PANEL

The following were the reasons for getting data of critical process parameters from the control panel:

- To get actual values of critical process parameters in order to confirm if there are deviations from the expected values
- Synergizing the raw values of process conditions and the physical conditions of the membrane unit on the plant

In conclusion, the aforementioned gives the mode of data collection and conducting of fieldwork carried out for this research work. In the next chapter, the results obtained from the empirical investigation will be presented and thereafter, discussed.

CHAPTER FIVE

RESULTS AND DISCUSSION

5.1 INTRODUCTION

Chapter five presents the results obtained from the empirical investigation through the data sources discussed in the previous chapter. Results from the control panel, laboratory analysis, field observation, questionnaires and personal interviews are presented. Afterwards, the respective results are analyzed and discussed in order to determine their implications in respect to the research work at hand. Thereafter, comparative discussions are also made with reference to what is obtainable in literature.

5.2 PRESENTATION OF RESULTS

5.2.1 CONTROL PANEL

Table 5.1: Control Panel Data for the Feed, Permeate and Non-Permeate streams

Feed		Permeate Stream				Non-Permeate Stream
Date	Flow rate (kNm ³ /hr)	Flow rate (kNm ³ /hr)	Differential pressure (kpa)	H ₂ Purity (mol%)	CO concentration (mol%)	Hydrogen/Carbon Monoxide Ratio
04/12/06	186.567	36.887	1628.2	90.43	5.98	1.86
07/12/06	186.534	36.885	1629.4	90.22	5.94	1.85
12/12/06	186.458	36.887	1632.1	90.23	6.03	1.87
14/12/06	186.553	36.886	1630.6	89.89	6.11	1.89
18/12/06	186.501	36.884	1630.9	89.94	6.12	1.89
20/12/06	186.497	36.885	1632.9	89.92	6.15	1.91
26/12/06	186.528	36.887	1633.4	89.89	6.18	1.94
29/12/06	186.545	36.887	1632.7	89.89	6.18	1.96
02/01/07	186.539	36.884	1633.8	89.85	6.18	1.91
05/01/07	186.557	36.886	1634.5	89.87	6.19	1.93
11/01/07	186.514	36.883	1634.6	89.76	6.21	1.89
16/01/07	186.496	36.883	1634.6	89.72	6.21	1.97
18/01/07	186.530	36.884	1634.8	89.89	6.20	1.98
25/01/07	186.559	36.883	1634.2	89.67	6.22	1.97
30/01/07	186.522	36.885	1635.3	89.65	6.22	1.99
05/02/07	186.505	36.884	1635.4	89.45	6.23	1.99
08/02/07	186.487	36.887	1635.9	89.52	6.26	2.01
14/02/07	186.495	36.887	1635.7	89.47	6.25	2.01
16/02/07	186.526	36.888	1636.0	89.44	6.24	2.02
20/02/07	186.542	36.886	1636.6	89.45	6.25	1.99
23/02/07	186.538	36.885	1635.9	89.43	6.27	2.03
27/02/07	186.552	36.887	1636.8	89.31	6.27	2.05

KEY: H₂ – Hydrogen

CO – Carbon Monoxide

mol% - Mole percent

5.2.2 LABORATORY ANALYSIS

Table 5.2: Laboratory Analysis of Membrane Permeate (Hydrogen) Stream

GAS PHASE							
Values in mol%							
H ₂	CH ₄	CO	CO ₂	N ₂	O ₂ + Ar	H ₂ O	NH ₃ + HCN
90.43	0.24	5.98	2.74	0.14	0.06	0.23	0.18
90.22	0.41	5.94	2.87	0.17	0.05	0.12	0.22
90.23	0.48	6.03	2.75	0.25	0.02	0.1	0.14
89.89	1.04	6.11	2.20	0.12	0.13	0.34	0.17
89.94	0.56	6.12	2.65	0.32	0.01	0.24	0.16
89.92	0.78	6.15	2.53	0.24	0.08	0.20	0.2
89.89	0.65	6.18	2.66	0.27	0.09	0.18	0.08
89.89	0.53	6.18	2.58	0.37	0.06	0.23	0.16
89.85	0.37	6.18	2.94	0.26	0.05	0.27	0.08
89.87	0.24	6.19	3.26	0.14	0.05	0.12	0.13
89.76	0.63	6.21	2.98	0.19	0.1	0.04	0.09
89.72	0.88	6.21	2.35	0.33	0.07	0.21	0.23
89.89	0.41	6.20	2.79	0.31	0.09	0.13	0.18
89.67	0.69	6.22	2.72	0.38	0.03	0.22	0.07
89.65	0.94	6.22	2.53	0.25	0.07	0.21	0.13
89.45	0.84	6.23	2.89	0.22	0.09	0.17	0.11
89.52	0.73	6.26	3.01	0.15	0.1	0.15	0.08
89.47	1.08	6.25	2.81	0.11	0.05	0.10	0.13
89.44	1.28	6.24	2.48	0.12	0.03	0.27	0.12
89.45	0.74	6.25	2.85	0.28	0.03	0.24	0.16
89.43	0.89	6.27	2.74	0.34	0.08	0.16	0.12
89.31	0.97	6.27	2.75	0.34	0.05	0.16	0.15

KEY: H₂ – Hydrogen CH₄ – Methane CO – Carbon Monoxide
N₂ – Nitrogen O₂ – Oxygen Ar – Argon H₂O – Water
NH₃ – Ammonia HCN – Hydrogen Cyanide CO₂ – Carbon Dioxide

5.2.3 FIELD OBSERVATION

Table 5.3: Observation of two decommissioned membrane modules

FINDINGS	
MEMBRANE SEPARTOR A	MEMBRANE SEPARATOR B
Wet membrane fibres with visible water condensation on the fibre surface	Droplets of water condensation on the surface of the fibres making them wet
Metal covering the membrane module still intact	Slightly dented metal covering for membrane module
A number of membrane fibres were brittle while some were broken	Some membrane fibres were broken while some were twisted

5.2.4 QUESTIONNAIRES

The results obtained from the questionnaires (Operators' and Senior personnel's) are presented in the tables below. Each set of results is displayed in two tables showing the raw data and percentages respectively.

NOTE:

1. The tables showing the raw data are displayed in Appendices D and G for the operators' questionnaire and senior personnel's questionnaire respectively.
2. In order to easily distinguish between the tables and figures that belong to the operators' questionnaire and those that belong to the senior personnel's questionnaire, the symbols "OP" and "SP" are put in parentheses at the end of each title. OP is used to denote operators' questionnaire while SP stands for senior personnel's questionnaire.

5.2.4.1 OPERATORS' QUESTIONNAIRE

Table 5.4: Process Background on work experience (Percentage) (OP)

Question	Yes (%)	No (%)	Total (%)
Have you at any time been delegated to work at the membrane unit of the plant?	88	12	100

Table 5.5: Process Background on operational knowledge (Percentage) (OP)

Question	Yes (%)	No (%)	Partially (%)	Total (%)
Do you fully understand the operational mode of the membrane unit?	94	0	6	100

Table 5.6: Process Background on knowledge of the process (Percentage) (OP)

Question	Strongly Agree (%)	Agree (%)	Strongly Disagree (%)	Disagree (%)	Cannot Say (%)	Total (%)
The membrane is critical to obtaining the right product quality for the plant	56	44	0	0	0	100

Table 5.7: Membrane performance (Percentage) (OP)

Question	Yes (%)	No (%)	Cannot Say (%)	Total (%)
Is the membrane unit performing according to design specifications?	3	75	22	100

Table 5.8: Frequency of low membrane performance (Percentage) (OP)

Question	Always (%)	Often (%)	Seldom (%)	Never (%)	Total (%)
Since your appointment as an operator in the plant, how often has the membrane witnessed failure or performed below expected performance?	0	66	19	15	100

Table 5.9: Factors Militating Against Membrane Efficiency (Percentage) (OP)

	Strongly Agree (%)	Agree (%)	Strongly Disagree (%)	Disagree (%)	Cannot Say (%)	Total (%)
High membrane feed gas temperature	0	9	13	78	0	100
High membrane feed gas pressure	0	3	6	91	0	100
High differential pressure across the membranes	66	22	0	9	3	100
High membrane feed gas speed	41	44	0	3	12	100
Presence of ammonia in the feed gas to the membrane fibres	44	31	0	6	19	100
Presence of methane in the feed gas to the membrane fibres	0	0	12	88	0	100
Presence of hydrogen cyanide in the feed gas to the membrane fibres	0	19	31	44	6	100
Presence of carbon monoxide in the feed gas to the membrane fibres	16	44	12	28	0	100
Presence of carbon dioxide in the feed gas to the membrane fibres	0	0	44	56	0	100
Presence of hydrogen sulphide in the feed gas to the membrane fibres	0	0	19	44	37	100
Presence of nitrogen in the feed gas to the membrane fibres	0	0	59	41	0	100
Insufficient heating of feed gas by the preheaters	12	47	0	29	12	100
Low membrane feed gas pressure	0	25	34	41	0	100
Low differential pressure across the membranes	0	9	0	66	25	100
Low membrane feed gas speed	0	12	9	69	9	100
Presence of cavity formations in the membrane structure	0	34	6	38	22	100
Presence of heavy hydrocarbons than methane in the feed gas	16	62	0	3	19	100
Occurrence of concentration polarization at points adjacent to the membrane	0	6	26	12	56	100

Table 5.10: Opinions of operators on possible causes of the conditions affecting the efficiency of the membranes (Percentage) (OP)

Suggestions on the factors affecting the efficient performance of the membrane unit with the most damaging effect amongst the listed possible causes in the questionnaire	
Response	Number of Respondents (%)
High membrane feed gas speed	91
Presence of ammonia in the feed gas to the membrane fibres	72
Insufficient heating of the feed gas by the preheaters	66
High differential pressure across the membranes	38

Table 5.11: Optimizing the membrane operations (Percentage) (OP)

	Strongly Agree (%)	Agree (%)	Strongly Disagree (%)	Disagree (%)	Cannot Say (%)	Total (%)
Making the feed gas flow directly adjacent to the membrane a turbulent one	0	0	22	66	12	100
Installing drains in the feed gas header in order to prevent condensate from getting to the membrane fibres	0	94	0	6	0	100
Checking the membrane feed header for liquid accumulation before the membrane groups are commissioned	47	53	0	0	0	100
Incorporating a Pressure Swing Adsorption system into the process line before the membrane unit, so as to remove any possible gaseous contaminants in the membrane feed gas stream.	0	9	0	12	79	100
Reducing the membrane feed gas speed through the reduction of individual partial pressures by removing other gaseous constituents of the membrane feed gas stream through the Pressure Swing Adsorption system	0	9	0	16	75	100
Cleaning the membranes by heating and purging with non-adsorbing gases	0	12	0	19	69	100
Periodic cleaning and backwashing in order to remove the high concentration phase formed by other constituents of the gas	28	44	0	12	16	100

5.2.4.2 SENIOR PERSONNEL'S QUESTIONNAIRE

Table 5.12: Process Background on work experience (Percentage) (SP)

	Yes (%)	No (%)	Total (%)
Have you at any time been delegated to work at the membrane unit of the plant?	83	17	100

Table 5.13: Process Background on operational knowledge (Percentage) (SP)

	Yes (%)	No (%)	Partially (%)	Total (%)
Do you fully understand the operational mode of the membrane unit?	75	0	25	100

Table 5.14: Process Background on knowledge of the process (Percentage) (SP)

	Strongly Agree (%)	Agree (%)	Strongly Disagree (%)	Disagree (%)	Cannot Say (%)	Total (%)
The membrane is critical to obtaining the right product quality for the plant	58	33	0	0	9	100

Table 5.15: Membrane performance (Percentage) (SP)

	Yes (%)	No (%)	Cannot Say (%)	Total (%)
Is the membrane unit performing according to design specifications?	0	75	25	100

Table 5.16: Frequency of low membrane performance (Percentage) (SP)

	Always (%)	Often (%)	Seldom (%)	Never (%)	Total (%)
Since your appointment as an operator in the plant, how often has the membrane witnessed failure or performed below expected performance?	0	67	33	0	100

Table 5.17: Factors Militating Against Membrane Efficiency (Percentage) (SP)

	Strongly Agree (%)	Agree (%)	Strongly Disagree (%)	Disagree (%)	Cannot Say (%)	Total (%)
High membrane feed gas temperature	0	8	17	75	0	100
High membrane feed gas pressure	0	33	0	67	0	100
High differential pressure across the membranes	25	58	0	17	0	100
High membrane feed gas speed	50	33	0	17	0	100
Presence of ammonia in the feed gas to the membrane fibres	42	42	0	17	0	100
Presence of methane in the feed gas to the membrane fibres	0	0	58	42	0	100
Presence of hydrogen cyanide in the feed gas to the membrane fibres	0	33	25	42	0	100
Presence of carbon monoxide in the feed gas to the membrane fibres	0	0	75	25	0	100
Presence of carbon dioxide in the feed gas to the membrane fibres	0	17	17	67	0	100
Presence of hydrogen sulphide in the feed gas to the membrane fibres	0	8	25	58	8	100
Presence of nitrogen in the feed gas to the membrane fibres	0	0	58	42	0	100
Insufficient heating of feed gas by the preheaters	17	58	0	25	0	100
Low membrane feed gas pressure	0	8	25	67	0	100
Low differential pressure across the membranes	0	17	25	58	0	100
Low membrane feed gas speed	0	8	17	67	8	100
Presence of cavity formations in the membrane structure	0	25	17	50	8	100
Presence of heavy hydrocarbons than methane in the feed gas	8	50	0	33	8	100
Occurrence of concentration polarization at points adjacent to the membrane	0	17	8	50	25	100

Table 5.18: Opinions of senior personnel on possible causes of the conditions affecting the efficiency of the membranes (Percentage) (SP)

Suggestions on the factors affecting the efficient performance of the membrane unit with the most damaging effect amongst the listed possible causes in the questionnaire	
Response	Number of Respondents (%)
Presence of ammonia in the feed gas to the membrane fibres	83
High membrane feed gas speed	75
High differential pressure across the membranes	67
Insufficient heating of feed gas by the preheaters	25

Table 5.19: Optimizing the membrane operations (Percentage) (SP)

	Strongly Agree (%)	Agree (%)	Strongly Disagree (%)	Disagree (%)	Cannot Say (%)	Total (%)
Making the feed gas flow directly adjacent to the membrane a turbulent one	0	0	33	42	25	100
Installing drains in the feed gas header in order to prevent condensate from getting to the membrane fibres	25	75	0	0	0	100
Checking the membrane feed header for liquid accumulation before the membrane groups are commissioned	83	17	0	0	0	100
Incorporating a Pressure Swing Adsorption system into the process line before the membrane unit, so as to remove any possible gaseous contaminants in the membrane feed gas stream	0	33	0	25	42	100
Reducing the membrane feed gas speed through the reduction of individual partial pressures by removing other gaseous constituents of the membrane feed gas stream through the Pressure Swing Adsorption system	0	33	0	17	50	100
Cleaning the membranes by heating and purging with non-adsorbing gases	0	25	8	58	8	100
Periodic cleaning and backwashing in order to remove the high concentration phase formed by other constituents of the gas	0	75	0	25	0	100

5.2.5 PERSONAL INTERVIEWS

A number of operators and senior personnel were interviewed personally with reference to their views on the conditions of the membranes and how to enhance the membrane's performance. The general responses given to the questions asked including the percentage of interviewees with such responses are listed below:

Question 1: In your opinion, what are other causes of the conditions affecting the efficiency of the membranes?

Responses:

"...The membrane unit has been showing signs of low performance for over a period now. You can never pinpoint a particular action as the main cause of the conditions affecting the efficiency of this section of the Autothermal Reforming plant". However, one of the major causes is the condensate which contains ammonia. The final condensate separator does not completely remove the condensate in the feed and this is a problem. The fibres become brittle as a result of the condensate and the ammonia which it contains. As the feed gas flows with a high velocity to the brittle membrane fibres, it causes them to break." – *Quote from a Personal Interview with a Shift Supervisor of the Autothermal Reforming plant, 01.17am, December 26, 2006.*

- a) The water (condensate) which carries over ammonia from the upstream process embrittles the fibres and the high flow velocity causes the brittle fibres to break [33% of the interviewees]
- b) Presence of gases which block the flow of feed gas to the membrane fibres [25% of the interviewees]
- c) No idea at the moment [25% of the interviewees]
- d) Membrane unit not being able to handle the current capacity of feed gas [17% of the interviewees]

Question 2: As an operator/senior personnel/engineer for the ATR plant, what adjustments do you feel could be made to the process parameters for efficient operation of the membrane unit?

Responses:

"...Changing the process parameters is not that easy as it seems. The membrane unit is sensitive to process variables such as temperature. But, I feel that if the temperature of

the reformed gas entering prisms is increased to say, 57°C to 59°C, the gas would not be able to condense due to heat losses in the pipe before it gets to the membranes...” – *Quote from a Personal Interview with a Senior Process Controller of the Autothermal Reforming Plant, 10.44pm, December 17, 2006.*

- a) No idea at the moment [58% of the interviewees]
- b) Differential pressure across the membranes should be lowered in order to reduce the flow of feed gas through the prisms (membrane modules) [33% of the interviewees]
- c) Increasing the reformed gas feed temperature to about 57°C to 59°C in order to prevent heat losses before the feed gas gets to the membranes. [9% of the interviewees]

Question 3: In your opinion, what changes do you feel can be made to the design of the membrane unit in order to optimize (enhance the effectiveness of) the membrane unit?

Responses:

“...It is still possible to have more quantity of hydrogen in the overall permeate. Some of the permeate stream can be rerouted back to the feed stream. I mean, resending an amount of the permeate with the feed into the membrane unit which would require installing a line joining the permeate stream with the feed header...” – *Quote from an engineer from the Research and Development unit, 02.13pm, December 28, 2006.*

“You cannot redesign the whole separation process like that. The cost implications are too high. But, a bypass could be installed around the membrane unit so as to send the gas straight to the clients. Which means the required syngas ratio would be obtained from the autothermal reforming process itself by using the Auto-control system. This would also increase the life span of the membranes...” – *Quote from a senior personnel of the Autothermal Reforming Plant, 12.05pm, January 5, 2007.*

- a) No idea at the moment [58% of the interviewees]
- b) More banks of membrane modules should be installed for backup purposes so that in case of other banks getting faulty, then the banks on stand-by can be commissioned. This would also increase the membrane unit's availability. [25% of the interviewees]

- c) Recycling the permeate back to the feed stream so as to have more yield of hydrogen in the permeate. [9% of the interviewees]
- d) A bypass should be installed around the membrane unit in order to increase the life span of the membranes [whereby the required syngas ratio would have been obtained for the product gas from the Autothermal reformer without any need for membrane separation]. [9% of the interviewees]

Question 4: As an operator/senior personnel/engineer who has acquired some working experience on the membrane unit of the ATR plant, please suggest ways by which the effect of the conditions affecting the membrane's efficiency could be eliminated or minimized in order to enhance its operation.

Responses:

"I feel the efficiency of the final condensate separator is reducing. If a demister unit is installed in the process line before the reformed gas enters the membrane unit, the condensate which could not be removed by the final condensate separator would be knocked off by the demister unit. By this, the unwanted condensate would be prevented from getting to the membrane fibres" – *Quote from a Process Controller of the Autothermal Reforming plant, 11.36am, January 2, 2007.*

- a) Maintenance work should be carried out on the membrane prisms more often in order to be able to detect faults and problems on the fibres on time. [50% of the interviewees]
- b) No idea at present. [25% of the interviewees]
- c) A demister unit should be installed just before the gas enters the membranes in order to ensure that any remaining traces of condensate in the feed are removed before it gets in contact with the membrane fibres. [8% of the interviewees]
- d) Unwanted vapours and gases should be removed from the feed gas with the use of adsorbents [8% of the interviewees]
- e) Dryers/a drying unit should be installed upstream of the membrane unit along the feed gas stream so as to remove any condensate present. [8% of the interviewees]

5.3 ANALYSIS OF RESULTS

Analysis of the results comprises the plots and charts drawn from the raw data obtained from the control panel, laboratory analysis and questionnaires. The representation of the data using charts is aimed at giving a graphical analysis of the displayed results.

Fig 5.1: Plot of non-permeate H_2/CO ratio against CO concentration in permeate

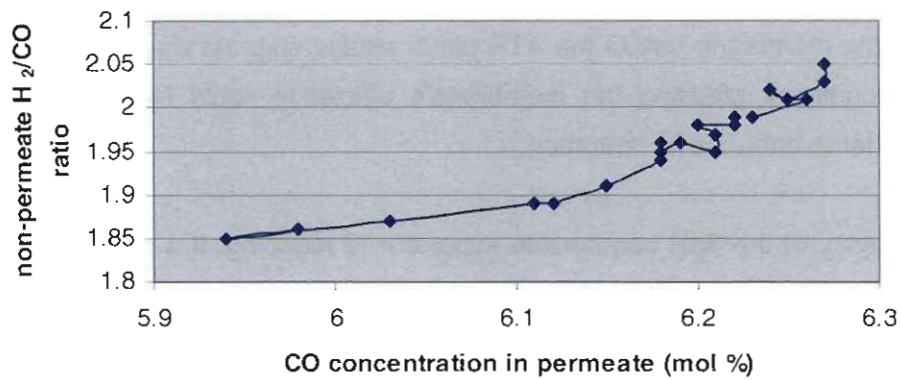
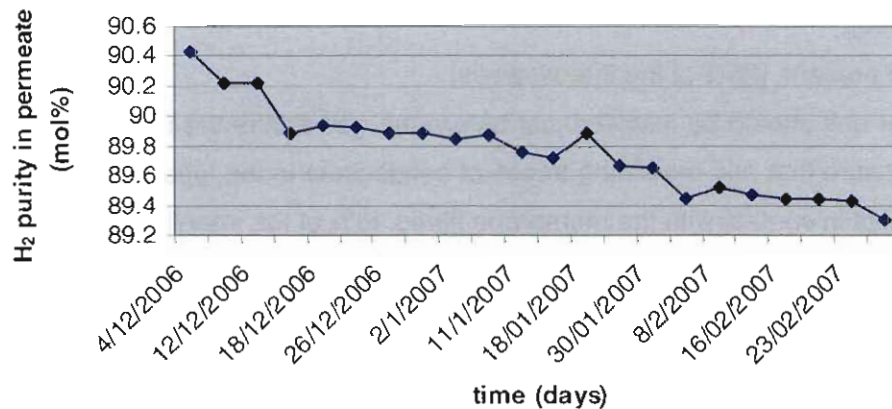


Fig 5.2: Plot of H_2 purity in permeate against time



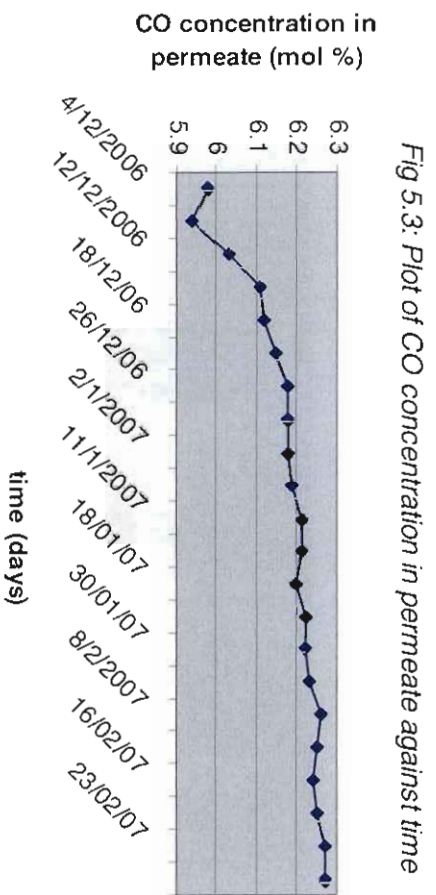


Fig 5.3: Plot of CO concentration in permeate against time

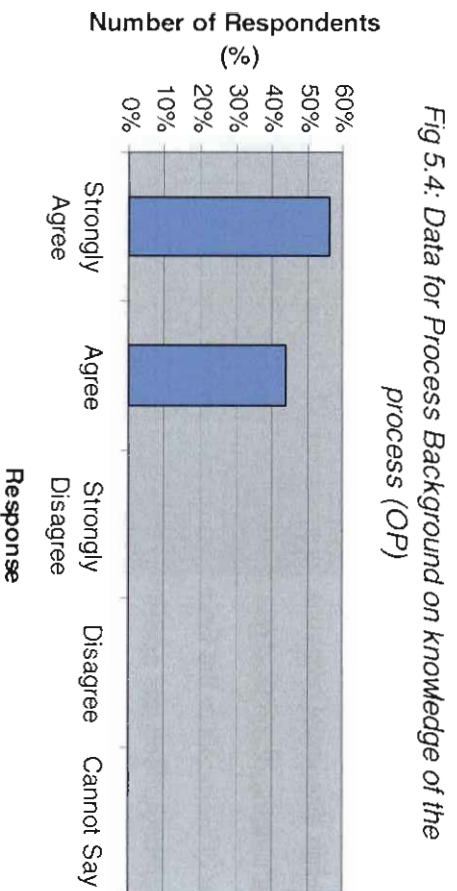


Fig 5.4: Data for Process Background on knowledge of the process (OP)

Fig 5.5: Data for High membrane feed gas temperature (OP)

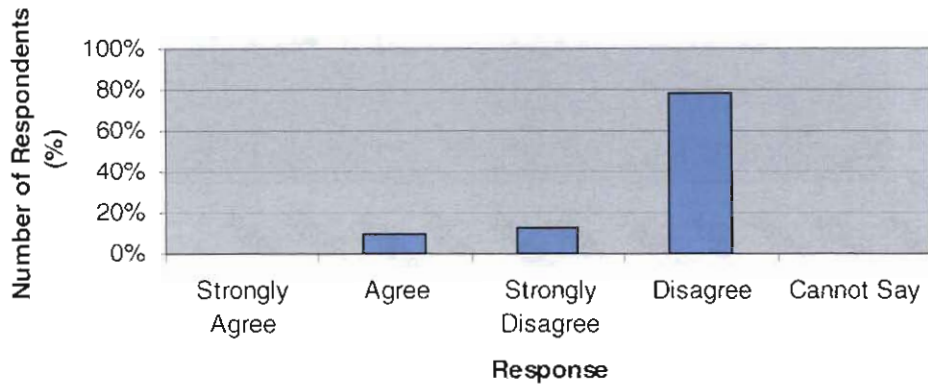
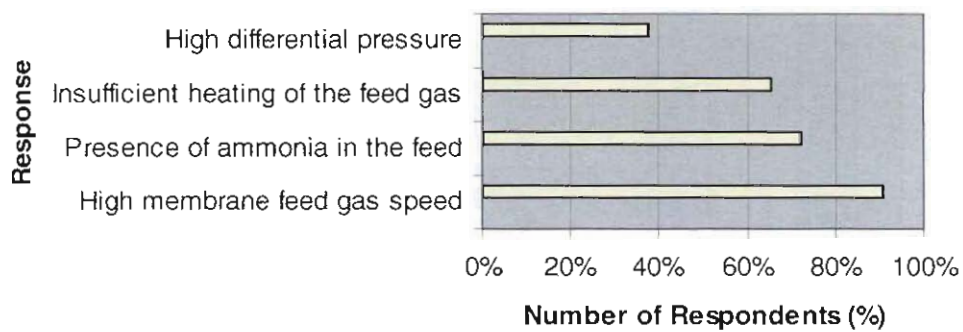
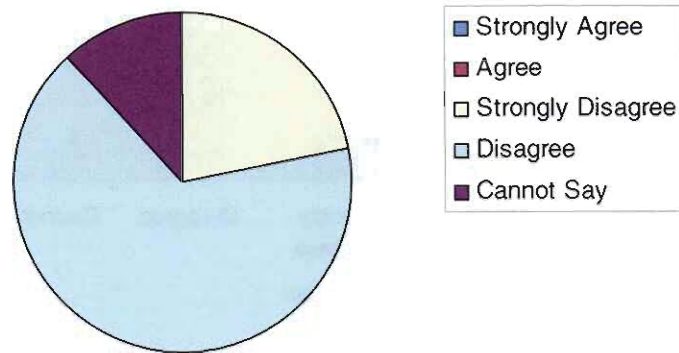


Fig 5.6: Opinions of operators on possible cause of conditions affecting the efficiency of the membranes (OP)



The other figures for results obtained on the factors militating against membrane efficiency for the operators' questionnaire are shown in Appendix E.

Fig 5.7: Data for Making the feed gas flow directly adjacent to the membrane a turbulent one (OP)



The other figures for results obtained on optimizing the membrane operations for the operators' questionnaire are shown in Appendix F.

Fig 5.8: Data for Process Background on knowledge of the process (SP)

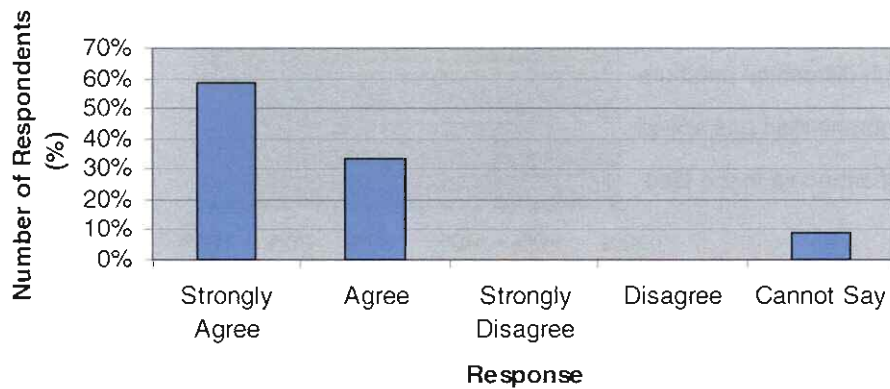
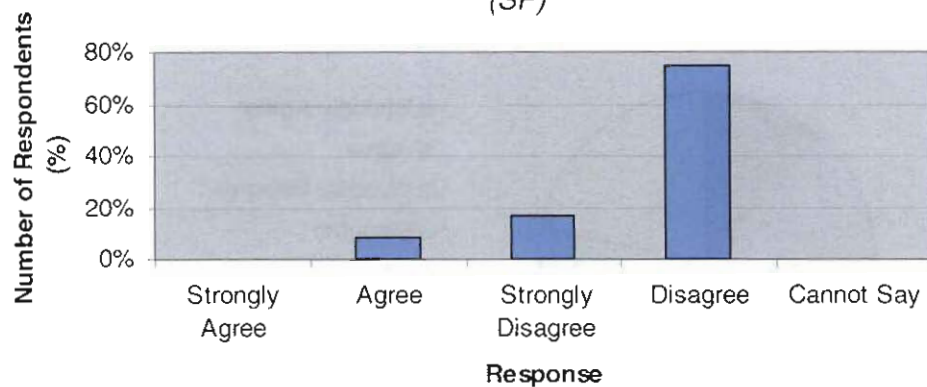


Fig 5.9: Data for High membrane feed gas temperature (SP)



The other figures for results obtained on the factors militating against membrane efficiency for the senior personnel's questionnaire are shown in Appendix H.

Fig 5.10: Opinions of senior personnel on possible cause of conditions affecting the efficiency of the membranes (SP)

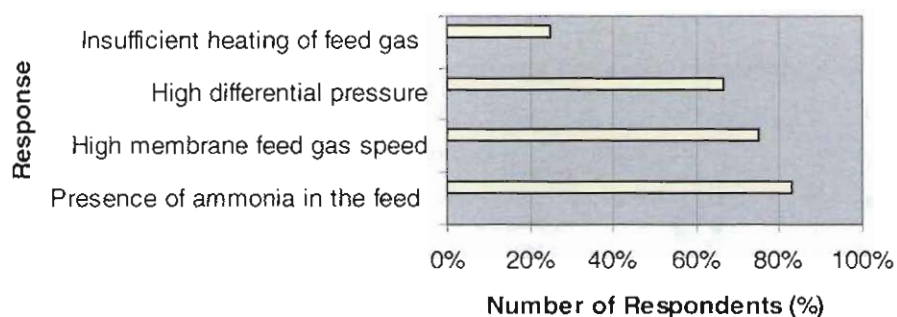
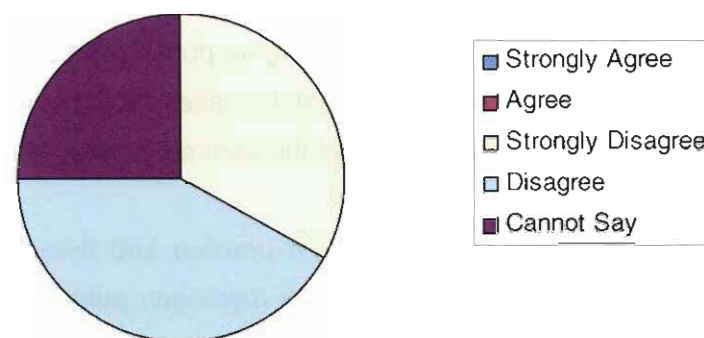


Fig 5.11: Data for Making the feed gas flow directly adjacent to the membrane a turbulent one (SP)



The other figures for results obtained on optimizing the membrane operations for the senior personnel's questionnaire are shown in Appendix I.

5.4 DISCUSSION OF RESULTS

The results displayed above give an indication of the awareness of a majority of the plant personnel towards the conditions of the membrane unit (its low selectivity for hydrogen gas) relatively compared with design specifications.

5.4.1 CONTROL PANEL, LABORATORY ANALYSIS AND FIELD OBSERVATION

A scrutiny of the data obtained from the control panel (see Table 5.1) including the plot drawn shows that as the concentration of carbon monoxide (CO) increased in the permeate (hydrogen) stream, the syngas ratio (hydrogen to carbon monoxide) increased likewise. (see Figure 5.1). This is an indication of the fact that the slippage of CO into the stream has an effect on the purity of the permeate.

This argument is further buttressed by the plot of hydrogen (H_2) purity in the permeate against time (see Figure 5.2). By design, the permeate is supposed to consist of a high purity of hydrogen gas with a maximum allowance of 2.5mol% (mole percent) of CO slippage. As a result, values of 5.98 to 6.27mol% of CO would greatly affect the purity of the H_2 gas needed by downstream plants where it is been utilized. In essence, the

membrane has a low selectivity for hydrogen gas (which is the component for which it has been designed to allow passage through the fibres).

However, from literature, Sentjens *et al.* (2003:1), apart from the presence of contaminants in the hydrogen gas stream affecting its purity, the flow rate also has an effect on this property. From Table 5.1, this is not the case. It can be seen that while the hydrogen purity was decreasing, the flow rate of the permeate remained fairly constant.

This discrepancy between what is obtainable in practice and theory stems from the presence of other factors affecting the selectivity (hydrogen purity) of the membrane. Although, when permeability increases, it is usually accompanied by a decrease in permeate purity. Luque & Alvarez (2001:381). However, this is not always the case because there are other factors which also affect the selectivity such as small defects (e.g. cracks, pinholes or pores), temperature and membrane differential pressure. Lu *et al.* (2007:7).

Also SRI International (1990:4-5) stated that "Gas permeance and selectivity are not the only criteria that determine suitability of membrane material for a given gas separation. High temperature resistance, high degree of strength, and reasonable resistance to a multitude of chemicals are also desired properties. "

From Table 5.1, the membrane differential pressure fairly increased with time. Therefore, this effect could have overridden the effect of flowrate. Furthermore, Lu *et al.* (2007:5) stated that even for materials with relatively high intrinsic permeabilities, commercially viable fluxes require that the effective thickness of the membrane be made as small as possible without introducing defects that destroy the intrinsic selectivity of the material. From the questionnaire, some of the respondents attested to the presence of cavity formations in the membrane structure as a possible cause of the low membrane performance. This effect could further nullify the effect of flowrate on the membrane selectivity.

The first point of argument above (low hydrogen selectivity) is also corroborated by the plot of the concentration of carbon monoxide in the permeate against time (see Figure 5.3). Obviously, the amount of CO increased with time.

A question which now readily comes to the mind is, “what is actually responsible for the high slippage of CO into the permeate stream causing the low membrane selectivity”? We now take a look into the results obtained from the questionnaires and interviews.

5.4.2 CAUSES OF THE MEMBRANES’ LOW PERFORMANCE

In order to be able to discuss the conditions affecting the performance of the membrane unit and proffer ways of optimizing it, an understanding of how to operate the unit is required by the plant personnel. Furthermore, knowledge of the separation process itself is also an important prerequisite for both the senior personnel as well as the operators.

From the results, majority of the plant personnel know how to operate the membrane unit (see Tables 5.5 and 5.13) and all of them are aware of the importance of the membrane unit in obtaining the right product quality for the plant (see Tables 5.6 and 5.14; Figures 5.4 and 5.8). Furthermore, most of the operators and senior personnel acknowledged the fact that the membrane unit is not performing at design efficiency (see Tables 5.7 and 5.15)

5.4.2.1 QUESTIONNAIRES

Concerning the possible causes of the conditions affecting the membrane unit, a greater number of the operators selected the following as the factors that might be the possible causes of the membrane’s low performance (see Table 5.9):

1. High membrane feed gas speed
2. Presence of ammonia in the feed gas to the membrane fibres
3. Presence of carbon monoxide in the feed gas to the membrane fibres
4. Insufficient heating of feed gas by the preheaters
5. High differential pressure across the membranes
6. Presence of heavy hydrocarbons than methane in the feed gas

For the senior personnel, the following were the factors which most of the respondents chose (see Table 5.17):

1. High membrane feed gas speed
2. Presence of ammonia in the feed gas to the membrane fibres
3. Insufficient heating of feed gas by the preheaters
4. High differential pressure across the membranes

5. Presence of heavy hydrocarbons than methane in the feed gas

Furthermore, a close look at the suggestions given by the plant personnel on the causes of the factors militating against the membrane's efficiency with the most damaging effect, shows that the following were common to both groups:

- a) High membrane feed gas speed
- b) Presence of ammonia in the feed gas to the membrane fibres
- c) High differential pressure across the membranes
- d) Insufficient heating of feed gas by the preheaters

Combining the results from the two sets of questionnaires, the respondents selected the following as the possible causes of the low membrane performance:

- 1. High membrane feed gas speed
- 2. Presence of ammonia in the feed gas to the membrane fibres
- 3. Presence of carbon monoxide in the feed gas to the membrane fibres
- 4. Insufficient heating of feed gas by the preheaters
- 5. High differential pressure across the membranes
- 6. Presence of heavy hydrocarbons than methane in the feed gas

Now, we would take a critical look into each of the six factors listed above.

5.4.2.1.1 Presence of heavy hydrocarbons than methane in the feed gas

Al-Juaied & Koros (2005:227) stated, "Natural gas streams contain numerous trace heavy hydrocarbons. Very heavy hydrocarbon contamination is believed to be the cause of some membrane failures and loss in performance even at low mass fractions. Due to this, it is very important to carefully consider the required pretreatment requirements for membrane systems".

However, with reference to this dissertation, chapter three gives a list of the chemical reactions that are involved in the entire autothermal reforming process. The reactions show that hydrocarbons (present in the natural gas) heavier than methane are broken down to hydrogen and carbon monoxide. Table 5.2 furthermore confirms this. Within the time frame chosen, there were no traces of heavy hydrocarbons in the membrane feed

gas. From these findings, the presence of heavy hydrocarbons than methane is not one of the causes of the low performance of the membranes.

Nonetheless, the reason why the respondents selected the presence of heavy hydrocarbons than methane in the feed gas could be linked to the laboratory analysis. There are times when the laboratory analysis displays small amounts of these hydrocarbons when these hydrocarbons are not completely broken down in the pre-reforming section (see chapter three). As a result, the respondents included it in the conditions affecting the performance of the membranes. However, within the time frame under consideration, the heavy hydrocarbons were not found in the feed gas.

5.4.2.1.2 High differential pressure across the membranes

SRI Consulting (2001:3-3) stated that pressure difference is the thermodynamic force that provides the driving force for mass transfer in gas separation membrane processes. In order to understand the relationship between the driving force and membrane selectivity, Lu *et al* (2007:7) said that selectivity decreases with increasing differential hydrogen pressure.

From the foregoing, it can be seen that a high differential pressure across the membranes would result in low selectivity. Therefore, the high transmembrane differential pressure (i.e. difference between feed gas pressure and permeate pressure) has a role to play in the reduction of the membrane selectivity for the desired component i.e. hydrogen.

5.4.2.1.3 Insufficient heating of the feed gas by the preheaters

From a report by SRI International (1990:4-5), apart from gas permeance and selectivity, high temperature resistance is also one of the criteria that determine suitability of membrane material for a given gas separation. In addition, Lu *et al* (2007:7) stated that selectivity increases with temperature. With these facts, the reduction in selectivity could be linked to low membrane feed gas temperature. This in turn could be linked to inadequate heating of the feed gas by the preheaters.

However, we need to consider the plant's design operating conditions. From the brief process description in chapter three, the design temperature of the feed gas to the

membranes is 47°C with an allowance within 38°C to 65°C. As a result, given this allowance, the heating of the gas has not gotten to the maximum allowable limit considering the design of the membrane unit. Therefore, insufficient heating of the feed gas is a possible cause of the membrane's low selectivity.

5.4.2.1.4 Presence of carbon monoxide in the feed gas to the membranes

Reformed gas is a mixture of hydrogen and carbon monoxide. From a news publication by Air Products and Chemicals, Inc. (© 1996–2006:1), the membrane unit in this dissertation has been designed for hydrogen/carbon monoxide ratio adjustment of syngas. The membrane system is used to adjust a non-permeate stream $H_2:CO$ molar ratio by withdrawing some of the hydrogen in the feedstream.

In essence, since the membrane unit in question has been designed to handle H_2 -CO mixture, the properties of carbon monoxide would have been put into consideration during the design of the unit. As a result, even if it would have any deleterious effect on the performance of the membrane, the material from which the membrane was to be designed would be made to resist attack by carbon monoxide. This line of argument therefore, nullifies the presence of carbon monoxide as a possible cause of the membranes' low performance.

5.4.2.1.5 Presence of ammonia in the feed gas to the membranes

From the study carried out by Tricoli & Cussler (1995:19-26) on membranes with hydrogen –ammonia mixtures, the presence of ammonia affected the selectivity of the membranes for hydrogen. With ammonia being one of the constituent gases of the membrane feed gas, not only does it reduce the selectivity of the membranes for hydrogen, it also attacks the mechanical integrity of the membrane fibres by causing them to become brittle.

5.4.2.1.6 High feed gas speed

As explained by Kluiters (2004:27), the problem of concentration polarization which plagues membrane processes, is a condition which could be corrected by making the gas flow which is adjacent the membrane to be turbulent. A confirmation of the turbulent flow to counteract the effect of concentration polarization could also be found in the report by SRI Consulting (2001:3-6).

The turbulent flow is an indication of high speed. As a result, the problem of concentration polarization would have been taken care of. However, from the design of the membrane fibres, a high feed gas velocity would cause a degree of damage by twisting them (see Table 5.3). In extreme cases, they get broken. Consequently, flow through the fibres would be hampered and therefore inability to selectively remove hydrogen would result.

5.4.2.2 PERSONAL INTERVIEWS

With reference to the personal interviews, the following were the suggestions given by the plant personnel on other causes of the conditions affecting the membrane's performance (which were not listed in the questionnaire):

- i. The water (condensate), which carries over ammonia from the process upstream, embrittles the fibres and the high flow velocity causes the brittle fibres to break.
- ii. Presence of gases which block permeation
- iii. Membrane unit not being able to handle the current capacity of feed gas.

In comparison with the field observation made on the two decommissioned membrane modules (see Table 5.3), a congruity is noticed. The presence of visible condensation on the surface of the fibres that made them wet and the observation of fibres that were brittle, twisted and broken are in consistency with the suggestions aforementioned.

Now, we would take another critical look into each of the factors listed above.

5.4.2.2.1 Presence of water (condensate) in the feed gas to the membrane fibres

This was an opinion from respondents about other possible causes of the low membrane performance. The final condensate separator is the equipment that has been designed to remove any traces of condensate from the feed gas (see chapter three). Its inability to completely remove the water from the feed makes the condensate to get to the membranes. From literature, Luque & Alvarez (2001:475, 478), water as a constituent of the feed gas has grave effects on the performance of the type of membranes under consideration in this dissertation. They are vulnerable to water. Water vapour adsorbs on

the membrane surface and on the pore walls thereby affecting the performance of the membrane.

5.4.2.2.2 Presence of gases which block permeation

Certain gases which are present in the feed have the tendency of preventing smooth permeation and therefore reducing the overall quantity of hydrogen in the permeate. This line of argument is confirmed by Kluiters (2004:27). This author described the adsorption of these gaseous components to the membrane surface (also inside the pores), limiting and even blocking permeation as fouling. H_2S and SO_2 were given as examples of gases that foul membranes. However, in relation to this dissertation, these two gases are not present in the feed gas to the membranes (see Table 5.2).

Furthermore, from literature, Luque & Alvarez (2001:453), presence of strongly adsorbed components such as carbon-1 (C_1), carbon-2 (C_2) and carbon-3 (C_3) could cause the membranes to significantly reject hydrogen. An example of C_1 components is methane (CH_4); for C_2 , we have ethane (C_2H_6), ethene (C_2H_4) and ethyne (C_2H_2); and for C_3 , we have propane (C_3H_8), propene (C_3H_6) and propyne (C_3H_4). Considering the feed gas components in this dissertation however, methane is the only gas in the feed to the membrane fibres amongst the aforementioned (see Table 5.2). As a result, the presence of methane is a possible cause of the conditions affecting the membranes' performance.

5.4.2.2.3 Inability of the membrane unit to handle the current capacity of feed gas

The suggestion that the membrane unit is not able to handle the capacity of feed gas is not agreed with. This is because from the design specifications (see chapter three); each prism (module) handles $10,000Nm^3/hr$ of feed (reformed gas). There are two banks of membranes, with each bank consisting of 18 prisms. Therefore, the total maximum capacity is supposed to be $360,000Nm^3/hr$. From the results, the range of flow rate for the feed gas was between $186,487Nm^3/hr$ and $186,567Nm^3/hr$ (see Table 5.1). As a result, the membrane modules could handle the capacity of gas flowing through them at that point in time. The implication of this is that the line of argument that states that the capacity of feed gas was too much for the membrane modules to handle is not supported.

Nevertheless, the interviewee had this as his opinion because not all the 36 prisms are usually put online during operation. As a result, it is logical to think that the amount of gas fed to the membrane unit was greater than its actual capacity. Following this line of argument, if the feed gas is greater than the capacity of the membrane unit, you expect to observe a dwindling performance in the separation capability of the unit.

In view of the discussions above, the following are therefore adopted as the major factors militating against the membrane efficiency:

- a) High differential pressure across the membranes
- b) High membrane feed gas speed
- c) Presence of ammonia in the feed gas to the membrane fibres.
- d) Insufficient heating of the feed gas giving rise to low membrane feed gas temperature
- e) Presence of water in the feed gas to the membrane fibres
- f) Presence of strongly adsorbed gases (such as methane), which block permeation.

5.4.3 WAYS OF OPTIMIZING THE MEMBRANE UNIT

5.4.3.1 QUESTIONNAIRES

For improving the performance of the membranes, majority of the operators selected the following actions to be taken:

1. Installing drains in the feed gas header in order to prevent condensate from getting to the membrane fibres
2. Checking the membrane feed header for liquid accumulation before the membrane groups are commissioned.
3. Periodic cleaning and backwashing in order to remove the high concentration phase formed by other constituents of the gas.

For the senior personnel, the three actions listed above were also selected.

However, a small percentage of the senior personnel selected the following optimization methods:

1. Incorporating a Pressure Swing Adsorption system into the process line before the membrane unit, so as to remove any possible gaseous contaminants in the membrane feed gas stream.
2. Reducing the membrane feed gas speed through the reduction of individual partial pressures by removing other gaseous constituents of the membrane feed gas stream through the Pressure Swing Adsorption system.

From the foregoing, combining the solutions to improving the membrane's efficiency as selected by the respondents, we have the following:

1. Incorporating a Pressure Swing Adsorption system into the process line before the membrane unit, so as to remove any possible gaseous contaminants in the membrane feed gas stream.
2. Reducing the membrane feed gas speed through the reduction of individual partial pressures by removing other gaseous constituents of the membrane feed gas stream through the Pressure Swing Adsorption system.
3. Installing drains in the feed gas header in order to prevent condensate from getting to the membrane fibres.
4. Checking the membrane feed header for liquid accumulation before the membrane groups are commissioned.
5. Periodic cleaning and backwashing in order to remove the high concentration phase formed by other constituents of the gas.

The results are discussed below.

5.4.3.1.1 Incorporating a Pressure Swing Adsorption system into the process line upstream of the membrane unit

Very few of the senior personnel selected this as a possible way of improving the efficiency of the membrane unit. Majority of the entire respondents could not say whether or not it could help optimize the performance of the membranes. This might be due to the fact that they are not very familiar with Pressure Swing Adsorption as a separation process.

From literature, Feng *et al* (1997:1696), "The improved separation performance of the integrated process lies in the fact that the two process components complement each

other by removing different species from the gas mixture. The adsorption process removes impurities from hydrogen, which is virtually non-adsorptive, while the permeation process extracts hydrogen from the impurities, which are much less permeable than hydrogen." Miller & Stocker (1999:25) corroborates this statement. They stated, "The combined system achieves both high recovery and high hydrogen purity, and low pressure tail gas is minimized." Therefore, the integrated process would not only help to solve the condition of low selectivity. It would also give the opportunity of obtaining high hydrogen throughput.

5.4.3.1.2 Reducing the membrane feed gas speed by the reduction of individual partial pressures through the Pressure Swing Adsorption system

Partial pressures of the components of a gas mixture are not related to the speed of the gas. With reference to Wikipedia (2007), the mole fraction of an individual gas component in an ideal gas mixture is equal to the ratio of its partial pressure to the total pressure of the mixture. Also, the mole fraction of the gas component is equal to the ratio of its moles in the mixture to the total moles of the mixture. (**Assumption:** *Reformed gas is taken as an ideal gas mixture for the purpose of this dissertation*).

From the above, it is clearly seen that by removing the other gaseous constituents of the membrane feed gas (apart from hydrogen), the total moles of the entire gas mixture would reduce. Furthermore, from Dalton's law of partial pressure, the total pressure of a gas mixture is the summation of the partial pressures of the individual gases in the mixture (Wikipedia, 2007). Therefore, removing the other gaseous constituents would reduce the total pressure of the mixture. However, the total moles of the mixture and its total pressure have no direct effect on the speed of the gas. As a result, a decrease in the pressure of the mixture does not necessarily translate to a reduction of the gas speed.

5.4.3.1.3 Installing drains in the feed gas header

As explained in section 5.4.2.2.1 above, the presence of water in the feed gas to the membrane fibres affects the membranes' selectivity. As a result, it should be prevented from getting to the fibres. The point of interest here is that the feed gas should be dried before it gets in contact with the fibres. Luque & Alvarez (2001:478) (see section 5.4.3.2.2).

Condensate is present as a result of incomplete removal of water by the final condensate separator (see chapter three). It accumulates in the process line which leads to the feed gas header to the membrane unit. Logically, incorporating drains in the process line would relieve the feed gas header of any possible condensate formation. These drains could be located at low points in the process line.

5.4.3.1.4 Checking the membrane feed header for liquid accumulation before the membrane groups are commissioned

This is also a follow up to the action of drying the feed gas before it enters the membranes. Luque & Alvarez (2001:478). From a clear rational thought and operations perspective, since water affects the performance of the membranes, it is reasonable to take necessary precautions before starting up the membrane unit. The production operators are therefore saddled with the responsibility of ensuring that there is no accumulation of condensate in the membrane feed gas header before the membrane groups are commissioned.

5.4.3.1.5 Periodic cleaning and backwashing of the membrane

SRI Consulting (2001:3-6) in its report on concentration polarization as it affects membranes and how to mitigate its effect, talked about increasing the cross-flow velocity of the gas. This method however has a damaging effect on the membrane fibres (see section 5.4.2.1.6). Also, in the same report, another method for combating concentration polarization was discussed. It is the regular cleaning and backwashing of the membranes. The effect of this action is to eliminate the deposition of the less permeable gas species from the points adjacent the membrane.

However, the types of fluid to be used for the cleaning and backwashing processes were not explicitly stated in the report. Nonetheless, this cleaning and backwashing processes offer effective means of alleviating the effect of concentration polarization on membrane performance.

5.4.3.2 PERSONAL INTERVIEWS

For the ways of optimizing the performance of the membrane unit, the following were the results obtained from the personal interviews:

1. Differential pressure across the membranes should be lowered in order to reduce the flow of feed gas through the prisms
2. A drying unit should be installed upstream of the membrane unit along the feed gas stream so as to remove any condensate present.
3. A demister unit should be installed just before the gas enters the membranes in order to ensure that any remaining traces of condensate in the feed are removed.
4. Recycling the permeate back to the feed stream so as to have more yield of hydrogen in the permeate
5. Maintenance work should be carried out on the membrane prisms more often in order to be able to detect faults and problems on the fibres on time.
6. A bypass should be installed around the membrane unit in order to increase the life span of the membranes [whereby the required syngas ratio would have been obtained for the product gas from the Autothermal reformer without any need for membrane separation].
7. Increasing the reformed gas feed temperature to around 57°C to 59°C in order to prevent heat losses before the feed gas gets to the membranes. This is also required to keep the gas above its saturation temperature so as to forestall condensate formation.
8. More banks of membrane modules should be installed for backup purposes so that in case of other banks getting faulty, then the banks on stand-by can be commissioned. This would also increase the membrane unit's availability.
9. Unwanted vapours and gases should be removed from the feed gas with the use of adsorbents.

The aforementioned suggestions raised by the interviewees are discussed below.

5.4.3.2.1 Lowering the differential pressure across the membranes

With reference to section 5.4.2.1.2, the effect of high transmembrane differential pressure on the selectivity of the membrane was discussed. In order to arrest this situation, SRI International (1990:4-7) wrote, "Membrane materials with high permeance

are desired to minimize the need for a high transmembrane driving force to achieve the desired separation.”

Furthermore, from Fick's law of diffusion, National Oceanic and Atmospheric Administration (2001:3), an increase in the pressure difference on the two sides of the membrane would cause the gas flow to increase. In addition, when permeability increases, it is usually accompanied by a decrease in permeate purity. Luque & Alvarez (2001:381).

Therefore, lowering the differential pressure would reduce the feed gas flow through the membrane modules and the resultant effect would be an increase in the membranes' selectivity.

5.4.3.2.2 Installation of a drying unit upstream of the membrane unit

A paper presented at the “Engineering with membranes” conference in Spain, dealt with the effect of water content on the selectivity of microporous hydrogen separation carbon-membranes. Luque & Alvarez (2001:478). In order to prevent the slippage of unwanted constituents of the gas through the permeate, solutions such as drying the feed before the membranes (as a crucial step) were proffered. This is to prevent the attack of water on the membrane selectivity.

However, any action that would ensure the feed gas is dried before it contacts the membranes would serve as a solution to the undesirable situation of condensate presence. The actions described in sections 5.4.3.1.3 and 5.4.3.1.4 fall under this category.

5.4.3.2.3 Installing a demister unit just before the gas enters the membranes

A demister is a piece of equipment that clears away mist or condensation from a process fluid. Installing a demister unit is also a follow up to the action of drying the feed gas before it enters the membranes.

A demister unit removes condensate with the help of baffles. A baffle is a device used to control or impede the flow or condensate. As the gas passes through the baffles, it makes several turns and negotiates in order to pass through the baffles. However, due

to the nature of the liquid (i.e. the condensate), it cannot make the same turns as the gas. As a result, it falls down to the bottom of the demister unit to be drained off.

5.4.3.2.4 Recycling the permeate back to the feed stream

From literature, Luque & Alvarez (2001:478), in order to increase the amount of hydrogen in the permeate relative to the amount of other constituents of the gas, the permeate stream should be recycled. There were two configuration options given. The first was a fraction of the total permeate recycled to the feed (for the case of one membrane separator). The second configuration was the cascade of two separators. Here, the permeate from the first module serves as feed for the second module.

The second configuration gives more hydrogen yield. However, it consists of more membrane separators. Therefore, a trade-off between having more hydrogen yield (using two separators) and economizing financial resources (using one separator) come into play.

5.4.3.2.5 Carrying out periodic maintenance work on the membrane prisms

This suggestion is from an operations perspective. By logical reasoning, performing regular maintenance work on the membrane unit would keep it in good condition. In addition, the onset of faults and defects would be detected on time before the situations escalate.

5.4.3.2.6 Installation of a bypass around the membrane unit

The installation of a bypass as a way of optimizing the membrane unit's performance is not supported. The unit is required to convert a reformed gas feed ($H_2:CO$ ratio of 2.24) to synthesis gas ($H_2:CO$ ratio of 1.89) to be used by downstream plants such as the *Fischer-Tropsch* (F-T) process. The conversion is made possible by separating some of the hydrogen from the feed (see chapter three). As a result, if the feed gas is made to bypass the membrane unit, the desired syngas ratio required downstream would not be achievable.

This action would only make the membranes to last longer but it would not necessarily improve their performance based on low selectivity.

5.4.3.2.7 Increasing the temperature of the feed gas (with the aid of the preheaters)

As explained previously in section 5.4.2.1.3, selectivity increases with temperature, Lu *et al* (2007:7). Since the maximum allowable final feed temperature of the reformed gas i.e. 65°C has not been reached (see chapter three), there is still room for temperature increase in order to achieve a significant improvement in the membranes' selectivity.

However, increasing the feed gas temperature with the preheaters would not keep the reformed gas away from saturation. A gas is not condensable by itself, except it is compressed. However, a vapour such as steam can condense by itself at room temperature. Therefore, increasing the reformed gas temperature would help to flash any water present to the vapour phase. This does not remove the water itself from the gas; rather the water is just present in the gaseous state.

Furthermore, one of the interviewees suggested that the feed gas temperature be increased to about 57°C to 59°C. However, this gives no assurance of how effective the temperature range would be in ensuring optimum selectivity of the membranes. Since simulations are not actually carried out, there is no conviction that stipulated values of process variables would give the exact solution required. Process variables are usually sensitive to changes. Therefore, it is suggested that the temperature to which the reformed gas be increased to, be included in further research.

5.4.3.2.8 Installing more banks of membrane modules

This suggestion does not proffer a means of improving the membrane unit's performance because it is already in place. The membrane unit has been designed with additional membrane modules. These additional set of separators are meant to serve as backup for the first set of 18 modules (see chapter three). Some of the 18 modules that are on stand by are commissioned depending on the capacity required by the plant.

5.4.3.2.9 Removal of unwanted vapours and gases from the feed gas with the use of adsorbents

This action is synonymous to that which occurs during the PSA process. The PSA process for hydrogen purification is based on the capacity of adsorbents to adsorb more impurities at high gas-phase partial pressure and then desorb them at low partial pressure. Miller & Stocker (1999:1). Therefore, this suggestion would be considered as being part of the installation of a PSA unit upstream the membrane unit as described in section 5.4.3.1.1.

From the foregoing, the adopted ways of improving the performance of the membranes are:

- a) Incorporating a Pressure Swing Adsorption system into the process line before the membrane unit, so as to remove any possible gaseous contaminants in the membrane feed gas stream.
- b) Installing drains in the feed gas header in order to prevent condensate from getting to the membrane fibres
- c) Checking the membrane feed header for liquid accumulation before the membrane groups are commissioned
- d) Periodic cleaning and backwashing of the membrane in order to remove the high concentration phase formed by other constituents of the gas
- e) Lowering the differential pressure across the membranes in order to reduce the flow of feed gas through the prisms
- f) Installation of a drying unit upstream of the membrane unit so as to remove any condensate present
- g) Installing a demister unit just before the gas enters the membranes to knock out any remaining traces of condensate in the feed
- h) Recycling the permeate back to the feed stream so as to have more yield of hydrogen in the permeate
- i) Carrying out periodic maintenance work on the membrane prisms in order to detect defects on the fibres on time
- j) Increasing the temperature of the feed gas (with the preheaters) so as to increase the membranes' selectivity

CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

This section gives a concise overview of the entire work carried out in this dissertation. The results obtained from the experimental investigation as well as the resulting solutions proffered in order to enhance the performance of the membrane unit are presented.

The performance of hydrogen separation membranes, which is a function of their selectivity and permeability, is greatly affected by a number of factors. Depending on the type of membrane and conditions surrounding its operation, process variables (such as temperature and pressure), presence of gaseous contaminants and chemicals have deleterious effects on the efficiency of the membrane.

With reference to this dissertation, the following were investigated for the membrane unit of the autothermal reforming plant under consideration:

1. The causes of decreasing hydrogen purity (decreasing selectivity).
2. The causes of insufficient membrane capacity to achieve the required synthesis gas (non-permeate) ratio.

From the empirical investigation and results obtained thereafter, the causes of the decreasing selectivity and deviation of the synthesis gas ratio from design were high differential pressure across the membranes and high membrane feed gas speed.

In addition, the presence of ammonia in the feed gas to the membrane fibres and insufficient heating of the feed gas giving rise to low membrane feed gas temperature were other causes. Also, the presence of water in the feed gas to the membrane fibres and the presence of strongly adsorbed gases (such as methane), which block permeation, affected the membranes' performance.

The aqueous ammonia from the upstream process embrittled the fibres and the high speed of flow caused the brittle fibres to become twisted while some got broken. The broken and twisted fibres resulted in the slippage of carbon monoxide and other constituents into the permeate stream.

However, in a quest to optimize (enhance the effectiveness of) the membrane unit, a number of solutions were proffered. They include reduction of the transmembrane differential pressure and recycling the permeate back to the feed stream with the intention of increasing the hydrogen yield in the permeate stream.

In addition, condensate should be prevented from getting to the membranes by installing a drying unit, and/or a demister unit into the process line upstream of the membranes. Moreover, the feed gas header should be checked for liquid accumulation before commissioning the membrane groups and drains should be installed to ensure no condensate gets to the membrane fibres.

Furthermore, a pressure swing adsorption system should be incorporated in order to remove the gaseous contaminants in the membrane feed gas. Also, the feed gas temperature should be increased to enhance the selectivity of the membranes. In addition, maintenance work and backwashing should be carried out periodically in order to forestall the onset of defects in the membrane unit.

6.2 RECOMMENDATIONS

From the results of the research work carried out, the recommendations to enhance the performance of the autothermal reforming plant's membrane unit are outlined as follows:

1. The empirical investigation methods – questionnaire and personal interviews, should be made to encompass a greater research population. For the purpose of further study on this dissertation, the manufacturer of the membrane unit, engineering contractors involved in the plant design and other membrane specialists not working on the ATR plant should be consulted.
2. A subject of further research should delve into finding the best possible membrane type amongst those suitable for hydrogen separation, putting into consideration the gaseous contaminants typical of those encountered in this dissertation.
3. Lastly, the economic implications of implementing the ways of optimizing the membranes' performance into the current design of the membrane unit were not treated in this dissertation. Therefore, the cost impacts of implementing the optimization

solutions on the plant's profitability should be the objective of another research work to be carried out in future.

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PERSONAL INTERVIEWS

Personal Interview with an ATR plant engineer, 10.38am, November 2, 2006

Personal Interview with a Shift Supervisor of the Autothermal Reforming plant, 01.17am, December 26, 2006.

Personal Interview with a Senior Process Controller of the Autothermal Reforming Plant, 10.44pm, December 17, 2006.

Personal Interview with an engineer from the Research and Development unit, 02.13pm, December 28, 2006.

Personal Interview with a senior personnel of the Autothermal Reforming Plant, 12.05pm, January 5, 2007.

Personal Interview with a Process Controller of the Autothermal Reforming plant, 11.36am, January 2, 2007.

APPENDICES
APPENDIX A
OPERATORS' QUESTIONNAIRE ON OPTIMIZATION OF THE MEMBRANE UNIT OF
THE ATR PLANT

Please tick the appropriate boxes and fill in the blank spaces where applicable

PART 1: RESPONDENT'S INFORMATION

Gender: ☐ Male ☐ Female

Age: ☐ 21-30 ☐ 31-40 ☐ 41-50 ☐ 51-60 ☐ 61-70

Division: _____

Level of Operator: ☐ Specialist Senior Process Controller (SSPC)
☐ Senior Process Controller (SPC)
☐ Process Controller 1 (PC1)
☐ Process Controller 2 (PC2)

Date: _____

PART 2: PROCESS BACKGROUND

1. Have you at any time been delegated to work at the membrane unit of the ATR plant?

☐ Yes ☐ No

2. Do you fully understand the operational mode of the membrane unit?

☐ Yes ☐ No ☐ Partially

3. Kindly describe the function of the membrane unit briefly-

4. Which section(s) is/are upstream of the membrane unit?

5. Which of the following gases constitute the membrane feed gas stream?

- ☐ Hydrogen (H₂) ☐ Methane (CH₄) ☐ Nitrogen (N₂)
☐ Carbon monoxide (CO) ☐ Carbon dioxide (CO₂) ☐ Oxygen (O₂)
☐ Water (H₂O) ☐ Argon (Ar) ☐ Hydrogen Sulphide (H₂S)
☐ Carbon-2 compounds (C₂+) such as Ethyne (C₂H₂), Ethene (C₂H₄) and Ethane (C₂H₆)

6. Which of the following process parameters is/are crucial to the performance of the membranes?

- ☐ Temperature ☐ Pressure ☐ Composition
☐ Level ☐ Flowrate

7. Which equipment is/are critical to the efficient performance of the membranes?

_____	_____	_____
_____	_____	_____
_____	_____	_____

8. The membrane is critical to obtaining the right product quality for the ATR plant

- ☐ Strongly Agree ☐ Agree ☐ Cannot say
☐ Strongly Disagree ☐ Disagree

PART 3: FACTORS MILITATING AGAINST MEMBRANE EFFICIENCY

9. Is the membrane unit performing according to design specifications?

- ☐ Yes ☐ No ☐ Cannot say

10. How would you rate the efficiency of the membrane unit?

- ☐ 0-10% ☐ 11-20% ☐ 21-30%
☐ 31-40% ☐ 41-50% ☐ 51-60%
☐ 61-70% ☐ 71-80% ☐ 81-90% ☐ 91-100%

11. Since your appointment as an operator in the ATR plant, how often has the membrane witnessed failure or performed below expected performance?

- ☐ Always ☐ Often ☐ Seldom ☐ Never

12. Which of the following is/are the conditions affecting the efficiency of the membranes?

- ☐ Broken membrane fibres ☐ Poor permeability of membrane fibres
☐ Brittle membrane fibres ☐ Condensate formation ☐ Low H₂ recovery
☐ Low separation factor ☐ High CO slippage to the permeate stream
☐ Deviation of synthesis gas ratio from design value

In your opinion, if there are other conditions not listed above; please fill them in the spaces below:

NOTE: Questions 13 to 30 contain a statement each. Identify if each statement is a **possible cause** of the conditions affecting the efficiency of the membranes in Question 12 by selecting either 'Strongly Agree', 'Agree', 'Strongly Disagree', 'Disagree' or 'Cannot say' and writing the number (representing the option you pick) in the boxes provided.

Key:

- 1 – Strongly Agree
- 2 – Agree
- 3 – Strongly Disagree
- 4 – Disagree
- 5 – Cannot say

- 13. High membrane feed gas temperature ☐
- 14. High membrane feed gas pressure ☐
- 15. High differential pressure across the membranes ☐
- 16. High membrane feed gas speed ☐
- 17. Presence of ammonia in the feed gas to the membrane fibres ☐
- 18. Presence of methane in the feed gas to the membrane fibres ☐
- 19. Presence of hydrogen cyanide in the feed gas to the membrane fibres ☐
- 20. Presence of carbon monoxide in the feed gas to the membrane fibres ☐
- 21. Presence of carbon dioxide in the feed gas to the membrane fibres ☐
- 22. Presence of hydrogen sulphide in the feed gas to the membrane fibres ☐
- 23. Presence of nitrogen in the feed gas to the membrane fibres ☐
- 24. Insufficient heating of feed gas by the preheaters ☐
- 25. Low membrane feed gas pressure ☐
- 26. Low differential pressure across the membranes ☐
- 27. Low membrane feed gas speed ☐

28. Presence of cavity formations in the membrane structure ☐
29. Presence of heavy hydrocarbons than methane in the feed gas ☐
30. Occurrence of concentration polarization at points adjacent to the membrane ☐

31. Amongst all the factors militating against the efficient performance of the membrane unit in Questions 13 to 30 above, which of them do you think has/have the most damaging effect?

PART 4: OPTIMIZING THE MEMBRANE OPERATIONS

32. In your opinion, the conditions affecting the efficiency of the membrane unit
- ☐ Can be minimized ☐ Can be eliminated ☐ Cannot be solved

NOTE: Questions 33 to 39 contain a statement each. Identify if each statement is a **possible solution** to improving the operations of the membranes by selecting either 'Strongly Agree', 'Agree', 'Strongly Disagree', 'Disagree' or 'Cannot say' and writing the number (representing the option you pick) in the boxes provided.

Key:

- 1 – Strongly Agree
 2 – Agree
 3 – Strongly Disagree
 4 – Disagree
 5 – Cannot say

33. Making the feed gas flow directly adjacent to the membrane a turbulent one. ☐
34. Installing drains in the feed gas header in order to prevent condensate from getting to the membrane fibres. ☐

35. Checking the membrane feed header for liquid accumulation before the membrane groups are commissioned. ☐
36. Incorporating a *Pressure Swing Adsorption system* into the process line before the membrane unit, so as to remove any possible gaseous contaminants in the membrane feed gas stream. ☐
37. Reducing the membrane feed gas speed through the reduction of individual partial pressures by removing other gaseous constituents of the membrane feed gas stream through the *Pressure Swing Adsorption system*. ☐
38. Cleaning the membranes by heating and purging with non-adsorbing gases. ☐
39. Periodic cleaning and backwashing in order to remove the high concentration phase formed by other constituents of the gas. ☐

Please give your personal comments about the questionnaire here:

APPENDIX B
SENIOR PERSONNEL'S QUESTIONNAIRE ON OPTIMIZATION OF THE MEMBRANE
UNIT OF THE ATR PLANT

Please tick the appropriate boxes and fill in the blank spaces where applicable

PART 1: RESPONDENT'S INFORMATION

Gender: ☐ Male ☐ Female

Age: ☐ 21-30 ☐ 31-40 ☐ 41-50 ☐ 51-60 ☐ 61-70

Division: _____

Designation: _____

Date: _____

PART 2: PROCESS BACKGROUND

1. Have you at any time been delegated to work at the membrane unit of the ATR plant?

☐ Yes ☐ No

2. Do you fully understand the operational mode of the membrane unit?

☐ Yes ☐ No ☐ Partially

3. Kindly describe the function of the membrane unit briefly-

4. Which section(s) is/are upstream of the membrane unit?

5. Which of the following gases constitute the membrane feed gas stream?

- ☐ Hydrogen (H₂) ☐ Methane (CH₄) ☐ Nitrogen (N₂)
☐ Carbon monoxide (CO) ☐ Carbon dioxide (CO₂) ☐ Oxygen (O₂)
☐ Water (H₂O) ☐ Argon (Ar) ☐ Hydrogen Sulphide (H₂S)
☐ Carbon-2 compounds (C₂+) such as Ethyne (C₂H₂), Ethene (C₂H₄) and Ethane (C₂H₆)

6. Which of the following process parameters is/are crucial to the performance of the membranes?

- ☐ Temperature ☐ Pressure ☐ Composition
☐ Level ☐ Flowrate

7. Which equipment is/are critical to the efficient performance of the membranes?

8. The membrane is critical to obtaining the right product quality for the ATR plant

- ☐ Strongly Agree ☐ Agree
☐ Strongly Disagree ☐ Disagree ☐ Cannot say

PART 3: FACTORS MILITATING AGAINST MEMBRANE EFFICIENCY

9. Is the membrane unit performing according to design specifications?

- ☐ Yes ☐ No ☐ Cannot say

10. How would you rate the efficiency of the membrane unit?

- ☐ 0-10% ☐ 11-20% ☐ 21-30%
☐ 31-40% ☐ 41-50% ☐ 51-60%
☐ 61-70% ☐ 71-80% ☐ 81-90% ☐ 91-100%

11. Since your appointment as an operator in the ATR plant, how often has the membrane witnessed failure or performed below expected performance?

- ☐ Always ☐ Often ☐ Seldom ☐ Never

12. Which of the following is/are the conditions affecting the efficiency of the membranes?

- ☐ Broken membrane fibres ☐ Poor permeability of membrane fibres
☐ Brittle membrane fibres ☐ Condensate formation ☐ Low H₂ recovery
☐ Low separation factor ☐ High CO slippage to the permeate stream
☐ Deviation of synthesis gas ratio from design value

In your opinion, if there are other conditions not listed above; please fill them in the spaces below:

NOTE: Questions 13 to 30 contain a statement each. Identify if each statement is a **possible cause** of the conditions affecting the efficiency of the membranes in Question 12 by selecting either 'Strongly Agree', 'Agree', 'Strongly Disagree', 'Disagree' or 'Cannot say' and writing the number (representing the option you pick) in the boxes provided.

Key:

1 – Strongly Agree

2 – Agree

3 – Strongly Disagree

4 – Disagree

5 – Cannot say

- 13. High membrane feed gas temperature ☐
- 14. High membrane feed gas pressure ☐
- 15. High differential pressure across the membranes ☐
- 16. High membrane feed gas speed ☐
- 17. Presence of ammonia in the feed gas to the membrane fibres ☐
- 18. Presence of methane in the feed gas to the membrane fibres ☐
- 19. Presence of hydrogen cyanide in the feed gas to the membrane fibres ☐
- 20. Presence of carbon monoxide in the feed gas to the membrane fibres ☐
- 21. Presence of carbon dioxide in the feed gas to the membrane fibres ☐
- 22. Presence of hydrogen sulphide in the feed gas to the membrane fibres ☐
- 23. Presence of nitrogen in the feed gas to the membrane fibres ☐
- 24. Insufficient heating of feed gas by the preheaters ☐
- 25. Low membrane feed gas pressure ☐
- 26. Low differential pressure across the membranes ☐
- 27. Low membrane feed gas speed ☐
- 28. Presence of cavity formations in the membrane structure ☐
- 29. Presence of heavy hydrocarbons than methane in the feed gas ☐
- 30. Occurrence of concentration polarization at points adjacent to the membrane ☐

31. Amongst all the factors militating against the efficient performance of the membrane unit in Questions 13 to 30 above, which of them do you think has/have the most damaging effect?

PART 4: OPTIMIZING THE MEMBRANE OPERATIONS

32. In your opinion, the conditions affecting the efficiency of the membrane unit

☐ Can be minimized ☐ Can be eliminated ☐ Cannot be solved

NOTE: Questions 33 to 39 contain a statement each. Identify if each statement is a **possible solution** to improving the operations of the membranes by selecting either 'Strongly Agree', 'Agree', 'Strongly Disagree', 'Disagree' or 'Cannot say' and writing the number (representing the option you pick) in the boxes provided.

Key:

1 – Strongly Agree

2 – Agree

3 – Strongly Disagree

4 – Disagree

5 – Cannot say

33. Making the feed gas flow directly adjacent to the membrane a turbulent one. ☐

34. Installing drains in the feed gas header in order to prevent condensate from getting to the membrane fibres. ☐

35. Checking the membrane feed header for liquid accumulation before the membrane groups are commissioned. ☐

36. Incorporating a *Pressure Swing Adsorption system* into the process line before the membrane unit, so as to remove any possible gaseous contaminants in the membrane feed gas stream. ☐
37. Reducing the membrane feed gas speed through the reduction of individual partial pressures by removing other gaseous constituents of the membrane feed gas stream through the *Pressure Swing Adsorption system*. ☐
38. Cleaning the membranes by heating and purging with non-adsorbing gases. ☐
39. Periodic cleaning and backwashing in order to remove the high concentration phase formed by other constituents of the gas. ☐

Please give your personal comments about the questionnaire here:

APPENDIX C
PERSONAL INTERVIEW QUESTIONS ON OPTIMIZATION OF THE MEMBRANE
UNIT OF THE ATR PLANT

Question 1: In your opinion, what are other causes of the conditions affecting the efficiency of the membranes?

Question 2: As an operator/senior personnel/engineer for the ATR plant, what adjustments do you feel could be made to the process parameters for efficient operation of the membrane unit?

Question 3: In your opinion, what changes do you feel can be made to the design of the membrane unit in order to optimize (enhance the effectiveness of) the membrane unit?

Question 4: As an operator/senior personnel/engineer who has acquired some working experience on the membrane unit of the ATR plant, please suggest ways by which the conditions affecting the efficiency of the membrane unit could be eliminated or minimized in order to enhance its operation.

APPENDIX D

TABLES OF RAW DATA FOR RESULTS OBTAINED FROM THE OPERATORS' QUESTIONNAIRE

Table 5.20: Process Background on work experience (Raw Data) (OP)

	Yes	No	Total
Have you at any time been delegated to work at the membrane unit of the plant?	28	4	32

Table 5.21: Process Background on operational knowledge (Raw Data) (OP)

	Yes	No	Partially	Total
Do you fully understand the operational mode of the membrane unit?	30	0	2	32

Table 5.22: Process Background on knowledge of the process (Raw data) (OP)

	Strongly Agree	Agree	Strongly Disagree	Disagree	Cannot Say	Total
The membrane is critical to obtaining the right product quality for the plant	18	14	0	0	0	32

Table 5.23: Membrane performance (Raw Data) (OP)

	Yes	No	Cannot Say	Total
Is the membrane unit performing according to design specifications?	1	24	7	32

Table 5.24: Frequency of low membrane performance (Raw Data) (OP)

	Always	Often	Seldom	Never	Total
Since your appointment as an operator in the plant, how often has the membrane witnessed failure or performed below expected performance?	0	21	6	5	32

Table 5.25: Factors Militating Against Membrane Efficiency (Raw Data) (OP)

	Strongly Agree	Agree	Strongly Disagree	Disagree	Cannot Say	Total
High membrane feed gas temperature	0	3	4	25	0	32
High membrane feed gas pressure	0	1	2	29	0	32
High differential pressure across the membranes	21	7	0	3	1	32
High membrane feed gas speed	13	14	0	1	4	32
Presence of ammonia in the feed gas to the membrane fibres	14	10	0	2	6	32
Presence of methane in the feed gas to the membrane fibres	0	0	4	28	0	32
Presence of hydrogen cyanide in the feed gas to the membrane fibres	0	6	10	14	2	32
Presence of carbon monoxide in the feed gas to the membrane fibres	5	14	4	9	0	32
Presence of carbon dioxide in the feed gas to the membrane fibres	0	0	14	18	0	32
Presence of hydrogen sulphide in the feed gas to the membrane fibres	0	0	6	14	12	32
Presence of nitrogen in the feed gas to the membrane fibres	0	0	19	13	0	32
Insufficient heating of feed gas by the preheaters	4	15	0	9	4	32
Low membrane feed gas pressure	0	8	11	13	0	32
Low differential pressure across the membranes	0	3	0	21	8	32
Low membrane feed gas speed	0	4	3	22	3	32
Presence of cavity formations in the membrane structure	0	11	2	12	7	32
Presence of heavy hydrocarbons than methane in the feed gas	5	20	0	1	6	32
Occurrence of concentration polarization at points adjacent to the membrane	0	2	8	4	18	32

Table 5.26: Opinions of operators on possible causes of the conditions affecting the efficiency of the membranes (Raw Data) (OP)

Suggestions on the factors affecting the efficient performance of the membrane unit with the most damaging effect amongst the listed possible causes in the questionnaire	
Response	Number of Respondents
High membrane feed gas speed	29
Presence of ammonia in the feed gas to the membrane fibres	23
Insufficient heating of the feed gas by the preheaters	21
High differential pressure across the membranes	12

Table 5.27: Optimizing the membrane operations (Raw Data) (OP)

	Strongly Agree	Agree	Strongly Disagree	Disagree	Cannot Say	Total
Making the feed gas flow directly adjacent to the membrane a turbulent one	0	0	7	21	4	32
Installing drains in the feed gas header in order to prevent condensate from getting to the membrane fibres	0	30	0	2	0	32
Checking the membrane feed header for liquid accumulation before the membrane groups are commissioned	15	17	0	0	0	32
Incorporating a Pressure Swing Adsorption system into the process line before the membrane unit, so as to remove any possible gaseous contaminants in the membrane feed gas stream	0	3	0	4	25	32
Reducing the membrane feed gas speed through the reduction of individual partial pressures by removing other gaseous constituents of the membrane feed gas stream through the Pressure Swing Adsorption system	0	3	0	5	24	32
Cleaning the membranes by heating and purging with non-adsorbing gases	0	4	0	6	22	32
Periodic cleaning and backwashing in order to remove the high concentration phase formed by other constituents of the gas	9	14	0	4	5	32

APPENDIX E

FIGURES FOR RESULTS OBTAINED ON THE FACTORS MILITATING AGAINST MEMBRANE EFFICIENCY FOR THE OPERATORS' QUESTIONNAIRE

Fig 5.12: Data for High membrane feed gas pressure (OP)

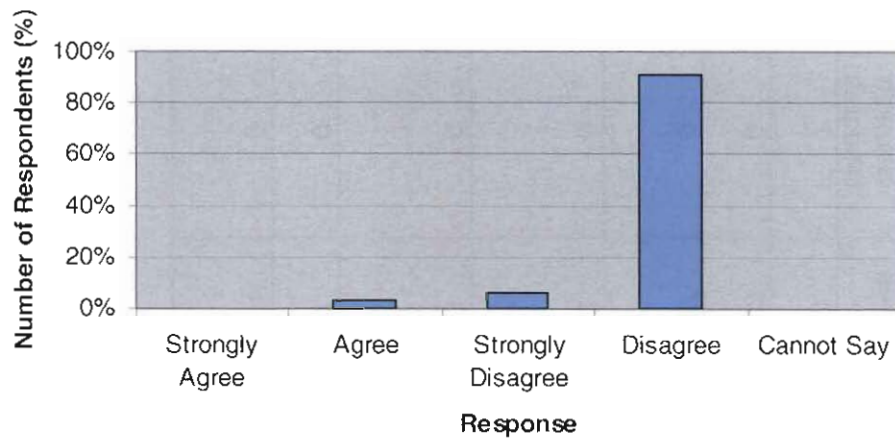


Fig 5.13: Data for High differential pressure across the membranes (OP)

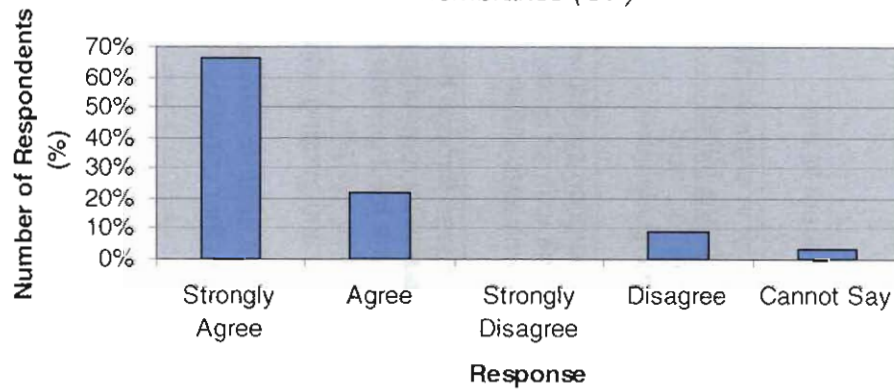


Fig 5.14: Data for High membrane feed gas speed (OP)

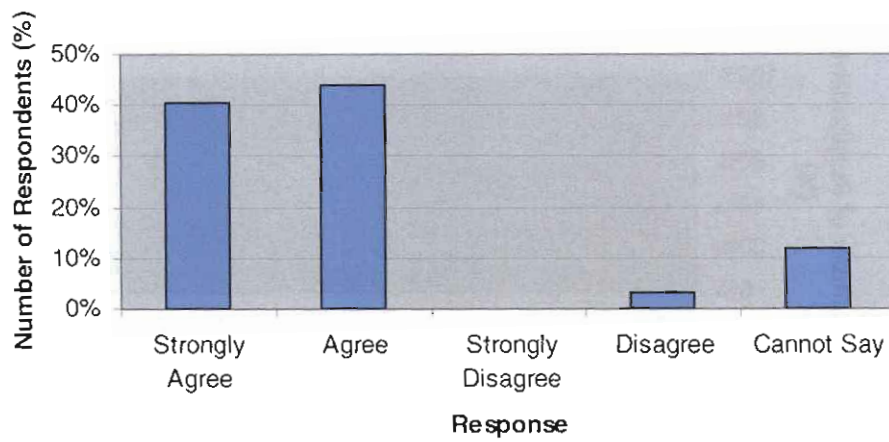


Fig 5.15: Data for Presence of ammonia in the feed gas to the membrane fibres (OP)

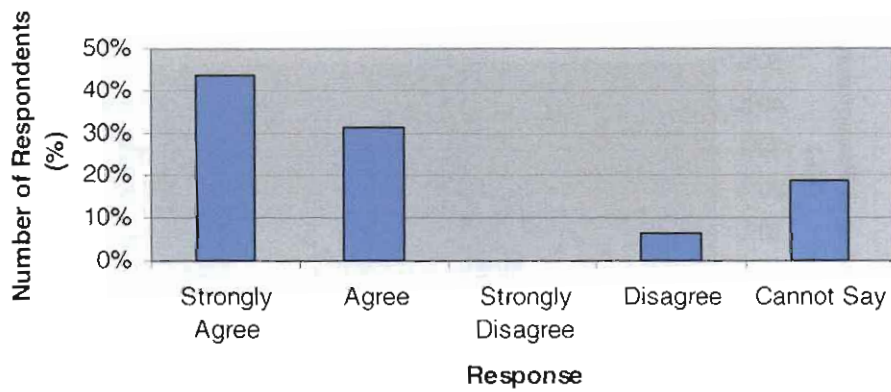


Fig 5.16: Data for Presence of methane in the feed gas to the membrane fibres (OP)

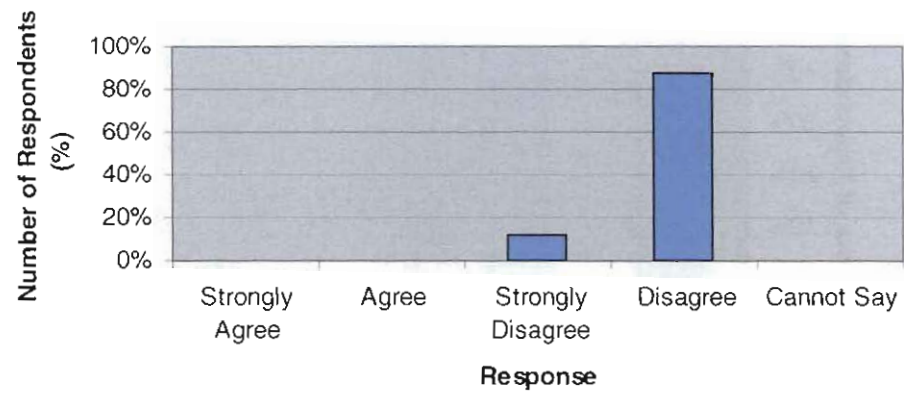


Fig 5.17: Data for Presence of hydrogen cyanide in the feed gas to the membrane fibres (OP)

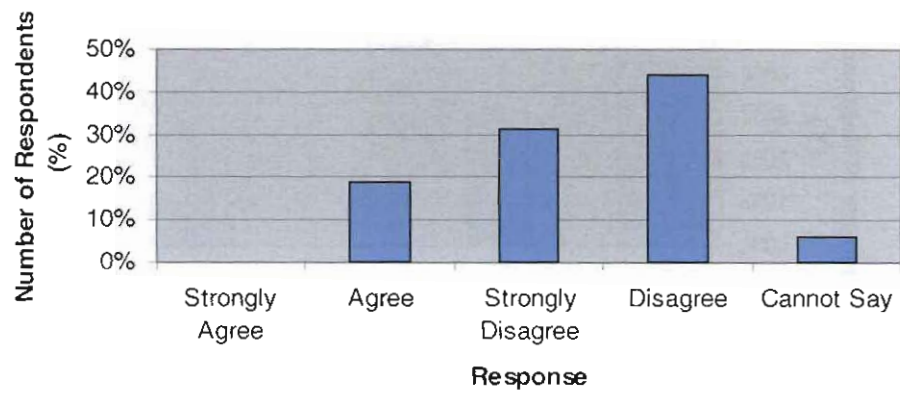


Fig 5.18: Data for Presence of carbon monoxide in the feed gas to the membrane fibres (OP)

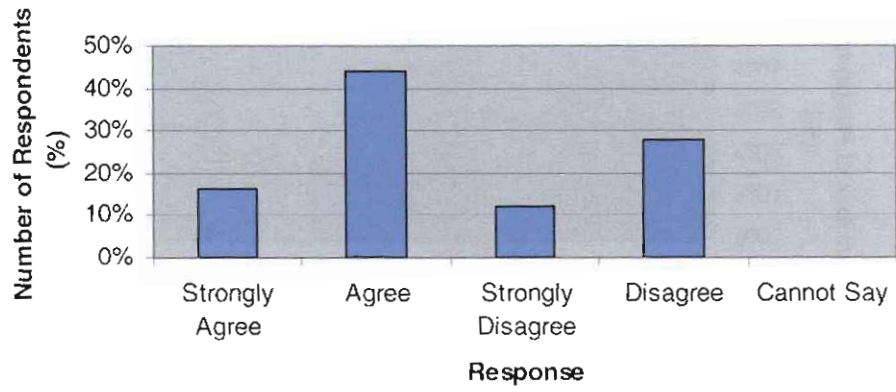


Fig 5.19: Data for Presence of carbon dioxide in the feed gas to the membrane fibres (OP)

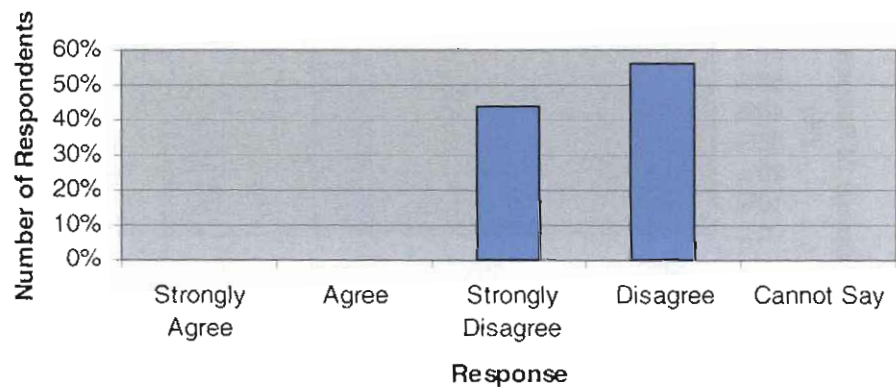


Fig 5.20: Data for Presence of hydrogen sulphide in the feed gas to the membrane fibres (OP)

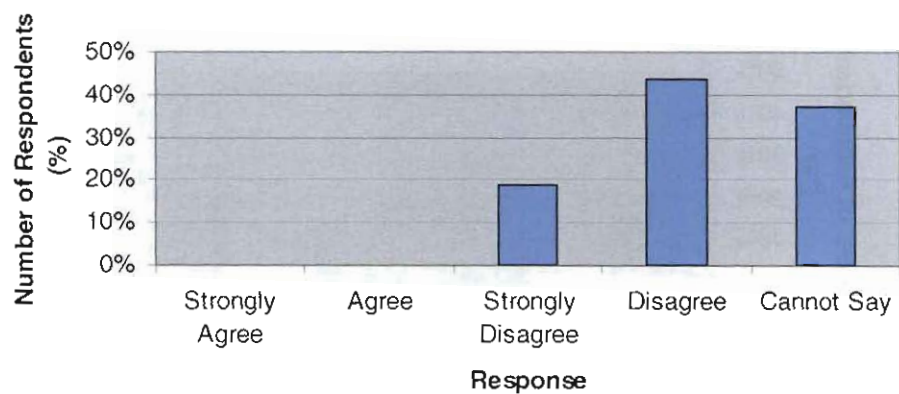


Fig 5.21: Data for Presence of nitrogen in the feed gas to the membrane fibres (OP)

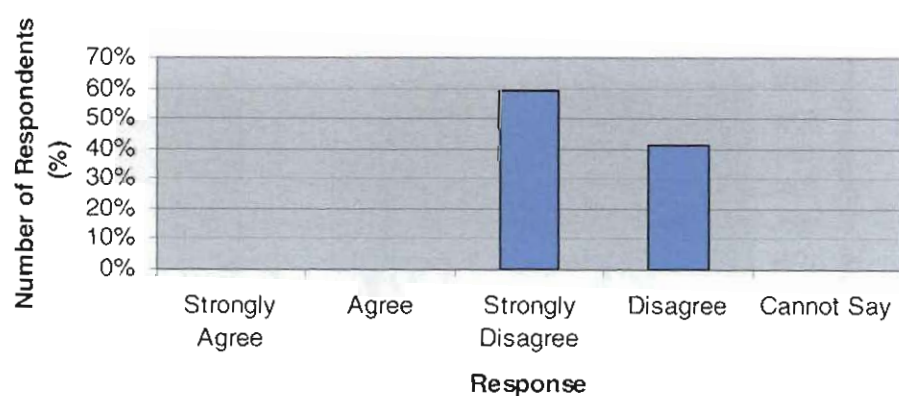


Fig 5.22: Data for Insufficient heating of feed gas by the preheaters (OP)

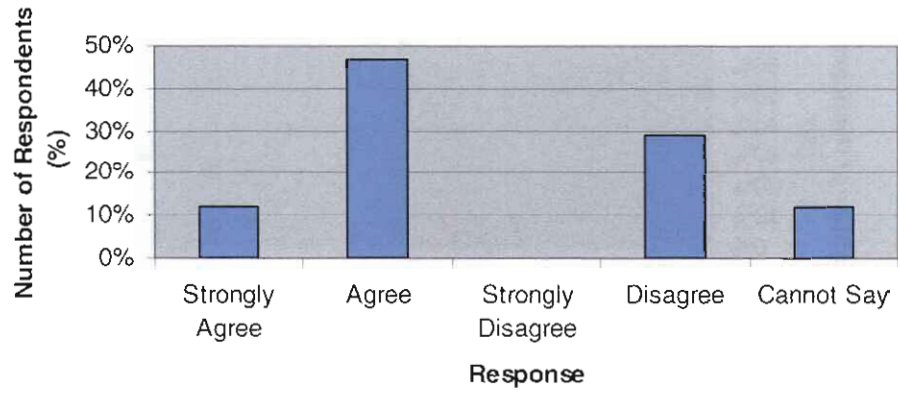


Fig 5.23: Data for Low membrane feed gas pressure (OP)

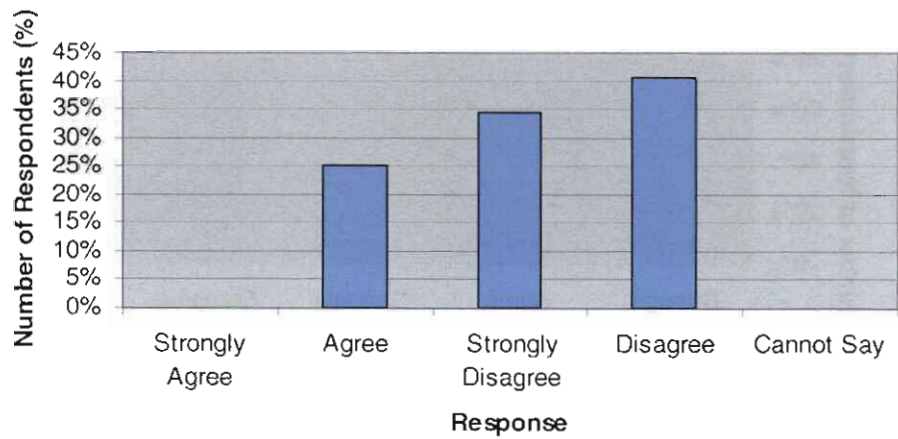


Fig 5.24: Data for Low differential pressure across the membranes (OP)

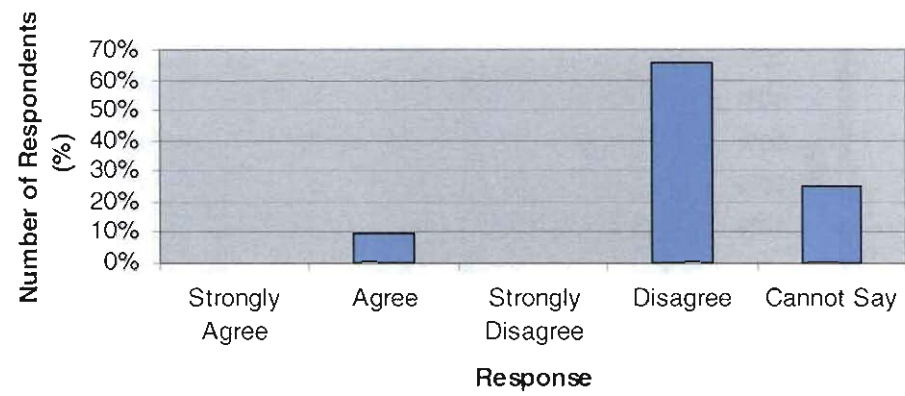


Fig 5.25: Data for Low membrane feed gas speed (OP)

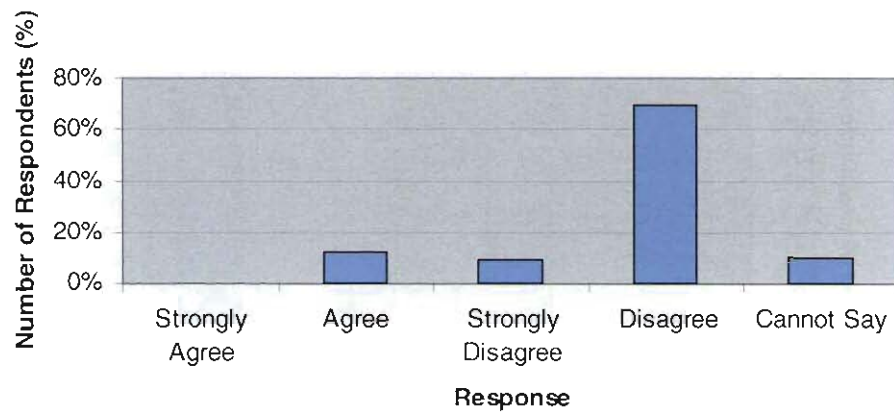


Fig 5.26: Data for Presence of cavity formations in the membrane structure (OP)

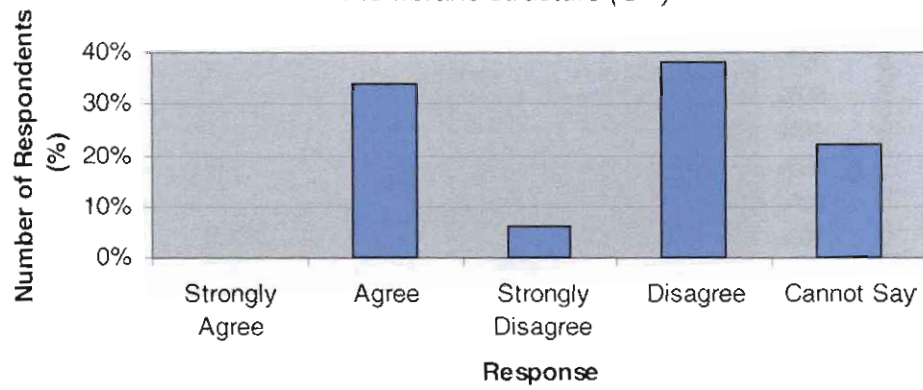


Fig 5.27: Data for Presence of heavy hydrocarbons than methane in the feed gas (OP)

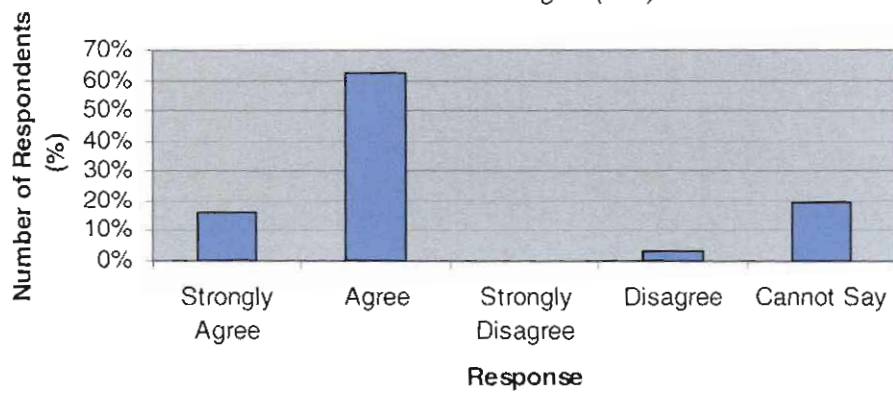
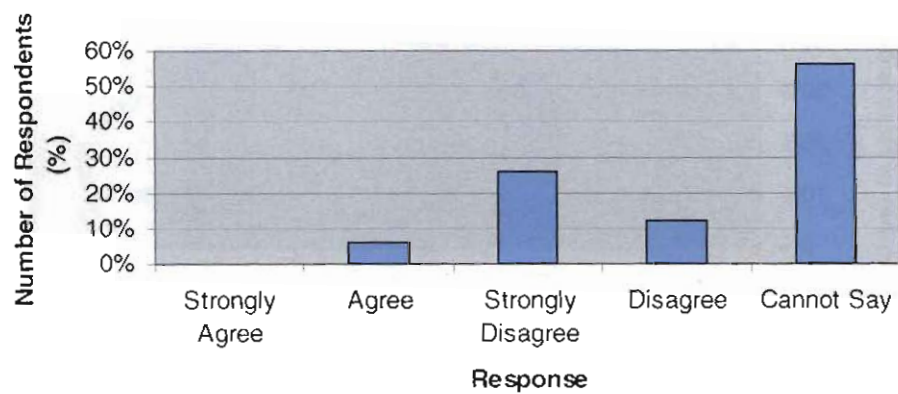


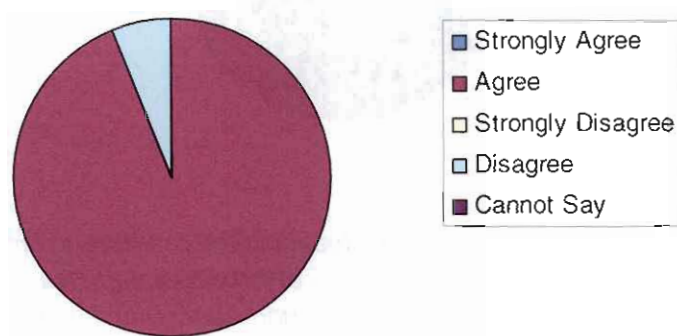
Fig 5.28: Data for Occurrence of concentration polarization at points adjacent to the membrane (OP)



APPENDIX F

FIGURES FOR RESULTS OBTAINED ON OPTIMIZING THE MEMBRANE OPERATIONS FOR THE OPERATORS' QUESTIONNAIRE

*Fig 5.29: Data for Installing drains in the feed gas header
(OP)*



*Fig 5.30: Data for Checking the membrane feed header
for liquid accumulation before the membrane groups are
commissioned (OP)*

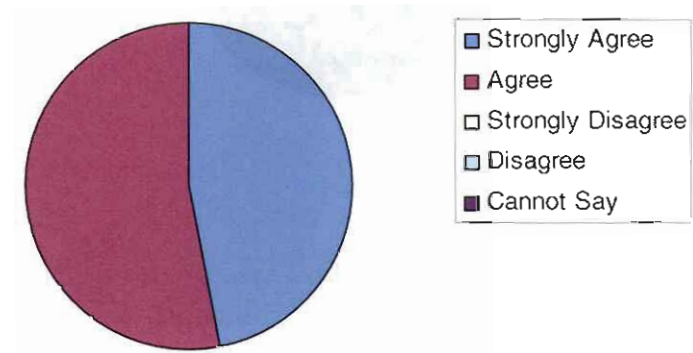


Fig 5.31: Data for Incorporating a Pressure Swing Adsorption system into the process line before the membrane unit (OP)

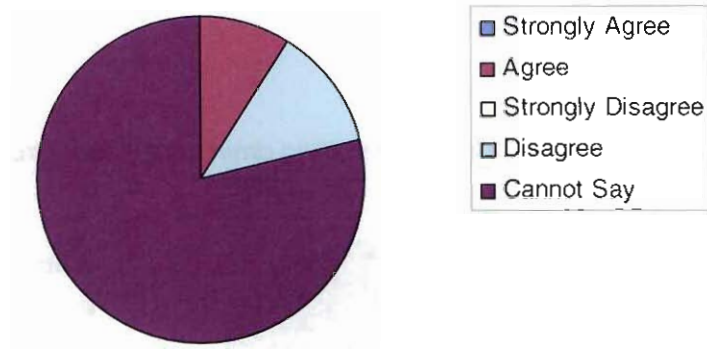


Fig 5.32: Data for Reducing the membrane feed gas speed by the reduction of individual partial pressures through the Pressure Swing Adsorption system (OP)

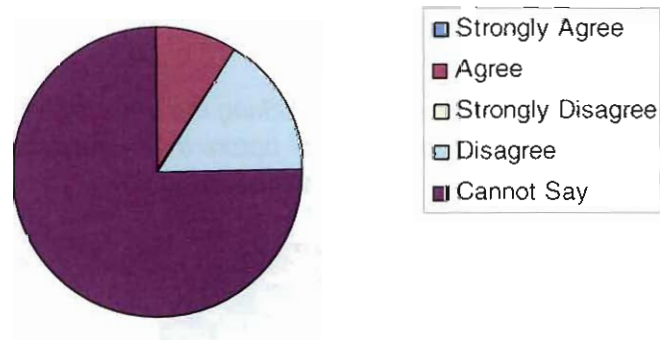


Fig 5.33: Data for Cleaning the membranes by heating and purging with non-adsorbing gases (OP)

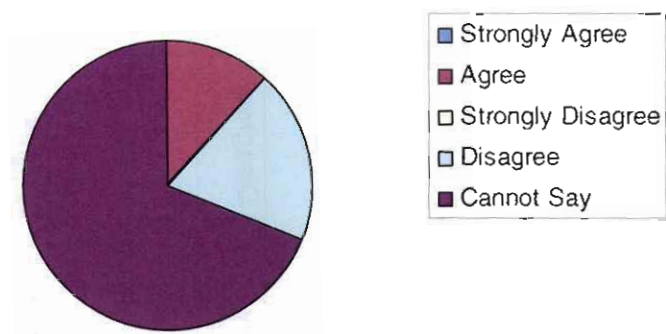
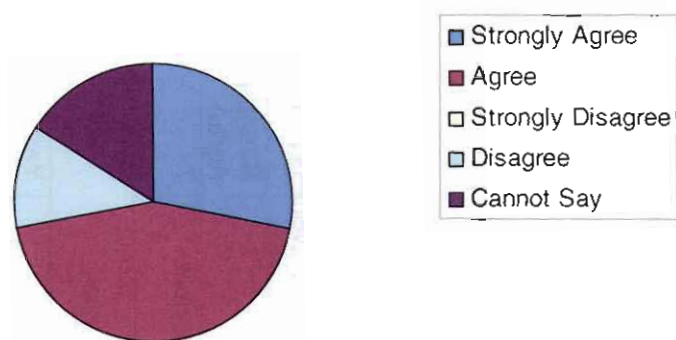


Fig 5.34: Data for Periodic cleaning and backwashing in order to remove the high concentration phase formed by other constituents (OP)



APPENDIX G

TABLES OF RAW DATA FOR RESULTS OBTAINED FROM THE SENIOR PERSONNEL'S QUESTIONNAIRE

Table 5.28: Process Background on work experience (Raw Data) (SP)

	Yes	No	Total
Have you at any time been delegated to work at the membrane unit of the plant?	10	2	12

Table 5.29: Process Background on operational knowledge (Raw Data) (SP)

	Yes	No	Partially	Total
Do you fully understand the operational mode of the membrane unit?	9	0	3	12

Table 5.30: Process Background on knowledge of the process (Raw data) (SP)

	Strongly Agree	Agree	Strongly Disagree	Disagree	Cannot Say	Total
The membrane is critical to obtaining the right product quality for the plant	7	4	0	0	1	12

Table 5.31: Membrane performance (Raw Data) (SP)

	Yes	No	Cannot Say	Total
Is the membrane unit performing according to design specifications?	0	9	3	12

Table 5.32: Frequency of low membrane performance (Raw Data) (SP)

	Always	Often	Seldom	Never	Total
Since your appointment as an operator in the plant, how often has the membrane witnessed failure or performed below expected performance?	0	8	4	0	12

Table 5.33: Factors Militating Against Membrane Efficiency (Raw Data) (SP)

	Strongly Agree	Agree	Strongly Disagree	Disagree	Cannot Say	Total
High membrane feed gas temperature	0	1	2	9	0	12
High membrane feed gas pressure	0	4	0	8	0	12
High differential pressure across the membranes	3	7	0	2	0	12
High membrane feed gas speed	6	4	0	2	0	12
Presence of ammonia in the feed gas to the membrane fibres	5	5	0	2	0	12
Presence of methane in the feed gas to the membrane fibres	0	0	7	5	0	12
Presence of hydrogen cyanide in the feed gas to the membrane fibres	0	4	3	5	0	12
Presence of carbon monoxide in the feed gas to the membrane fibres	0	0	9	3	0	12
Presence of carbon dioxide in the feed gas to the membrane fibres	0	2	2	8	0	12
Presence of hydrogen sulphide in the feed gas to the membrane fibres	0	1	3	7	1	12
Presence of nitrogen in the feed gas to the membrane fibres	0	0	7	5	0	12
Insufficient heating of feed gas by the preheaters	2	7	0	3	0	12
Low membrane feed gas pressure	0	1	3	8	0	12
Low differential pressure across the membranes	0	2	3	7	0	12
Low membrane feed gas speed	0	1	2	8	1	12
Presence of cavity formations in the membrane structure	0	3	2	6	1	12
Presence of heavy hydrocarbons than methane in the feed gas	1	6	0	4	1	12
Occurrence of concentration polarization at points adjacent to the membrane	0	2	1	6	3	12

Table 5.34: Opinions of senior personnel on possible causes of the conditions affecting the efficiency of the membranes (Raw Data) (SP)

Suggestions on the factors affecting the efficient performance of the membrane unit with the most damaging effect amongst the listed possible causes in the questionnaire	
Response	Number of Respondents
Presence of ammonia in the feed gas to the membrane fibres	10
High membrane feed gas speed	9
High differential pressure across the membranes	8
Insufficient heating of feed gas by the preheaters	3

Table 5.35: Optimizing the membrane operations (Raw Data) (SP)

	Strongly Agree	Agree	Strongly Disagree	Disagree	Cannot Say	Total
Making the feed gas flow directly adjacent to the membrane a turbulent one	0	0	4	5	3	12
Installing drains in the feed gas header in order to prevent condensate from getting to the membrane fibres	3	9	0	0	0	12
Checking the membrane feed header for liquid accumulation before the membrane groups are commissioned	10	2	0	0	0	12
Incorporating a Pressure Swing Adsorption system into the process line before the membrane unit, so as to remove any possible gaseous contaminants in the membrane feed gas stream	0	4	0	3	5	12
Reducing the membrane feed gas speed through the reduction of individual partial pressures by removing other gaseous constituents of the membrane feed gas stream through the Pressure Swing Adsorption system	0	4	0	2	6	12
Cleaning the membranes by heating and purging with non-adsorbing gases	0	3	1	7	1	12
Periodic cleaning and backwashing in order to remove the high concentration phase formed by other constituents of the gas	0	9	0	3	0	12

Table 5.35: Optimizing the membrane operations (Raw Data) (SP)

APPENDIX H

FIGURES FOR RESULTS OBTAINED ON THE FACTORS MILITATING AGAINST MEMBRANE EFFICIENCY FOR THE SENIOR PERSONNEL'S QUESTIONNAIRE

Fig 5.35: Data for High membrane feed gas pressure (SP)

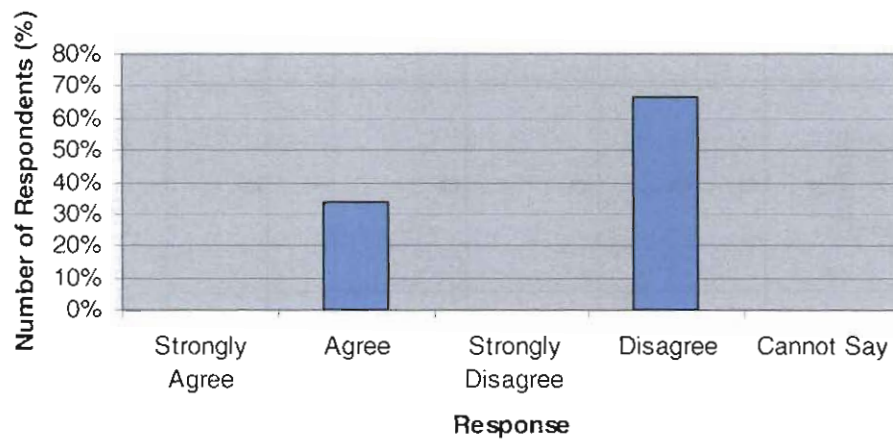


Fig 5.36: Data for High differential pressure across the membranes (SP)

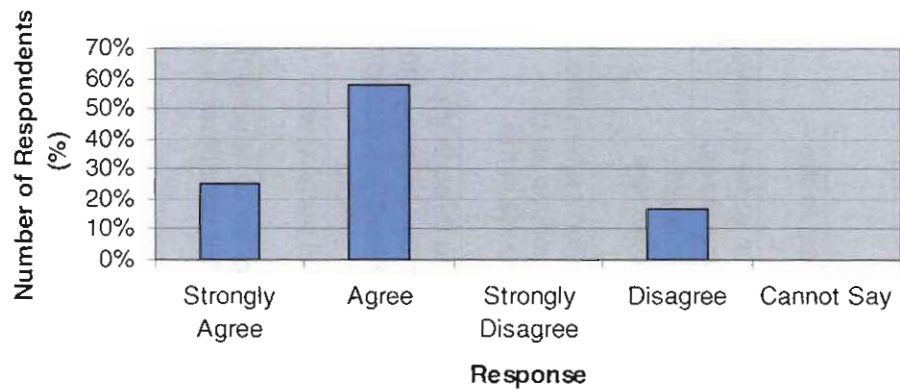


Fig 5.37: Data for High membrane feed gas speed (SP)

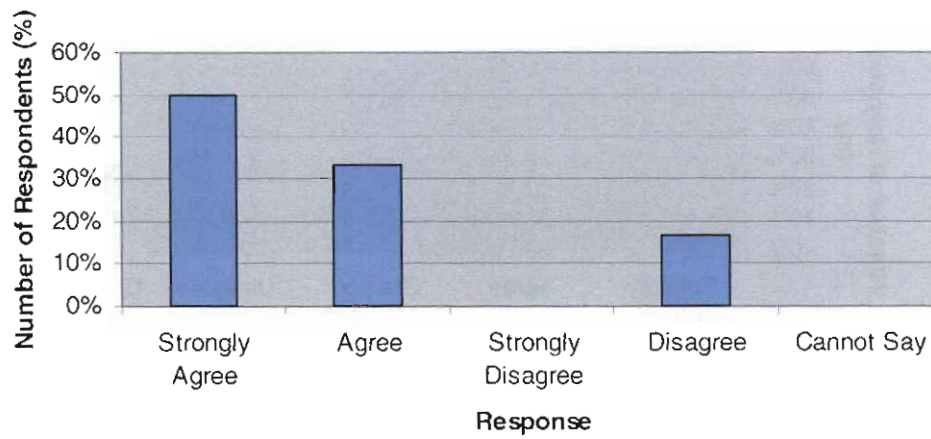


Fig 5.38: Data for Presence of ammonia in the feed gas to the membrane fibres (SP)

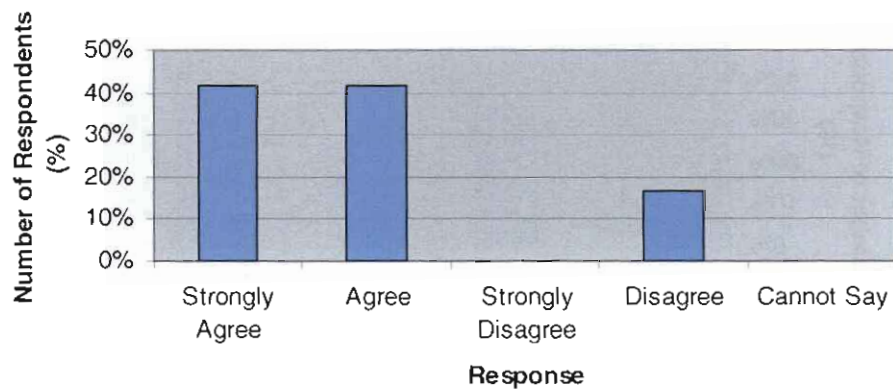


Fig 5.39: Data for Presence of methane in the feed gas to the membrane fibres (SP)

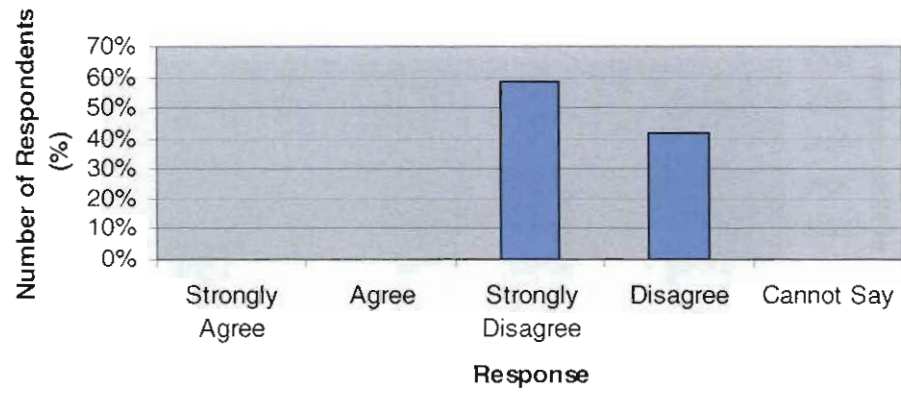


Fig 5.40: Data for Presence of hydrogen cyanide in the feed gas to the membrane fibres (SP)

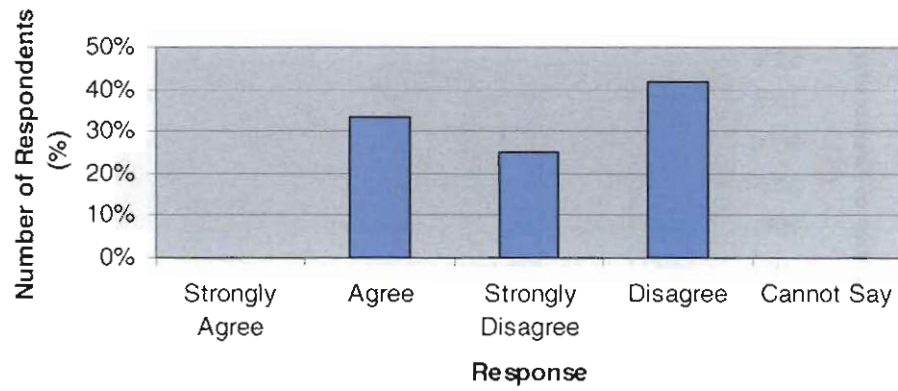


Fig 5.41: Data for Presence of carbon monoxide in the feed gas to the membrane fibres (SP)

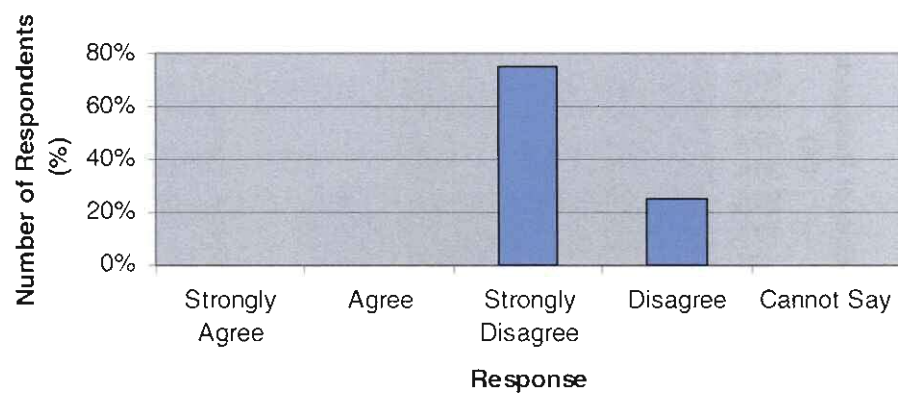


Fig 5.42: Data for Presence of carbon dioxide in the feed gas to the membrane fibres (SP)

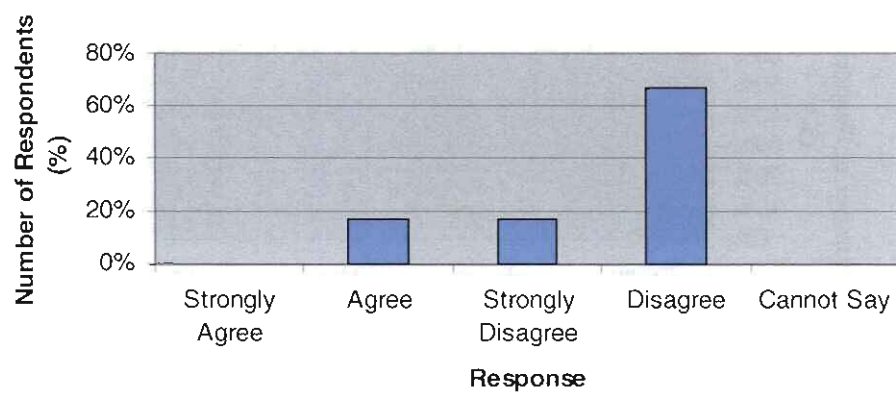


Fig 5.43: Data for Presence of hydrogen sulphide in the feed gas to the membrane fibres (SP)

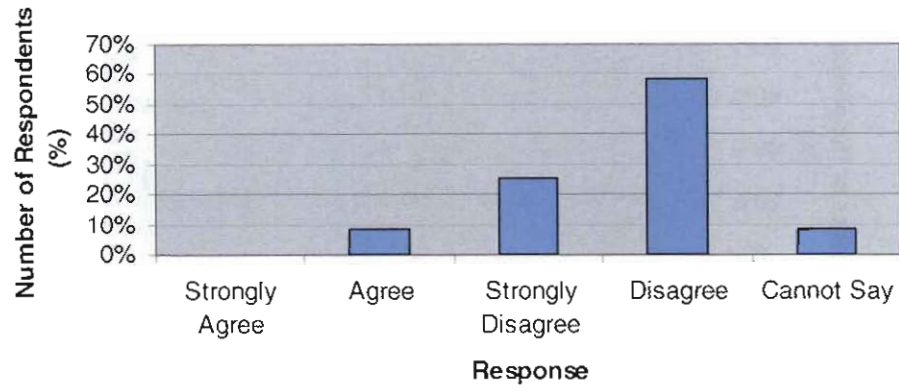


Fig 5.44: Data for Presence of nitrogen in the feed gas to the membrane fibres (SP)

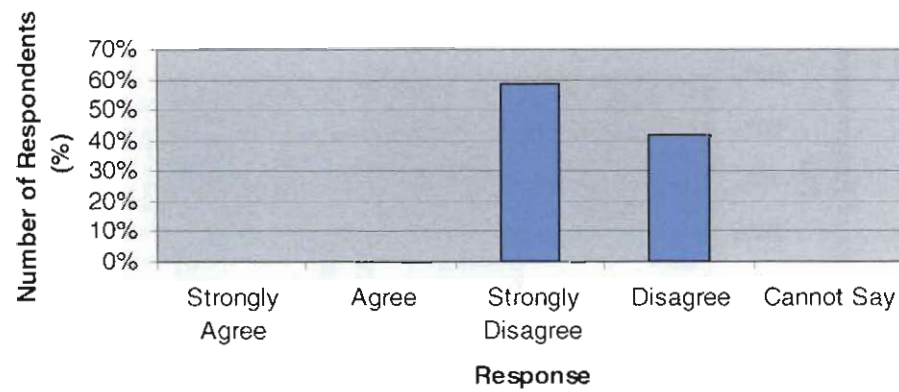


Fig 5.45: Data for Insufficient heating of feed gas by the preheaters (SP)

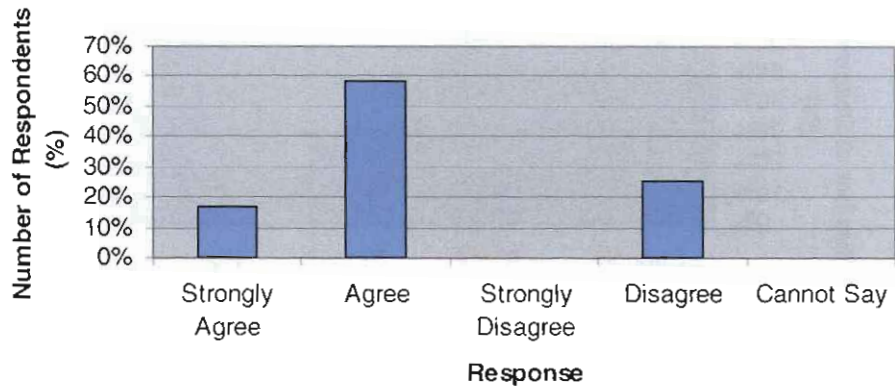


Fig 5.46: Data for Low membrane feed gas pressure (SP)

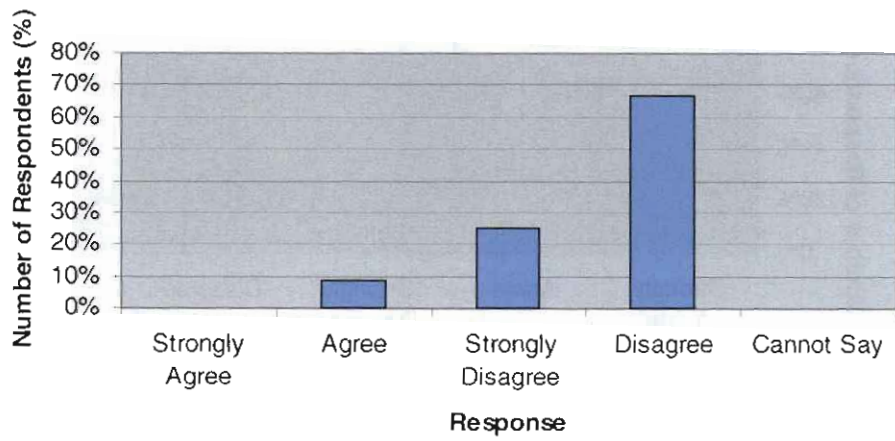


Fig 5.47: Data for Low differential pressure across the membranes (SP)

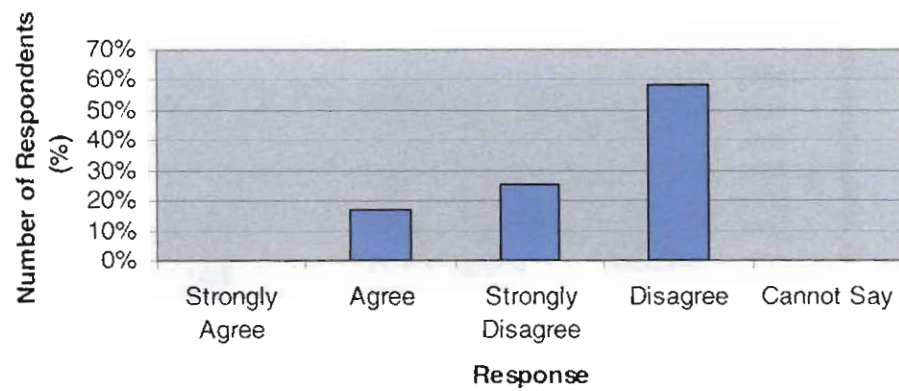


Fig 5.48: Data for Low membrane feed gas speed (SP)

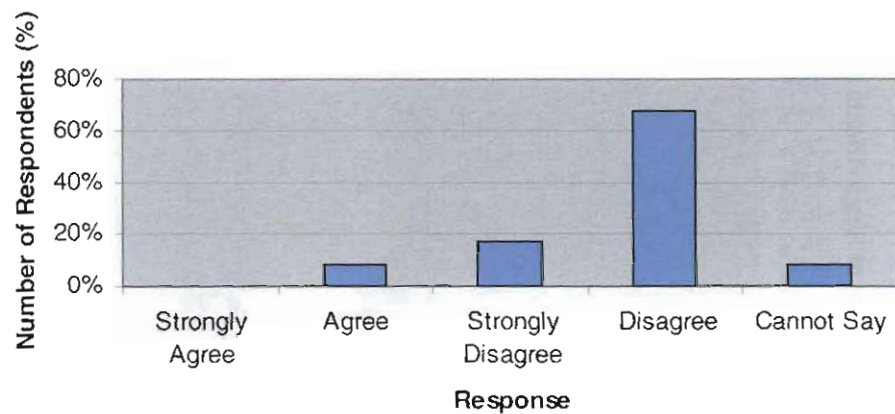


Fig 5.49: Data for Presence of cavity formations in the membrane structure (SP)

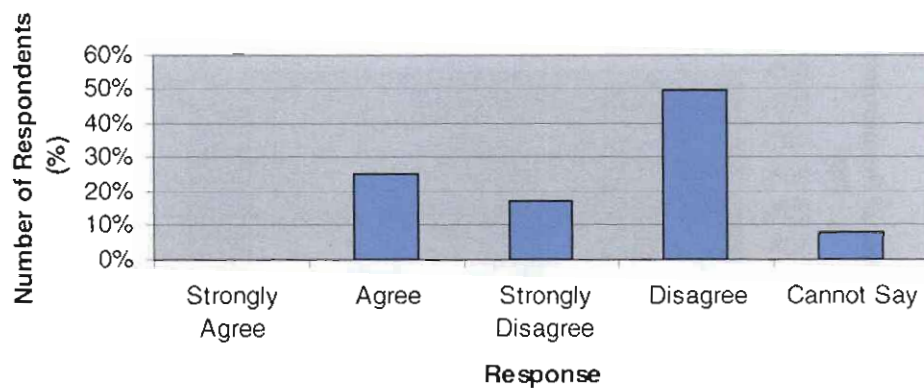


Fig 5.50: Data for Presence of heavy hydrocarbons than methane in the feed gas (SP)

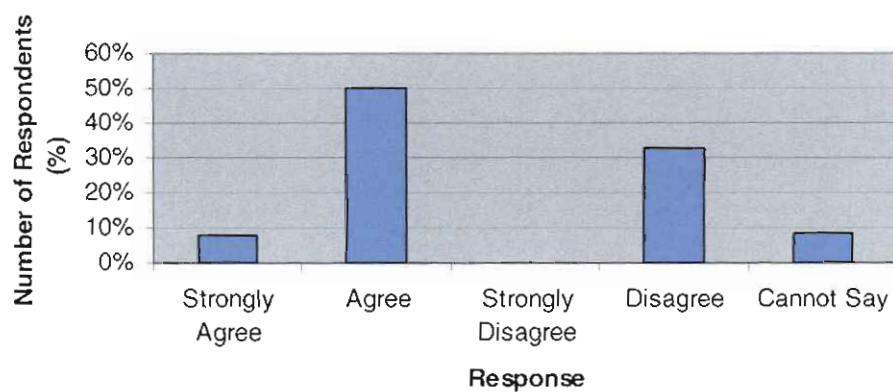
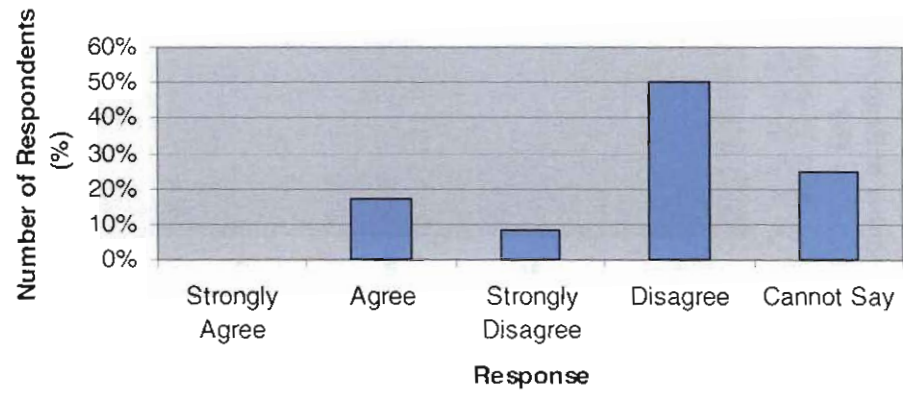


Fig 5.51: Data for Occurrence of concentration polarization at points adjacent to the membrane (SP)



APPENDIX I

FIGURES FOR RESULTS OBTAINED ON OPTIMIZING THE MEMBRANE OPERATIONS FOR THE SENIOR PERSONNEL'S QUESTIONNAIRE

Fig 5.52: Data for Installing drains in the feed gas header (SP)

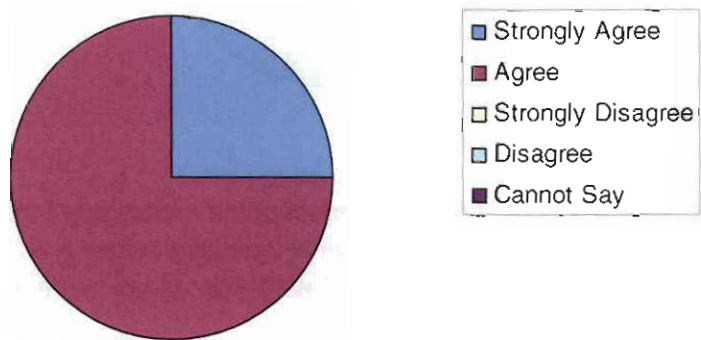


Fig 5.53: Data for Checking the membrane feed header for liquid accumulation before the membrane groups are commissioned (SP)

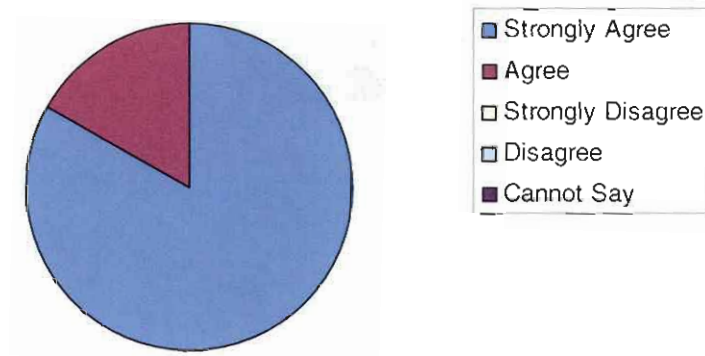


Fig 5.54: Data for Incorporating a Pressure Swing Adsorption system into the process line before the membrane unit (SP)

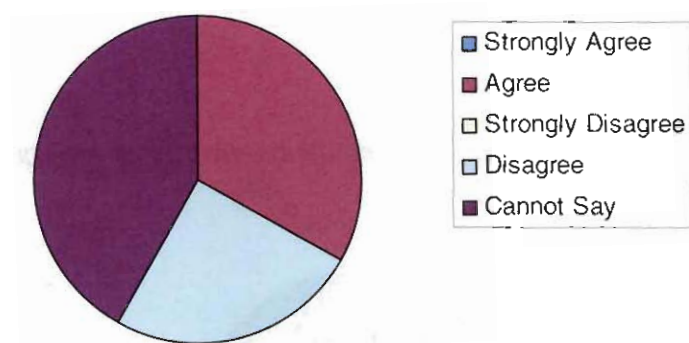


Fig 5.55: Data for Reducing the membrane feed gas speed by the reduction of individual partial pressures through the Pressure Swing Adsorption system (SP)

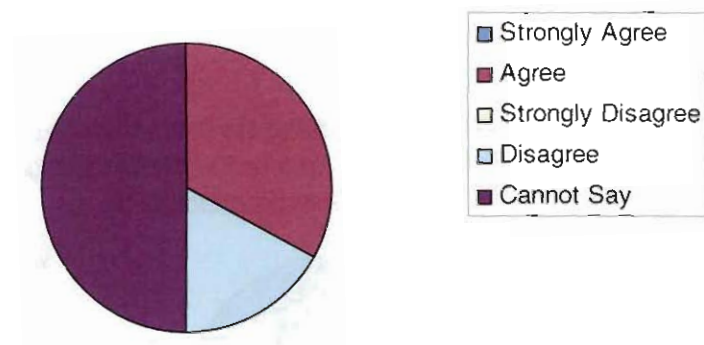


Fig 5.56: Data for Cleaning the membranes by heating and purging with non-adsorbing gases (SP)

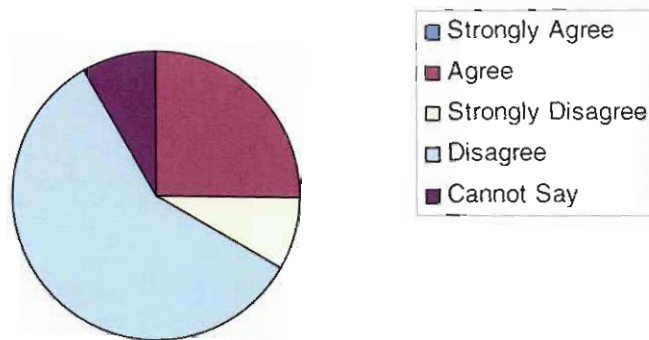


Fig 5.57: Data for Periodic cleaning and backwashing in order to remove the high concentration phase formed by other constituents (SP)

