

**An investigation into the feasibility of applying the watergas shift process to  
increase hydrogen production rate of the hybrid sulphur process.**

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## **ABSTRACT**

An investigation was undertaken to determine the feasibility of increasing the hydrogen production rate by coupling the water gas shift (WGS) process to the hybrid sulphur process (HyS). This investigation also involved the technical and economical analysis of the water gas shift and the H<sub>2</sub> separation by means of Pressure swing adsorption (PSA) process. A technical analysis of the water gas shift reaction was determined under the operating conditions selected on the basis of some information available in the literature. The high temperature system (HTS) and low temperature system (LTS) reactors were assumed to be operated at temperatures of 350°C and 200°C, respectively. The operating pressure for both reactors was assumed to be 30 atmospheres. The H<sub>2</sub> production rate of the partial oxidation (POX) and the WGS processes was 242T/D, which is approximately two times the amount produced by the HyS process alone. The PSA was used for the purification process leading to a hydrogen product with a purity of 99.99%. From the total H<sub>2</sub> produced by the POX and the WGS processes only 90 percent of H<sub>2</sub> is recovered in the PSA. The unrecovered H<sub>2</sub> leaves the PSA as a purge gas together with CO<sub>2</sub> and traces of CH<sub>4</sub>, CO, and saturated H<sub>2</sub>O. The estimated capital cost of the WGS plant with PSA is about US\$50 million. The production cost is highly dependent on the cost of all of the required raw materials and utilities involved. The production cost obtained was US \$1.41/kg H<sub>2</sub> based on the input cost of synthesis gas as produced by the POX process. In this case the production cost of synthesis gas based on US \$6/GJ for natural gas and US \$0/Ton for oxygen was estimated to be US \$0.154/kg. By increasing the oxygen and natural gas cost, the corresponding increase in synthesis gas has resulted in an increase in H<sub>2</sub> production cost of US \$1.84/kg.

Keywords: Partial oxidation of Methane, Water gas shift reaction, Increasing H<sub>2</sub> production, High and low temperature, Reactor sizing, Economic Analysis, Pressure Swing Adsorption,

## **UITTREKSEL**

'n Ondersoek is gedoen om die ekonomiese gangbaarheid te bepaal wanneer die waterstofproduksie deur die HYS proses verhoog word deur van 'n watergas skuifproses (WGS) gebruik te maak. Die ondersoek sluit ook die tegniese en ekonomiese ondersoek in van die watergas en -waterstof skeidingsproses deur van 'n PSA gebruik te maak. Die tegniese ondersoek van die watergas skuifreaksie is gebaseer op bedryfskondisies soos verkry in die literatuur. Beide hoë en lae temperatuur reaktor sisteme wat bedryf word by 350 °C en 200 °C onderskeidelik is ondersoek. Die bedryfsdrukke van beide reaktore is as 30 bar aanvaar. Die totale waterstof produksietempo van die parsiële oksidasie proses (POX) gekoppel aan die WGS proses is bereken as 242 ton per dag wat ongeveer twee keer die hoeveelheid is wat deur die HYS proses alleen geproduseer word. Die PSA proses is aangewend as 'n skeidingsproses wat 'n waterstofsuiwerheid van 99,99 % tot gevolg het. 90% van die waterstof wat deur die POX en die WGS geproduseer word word deur die PSA herwin. Die waterstof wat nie herwin word nie verlaat die PSA as 'n bloeistroom tesame met CO<sub>2</sub> en spore van CH<sub>4</sub>, CO en versadigde waterdamp. Die beraamde kapitaalkoste van die WGS aanleg tesame met die PSA is in die orde van US\$50 miljoen. Die produksiekoste is hoogs afhanklik van al die roumateriale en utiliteite benodig. Die waterstof produksiekoste was bereken as US\$1.41 per kg waterstof gebaseer op die insetkoste van sintese gas soos deur die POX geproduseer. In heidie geval was die produksiekoste van sintese gas gebaseer op 'n natuurlike aardgaskoste van \$6 /Gj en 'n suurstofkoste van \$0 per ton suurstof bereken as US\$0.154 per kg. Deur die suurstof en natuurlike aardgaskoste te verhoog het die ooreenstemmende toename in sintese gas 'n verhoging in waterstof produksiekoste van US\$1.84 per kg tot gevolg gehad.

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# NOMENCLATURE

## Symbols

A, B, C, D	- Constants
$C_p$	- Molar specific heat capacity
exp	- Exponent
$F$	- Flow rates
$H$	- Molar or specific enthalpy
$k$	- Rate constant
$K_{eq}$	- Equilibrium constant
$P$	- Pressure
$r_A$	- Reaction rates of A
$R$	- Ideal gas law constant
$X$	- Conversion
$y$	- Mole fraction
$\psi$	- Activity factor
$\varepsilon$	- Expansion factor, fractional volume change on conversion
$W$	- Weight
$\tau$	- Temperature ratio ( $T/T_0$ )

## Subscripts

$_A$	- gas component
eq	- equilibrium
$in$	- inlet
$out$	- outlet
$t$	- time

## Abbreviations

BET	- Brunauer Emmett and Teller
CNF	- Carbon nanofiber
$CH_4$	- Methane
CO	- Carbon monoxide
$CO_2$	- Carbon dioxide

FID	- Flame ionization detector
GC	- Gas chromatograph
H <sub>2</sub>	- Hydrogen
H <sub>2</sub> O	- Steam/water
H <sub>2</sub> S	- Hydrogen sulphide
HP	- High pressure
ID	- Internal diameter
MEA	- Monoethanolamine
Min	- Minutes
MMO	- Mixed metal oxide
MMscfd	- Million standard cubic feet per day
MPa	- Megapascal
PSA	- Pressure swing adsorption
POX	- Partial oxidation
RPM	- Revolutions per minute
STP	- Standard temperature and pressure
TSA	- Temperature swing adsorption
TPR	- Temperature programmed reduction
WGS	- Water gas shift

# **Chapter 1**

## **Introduction**

### **1.1 Background**

There is a general universal increase in energy demand due to the global economic growth. The environmental concerns and supply uncertainty of fossil fuel based energy have led to a shift in focus to nuclear and renewable energy systems. However, South Africa, which recently experienced electricity power supply disruptions due to the generation capacity failing to meet demand, is on the forefront of alternative energy research such as nuclear energy (Pebble Bed Modular Reactor) to reduce dependence on coal.

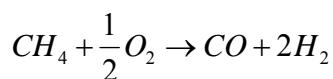
One positive factor is that in-roads have been made to address political and environmental issues concerning the generation of nuclear energy, as a result fear concerning nuclear processes safety has been addressed to an extend. There are environmental benefits linked directly to nuclear power generation due to minimal emission levels if any has made nuclear energy more attractive. Another benefit is that excess and residual process heat generated from nuclear reactors can be used for other vital processes. Chemical processes such as hydrogen production are some of the areas which can utilize energy derived from nuclear process. Besides being a raw material in many chemical processes, hydrogen is a clean source of energy and can be used as a fossil fuel substitute, this will to an extend address some of the key environmental concerns such as green house gas emissions.

Prohibitive costs for hydrogen production processes have been a major limiting factor on its usage as a source of energy. Hydrogen finds extensive usage in the oil industry to lighten crude oils, and is a key raw material in the manufacture of fertilizers, glass, refined metals, cosmetics, soaps and lubricants. There is a great interest in changing from petroleum based fuel to hydrogen in the automobile transportation sector (under development), hence the need to invest in new technologies for hydrogen production (Forsberg, 2003). The nuclear energy generation process leads to the production of high temperature process heat which can be utilized as a key attribute in a hydrogen production process, thus increasing the scale that match the needs for hydrogen.

The most important processes for hydrogen production described in literature, are thermo-chemical based (Nelson et al., 2007, Yildiz and Kazimi, 2006, Shinji et al., 2004, Forsberg, 2003, Schultz, 2003, Brown et al., 2002), electrochemical (Harvergo et al., 2006, Yildiz and Kazimi, 2006, Hino et al., 2004, Forsberg, 2003) and thermo - chemical hybrid sulphur processes (Yildiz and Kazimi, 2006, Jeong et al., 2005, Summers et al., 2005) of which some are still under development. Several investigations have been conducted by researchers over the past years on these processes and the hybrid sulphur (HyS) process, also known as a Westinghouse process and is regarded as a basis for hydrogen production (Summers et al., 2005). Although the HyS process is still under development, its potential and advantages makes it strongly eligible for future economical production of hydrogen. The HyS main product is hydrogen and produces oxygen as a by - product, which among other uses, can be used as a raw material for further production of hydrogen, hence increasing the overall hydrogen yield.

Oxygen produced by the HyS process can be used for the production of synthesis gas (mixture of carbon monoxide and hydrogen). These gases are normally produced from coal gasification and also from steam reforming of natural gas (methane) (Nelson, et al. 2007, Yildiz and Kazimi, 2006, Uhrig, 2005). The process is an endothermic reaction that needs a high input of energy of approximately 206 kJ/mol of methane. There are other processes such as partial oxidation of methane (non-catalytic or catalytic), automatic thermal reforming and compound reforming (Petroleum Energy Center, 1999) that can be applied for methane reforming, but have so far not get much attention. Problems related to these processes such as setting up an oxygen plant has been resolved in this case by the HyS process. A survey conducted by Petroleum Energy Center (Japan) in 1999 on these different processes showed that catalytic partial oxidation of methane is economically and thermodynamically viable for the production of synthesis gas.

If the oxygen produced by the HyS process is utilized in the partial oxidation of methane, the hydrogen production in a combination of the two systems is doubled and results in the production of carbon monoxide (CO) as another by - product of the process. The CO is converted even further by means of the water gas shift (WGS) reaction to carbon dioxide (CO<sub>2</sub>) and hydrogen (H<sub>2</sub>) resulting in a theoretical fourfold hydrogen production overall according to the following chemical reactions involved:



1

However, these H<sub>2</sub> production processes also produce CO<sub>2</sub> as a by - product which can be separated and be used for commercial purposes or can be sequestered to avoid releasing it into the atmosphere. Sequestration involves taking CO<sub>2</sub> directly from industrial plants and storing it in deep saline reservoirs. It can also be injected into a porous permeable reservoir that is covered with a cap rock at least 800 meters beneath the earth surface. Another option is deep ocean storage where CO<sub>2</sub> is pumped to a 1000 meters or more depth allowing it to disperse forming a sinking plume.

Current H<sub>2</sub> production rates in the world are difficult to determine because some of the H<sub>2</sub> is used internally in the refineries. A rough estimate of global production rate is approximately 45 million tons per year (Ritter and Ebner, 2005, Climate Technology, 2003). About 48% of H<sub>2</sub> is produced from natural gas, 30% from oil, 18% from coal and the remaining 4% via electrolysis (Climate Technology, 2003). At present several organisations around the world are engaged in research with the purpose of advancing the current and potential technologies that can be used in increasing H<sub>2</sub> production. Some organisations in South Africa have shown great interest in increasing the national H<sub>2</sub> economy; hence, South Africa is partaking in research to improve the currently available processes for H<sub>2</sub> production technologies.

## 1.2 Motivation

The Pebble Bed Modular Reactor (PBMR) process produces high temperature process heat of up to about 950°C that can be economically used as an energy input to various chemical processes. The PBMR Limited organization in conjunction with the Post graduate School of Nuclear Science and Engineering at the North West University (Potchefstroom campus) have seen a need for a detailed investigation on the use of this energy for process heat applications. Currently PBMR Limited and others (Westinghouse) are further developing the HyS process for the production of H<sub>2</sub>. There is also a need to further investigate other possible processes that can be used to increase the H<sub>2</sub> production by the HyS process. A promising method for increasing the H<sub>2</sub> production involves the utilization of the O<sub>2</sub> produced from a HyS process downstream in processes such as POX of natural gas process coupled to a WGS process.

Production of synthesis gas ( $\text{CO} + \text{H}_2$ ) like partial oxidation of natural gas is normally expensive due to the expenses related to the mandatory  $\text{O}_2$  production plant required. In this case  $\text{O}_2$  will be readily available as a by – product from the HyS process at a low or no cost. Therefore, the  $\text{O}_2$  from the HyS process can be used to partially oxidize methane ( $\text{CH}_4$ ) and this process leads to the production of  $\text{H}_2$  and CO. The carbon monoxide produced can be reacted with steam in the WGS reaction leading to further  $\text{H}_2$  production. By coupling these plants, a threefold production of  $\text{H}_2$  is theoretically possible. Coupling of HyS, POX and WGS processes have never been investigated in the past and the outcome is expected to make a significant impact on the overall amount of  $\text{H}_2$  that can be produced by this system as well as make an improvement in the techno – economics of the process.

### 1.3 Research Objectives

The purpose of this study is to investigate the feasibility of applying the water gas shift reaction process in order to increase the hydrogen production rate of the hybrid sulphur process. This was accomplished by the following:

- An energy balance analysis of the WGS reaction process was undertaken to assess the energy requirements of the process. This was based on the thermodynamic data available in literature and the operating conditions of the reactions. The key parameter to be determined was the temperature increase due to the reaction (equilibrium temperature) followed by calculation of the equilibrium constant values as a function of temperature.
- Material balance analysis was conducted where synthesis gas (CO and  $\text{H}_2$ ) produced by the partial oxidation of methane process was used as a feed - stock to the water gas shift reaction process. The input quantities of synthesis gas (CO and  $\text{H}_2$ ) were known from the POX computations and the steam ( $\text{H}_2\text{O}$ ) required was computed using the material balance and the equilibrium conditions.
- Economic evaluation of using the WGS reaction process to increase the  $\text{H}_2$  production was conducted, with the main focus on determining the capital and production cost of the WGS and PSA processes.

## **1.4. Scope of this dissertation**

This study mainly focused on the water gas shift process, which coupled the partial oxidation of methane and hybrid sulphur processes, to increase the H<sub>2</sub> production. Technical and economic evaluations of the WGS reaction and PSA process were undertaken to attain the objectives of this study. The outline followed is as follows:

- Chapter 1 presents an overview of the background, motivation of the investigation and description of the objectives of the study.
- A detailed review of the WGS and H<sub>2</sub> purification processes is discussed in chapter 2. This elaborates the main process parameters involved, namely, operating temperature and pressure, steam to CO ratio, commercial catalysts available, and the chemistry and kinetics of the reaction.
- Chapter 3 presents a description of the path followed in conducting both the technical analysis of the WGS reaction and PSA processes as well as an economic evaluation of the processes.
- Chapter 4 presents the results obtained and a discussion of the analysis as discussed in chapter 3.
- Finally, conclusions which were drawn from the results and recommendations made based on the findings are given in chapter 5.

# Chapter 2

## Literature Review

### 2.1. Introduction

A literature review of the water gas shift reaction is presented in this chapter. Section 2.2 gives an overview of the technologies that can be used for the production of synthetic gas. The water gas shift reaction is discussed in section 2.3, followed by the process parameters in section 2.4. Finally, the hydrogen purification processes are presented in section 2.5.

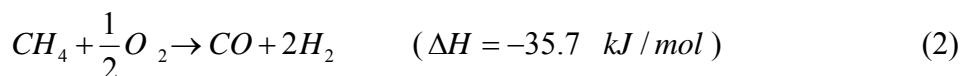
### 2.2 Synthesis gas production

The major source of energy world over is fossil fuels (coal, natural gas, oil, and biomass) and hydrogen is mainly classified as an energy carrier, which is produced from the fossil fuels. Hydrogen can be synthesized using various technologies (methane reforming) including steam reforming, partial oxidation (catalytic or non catalytic), automatic thermal reforming, compound reforming (Keshav and Basu, 2007, Song and Guo, 2006, Koh et al., 2006, Petroleum Energy Center, 1999). The resultant product from these processes is a mixture of hydrogen and carbon monoxide collectively known as a synthesis gas. Carbon monoxide (CO) produced can further be reacted with H<sub>2</sub>O to produce CO<sub>2</sub> and additional H<sub>2</sub> using the water gas shift reaction (Levent, 2001). Water gas shift reaction (WGS) process has been extensively used for further production of hydrogen from synthesis gas. It is mainly applied in fuel cell technology, coal gasification as well as in gas to liquid systems.

Steam methane reforming (SMR) is the most widely used and an economically viable technology for the production of hydrogen (traditionally combined with CO). The SMR reaction presented in equation 1 is endothermic and needs an input of energy of approximately 206 kJ/mol of methane (Yildiz and Kazimi, 2006, Petroleum Energy Center, 1999). It is operated within the temperatures of 750 - 900 °C and a pressure range of 30 – 60 atmospheres and employs a nickel based catalyst to reform methane to CO and H<sub>2</sub> (Song and Guo, 2006, Steinberg, 1999).



The other alternative process for the synthesis gas production is the partial oxidation of methane (catalytic or non - catalytic). Methane gas is oxidized either in the presence or absence of a catalyst. Partial oxidation of methane requires the setting up of an oxygen plant which demands a high capital expenditure. Partial oxidation of methane to synthesis gas as presented in equation 2 is exothermic hence energy is generated compared to the steam reforming process (Keshav and Basu, 2007, Koh et al., 2006, Petroleum Energy Center, 1999).



However, the negative effect of the methane partial oxidation process is that there is a high outlet temperature of the product gases, of approximately 1500 °C, that increases the reactor cost and also leads to the formation of soot (Keshav and Basu, 2007).

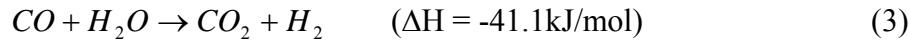
In the automatic thermal reforming process both partial oxidation and methane reforming processes occur in one reactor (Moulijn et al., 2004, Petroleum Energy Center, 1999). The automatic thermal reforming process can be used to compensate for steam reforming or partial oxidation drawbacks. The main disadvantage of using this method is that high volumes of CO<sub>2</sub> are produced, whereas on a positive note, high pressure synthetic gas can be obtained.

Another alternative route that can be used to produce hydrogen is the compound reforming method. In this case steam reforming is combined with the automatic thermal reactor (Keshav and Basu, 2007, Song and Guo, 2006, Petroleum Energy Centre, 1999). Although separate reactors are used, which appears to lead to a high construction costs, a reduction in the operating costs is experienced since there is no need for installing a compressor. A low pressure gas exiting the steam reformer can be converted into a high pressure gas by means of automatic thermal reforming. This study will focus on using a WGS reaction process to convert the CO present in the synthesis gas as produced by a partial oxidation process for the production of H<sub>2</sub>.

## 2.3 Water gas shift process

In the water gas shift process, steam (H<sub>2</sub>O) reacts with carbon monoxide (CO) to produce a mixture of carbon dioxide (CO<sub>2</sub>) and hydrogen (H<sub>2</sub>) as shown in equation 3. The WGS is an exothermic, reversible reaction that takes place in the presence of a catalyst (Mukherjee et al.,

2007, Batista et al. 2006, Callaghan, 2006, Wheeler et al. 2004, Levent, 2001, Tonkovich et al., 1999, Rhodes et al., 1995, Shah et al., 1984).



The WGS can be carried out in a single or multistage (two stages) reactors depending on the conversion rate of CO and steam to H<sub>2</sub> (Shah et al., 1984, Rhodes et al., 1995). In a single stage shift reactor, CO and steam are introduced into the shift reactor in the presence of a catalyst, and the product gas (CO<sub>2</sub> and H<sub>2</sub>) leaving the WGS reactor is sent to the CO<sub>2</sub>/H<sub>2</sub> separators, thus increasing the H<sub>2</sub> concentration. Schematic presentations of the process layout applicable to both processes are given in figures 2.1 and 2.2.

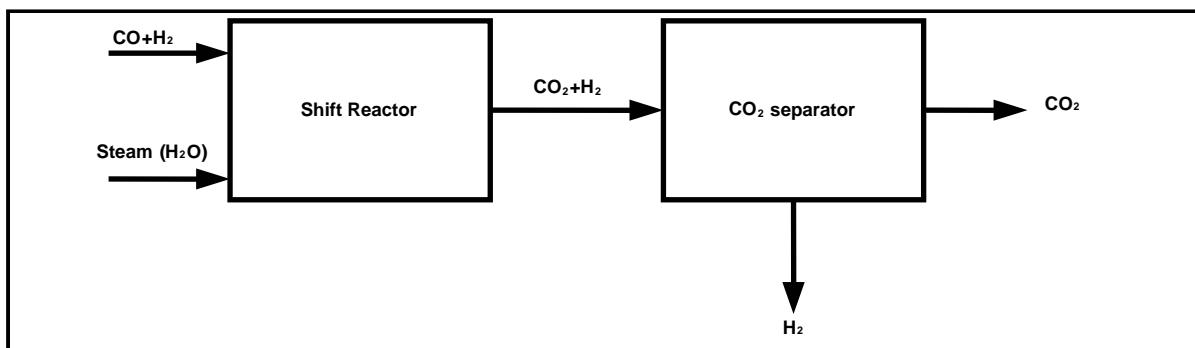


Figure 2.1: Single Stage Shift Process

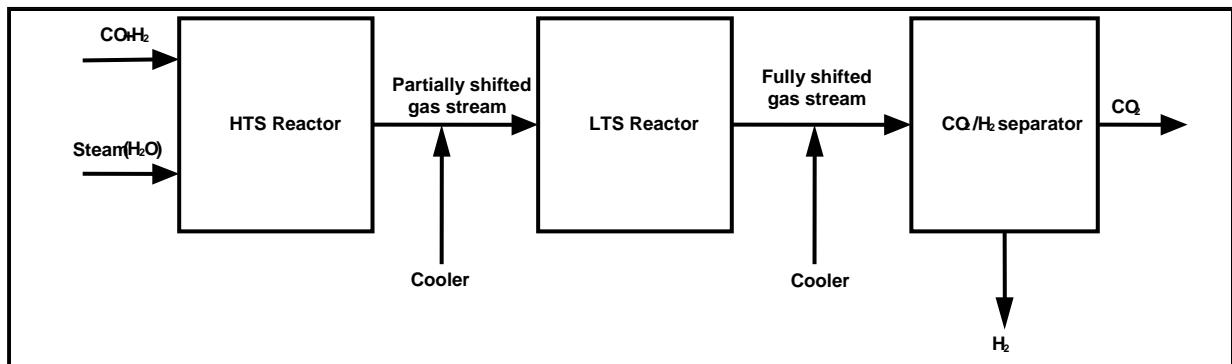


Figure 2.2: Two Stage Shift Process

In an adiabatic two - stage reactor process, as shown in Figure 2.2, catalytic reactors that are operating at high and low temperatures are used consecutively. The partially shifted stream exiting the first reactor (high temperature) is cooled to a temperature of approximately 220°C prior to entering the second shift reactor that is operated at low temperatures. The fully shifted

stream leaving the second shift reactor is cooled to a temperature suitable for CO<sub>2</sub>/H<sub>2</sub> separation process. The two - stage shift reactor option is used in cases where high purity H<sub>2</sub> is required, hence this is advantageous to the steam economy, (Newsome, 1980). Steam required for a two - stage shift reactor process is less than that needed for a one stage shift reactor.

## 2.4 Process parameters

The WGS reaction performance is dependent on a number of variables such as the type of catalysts used, operating temperature, Steam to CO ratio and to a lesser extent the pressure of operation. These parameters are discussed in more detail.

### 2.4.1 Temperature

Temperature plays an important role in most chemical reactions. It is commonly known that for most endothermic reactions, the reaction rates generally increase with an increase in temperature (Arrhenius equation). Since the WGS reaction is reported to be exothermic, it is, therefore, thermodynamically necessary to avoid high temperatures for the reasons of catalysts sintering or deactivation (e.g recrystallization of copper in copper – zinc aluminium catalysts) as well as equipment mechanical design considerations (Rhodes et al., 1995, Callaghan, 2006). On the other hand, the catalytic reaction kinetics is highly favoured by higher temperatures. It is therefore important to strike a balance so as to meet these thermodynamic limitations and ensure that high conversion rates are obtained. Higher reaction rates for equilibrium determined systems reduce the approach to equilibrium (difference between actual outlet temperature and the equilibrium temperature to which the unit product gases correspond). As a result, the WGS reaction is conducted in two stages. The first stage consists of a high temperature reactor operating at a temperature range of 350 - 600°C and the second stage (consisting of a low temperature reactor) operates within a temperature range of 150 - 300°C (Callaghan, 2006).

The catalysts used for the WGS reaction are also affected by the operating temperature. This has led to the development of high temperature shift (HTS) catalysts (iron and chromium oxides) and low temperature shift (LTS) catalysts (copper, zinc and aluminium oxides), (Batista et al., 2006, Lei et al., 2005, Xue et al., 1996, Rhodes, et al. 1995). Ettouney et al., 1995, pointed out some advantages of operating at low temperatures such as low energy consumption, high hydrogen

yield, low operating pressures and reduced equipment cost. Unfortunately these catalysts have lower resistance to poisoning and thermal stresses which lead to a shorter catalyst life span.

## 2.4.2 Catalysts

Catalysts contribute significantly to the WGS reaction mechanism and many studies (Huber, et al. 2007, Nagai and Matsuda, 2006, Lei et al., 2005, Luengnaruemichai et al., 2003, Andreeva et al., 2002, Li et al., 2000, Bocuzzi et al., 1999, Bunluesin et al., 1998, Ovesen et al., 1996, Xue et al., 1996) have been conducted to unlock the uncertainties concerning catalysts that are commercially available. These are iron, copper, rhodium, cobalt, gold and platinum based catalysts. Although there are a number of metal catalysts available that can be used for the WGS reaction, iron based catalysts, commonly used for the high temperature shift reaction, have been favorites due to their excellence in thermal stability, poison resistance, and good selectivity (Iyoha, 2007, Ladebeck and Wagner, 2003). The catalysts are available as pellets on a chromium oxide support composed of 8 -12% Cr<sub>2</sub>O<sub>3</sub>. The Cr<sub>2</sub>O<sub>3</sub> support is vital because it prohibits catalyst sintering resulting in a longer life span of the catalyst (Iyoha, 2007).

In the case of a low temperature shift (LTS) reaction, copper based catalysts are normally employed; they are preferred due to their high activity, high reaction selectivity, and minimal side reactions (Iyoha, 2007, Newsome, 1980). LTS catalysts are susceptible to sulphur poisoning, and their usage is recommended in cases where sulphur levels are reduced to about 10 -100 ppb (Rhodes et al., 1995). The catalysts are normally applied in the form of tablets, extrusions, or spheres (Ladebeck and Wagner, 2003). Some other metals that have been studied to facilitate the WGS reaction are discussed in more detail below.

### 2.4.2.1 Fe based catalysts

Xue et al., 1996 conducted a study on the iron chromium (Fe - Cr) catalyst. The main objective of the experiments was to measure the activity of the catalyst. The catalyst samples were crushed to particle sizes of between 0.212 and 0.425 mm. Each loading was 200 mg and the reduction pretreatment of the catalyst was conducted prior to their use in the experiments. The catalyst was tested using a quartz tubular reactor in a Eurotherm-controlled furnace. Experiments were carried out at atmospheric pressure and temperatures of about 150 to 450°C. The feed rate was 50 cm<sup>3</sup> (STP)/min composed of a H<sub>2</sub>O to CO ratio of 1.33, with 15% CO, 20% H<sub>2</sub>O, 5% CO<sub>2</sub>, 5% H<sub>2</sub> and the balance being N<sub>2</sub>. The dry gas mixture was introduced into H<sub>2</sub>O by passing it through a

water saturator. The gas concentration was determined by HP 5780 II GC equipped with a Carboxen 1000 column. The following findings for Fe - Cr catalysts have been observed. A high activity was observed at temperatures above 300°C and the conversion of CO came close to equilibrium at temperatures above 450°C. Equation 4 was used to calculate the activity of the catalyst, where  $Y_{CO,in}$ ,  $Y_{CO,out}$  are the number of moles of CO in the feed and exit flow respectively, and  $X_{CO}$  expresses the percent of CO converted.

$$X_{CO}(\%) = \frac{Y_{CO,in} - Y_{CO,out}}{Y_{CO,in}} \times 100 \quad (4)$$

The study also involved a blank test that were conducted for comparison purposes at 150 - 450°C. No conversion of CO was observed during these blank tests. Only a thin layer of carbon was formed on the wall of the quartz reactor during the heating of the mixture to temperatures above 375°C.

Lei et al., 2005 conducted the WGS reaction kinetics study over a rhodium promoted iron chromium oxide catalyst. This was done due to results obtained from previous studies (Edwards et al., 2002, Rhodes et al., 2002) where it was discovered that using metals as promoters can be advantageous to the high temperature water gas shift reaction. The best promoter was found to be rhodium. Consequently, the study to quantify the advantages that can be achieved by using rhodium as a promoter was initiated. Experiments were carried out in a tubular flow reactor. Brookes 5850 mass flow meters were used to control the flow. A pre - heater was used to generate steam which was pumped using an ISCO LC – 260D stainless steel pump. The height of a reactor was 40 cm with an internal diameter of 1 cm. The amount of catalyst used was 50 mg with a particle size of -250 to 150  $\mu$ m. More details about the experimental procedure can be found in Lei et al., 2005. The findings of the study were that the reaction rates increase with a decrease in particle size of the catalyst; however, there was evidence of an influence in mass transfer.

#### **2.4.2.2 Copper based catalyst**

Ovesen et al., 1996 conducted a study on three different types of Cu - based catalysts in order to obtain kinetic data for the WGS reaction. The catalysts used were Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>, Cu/Al<sub>2</sub>O<sub>3</sub> and

$\text{Cu/SiO}_2$ . The  $\text{Cu/ZnO/Al}_2\text{O}_3$  catalyst with a surface area of  $10 \text{ m}^2 / \text{g}$ , consisted of: 40% Cu, 22% Zn and 5% Al; the  $\text{Cu/Al}_2\text{O}_3$  catalyst was composed of 35% Cu, whereas the catalyst  $\text{Cu/SiO}_2$  was composed of 21% Cu and had surface areas of 15 and  $5 \text{ m}^2 / \text{g}$  respectively.

A continuous - flow tubular reactor was used for these experiments. The feed gas stream was pre-mixed and mass flow meters were used to control the feed. Impurities (sulphur and chlorine) in the gas were removed by means of  $\text{ZnO}$  and  $\text{Cu/ZnO}$  catalysts at ambient temperature. A high - precision pump used was to feed ionized and degassed water, into a heated stainless steel tube where it was evaporated. The evaporated water was then fed into the inlet of the reactor which was pre-loaded with 0.1 to 0.2 g of  $\text{ZnO}$  catalyst of 0.5 to 0.8 mm particle size mixed with crushed alumina.. The stainless steel tube with a copper lining was heated externally and its temperature was determined by means of a chromel – alumel thermocouple placed in the catalyst bed. The product gases were analyzed using a gas chromatograph with a system of packed and capillary columns. The process was repeated with the catalyst  $\text{Cu/ZnO}$ .

Prior to the above experiment, activation of each catalyst was carried out at atmospheric pressure, whereby the catalyst was heated in a gas mixture containing 0.5% CO, 4%  $\text{CO}_2$  and 4%  $\text{H}_2$  in helium (He) balance with an increment of 0.6 K/min to 493K. Kinetic measurements conducted on  $\text{Cu/ZnO/Al}_2\text{O}_3$  catalyst were at 5 and 20 bar and for  $\text{Cu/Al}_2\text{O}_3$  and  $\text{Cu/SiO}_2$  catalysts were at 20 bar. Four different dry gas compositions as given below were used for the study.

- (1) 2.5% CO, 22%  $\text{CO}_2$ , balance  $\text{H}_2$
- (2) 2.5% CO, 11%  $\text{CO}_2$ , 73%  $\text{H}_2$  and balance He
- (3) 2.5% CO, 22%  $\text{CO}_2$ , 40%  $\text{H}_2$  and balance He and
- (4) 25%  $\text{CO}_2$  and balance  $\text{H}_2$

Kinetic data was analyzed using both a micro kinetic model and a power law model. The analysis showed that the micro kinetic model can be used to elucidate the WGS kinetics through surface redox mechanism, yet the power law model gave a best fit for the experimental WGS kinetic data.

Huber et al., 2007 examined the activity of a nano - composite catalyst containing carbon nano - fiber (CNF) and mixed metal oxide (MMO) of Cu – Ce - Zr over a WGS reaction. Experiments

were carried out at atmospheric pressure in a tubular fixed bed reactor. Details on the experimental procedure can be found in Huber et al., 2007. During the tests, temperature increment was made from 15 to 25°C and stabilized for about 30 minutes before starting the test. Analysis results were taken every 3 minutes for about 15 hours to observe the deactivation behaviour. Observation on the catalytic activity analysis for the WGS reaction revealed that the activity and stability of the CNF containing catalysts and that of the CNF free catalysts is the same resulting in a conclusion that there is no need for the addition of CNF in a MMO catalyst.

Xue et al., 1996 also studied a Cu - Zn catalyst using the method described above. It was concluded that the (Cu - Zn) catalyst is very active for the WGS reaction. CO conversion of 70 % was obtained at temperatures of around 200°C and equilibrium at temperatures above 350°C. In cases where low steam ratios were used, the observation was that the Cu - Zn catalysts is very selective. Under the same conditions, the poison effect was investigated where findings showed that the Cu - Zn catalyst is highly sensitive to sulphur poisoning which is in agreement with other results in literature (Rhodes et al., 1995).

Li et al., 2000 studied the activity of the cerium oxide promoted copper catalyst for the WGS reaction; this was done in order to verify previous studies that revealed that Cu - CeO<sub>2</sub> is active at low temperatures. The study involved the steady state kinetics measurements of the WGS reaction over temperatures of about 175 - 300°C. Experiments were conducted in a quartz tube flow reactor with an internal diameter (ID – 1cm). They were performed at atmospheric pressure with 150 mg of the catalyst powdered into about 50 – 150 µm particle sizes. The feed gas composition was 2 mol% CO, 10.7 mol% H<sub>2</sub>O and the balance was helium. Whenever necessary, 40 mol% of H<sub>2</sub> was added into the feed gas. Gas flow rate was 100cm<sup>3</sup>/min corresponding to a space velocity of 8000/h. Cerium oxide promoted copper catalyst was found to be a good catalyst and 90% CO conversion was obtained.

#### **2.4.2.3 Rhodium based**

Bunluesin et al., 1998 conducted a study on the Rh/ceria, Rh/Al, and ceria catalysts separately. The WGS reaction rates were measured using a ¼ inch quartz tubular reactor, operating under atmospheric pressure. Water vapour was fed into the reactor by bubbling N<sub>2</sub> through de-ionized, distilled water. CO was cleaned by passing it through activated carbon for carbonyls removal and then sent to a packed bed with NaOH pellets to remove the remaining CO<sub>2</sub>. Gas leaving the reactor was measured using an online chromatograph with a methanator and an FID detector.

The results showed that reaction rates on the Rh/ceria catalyst are one order of magnitude higher when compared to the use of ceria on its own and two orders of magnitude higher than that of the Rh/Al catalyst.

#### **2.4.2.4 Cobalt based catalyst**

Nagai and Matsuda, 2006 examined the ability of the Co - Mo oxides to catalyze the WGS reaction at low temperature. The procedure used to prepare catalysts and characterize them is discussed in Nagai and Matsuda, 2006. The WGS reaction has been conducted at a temperature of about 453 K. A gas composition of 10.5% CO, 21% H<sub>2</sub>O, and the balance He was introduced at a rate of 60 ml/min. A micro - pump (Lab – Quatec model LP - 6300) was used to pump water at a flow rate of 0.006 ml/min. The exit gas (CO, CO<sub>2</sub>, H<sub>2</sub>) was analyzed using an on line gas chromatograph with a thermal conductivity detector (ID = 6 mm and Length = 2 m). A gas chromatograph temperature was initially kept at 413 K (about 6 minutes) and increased to 473 K at a rate of 20 K/min where it was kept again for another 6 minutes. The WGS reaction gas was sampled at 30 minutes intervals from 5 minutes after starting the run and ending after 300 minutes.

Findings showed that the activity of Co - Mo at the beginning of the reaction is higher than that of a commercial Cu - Zn catalyst, but it decreased at a later stage of the reaction. The activity of the Co - Mo catalyst is attributed to the content of the Co present. However the reactivity showed to be sensitive to the operating temperatures which can lead to formation of different carbide species. In Ullmann's Encyclopedia of Industrial Chemistry, 2002, it is reported that Co - Mo catalysts are most effective for cases where a feed gas has high impurities of sulfur or heavy hydrocarbons. It helps in the hydrogenation of hydrocarbons.

Another investigation on the Co – Cr commercial catalyst was conducted by Xue et al., 1996. According to this study it was concluded that Co - Cr catalyst is very active nevertheless it cannot be chosen over Fe - Cr or Cu - Zn catalysts due to lack of selectivity. It also contributes to the formation of methane and carbon in the reactor.

#### **2.4.2.5 Platinum based catalyst**

Luengnaruemitchai et al., 2003, studied a low temperature WGS reaction over Pt/CeO<sub>2</sub>. The catalyst was prepared using a sol gel method. The BET surface area of the samples was analyzed by nitrogen adsorption with an auto – sorb automated gas sorption analyzer. The activity of the catalyst was carried out at atmospheric pressure at a reaction temperature of 120 – 360°C. A pyrex U – tube reactor with an internal diameter of 6 mm was used for the experiments. The gas mixture composition was 4% CO, 2.6% H<sub>2</sub>O and the balance was helium. The space velocity was 30000 /h. The pre - treatment of the catalyst was done at 110°C under an oxygen atmosphere for 2 hours. A gas chromatograph equipped with a thermal conductivity detector and a 10 feet × 1/8 inch stainless steel packed column filled with carbosphere was used to analyze the reactant and product gas composition. The findings were that the Pt/CeO<sub>2</sub> catalyst is very active. The effects of steam and the CO concentration on Pt/CeO<sub>2</sub> catalyst were also tested. A positive increment in CO conversion was observed due to an increase in steam. Whereas a decrease in CO conversion rate was observed during an increase in the feed CO concentration which may be due to the poisoning effect of CO on Pt sites.

#### **2.4.2.6 Nickel based catalyst**

Li et al., 2000 also studied the WGS reaction over a nickel - loaded cerium oxide catalyst. The experiments were carried out at temperatures ranging from 250 to 300°C under atmospheric pressure. The experiments were conducted in a quartz tube reactor as described above. Catalysts were also used as prepared with no activation. It was found that the nickel cerium catalyst was better than the copper cerium catalyst. However, it is reported in Ullmann's Encyclopedia of Industrial Chemistry, 2002 that nickel based catalysts enhance the formation of methane from carbon oxides which is a disadvantage.

#### **2.4.2.7 Gold based catalyst**

Bocciuzzi et al., 1999 conducted a study on the Au/Fe<sub>2</sub>O<sub>3</sub> and Au/TiO<sub>2</sub> catalysts. These catalysts have gained much attention because of their high catalytic activity at low temperatures for a number of reactions. The catalysts were prepared using the deposition precipitation method. A laboratory reactor (Contraves AG, Switzerland) was used which was operated with full control of the temperature, pH, stirrer speed, and reactant flow rates. The operating temperature was 333 K, the stirrer speed was 250 rpm and the flow rate was 8 ml/min. The observation during

examination of these two catalysts in a WGS reaction was different from what was observed on other chemical reactions.  $\text{Fe}_2\text{O}_3$  showed high activity at high temperature whilst  $\text{TiO}_2$  did not show any sign of activity at all.

Andreeva et al., 2002 conducted a study of low temperature WGS reaction over an  $\text{Au}/\text{CeO}_2$  catalyst. Different samples were prepared with three different gold loadings: 1, 3, and 5 % gold content, expressed as  $1\text{Au}/\text{CeO}_2$ ,  $3\text{Au}/\text{CeO}_2$ , and  $5\text{Au}/\text{CeO}_2$ . The main focus was on the reaction contact time,  $\text{H}_2\text{O}/\text{CO}$  ratio, and the catalyst stability. The experiments were performed in a temperature range of  $140 - 350^\circ\text{C}$  at atmospheric pressure where the catalyst activity was set forth as a degree of CO conversion. An inlet gas mixture used was 4.498 vol.% CO and the balance was argon. The catalysts bed volume was  $0.5 \text{ cm}^3$  sieved into 0.63 - 0.80 mm with a space velocity of the dry gas of 4000/h. The partial pressure of steam was 31.1 kPa. An "Infralit" gas analyzer was used to determine the amount of CO and  $\text{CO}_2$  from the exit gas. Prior to the tests, samples were preliminary reduced in the hydrogen – argon mixture (1%  $\text{H}_2$ ) at about  $100^\circ\text{C}$  for an hour. The stability of the catalysts tests were conducted under different space velocities (4000/h, 8000/h and 12000/h) and steam partial pressures ranging from 10 – 50 kPa.

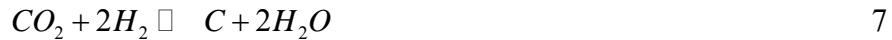
It was found that the samples with the highest gold loadings showed the highest CO conversions irrespective of change in space velocity. But the samples with the lowest gold content showed an evident decrease in CO conversion when the space velocity was increased. Observations during  $\text{H}_2\text{O}/\text{CO}$  effect examinations were that the catalyst activity increased with an increase in  $\text{H}_2\text{O}/\text{CO}$  ratio.

#### **2.4.3 Steam to carbon ratio**

Steam to carbon monoxide ( $\text{H}_2\text{O}/\text{CO}$ ) ratio is one of the main parameters that determine the WGS reaction direction. For the forward reaction to proceed in converting CO in the process gas to  $\text{CO}_2$  and  $\text{H}_2$ , a higher  $\text{H}_2\text{O}/\text{CO}$  ratio is required. The ratio must be higher than that needed stoichiometrically by the reaction ( $R=1$ ) (Xue et al., 1996). Most investigators (Raggio et al., 2005, Maiya et al., 2000, Tokovinch et al., 1999, Rase, 1977) have reported R values ranging from 2 to 4. In the studies conducted by Luengnaruemitchai et al., 2003 when examining the effects of  $\text{H}_2\text{O}$  content on the WGS reaction over a  $\text{Pt}/\text{CeO}_2$  catalyst, he discovered that the conversion rate of CO increases rapidly with an increase in  $\text{H}_2\text{O}$  content. This is in agreement

with results reported by Raggio et al., 2005, Andreeva et al., 2002 and Li et al., 2000 whom all observed the same behaviour.

Maiya et al., 2000 investigated the effect of H<sub>2</sub>O/CO ratios at temperatures of 400°C and discovered that, with a H<sub>2</sub>O/CO ratio of (0 - 2) the WGS reaction rate increased but at values above that, there was no significant effect observed. The information given by Cheng and Jheng, 2007, in their examination of the performance of the WGS reaction with a varying steam to CO ratio in a HTS reactor, is that at high temperatures, the effect of increasing the steam to CO ratio was not significant since higher conversions are also attributed to an increase in reaction temperature. However with the LTS reactor the increase in CO conversion can be attributed to an increase in the H<sub>2</sub>O/CO ratio. Rase, 1977, reported optimum value of the H<sub>2</sub>O/CO ratio of 4:1 or higher, an increase in the H<sub>2</sub>O/CO ratio needs careful economic consideration because higher steam rates might result in overall high flows, thus larger reactors will be needed by the process for the same output. Similarly low H<sub>2</sub>O/CO ratio in the feed can result in the following side reactions (Xue et al., 1996).



Most of the products produced by these side reactions may have a negative effect on the WGS reaction. For example, carbon may block the catalyst bed and result in catalyst deactivation thus increasing a pressure drop across the reactor. Methane formation will consume H<sub>2</sub> which results in a lower H<sub>2</sub> output by the process. However in the LTS, the serious constraint is the dew point of the process gas entering the reactor. The inlet process gas temperature must be above its dew point by a reasonable limit to avoid water condensation that can result in damage of a catalyst

(Maxwell, 2004). This limits the minimum inlet process gas temperature entering the LT shift reactor to about 190 to 200°C (Satterfield, 1980, Maxwell, 2004), which is the lowest temperature that can be used without condensation at elevated pressures.

#### **2.4.4 Pressure**

Normally the reaction rate is affected by the operating pressure as far as the reaction kinetics is concerned. The reaction is favored by pressure if there is a decrease in volume and negatively affected by pressure if there is an increase in volume with the reaction. The WGS reaction is equimolar, and thus the effect of pressure is minimal (Ladebeck and Wagner, 2003, Rhodes et al., 1995). It is observed from Ladebeck and Wagner's work that a small change in pressure does not affect the concentration of CO. It can only be affected if the pressure difference is approximately 100 times more than the actual value.

In spite of the minimal dependency of the WGS reaction on pressure, it is reported that the operational pressure is mainly determined by other unit operations inside the plant and values as high as 3 MPa have been proposed (Satterfield, 1980). The high pressure operation may allow the use of smaller equipment. Higher pressures may also decrease the contact time in the reactor which is in the order of 3 to 9 seconds to about 1 second or less (Satterfield, 1980). Rase, 1977 is in agreement with Satterfield, 1980 that the WGS reactor pressure can be determined by other operating units in the plant. He pointed out that shift reactors should operate at 0.068 MPa less than the reformer pressure. Rase, 1977 used 2.69 MPa and 2.63 MPa for the first and second shift reactors respectively when conducting a case study on the WGS reaction process. Moe, 1962 reported in his study that an increase in pressure increases the rate constant of the WGS reaction but does not affect the equilibrium. In studies conducted by Ettouney et al., 1995, the effect of the total pressure on the WGS reaction rate was shown to be minimal. The degree of increase in the reaction rate revealed no valuable effect on the overall conversion of CO.

Table 2.1: Water gas shift process parameters used by other researches.

	Process Parameters							
Investigators	Temperature (°C)		Pressure (atmospheres)	Catalysts		Steam/CO ratio	CO exit concentration (%)	CO <sub>2</sub> separation method
	HTS	LTS		HTS	LTS			
Bruck et al., 2004	320 - 420	180	-	Fe/Cr	ZnO	-	-	-
Callaghan, 2006	350-600	150-300	30	Fe - based	Cu - based	-	-	-
Chiesa et al., 2005	<400	200		Co - Mo		-	-	PSA
Ritter and Ebner, 2005	315-430	205-230	20	Fe <sub>3</sub> O <sub>4</sub> /Cr <sub>2</sub> O <sub>3</sub>	ZnO/CuO	-	-	PSA MEA or MDEA Membrane revisit
Duante, 2007	350	-	-	Fe/Cr	Cu/Zn	-	-	-
Elnashaie and Alhabdan, 1989	350	-	23 – 31	Fe <sub>3</sub> O <sub>4</sub> /Cr <sub>2</sub> O <sub>3</sub>	ZnO/CuO	-	-	-
Ettonney et al., 1995	370	212	26.8 (LTS) 27.4 (HTS)	Fe <sub>3</sub> O <sub>4</sub> -Cr <sub>2</sub> O <sub>3</sub>	Cu/Zn/Cr	0.524 (LTS) 0.662 (HTS)	-	-
Ladebeck and Wagner, 2003	330	190 - 230	10 - 60	Fe/Cr/Cu	Cu/Zn/Al	-	-	-
Lei et al., 2005	360	-	-	Fe <sub>3</sub> O <sub>4</sub> /Cr <sub>2</sub> O <sub>3</sub>	Cu/ZnO/Al <sub>2</sub> O <sub>3</sub>	-	-	-
Levent, 2001	310-450	200-250	30	Cr/Fe based	-	-	0.1 - 0.3	-
Newsome, 1980	320 - 450	200 - 250		Fe <sub>3</sub> O <sub>4</sub> /Cr <sub>2</sub> O <sub>3</sub>	Cu/ZnO/Al <sub>2</sub> O <sub>3</sub>		-	-
Ovesen et al., 1996	-	180-220	30	-	Cu/ZnO/Al <sub>2</sub> O <sub>3</sub> Cu/Al <sub>2</sub> O <sub>3</sub> Cu/SiO <sub>2</sub>	-	0.4	-
Raggio et al., 2005	350-400	250	1	-	-	2.5	<1	MEA

Table 2.1 Continue

Rhodes et al., 1995	310 - 450	219-240	25 - 35	$\text{Cr}_2\text{O}_3/\text{Fe}_3\text{O}_4$	Cu/ZnO/Al	-	-	-
Tarun, 2006	400 - 423	19 - 210	-	-	-	-	-	-
Tonkovich et al., 1999	330 - 530	-	-	Fe /Cr/Zn	CuO	3:1	$\sim 0.2$	--
Xue et al., 1996	300 - 400	200 - 300	-	Fe-Cr	Cu-Zn C0 - Cr	-	-	-
Wheeler et al., 2004	500	200	-	Fe/ $\text{Cr}_2\text{O}_3$	Cu/ZnO	-	-	-

## **2.5 Hydrogen purification processes**

Studies have been conducted over the years on H<sub>2</sub> purification processes and some are still in progress. There are already a number of different technologies that are commercially available to purify a H<sub>2</sub> rich process gas. There are amine absorption based processes, adsorption (pressure and temperature swing), cryogenic processes and polymer membranes (Berchtold, et al., 2006, Tarun, 2006, Wong and Bioletti, 2002).

In absorption processes, monoethanolamine (MEA) absorbent has generated a great interest due to its ability to remove acidic gases such as H<sub>2</sub>S and CO<sub>2</sub> (Rao et al., 2004). Adsorption became popular in the industry during the early 1970's through pressure swing and temperature swing adsorption. Membranes are also under development (research) for the H<sub>2</sub> purification applications. Cryogenic distillation process has put its mark in refineries. There are some other processes such as NaOH scrubbing that are available for the same applications but do not get much attention due to lack of efficiency for high scale operations (Wong and Bioletti, 2002, Tarun, 2006).

### **2.5.1. Monoethanolamine**

Monoethanolamine (MEA) absorbent is widely used in refineries to capture CO<sub>2</sub> in the process gas. MEA (molecular formula = HO-CH<sub>2</sub>-CH<sub>2</sub>-NH<sub>2</sub>) is a primary amine with a high pH and it has a low molecular weight, high solubility and is readily biodegradable.

The MEA absorption process is currently used in many conventional plants world wide, one of these plants is Natref, South Africa. These plants use an amine scrubbing together with a methanator. The negative effect of this process is that it uses some of the product H<sub>2</sub>, reacting it with carbon oxides in the methanator to form more CH<sub>4</sub>. This results in a relatively lower H<sub>2</sub> product purity of 95 - 97% (Ritter and Ebner, 2005) hence it may be used in cases where high H<sub>2</sub> purity is not required such as ammonia production for example. On the other hand MEA separation technology has two highly purified products (H<sub>2</sub> and CO<sub>2</sub>). An example of the conventional plant with MEA absorption process is represented in Figure 2.3.

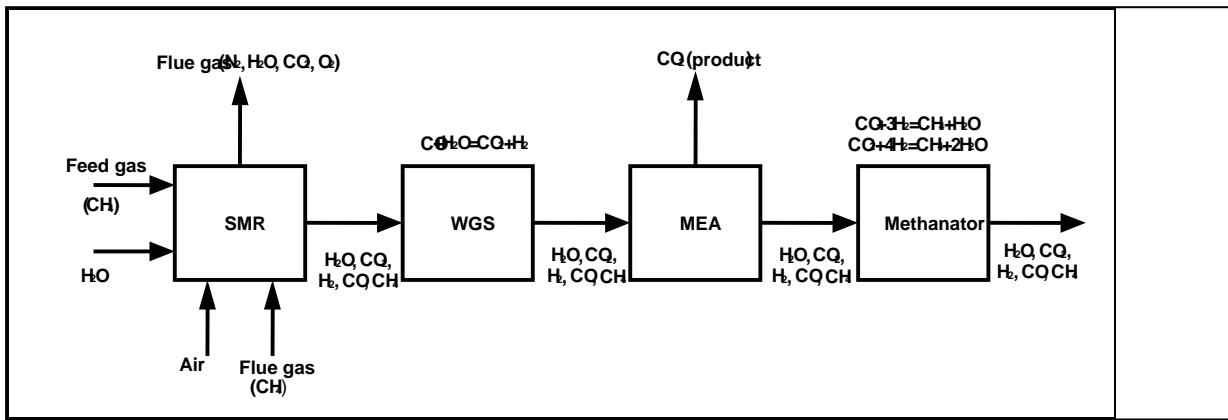


Figure 2.3: Conventional H<sub>2</sub> plant –MEA

The WGS exiting gas stream containing (CO<sub>2</sub>, H<sub>2</sub> and other impurities) enters the bottom part of an absorber and get into contact with a countercurrent flowing aqueous solution of MEA introduced into the column from the top part. CO<sub>2</sub> (known as a weak acid) reacts with MEA (known as weak base) to form a water soluble salt. Then, rich CO<sub>2</sub> containing MEA solution leaving the absorber column is fed to the stripper where it enters the top part of the regenerating stripper. In the stripper the reaction is reversed and the CO<sub>2</sub>, water solution is stripped out of the MEA leaving a lean amine solution ready for reuse (recycle). The CO<sub>2</sub> and water vapor containing stream is directly sent into a condenser where a huge amount of water vapor available condenses. The condensate is then sent back to the stripper column. The objective of this process is to avoid continuous over concentration of amine solution. A heat exchanged operation is done by heating a rich lean solution leaving the bottom part of the absorber with the hot lean solution from the stripper. This lean solution stream is then cooled using a heat exchanger before entering the absorber.

The MEA absorption system is normally operated at temperatures of 30°C and at atmospheric pressure. The stripping temperature is 100°C. Figure 2.4 is representation of the MEA – CO<sub>2</sub> capture flow process (Tarun, 2006).

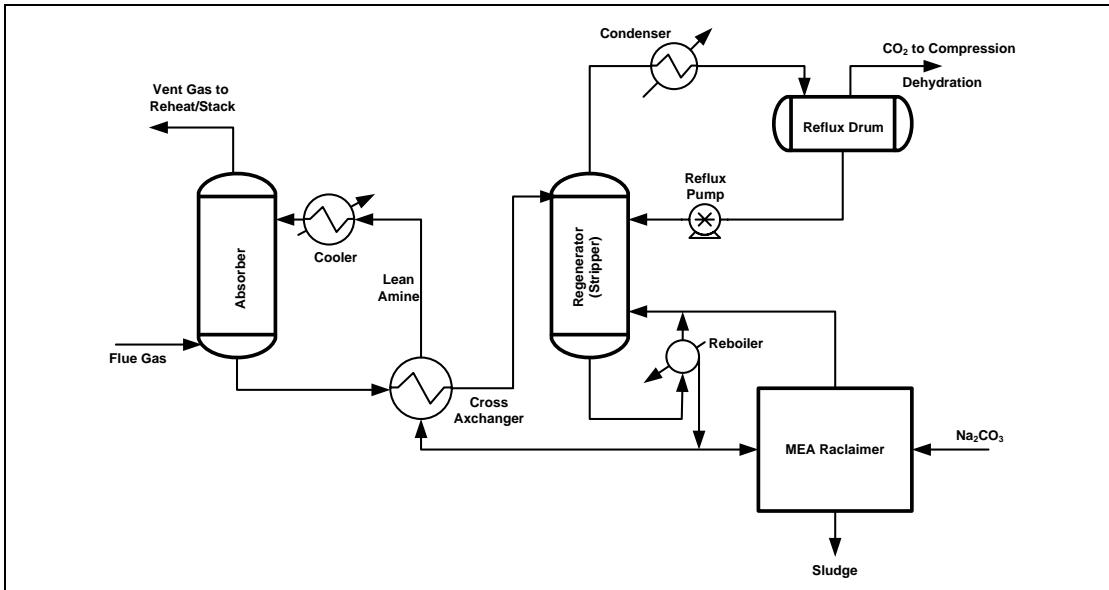


Figure 2.4: Basic flow diagram for MEA – CO<sub>2</sub> capture

## 2.5.2 Polymer membranes

Studies on polymer membrane materials have been undertaken to improve the CO<sub>2</sub> capture technology. Some different membranes that have been so far looked into are reported by Tarun, 2006. These materials differ from each other by means of mass transfer through the membrane, predominant transport mechanism and the phases that are present. The main characteristics of these membranes are excellent permeability and permselectivity. The latest developments were on a cardo polyimide hollow fiber membrane material (Tarun, 2006). It has showed excellent properties for CO<sub>2</sub> separation from H<sub>2</sub> rich gas with a permeation rate in the order of 10<sup>-3</sup> cm<sup>3</sup> (STP)/ (cm<sup>3</sup> sec cmHg) and CO<sub>2</sub>/N<sub>2</sub> selectivity.

However, with membrane technology the high pressure drop characteristic makes them unattractive because expensive compressors are required to meet the downstream demand (H<sub>2</sub> users) (Lin, et al., 2006, Marano, 2003). An illustration of the membrane process is shown in figure 2.5 below. The membrane's systems driving force is the difference in permeation of H<sub>2</sub> and other gases across a polymer membrane. Gas phase component dissolves into the membrane and diffuses through it into the permeate side.

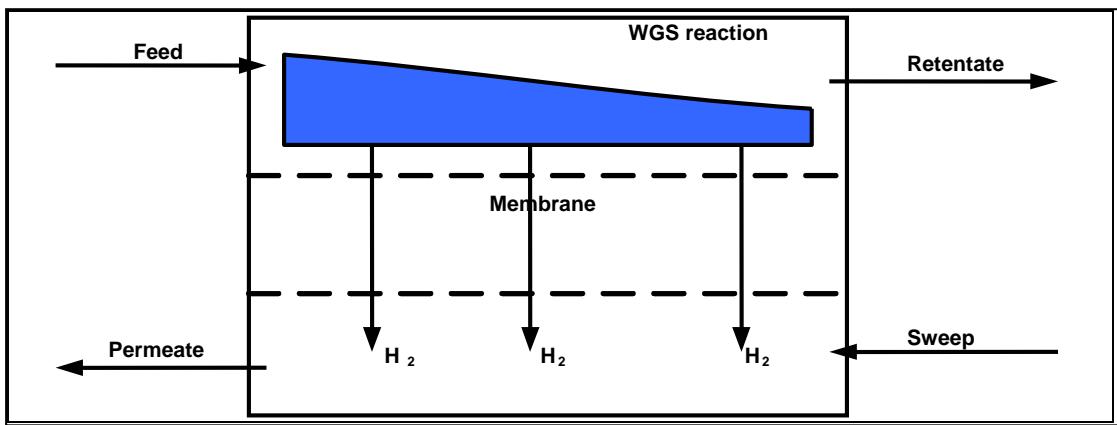


Figure 2.5: Membrane

Polymer membranes for use in synthesis separation need to be thermally, chemically, and mechanically stable under high temperature and pressure conditions (Berchtold, et al., 2006). The development of polymer membranes is underway to address the limitations of this technology. A proposition made by Lin et al., 2006, is to develop current available membranes to be reverse selective (more permeable to heavy components such as CO than to smaller components such as H<sub>2</sub>). In their first attempt in addressing this, they have prepared polymers based on polyethylene oxide that show favourable interaction with CO<sub>2</sub>. This has shown an outstanding performance but more work is still required to acquire more practical information on this technology.

### 2.5.3. Solid Physical adsorption

One of the most promising and economical viable gas separation processes discussed in literature is the solid physical adsorption process, either pressure swing adsorption (PSA) or temperature swing adsorption (TSA) (Gaffney et al., 1999) can be utilized.

#### 2.5.3.1 PSA

PSA is the most attractive technique due to its economical characteristics and ease in operation compared to TSA. It is operated making use of one or more reactors (typically 7 to 16 beds) using four different adsorbents (silica gel/ alumina for water, activated carbon for CO<sub>2</sub>, and 5A zeolite for CH<sub>4</sub>, CO and N<sub>2</sub>) Ritter and Ebner, 2005, Stenberg, 1999. The operation temperature

of the reactor system is 35°C and pressure range of 20 to 60 bar. In a PSA process, desorption occurs at a pressure lower than that of adsorption (Whysall and Picioccio, 1999, Perry and Green, 1997). It uses a pressure difference to shift the adsorption equilibrium. Feed gas containing the adsorbate is passed through adsorbent beds at a certain temperature and pressure, where adsorption will continue until the loading equilibrium is achieved. The regeneration process is achieved by depressurization the reactor, where partial pressure of the adsorbates is reduced allowing desorption to take place. The PSA process is operated at a constant temperature, without requiring any heating or cooling step. Instead, it uses the exothermic heat of adsorption remaining in the adsorbent to supply heat required for adsorption.

Adsorption and regeneration cycle steps take place in each bed. These involve pressurization, high pressure feed, concurrent depressurization, countercurrent depressurization and counter current purge and equalization (Whysall and Picioccio, 1999, Raghavan and Ruthven, 1985). The separation process is driven by the difference in partial pressure of the impurities between the feed and purge gas. A recommended pressure ratio for H<sub>2</sub> separation is 4:1 (Whysall and Picioccio, 1999).

PSA technology is the preferred and recommended technology for modern refining industries. A multistage PSA unit is under operation at Catalyst and Chemical Europe, operating at a pressure of 20 bar and at Hytex where the PSA is operated at 60 bar (Amphlett et al., 1995, Chiesa et al., 2005). From this process, H<sub>2</sub> purity of 99.99% with a recovery of 85 to 90% has been reported. Emphasis on possible high purity H<sub>2</sub> output from PSA units was demonstrated by Peramanu and others, 1999 when reviewing the productive H<sub>2</sub> purification technologies. The H<sub>2</sub> recovery ranges from 65 to 90%. The purge gas leaving the PSA unit contains H<sub>2</sub>O, CO<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub>, and CO. Since H<sub>2</sub> is not adsorbed, it possibly leaves the PSA plant at a pressure close to the feed pressure (Whysall and Picioccio, 1999). Interesting work has been conducted by Heck and Johansen, 1978 where they compared a conventional plant to that using PSA for the production of 50 MM scfd of H<sub>2</sub>. In both systems, the available energy was recovered to practical possible values and the difference in thermal efficiency is due to the operating conditions. The results of the comparison of the two systems showed a thermal efficiency of 84.6% for the PSA H<sub>2</sub> plant and 83.2% for the conventional plant. The higher efficiency obtained in the PSA plant results in lower production costs compared to that of a conventional plant.

There are other possible approaches that can be undertaken to improve the efficiency of the PSA technology such as applying PSA for simultaneous purification of both CO<sub>2</sub> and H<sub>2</sub> (Tarun,

2006, Kumar et al., 1995, Ritter and Ebner, 2005). In this case, one set of adsorbent beds is capable of recovering more than one component from a single gas stream in one plant. Kumar et al., 1995 discussed a new method that can be used to achieve simultaneous separation. By applying this method it is possible that a 100% H<sub>2</sub> recovery can be obtained. A typical example of a hydrogen production plant with PSA is shown in figure 2.6. The fact that the purge gas from the PSA can be recycled makes it possible for the LTS reactor to be neglected because the unreacted CO from the HTS reactor is recirculated. Nowadays the H<sub>2</sub> production plants making use of PSA have become a world standard.

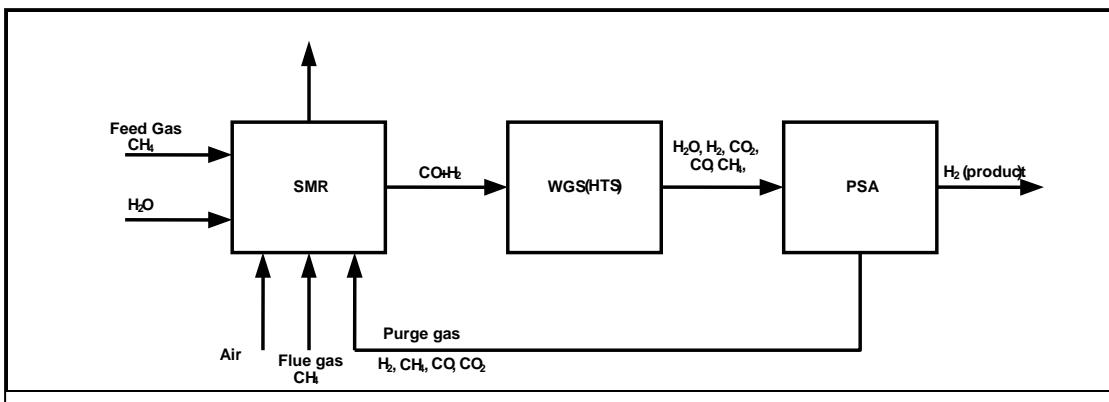


Figure 2.6: Typical H<sub>2</sub> plant with PSA

### 2.5.3.2 TSA

In the TSA process, desorption occurs at higher temperatures compared to that of adsorption. It uses elevated temperatures to shift the adsorption equilibrium which affects the regeneration of the adsorbent. The feed gas containing the adsorbate is passed through an adsorbent at a certain temperature. The adsorption step continues until the equilibrium loading is achieved. The adsorbent temperature is then raised for the desorption process to take place. This heating step must provide the thermal energy required to raise the adsorbate, adsorbent and adsorber temperatures for the desorption process to take place (Perry and Green, 1997).

During the TSA purification process, CO<sub>2</sub> is removed from the adsorbent by the use of heat in the regeneration step. The disadvantage of using TSA is that it requires a large adsorbent inventory is required and the regeneration step is fairly longer compared to that of PSA, this makes these beds unattractive (Bonjour et al., 2005).

## **2.5.4 Cryogenic**

A cryogenic process is normally used in adjusting the synthesis gas composition for a chemical unit feed - stock such as a feed for ammonia production plants (Whysall and Picioccio, 1999). It is based on the boiling temperatures of the feed components. H<sub>2</sub> is a component of interest and has a high volatility compared to that of hydrocarbons. In this process, feed impurities are condensed by cooling the feed stream against the warming product and tail gas stream in a heat exchanger. Refrigeration can be achieved by Joule Thompson refrigeration which is derived from regulating the flow of condensed liquid hydrocarbons. Pretreatment is required to remove water and other components that could freeze up in the system. The pretreated stream is cooled to a temperature where the hydrocarbons could condense and then sent to a separator for the separation of H<sub>2</sub>.

The cryogenic process that is mostly used is known as partial condensation. The disadvantage of the cryogenic separation process is that H<sub>2</sub> recovery is inversely proportional to the purity, which is absolutely not ideal for large industries (Miller and Stocker, 1999). A hydrogen recovery of 92 to 97% and purity of 95% can be achieved. The cryogenic process is reported to be thermodynamically more efficient compared to other H<sub>2</sub> purification processes but it has not got as much attention as the PSA process (Whysall and Picioccio, 1999).

# **Chapter 3**

## **Project analysis**

### **3.1 Introduction**

This chapter discusses technical and economical analysis conducted to address the problem statement of this study. The capacity of the WGS reactors and H<sub>2</sub> purification unit (PSA) were evaluated based on the synthesis gas supplied by partial oxidation process. The main focus was on the amount of steam required for the WGS reaction to take place and the H<sub>2</sub> that can be produced and recovered as a product. Detailed description of the process is given in section 3.2. The method used to analyze WGS and PSA processes is discussed in section 3.3. Reactor sizing equations used and economic evaluation procedure are discussed in sections 3.4 and 3.5 respectively.

### **3.2 Process description**

The H<sub>2</sub> production process selected incorporates the two stage WGS reactors (see Figure 3.1) operating in series at high and low temperatures. Both reactors operate at 30 atmospheres. Other process units are heat exchangers that are used to cool the process gas that leaves both WGS reactors. The purification process of the resultant product gas is conducted by the use of PSA beds in series.

The synthesis gas production by POX is based on the O<sub>2</sub> available from a HyS plant coupled to a 500 MWt PBMR nuclear plant which contains approximately 2:1 mol ratio of H<sub>2</sub>/CO and the rest is H<sub>2</sub>O, CH<sub>4</sub>, and CO<sub>2</sub> (stream 1). The process gas as introduced in stream 1 is produced by the POX process study by Conradie, 2008 that was conducted consecutively with this study and was cooled to a temperature of 350°C as a selected operating temperature for the HTS system. POX process produced synthesis gas at approximately 750°C which was then sent to a heat exchanger where a high pressure steam was generated whilst the synthesis gas was cooled to 350°C. The process gas is introduced into the HTS reactor operating at 350°C where it reacts with H<sub>2</sub>O

(stream 6) in the presence of catalyst ( $\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3/\text{CuO}$ ) to convert CO into  $\text{H}_2$  and  $\text{CO}_2$ . The process gas leaves the HTS reactor at  $450^\circ\text{C}$  (stream 2) and is then cooled in a heat exchanger to a temperature of  $200^\circ\text{C}$  (stream 3), whilst producing a high pressure process steam (stream 11). The steam produced is utilized in house. In the HTS reactor, about 85% of CO is converted, leaving 15% unconverted CO in stream 3. The unconverted CO (15%) is introduced into the second shift reactor that operates at a relatively lower temperature ( $200^\circ\text{C}$ ). In the second reactor, 90% conversion of CO takes place which results in an overall conversion of CO achieved to be 98.5%. A low temperature catalyst ( $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$ ) is used to promote the reaction between  $\text{H}_2\text{O}$  (stream 7) and CO in stream 3. The fully converted process gas (stream 4) exiting the low temperature shift reactor has a temperature of  $300^\circ\text{C}$ . This stream is also cooled in a heat exchanger (condenser) to about  $30^\circ\text{C}$  which is the operating temperature of the PSA purification process. In the condenser, most of the steam present condenses (stream 14) leaving non-condensable gases and a small amount of saturated water as the exiting stream. Another high pressure steam (stream 13) has been produced in this cooling process. Streams 10 and 12 are boiler feed and cooling water respectively, which is at a temperature of about  $30^\circ\text{C}$ . The process gas leaving the condenser (stream 5) is fed into a PSA where high purity (about 99.99%)  $\text{H}_2$  can be recovered in stream 8. The  $\text{CO}_2$  containing stream with traces of  $\text{H}_2$ ,  $\text{CH}_4$ , CO, and  $\text{H}_2\text{O}$  (stream 9) is sent for sequestration. The PSA is designed to recover 90% of the hydrogen produced (Chiesa et al., 2005, Peramanu, 1999, Amphlett et al., 1996). A schematic presentation of the process described above is shown in Figure 3.1.

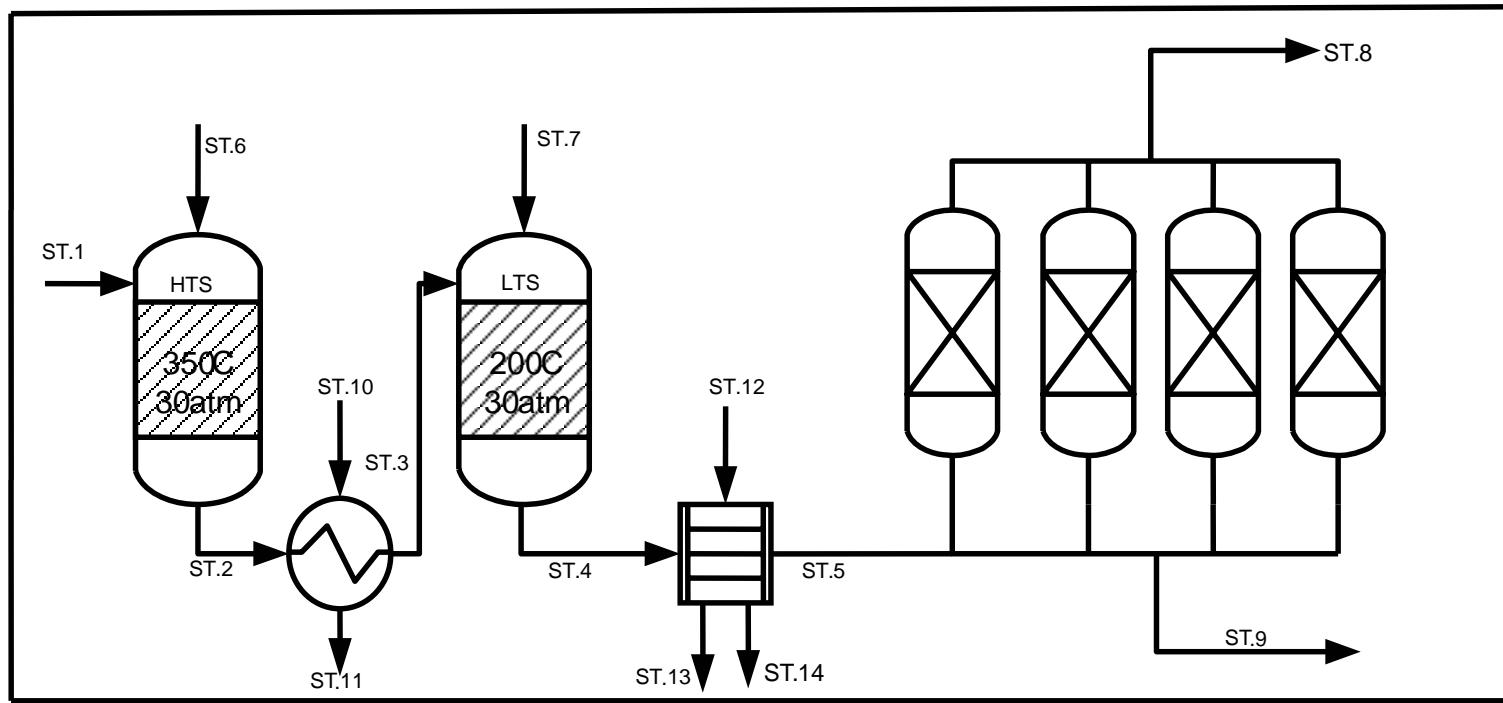


Figure 3.1: Schematic layout of WGS reactors with PSA

### 3.3 Process technical analysis

#### 3.3.1 Water Gas Shift reaction

The question on hold is how much steam is required to convert CO in the WGS reaction? This has been tackled by conducting an energy balance across the reactors. Specific operating conditions (discussed in section 3.2) for the analysis were selected based on literature. To begin with, the thermodynamic behaviour of the reaction was a key aspect to the solution. Therefore, it was necessary that the heat of reaction be determined, where a simplified heat of reaction equation taken from Ettouney et al., 1995 was used. It is expressed by equation 11.

$$-\Delta H = 9.88T - 44754$$

11

The heat of reaction as determined for both HTS and LTS reactors led to the determination of product gas exiting temperatures at which equilibrium is assumed. The temperature of the gases leaving the reactors has increased due to the exothermic nature of the reaction of CO with H<sub>2</sub>O and their values were obtained using equation 12, from Smith et al., 1996.

$$T = 298.15 - \frac{\Delta H_{298}^o}{\langle C_p^o \rangle_H} \quad 12$$

The temperature dependent molar heat capacity of the reaction is required to solve for the temperature in equation 12. Thus far, the molar heat capacity was determined using equation 13, integrated by Smith et al., 1996.

$$\int_{T_0}^T \frac{C_p}{R} \frac{dT}{T} = A \ln \tau + \left[ BT_0 + \left( CT_0^2 + \frac{D}{\tau^2 T_0^2} \right) \left( \frac{\tau+1}{2} \right) \right] (\tau+1) \quad 13$$

After determining the heat of reaction, the molar heat capacity and the temperature increase due to the reaction, the equilibrium constant at exit temperatures of both HTS and LTS reactors was determined since it is a key variable in handling a material balance of the WGS reaction. The equation for determining the equilibrium constant as given by equation 14 is available in literature (Newsome, 1980, Prakash, 1994, Tarun, 2006).

$$K_{eq} = \exp\left(\frac{4577.8}{T} - 4.33\right)$$

14

For this analysis, the WGS reaction is assumed to reach equilibrium which is practically not the case but since this is an equimolar reaction would not a significant impact on the results. Having solved all the necessary thermodynamic data of the reaction, the material balance was then conducted in order to determine the amount of steam required to convert the available CO and the exit process gas composition from each reactor. For a successful analysis of the processes, the following assumptions were made, that the feed contains  $a$  moles of H<sub>2</sub>,  $b$  moles of CO,  $c$  moles of CO<sub>2</sub> and  $d$  moles of steam are added. The degree of conversion was given as X. At equilibrium, the number of moles of each component can be written as (Mearns, 1973).

Having solved all the necessary thermodynamic data of the reaction, the material balance was then conducted in order to determine the amount of steam required to convert the available CO and the exit process gas composition from each reactor. For a successful analysis of the processes, the following assumptions were made, the feed was assumed to contain  $a$  moles of H<sub>2</sub>,  $b$  moles of CO,  $c$  moles of CO<sub>2</sub>. If X is the degree of conversion and  $d$  the moles of external steam added. At equilibrium, the number of moles of each component can be written as: (Mearns, 1973).



15

Hence looking at equation 15, the equilibrium constant ( $K_{eq}$ ) can be obtained by:

$$K_{eq} = \frac{(c + bX)(a + bX)}{(b - bX)(d - bX)}$$

16

And

$$d = \frac{(c + bX)(a + bX)}{(b - bX)K_{eq}} + bX$$

17

By solving equations 16 and 17, the amount of steam that is needed to convert CO into CO<sub>2</sub> and H<sub>2</sub> under the conditions selected was obtained together with the composition of the process gas

leaving both reactors. A material balance across both heat exchangers was also conducted to determine the amount of cooling water needed and that of the steam that can be produced.

### **3.3.2 Pressure swing adsorption**

In this work, PSA is chosen for the H<sub>2</sub> purification on the basis of its historical advantages with respect to product purity, product cost, product recovery, operating cost, and high efficiency (Kamarudin et al., 2004). The analysis in this section was conducted on the basis that PSA is designed to recover 90% of H<sub>2</sub> from the feed at 99.99% purity. Equation 18 was used to determine the amount of H<sub>2</sub> that can be recovered by PSA. All the other gases and the 10% H<sub>2</sub> that is not recoverable leave the PSA as a purge gas. As far as this study is concerned the purge gas (stream 9) will be sent for sequestration. However there are high possibilities of also recovering CO<sub>2</sub> present for other commercial purposes and recycle the remaining gases.

$$F_{H_2,out} = \frac{0.9x_{H_2,in} F_{PSA,in}}{0.9999} \quad 18$$

### **3.4 Water gas shift reactor sizing**

To predict the volume of the WGS reactors, the weight of the catalyst equation was used as given by equation 19 taken from Levenspiel, 1999. Derivation of the catalyst weight equation is given in appendix A; the reaction rate equations used to determine the size of the reactors are given as well. Appendix B gives the examples of the calculations as discussed.

$$W = \frac{F_{AO}}{kC_{AO}} \left( \ln \frac{1}{1 - X_A} \right) \quad 19$$

### **3.5 Project economic analysis**

This section presents the evaluation of technical economic viability of the WGS reaction and the PSA process. The main focus is on capital cost of the plant and the production cost of H<sub>2</sub>.

Detailed discussion on the method used for cost estimation is given in section 3.5.1 and the sensitivity analysis is given in section 3.5.2.

### **3.5.1 Costs estimation**

The total capital cost of a hydrogen plant with a capacity of 2.5 MM Nm<sup>3</sup>/day (220T/D) based on the technical analysis determined above was estimated. This involved the cost of engineering, procurement, fabrication and installation. The capital cost required was directly obtained from a design and fabrication engineering H<sub>2</sub> plants supplier using the preliminary analysis at hand for the study.

The production cost of the hydrogen gas was also estimated based on the consumables such as raw materials, catalyst, utilities and the expenses like man - hours required for the operation of the plant. Raw materials (synthesis gas) prices were taken from the POX analysis results that were undertaken concurrently with this study (Conradie, 2008). The production cost of synthetic gas was found to be \$0.154/kg when natural gas was estimated to be \$6/GJ and \$0/Ton of H<sub>2</sub> as assumed to be supplied by the HyS process. To estimate the production cost of the catalysts used, today's catalysts prices were supplied by Sud - Chemie in Euros/kg, and the catalyst lifetime was used to determine the hydrogen production cost per kilogram. Utilities such as water required for the process was estimated using technical data as given in Table 4.1 and was priced using the current water tariffs rates. Steam required as obtained from the analysis discussed in section 3.31 is assumed to be available at no cost since it is produced in house during the cooling processes from both POX and WGS stages. Estimation of electricity needed for a hydrogen plant was determined from the plant data available in Chemical Engineering Journals and priced according to the current electricity tariffs. Lastly, the operating labour was estimated using an operating labour graph (man – hours/day versus plant capacity) from Peters and Timmerhaus, 2003. The above costing was conducted as per amount of product produced (hydrogen).

### **3.5.2 Sensitivity analysis**

The sensitivity on costs analysis was evaluated by increasing the cost of oxygen as an input to the POX from \$0/T to \$30/T, \$60/T and \$100/T whilst that of natural gas was increased from \$6/GJ to \$8/GJ, \$10/GJ and \$12/GJ. The evaluation was conducted in the POX stage which then resulted in an increase in the production cost of the synthesis gas as an input of the WGS

reaction. The costing of H<sub>2</sub> plant was based on a free (\$0 oxygen) being supplied by the HyS process and the cost of natural gas (CH<sub>4</sub>) to be \$6/GJ. After that the cost analysis was conducted to determine the effect of varying the oxygen cost. The increased values of production cost for the synthesis gas was given by POX process to determine the economical sensitivity of the WGS reaction stage. All other input parameters of the WGS reaction processes remained the same.

# **Chapter 4**

## **Results and discussions**

### **4.1 Introduction**

In this chapter, results obtained during the investigations are presented. Technical and economical analyses undertaken are discussed in section 4.2 and 4.3 consecutively.

### **4.2 Technical analysis**

The technical analysis results of the WGS and the PSA processes shown in figure 3.1 are given in table 4.1. The findings of the study show that by utilizing the WGS reaction to produce H<sub>2</sub>, the process yields a threefold production as was expected. The H<sub>2</sub> that can be produced in the POX process is 160T/D and that which can be produced in the WGS reaction process is 82T/D collectively resulting in a total of 242T/D. However, not all of the H<sub>2</sub> produced from POX and WGS reaction processes can be recovered in the PSA purification stage since it is designed to recover only 90 percent of the total H<sub>2</sub> produced. Therefore, the amount of H<sub>2</sub> recovered by PSA purification process is 218T/D. About 10% H<sub>2</sub> is lost to the purge gas which is mainly composed of CO<sub>2</sub>. Another significant contribution made by the WGS reaction process is the production of high pressure steam (as a by -product) which is a valuable product. The steam is used in house, as a result it would not be necessary to continuously buy steam from external sources or install a steam generator like a boiler.

It was also observed that the steam required by the HTS reactor is less than the steam required by the LTS reactor. This can be attributed to the operating conditions, as reported in literature because the WGS reaction is thermodynamically unfavoured by high temperature which is illustrated by a decrease in equilibrium constant with an increase in temperature, however catalytic kinetics are favoured (Callaghan, 2006). Consequently in the LTS, it is vice versa. The reaction rate is relatively low at LTS reactors (Chiesa et al., 2005) and this can also be due to the amount of H<sub>2</sub> already present in the process gas which can hinder the reaction rates.

Besides the thermodynamic limitations, high conversions can be achieved in both HTS and LTS reactors. The conversion obtained for both reactors was 85% and 90% respectively. The

conversion that can be achieved is relative to the amount of steam used and the operating temperature (which determines the equilibrium conditions). Since most of the steam is produced internally, its usage does not directly have a negative contribution into the overall production cost although there is a possibility of increasing the capital cost due to high flows that might result in a need of large reactors.

The amount of catalyst needed for the conversion of CO in both reactors was determined on the basis of reactor volume. Approximately 64000kg (58 m<sup>3</sup>) of Fe<sub>2</sub>O<sub>3</sub>/Cr<sub>2</sub>O<sub>3</sub>/CuO is required for the HTS reactor. The volume of the catalysts is actually the most important compared to the volume of the reactor since this is a heterogeneous reaction. For LTS reactor, 97000 kg (74m<sup>3</sup>) of ZnO/CuO/Al<sub>2</sub>O<sub>3</sub> is required to convert the residual CO in the process gas. The results obtained from theoretical analysis of the LTS reactor system were multiplied by 4 to obtain the reported value. This was done on the basis of a statement made by Ettouney et al., 1995 that the amount of catalysts that is practically required is actually four times the theoretical amount. The volume of the catalysts obtained in this study is also in agreement with the values reported by Ettouney et al., 1995.

Table 4.1: Material balance Analysis Results

	ST-stream							Recovered							
								H2 (90%)							
	Stream 1	stream 2	stream3	stream 4	stream 5	stream 6	stream 7	stream 8	stream 9	stream 10	stream 11	stream 12	stream 13	Stream 14	
Temperature (C)	350	450	200							30	280	30	290	condensate	
Pressure (atm)	45.4	30		30	30			20			63		73		
Flow rates															
Kmol /hr	6038.056	11610.087	11610.087	14.052183	6914.9078	5572.0306	3112.8383	4504.642	2410.2659	13691.895	13691.895	21082.023	21082.02306	14014.79235	
Cp (mass)										4186		4186			
Cp (mole)		273.6	273.6							232		232			
mole fraction															
H <sub>2</sub>	55.068	41.515512	41.515512	33.992276	72.374894			99.999	20.745232						
CO	29.128	2.2722892	2.2722892	0.5375591	1.1445478				3.2836387						
CO <sub>2</sub>	2.261	14.052183	14.052183	12.335463	26.264139				75.350233						
H <sub>2</sub> O	13.455	42.11425	42.11425	53.098612	0.1395789				0.4004436						
CH <sub>4</sub>	0.088	0.0457661	0.0457661	0.0360899	0.0768411				0.2204524						
Flow rates kg/hr	76696.88	177120.93	177120.93	222.58959	92339.889	100407.99	56093.346	9099.3767	83240.512	246727.95	246727.95	379898.06	379898.0556	252546.5582	
T/D	1840.7251	4250.9024	4250.9024	5.3421502	2216.1573	2409.7918	1346.2403	218.38504	1997.7723	5921.4709	5921.4709	9117.5533	9117.553335	6061.117396	
mass fraction															
H <sub>2</sub>	8.74	5.4970202	5.4970202	4.334815	10.94804				1.2133885						
CO	64.233	4.1719805	4.1719805	0.9505573	2.4007342				2.6631687						
CO <sub>2</sub>	7.833	40.537853	40.537853	34.2725	86.55887				96.020991						
H <sub>2</sub> O	19.083	49.744998	49.744998	60.40556	0.1883527				0.2089423						
CH <sub>4</sub>	0.111	0.0481487	0.0481487	0.0365679	0.0923561				0.1024519						

### 4.3 Costs Results

The total capital cost of a hydrogen plant with a capacity of 2.5 MM Nm<sup>3</sup>/day (220T/day of product H<sub>2</sub>) is estimated to be US\$50 million. This is divided into cost of engineering, procurement and fabrication of the equipment, which is estimated to be US\$35 million. The installation estimation value is US\$15 million.

The production cost results are given in table 4.2 and Figure 4.1 based on a dollar per kilogram of H<sub>2</sub> produced. They are tabulated as amount required in kg/hr, prices in \$/kg and the amount of product produced (hydrogen) also in \$/kg. The production cost determined when using \$0/Ton of oxygen and \$6/GJ of natural gas is given in table 4.2.

Table 4.2: H<sub>2</sub> production cost results

Production cost			
	capacity	Cost (\$/kg)	\$/kg of H <sub>2</sub>
Synthetic gas (kg/hr)	766977	0.154	1.2845
HTS catalyst (kg)	70000	13.2542	0.0012
LTS catalyst (kg)	97000	28.2136	0.0068
		Cost (\$/MWhr)	
Electricity (MWhr)	0.001323	45	0.0595
		Cost (\$/kl)	
Water (kl)	710	0.000413	0.0318
	Number of man	Cost (\$/hr)	
Man - hours	32	30	0.0238
total			1.4077

## 1. Raw materials

Synthesis Gas \$0.154/kg (POX),  
assuming CH<sub>4</sub> = \$6/GJ and O<sub>2</sub>=\$0/T  
Catalysts

HTS catalyst=7000kg, using catalyst's lifetime, the production cost will be = \$0.0012/kg of H<sub>2</sub>

LTS catalyst=97000kg, using catalyst's lifetime, the production cost will be = \$0.0068/kg of H<sub>2</sub>

**2. Man-hours**  
assumed using operating labor graph  
(Timmerhaus,2003)=\$0.0238/  
kg of H<sub>2</sub>

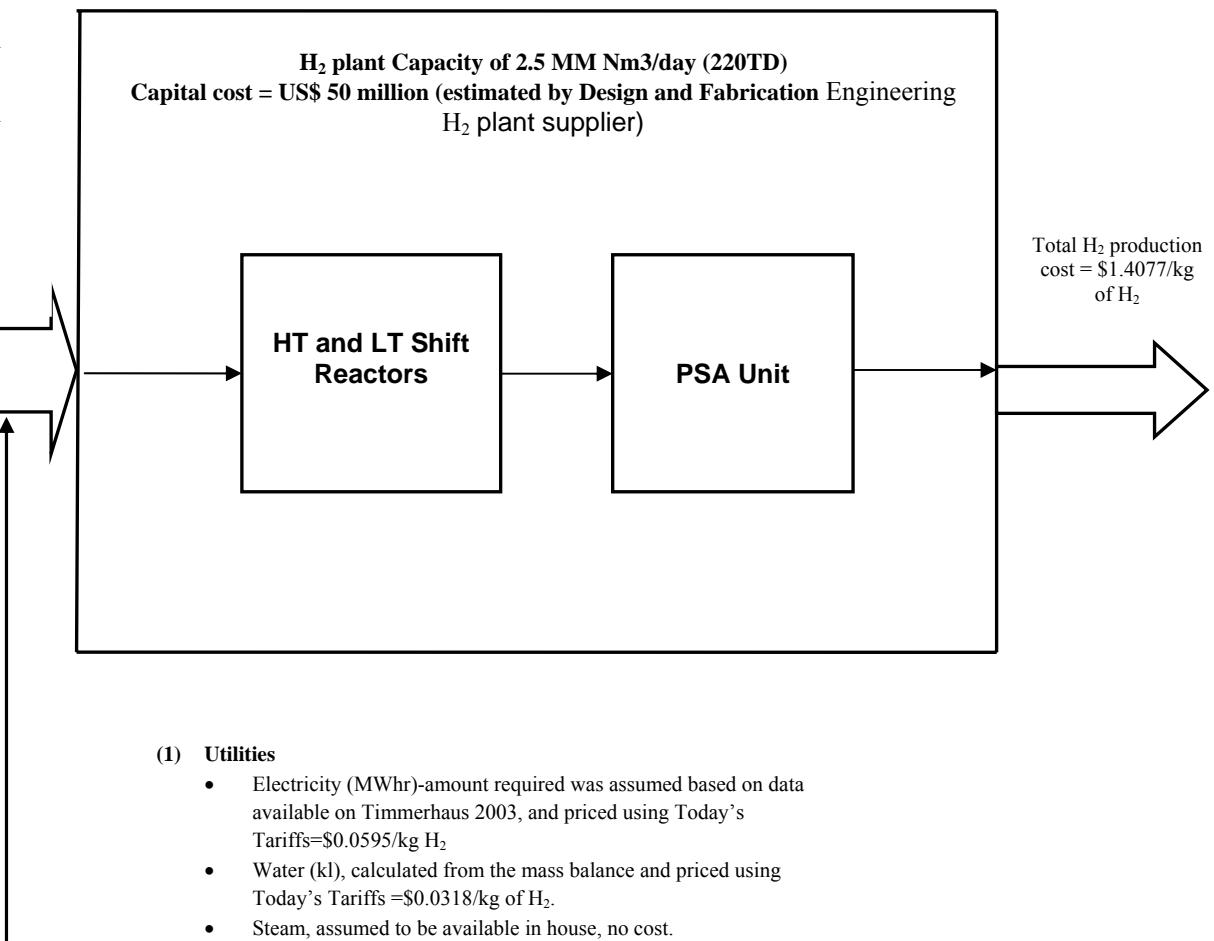


Figure 4.1: Cost item input-output diagram

The sensitivity study was then conducted where the natural gas and oxygen costs were varied and the results are given in Table 4.3. It can be clearly seen from the production cost results that an increase in the cost of oxygen and natural gas leads to an increase in the production costs of the synthesis gas and H<sub>2</sub> from the POX and the WGS plants respectively. The synthesis gas production costs values are the results of the preceding study (Conradie, 2008). The synthesis gas makes about 90 percent of the total H<sub>2</sub> production cost.

Table 4.3: Hydrogen Production Cost

Natural Gas (\$/GJ)		Hydrogen Production Cost (\$/kg)							
		6		8		10		12	
O <sub>2</sub> Price \$/ton	CH <sub>4</sub> price	Syn gas	H <sub>2</sub>	H <sub>2</sub>	Syn gas	Syn gas	H <sub>2</sub>	Syn gas	H <sub>2</sub>
	0	\$0.154	\$1.41	\$0.194	\$1.74	\$0.233	\$2.07	\$0.272	\$2.40
	30	\$0.170	\$1.54	\$0.209	\$1.87	\$0.249	\$2.20	\$0.288	\$2.53
	60	\$0.185	\$1.67	\$0.225	\$2.00	\$0.264	\$2.33	\$0.303	\$2.65
	100	\$0.206	\$1.84	\$0.245	\$2.17	\$0.285	\$2.50	\$0.324	\$2.83

The results obtained from this study have indicated that H<sub>2</sub> could be produced below or just above \$2/kg depending on the cost of natural gas and oxygen and these results are economically viable for H<sub>2</sub> current selling price.

# **Chapter 5**

## **Conclusions and recommendations**

### **5.1 Conclusions**

The conclusion made from the investigation on the possibility of increased H<sub>2</sub> production is that the coupling of the hybrid sulphur, the partial oxidation and the water gas shift processes has been demonstrated to increase the H<sub>2</sub> production by three times.

It can be concluded that the production of H<sub>2</sub> using oxygen from the HyS process as an input to the POX is more economical than when the oxygen had to be purchased from other sources. It can also be concluded that the production cost of H<sub>2</sub> is dependent on the cost of O<sub>2</sub> and natural gas.

### **5.2 Recommendation**

This study was confined to the two stage WGS reaction for the processing of synthesis gas produced by POX process. The PSA purification process was chosen for the study. It is recommended that the following be investigated further to give more light into the applicability of H<sub>2</sub> production systems.

- A single stage WGS with PSA should be examined, noting that the CO content present in the process gas that will be sent to the PSA will still be high, therefore the recycling of the gases will need to be considered. To achieve this, a PSA with multiple gas purification possibilities should also be considered.
- Usage of more than one separation technologies for purification process, for example both MEA and PSA to purify the gases exiting WGS reactors is strongly recommended. The main focus of this further study should be lined with an increase of the efficiency of the H<sub>2</sub> production systems mentioned above.

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## APPENDIX A

### Kinetic parameters for WGS (Tarun, 2006)

#### Rate of reaction

$$-r_{co} = 7.33e - 7\psi k \left( y_{CO} y_{H_2O} - \frac{y_{CO_2} y_{H_2}}{K_{eq}} \right), \frac{\text{kmole CO reacted}}{\text{kg cat s}} \quad \text{A.1}$$

#### Rate and equilibrium constants

$$k = \exp \left( 15.95 - \frac{4900}{T} \right), \text{ for iron catalyst} \quad \text{A.2}$$

$$k = \exp \left( 12.88 - \frac{3340}{T} \right), \text{ for copper catalyst} \quad \text{A.3}$$

For Iron catalyst: (Rase, 1977)

$$\psi = 0.816 + 0.184P_t, \text{ for } P_t \leq 11.8 \quad \text{A.4}$$

$$= 1.53 + 0.123P_t, \text{ for } 11.8 \leq P_t \leq 20$$

$$= 4.0, \text{ for } P_t \geq 20$$

For copper catalyst:

$$\psi = 0.86 + 0.14P_t, \text{ for } P_t \leq 24.8 \quad \text{A.5}$$

$$= 4.33, \text{ for } P_t \geq 24.8$$

#### Derivation of the catalyst weight equation (Levenspiel, 1999)

Assuming a plug flow reactor, a steady state material balance for reactant A gives

Input = output + accumulation

$$F_{A0} - F_{A0}X_{Ain} = F_{A0} - F_{A0}X_{Aout} + (-r_A')\square W \quad \text{A.6}$$

Differentiating results in:

$$F_{A0}dX_A = (-r_A')dW + (-r_A')dV_s \quad \text{A.7}$$

Integrating over the whole reactor gives:

$$\frac{W}{F_{A0}} = \int_0^{X_{Aout}} \frac{dF_A}{r_A'} \quad \text{or} \quad V_s = \int_0^{X_{Aout}} \frac{dF_A}{r_A'} \quad \text{A.8}$$

Where

$$\frac{WC_{A0}}{F_{A0}} = c' \quad \text{and} \quad \frac{V_s C_{A0}}{F_{A0}} = c'' \quad \text{A.9}$$

For first order catalytic reactions, equation A.8 may become:

$$k'c' = k''c'' = (1 + \varepsilon_A) \ln \frac{1}{1 + X_{Aout}} - \varepsilon_A X_{Aout} \quad \text{A.10}$$

For a mixed flow, we have

$$\frac{W}{F_{A0}} = \frac{X_{Aout} - X_{Ain}}{(-r_{Aout}')} \quad \text{or} \quad \frac{V_s}{F_{A0}} = \frac{X_{Aout} - X_{Ain}}{(-r_{Aout}'')} \quad \text{A.11}$$

$$\frac{W}{F_{A0}} = \int_0^{X_{Aout}} \frac{dF_A}{r_A'} \quad \text{or} \quad V_s = \int_0^{X_{Aout}} \frac{dF_A}{r_A''} \quad \text{A.12}$$

With  $C_{Ain} = C_{A0}$  and  $\varepsilon_A \neq 0$ , we can results in a catalysts weight equation as

$$W = \frac{F_{AO}}{kC_A} \left[ (1 + \varepsilon_A) \ln \frac{1}{1 + X_A} - \varepsilon_A X_A \right] \quad \text{A.13}$$

$$\text{Where, } \varepsilon_A = \frac{V_{X_A=1} - V_{X_A=0}}{V_{X_A=0}} \quad \text{A.14}$$

If  $\varepsilon_A = 0$ , equation A.13 reduces to

$$W = \frac{F_{AO}}{kC_{AO}} \left( \ln \frac{1}{1 + X_A} \right) \quad \text{A.15}$$

## APPENDIX B

### B.1 Examples: Reactor sizing

HTS

$$k = \exp\left(15.95 - \frac{4900}{623}\right)$$

$$= 3117.64$$

$$(-r_{CO}) = 7.33 \times 10^{-7} \times 3244.9 \left(0.0227 \times 0.42 - \frac{0.141 \times 0.415}{7.3}\right)$$

$$= 1.456 \times 10^{-5} \frac{\text{kmole CO reacted}}{\text{kg catalyst s}}$$

$$W = \frac{0.4885 \text{ kmole/s}}{1.456 \times 10^{-5} \frac{\text{kmole CO reacted}}{\text{Kg catalyst s}}} (1.897)$$

$$= 63645.9 \text{ kg}$$

$$V = \frac{63645.9 \text{ kg}}{1100 \text{ kg/m}^3} = 57.86 \text{ m}^3$$

LTS

$$k = \exp\left(12.88 - \frac{1855.56}{473}\right)$$

$$= 7762.348$$

$$(-r_{CO}) = 4.33 \times 7.33 \times 10^{-7} \times 7762.348 \left(0.00126 \times 0.66 - \frac{0.089 \times 0.24}{39}\right)$$

$$= 6.995 \times 10^{-6} \frac{\text{kmole CO reacted}}{\text{kg catalyst s}}$$

$$263 \frac{\text{kmole}}{\text{hr}} \times 3600 \frac{\text{1hr}}{\text{s}} = 0.733 \text{ kmole/s}$$

$$W = \frac{0.733 \text{ kmole/s}}{6.995 \times 10^{-6}} \left[ \ln\left(\frac{1}{1-0.9}\right) \right]$$

$$24132.94 \text{ kg} \times 4 = 96531.75 \text{ kg}$$

$$V = \frac{m}{\rho} = \frac{24132.94 \text{ kg}}{1300 \text{ kg/m}^3} = 18.56 \text{ m}^3 \times 4 = 74.26 \text{ m}^3$$

## B. 2 Examples of steam calculations

HTS							
			Texit=723K		H <sub>2</sub> O/CO=3.168149685	Exit comp	
						CO	2.2722
				X=0.85		CO <sub>2</sub>	14.052
	initial	X=Conversion		K <sub>eq</sub> (at exit T) =7.311		H <sub>2</sub> O	42.115
						H <sub>2</sub>	41.511
CO	29.128	b-bX	4.3692	d(H <sub>2</sub> O)=	92.28186	CH <sub>4</sub>	0.045
H <sub>2</sub> O	13.455	d-bX	80.97806			Total	100
CO <sub>2</sub>	2.261	c+bX	27.0198				57.885
H <sub>2</sub>	55.068	a+bX	79.8268				
CH <sub>4</sub>	0.088	bX	24.7588				
				Total=	192.2819		

**LTS**

			Texit = 573K				
			Keq = 39.22		H2O/CO=11.79		
		X= Conversion		X = 0.7			Exit composition
initial							CO 0.537559
							CO <sub>2</sub> 12.33546
CO	2.272289184	b-bX	0.681687	d (H <sub>2</sub> O)= 26.8115			H <sub>2</sub> O 53.09861
H <sub>2</sub> O	42.11424954	d-bX	67.33515				H <sub>2</sub> 33.99228
CO <sub>2</sub>	14.05218331	c+bX	15.64279				CH <sub>4</sub> 0.03609
H <sub>2</sub>	41.51551182	a+bX	43.10611				Total 100
CH <sub>4</sub>	0.045766147	bX	1.590602				
total	100		TOTAL	=126.8115			46.90139

Overall balance

kmol/hr							
ST1	6038.056	ST2	11610.09	ST4	14722.92	ST5	6914.908
CO=	1758.765	CO=	263.8147	CO=	79.14442	CO=	79.14442
H <sub>2</sub> =	3325.037	H <sub>2</sub> =	4819.987	H <sub>2</sub> =	5004.657	H <sub>2</sub> =	5004.657
H <sub>2</sub> O=	812.4204	H <sub>2</sub> O=	4889.501	H <sub>2</sub> O=	7817.669	H <sub>2</sub> O(sat)	9.651756
CO <sub>2</sub> =	136.5204	CO <sub>2</sub> =	1631.471	CO <sub>2</sub> =	1816.141	CO <sub>2</sub> =	1816.141
CH <sub>4</sub> =	5.313489	CH <sub>4</sub> =	5.313489	CH <sub>4</sub> =	5.313489	CH <sub>4</sub> =	5.313489
H <sub>2</sub> O(ST6)	5572.031	H <sub>2</sub> O(ST7)	3112.8383				

kmol/hr			
ST 8		ST 9	2410.266
H <sub>2</sub>	4504.642	CO <sub>2</sub>	1816.141
		CH <sub>4</sub>	5.313489
		H <sub>2</sub>	500.0153
		CO	79.14442
		H <sub>2</sub> O	9.651756