UTILIZING THE BY-PRODUCT OXYGEN OF THE HYBRID SULFUR PROCESS FOR SYNTHESIS GAS PRODUCTION

by

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Abstract

This study introduces an evaluation of the downstream utilization of oxygen produced by the hybrid sulfur process (HYS). Both technical and economic aspects were considered in the production of primarily synthesis gas and hydrogen. Both products could increase the economic potential of the hybrid sulfur process.

Based on an assumed 500MWt pebble bed modular nuclear reactor, the volume of hydrogen and oxygen produced by the scaled down HYS was found to be 121 and 959 ton per day respectively.

The partial oxidation plant (POX) could produce approximately 1840 ton synthesis gas per day based on the oxygen obtained from the HYS. The capital cost of the POX plant is in the order of $104 million (US dollars, Base year 2008). Compared to the capital cost of the HYS, this seems to be a relatively small additional investment. The production cost varied from a best case scenario $9.21 to a worst case scenario of $19.36 per GJ synthesis gas. The profitability analysis conducted showed favorable results, indicating that under the assumed conditions, and with 20 years of operation, a NPV of $87 mil. and an IRR of 19.5% could be obtained, for the assumed base case. The economic sensitivity analysis conducted, provided insight into the upper and lower limitations of favorable operation.

The second product that could be produced was hydrogen. With the addition of a water gas shift and a pressure swing adsorption process to the POX, it was found that an additional 221 ton of hydrogen per day could be produced. The hydrogen could be produced in the best case at $2.34/kg and in the worst case at $3.76/kg. The investment required would be in the order of $50 million. The profitability analysis for the base case analysis predicts an NPV of $206 million and a high IRR of 23.0% under the assumed conditions. On financial grounds it therefore seemed that the hydrogen production process was favorable.

The thermal efficiency of the synthesis gas production section was calculated and was in good agreement with that obtained from literature. The hydrogen production section's thermal efficiency was compared to that of steam methane reforming of natural gas (SMR) and it was found that the efficiencies were comparable but the SMR process was superior.

The hydrogen production capacity of the HYS process was increased by a factor of 1.83. This implied that for every 1 kg of hydrogen produced by the HYS an additional 1.83 kg was produced by the proposed process addition. This lowers the cost of hydrogen produced by the HYS from $6.83 to the range of approximately $3.93 - $4.85/kg.

In the event of a global hydrogen economy, traditional production methods could very well be supplemented with new and innovative methods. The integration of the well-known methods incorporated with the new nuclear based methods of hydrogen production and chemical synthesis could facilitate the smooth transition from fossil fuel based to environmentally friendly methods. This study presents one possible integration method of nuclear based hydrogen production and conventional processing methods. This process is technically possible, efficient and economically feasible.

Keywords: Hybrid Sulfur Process, Oxygen Utilization, PBMR, Partial Oxidation of Methane, Nuclear Hydrogen Production.

Opsomming

Hierdie studie onderneem ’n evaluasie van die stroomaf gebruik van suurstof wat geproduseer is deur die hibriedswawelproses (HYS). Beide tegniese en ekonomiese aspekte is in ag geneem in die produksie van merendeels sintesegas en waterstof. Beide produkte kan die finansiële potensiaal van die hibriedswawelproses verhoog.

Gebaseer op ’n veronderstelde 500MWt korrelbed-modulêre-kernreaktor is die volume waterstof en suurstof wat geproduseer is deur die afgeskaalde HYS bepaal om tussen 121 en 959 ton per dag onderskeidelik te wees.

Die parsiële oksidasie aanleg (POX) kon ongeveer 1840 ton sintesegas per dag produseer, gebaseer op die suurstof verkry van die HYS. Die kapitale koste van die POX aanleg was in die orde van $104 miljoen (VS dollers, Basis jaar 2008). Vergelyk met die kapitale koste van die HYS blyk dit ’n relatiewe klein addisionele belegging. Die produksie koste het gevarieer tussen ’n beste geval van $9.21 tot ’n slegste geval van $19.36 per GJ gesintetiseerde gas. Die winsgewendheidsanalise wat uitgevoer is het positiewe resultate getoon, wat aangedui het dat onder die aangenome kondisies, en met 20 jaar in bedryf, ’n NHW van $87 miljoen en ’n IRR van 19.5% verkry kon word, vir die aangenome basis geval. Die ekonomiese sensitiwiteitsanalise wat uitgevoer is, het insig gegee in die laagste en hoogste grense van gunstige bedryf.

Die tweede produk wat vervaardig kon word was waterstof. Met die byvoeging van ’n watergasskuif en ’n drukvariasie-adsorpsieproses tot die POX is dit gevind dat ’n addisionele 221 ton waterstof per dag geproduseer kon word. Die waterstof kon in die beste geval vervaardig word teen $2.34/kg en in die slegste geval teen $3.76/kg. Die belegging wat vereis word sal in die orde van $50 miljoen wees. Die winsgewendheidsanalise vir die basis geval analise voorspel ’n NHW van $206 miljoen en ’n hoë IRR van 23.0% onder die aangenome kondisies. Op finansiële gronde het dit dus geblyk dat die waterstofproduksieproses gunstig was.

Die termiese doeltreffendheid van die sintesegasproduksieafdeling is bereken en was in goeie ooreenstemming met wat verkry is uit literatuur. Die waterstofproduksieafdeling se termiese doeltreffendheid is vergelyk met die van stoom-metaan-hervorming van natuurlike gas (SMR) en daar is gevind dat die effektiwiteit vergelykbaar is, maar dat die SMR proses beter is. Die waterstofproduksiekapasiteit van die HYS proses is verhoog met ’n faktor van 1.83. Wat impliseer dat vir elke 1 kg vervaardig deur die HYS ’n addisionele 1.83 kg waterstof vervaardig is deur die byvoeging van die voorgestelde proses. Dit het die koste van waterstof vervaardig deur die HYS verlaag van $6.83 in die orde van ongeveer $3.39-$4.85/kg.

In die geval van ’n wêreldwye waterstofekonomie kan tradisionele produksie metodes baie goed aangevul word met nuwe en innoverende metodes. Die integrasie van die bekende metodes geïnkorporeer met die nuwe kern gebaseerde metodes van waterstofproduksie en chemiesesintese kan die gladde oorgang fasiliteer van fossielbrandstofgebaseerde na omgewingsvriendelike metodes. Hierdie studie verteenwoordig een moontlike integrasie metode van kerngebaseerde-waterstofproduksie en konvensionele prosesmetodes. Hierdie proses is tegnies moontlik, doeltreffend en ekonomies uitvoerbaar.

Sleutelterme: Hibried Swawel Proses, Suurstof Gebruik, PBMR, Parsiële Metaan Oksidasie, Kern Gebaseerde Waterstof Produksie.

Table of Contents

List of Figures

List of Tables

Nomenclature

AGR	Advance Gas Cooled Reactor
CW	Cooling Water
CEI	Chemical Engineering Index
FCI	Fixed Capital Investment
HP	High Pressure
HTTR	High Temperature Thermal Reactor
HYS	Hybrid Sulfur Cycle
IHX	Intermediate Heat Exchanger
IRR	Internal Rate of Return
MPG	Multi Purpose Gasification
MWe	Mega Watt Electric
MWt	Mega Watt Thermal
NG	Natural Gas
Nm^3	Normal Cubic Meters
NPV	Net Present Value
OTTO	Once Through Then Out
PBMR	Pebble Bed Modular Reactor
PCU	Power Conversion Unit
POX	Partial Oxidation of Methane
PSA	Pressure Swing Adsorption
SI Cycle	Sulfur Iodine Cycle
SMR	Steam Methane Reforming
SPG	Shell Gasification Process
SRNL	Savannah River National Laboratory
TCI	Total Capital Investment
TPD	Ton Per Day
Btu	British Thermal Unit
WGS	Water Gas Shift

Chapter 1 - General Introduction

This introductory chapter is subdivided into three sections. Section 1.1 provides a brief background and motivation to conduct the research. Section 1.2 clearly outlines the objectives and problem statement that will be addressed in the research and Section 1.3 outlines the scope of the study and explains the investigation method. The background primarily describes the energy problem which the world is facing and explains the possible hydrogen economy solution. It gives perspective on where the nuclear hydrogen production may feature and outlines its importance. Possible improvements to one of the thermo nuclear cycles are also suggested to make it more efficient and economical.

1.1 Background and Motivation

The continuous economic development of humanity causes an everlasting demand for energy. The average economic growth of the world is expected to increase by 4.1% annually, along with the expansion of the economic sector the world average demand for energy will increase by 1.8% annually, according to the EIA International Energy Outlook Report (2007:5), a projected increase from 471 in 2004 to 740 quadrillion kilojoules in 2030 is reported for the base case scenario. The problem with the current energy system is the fact that fossil fuel reserves are limited and causes environmental pollution. At some time the energy system will have to change, something more sustainable and less polluting needs to be implemented. A change in the energy system is inevitable.

One such solution might be the use of hydrogen as an energy carrier. The use of hydrogen was first suggested in 1820 by Rev. William Cecil of Cambridge for use in an engine. At that time the concept was not at all feasible on large scale and no sustainable primary energy source was mentioned. As time passed by and research continued in Germany by Erren and Haldane in Scotland and many other scientists across the world the possibility of a hydrogen economy became more promising (Hoffmann, 1981:106).

The fundamentals of a hydrogen economy lie in the fact that only hydrogen and electricity will be used as energy carriers. Hydrogen can be produced in a number of ways including fossil fuels, renewable resources and nuclear energy. Hydrogen has the advantage that it can be stored, unlike electricity. This makes it possible to store energy from solar and wind sources. The storage capability of hydrogen enables the elimination of costly backup systems which are maintenance intensive and only provides limited use in peak operation times. Another attractive possibility is the use of hydrogen as vehicle fuel. However certain practical challenges still remain with this technology. The capacity in terms of achievable distance in hydrogen powered vehicles disappoints in comparison to conventional gasoline powered vehicles, although research should find a solution to the problem (Häussinger et al, 2006:205). Currently hydrogen powered vehicles are capable of traveling distances up to 400 kilometers.

To accomplish the hydrogen economy on global scale, large volumes of hydrogen generated from fossil fuels as well as renewable and nuclear sources or even a combination of the two, will be needed. One alternative will be the splitting of water for the production of hydrogen and oxygen. Low temperature electrolysis is used to produce hydrogen and oxygen from water, Mathis (1976:17) reports this being done in India, Norway and Canada where cheap hydroelectric power is available or a lack of natural gas exists. The electricity consumption in electrolysis implies that the cost of hydrogen will never be less than the cost of electricity.

The development of advanced high temperature gas cooled nuclear reactors has made it possible to use high temperature thermochemical cycles, like the Hybrid Sulfur Cycle (HYS) and Sulfur Iodine Cycle (SI). The use of these cycles eliminates the need for ineffective electricity generation and will make the production of hydrogen more effective. The increased efficiency is a result of using the high temperature of the nuclear reactor to drive endothermic chemical reactions. These types of processes were developed in the early seventies and eighties and are receiving much more attention today. The HYS is currently under development at several research institutes world-wide, such as Savannah River National Laboratory in the United States. The initial investigation by Summers (2005:4) showed promising potential and with further research and development the HYS might become highly effective in the nuclear hydrogen production sector.

Mathis (1976:30) argues that for a hydrogen economy to succeed, hydrogen must be produced efficiently, inexpensively and for long periods of time on a large scale. The HYS process currently undergoing development, might even be more attractive if the by-product oxygen can be used to increase hydrogen production. It is expected that there would be an improvement in the economics of the process. The success of any process depends on the technical performance and the economic feasibility. This study will investigate the possibility of increasing the hydrogen production by making use of the by-product oxygen in a POX process for the production of synthesis gas. The synthesis gas will then be further converted to hydrogen by applying the water gas shift process in order to increase the hydrogen production.

1.2 Problem Statement and Objectives

The HYS process was designed to produce Hydrogen from nuclear energy essentially using only water as raw material. The oxygen produced in the process as a by-product is available at low or no cost and could be used in a downstream process to produce more hydrogen. In the case of the HYS, additional hydrogen could be produced when the oxygen is used for the partial oxidation of methane to produce synthesis gas and applying the WGS process to increase hydrogen output. It would be beneficial to determine whether the addition of a POX and WGS will enhance the economical potential of a HYS process.

The objective of the study is to determine the technical and economic feasibility of the HYS process by increasing the hydrogen production. The study makes provision for the following:

1. Determining the volume of hydrogen and oxygen that would be produced by a HYS process based on 500MWt thermal energy provided by a PBMR nuclear reactor.
2. Determining the cost-elements of the HYS process contributing to the total production cost of hydrogen in the combined system.
3. Determining the capacity of a partial methane oxidation (POX) plant coupled to a HYS process, based on the amount of oxygen produced by the HYS. The volume of synthesis gas (H_2 and CO) that could be produced as well as the capital cost of the above mentioned plant and the calculation of the production cost of synthesis gas. As well as a techno-economic evaluation on the process for synthesis gas production.
4. Determining the capacity of the water gas shift plant based on the available carbon monoxide in the synthesis gas. The amount of hydrogen that could be produced, the capital cost of the plant and the determining of the production cost of hydrogen. As well as a techno-economic evaluation on the process for the production of hydrogen.
5. Possible economic improvement. The objective being to gain an understanding of the individual contribution of each process in improving the overall economics of the process.

1.3 Scope of this Study

The research pathway followed in this study can be seen in Figure 1-1. The research project is divided into three core areas, namely, the process technical design, an economic study of the entire process and the comparison with other industrial processes currently available. A short review of each chapter highlighting important areas is presented.

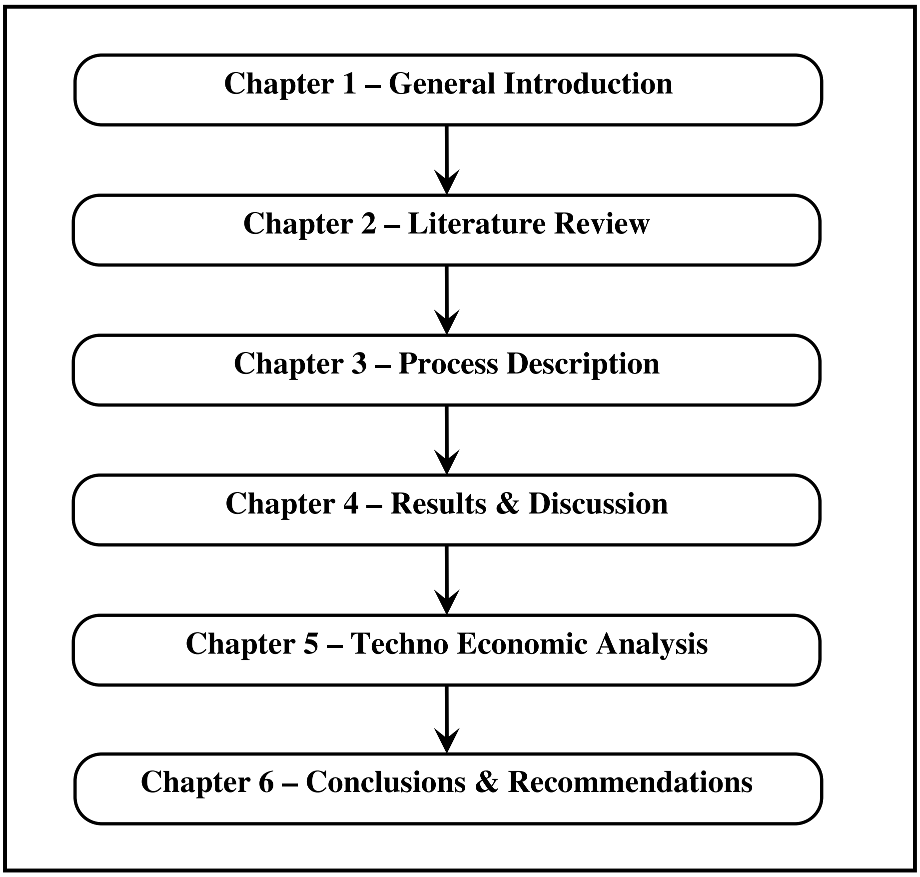

Figure 1-1: Research path followed in this study

An overview of each chapter highlighting important areas is described briefly.

The importance and the scope of the project, as well as the specific problem statement is described in Chapter 1. A detailed description of the objectives of the research is also given. A general overview of the research path is discussed.

Chapter 2 provides a brief overview of the most relevant processes that will be combined in the study in order to examine the relevant technical and economical aspects. The possibility and difficulties of combining them will also be explored.

The previous attempts to combine nuclear power and hydrogen production facilities are discussed in Chapter 3. Limitations to the type of applications are given and a description of the proposed combined PBMR/HYS/POX/WGS process is provided.

In Chapter 4, the conceptual design results are presented and discussed along with the limitations to the technical study.

Techno economic evaluations for synthesis gas and hydrogen production were carried out. The addition of a POX and WGS process contributed to the profitability of the HYS and the economical implication of each is presented in Chapter 5. The estimated production cost of synthesis gas and hydrogen as well as the capital cost of the POX and WGS plant were calculated and compared. Sensitivity analyses were carried out on the most prominent contributing economic factors. These include natural gas price and the oxygen price, capital investment and total production cost.

In Chapter 6, general conclusions are drawn and recommendations for future research are made.

Chapter 2 - Literature Review

2.1 Introduction

The objective of this chapter is to provide a literature overview of the research conducted concerning nuclear hydrogen production. The possible thermochemical cycles and their mechanisms are briefly explained, as well as the role which nuclear hydrogen production might play in the hydrogen economy. Mention of other industrial applications of process heat is made to give insight into the possibilities that high temperature nuclear reactors might have. The utilization of oxygen is discussed and an overview of the available POX processes in the industry today, namely, the Shell, Texaco and Lurgi process are given. The performance of these three processes is evaluated. A brief explanation of principals governing a POX reactor is also given.

2.2 Nuclear Reactors as Heat and Electricity Source

All methods of hydrogen production can theoretically be coupled to a nuclear reactor to provide electricity or heat except the photolytic processes. The Generation IV nuclear reactors are being designed not only to produce electricity, but hydrogen, heat and clean water as well.

A high temperature nuclear reactor as described by Kugler (2005:9) differs considerably from the conventional light water and heavy water reactors that exist today. According to Kugler (2005:18) these nuclear reactors had their origin in the Magnox type reactors that evolved into the advance gas cooled reactors (AGR) and eventually into the type that may be called the modern PBMR. The major difference is that it is designed with an all ceramic core and helium as the coolant. The ceramic allows for high temperature operation while the helium possesses high heat capacity. The chemical inertness of the helium allows for sufficient cooling and does not affect the neutron economy.

During the development of the PBMR at Jűlich in Germany, many process heat application possibilities have been suggested ranging from low temperature seawater desalination and district heating, to medium temperature applications like steam production for the chemical industry and refineries.

The coupling of a nuclear reactor to any process will require an intermediate heat exchanger (IHX) for safety. At the 10MWt KVK test facility in Germany, two heat exchangers, a Helical and a U-tube bundle, were operated and tested. The maximum heating temperatures of 950°C on the primary side and 900°C on the secondary side have been proven for both the helical and the U-tube IHX. The overall performance of the helical IHX was found to be better that the U-tube IHX.

With the development and operation of the High Temperature Engineering Test Reactor (HTTR) in Japan, the helical IHX design was further improved and operated for the first time with nuclear heating. The heat capacity was 10MWt with an inlet helium temperature of 950°C and on the secondary side an outlet temperature of 869°C. This demonstrates the high temperature heat application possibility.

One example is steam methane reforming (SMR). Hori (2003:174) reports the conversion efficiency of a conventional SMR process to be in the order of 80%. Approximately 2.7 mols of hydrogen are produced for every mol of CH_4 reacted. When nuclear process heat is applied to an SMR process, the need for using CH_4 for heating applications is eliminated allowing 100% of the CH_4 to be converted to synthesis gas or hydrogen. This also avoids the burning of approximately 30% of the fossil fuel to supply energy to drive the endothermic reaction, thus mitigating CO_2 emissions (Hori et al 2003:174). Kugler (2005:29) reports that the total thermal efficiency, including the nuclear heat, will be in the order of 65%.

At the EVA I and EVA II test facility in Germany two types of steam reformer bundles were tested; an annulus design and a baffle design. The maximum temperature of the helium to heat the reformer was 950°C at a pressure of 4MPa and operations were carried out for more than 6000 hours. The design did not include an intermediate heat exchanger, making the design simpler. Neglecting the IHX in the design could complicate licensing of the process.

A steam reformer was also tested in Japan. The design included the IHX. The new design adopted a bayonet type of catalyst tube, a double walled tube which can use both the outside and inside gas flow to heat up the process gas. The thermal energy input to the process gas increased from 3.6 to 4.9 MW. The coupling of the HTTR with a steam reformer was made possible by the employment of an IHX. The thermal efficiency of the improved design will be in the order of 78%, making it competitive with conventional fossil heated steam methane reforming.

Thermochemical water splitting is also one of the suggested processes that will benefit from high temperature nuclear process heat that is available in the range of 800°C to 1000°C. The next section is devoted to an insight into these types of processes.

2.3 Hydrogen Production by Thermochemical Water Cleavage

In the production of hydrogen the use of water as a raw material is very attractive due to its abundance. In normal electrolysis, conversion efficiency can be as high as 95%. The total energy efficiency based on the higher heating value can be as high as 73%, but when it is taken into account that for a thermal efficiency of a gas turbine power plant of 45%, the total thermal efficiency of hydrogen production would be in the order of 34%. The process could only be economical if low cost hydroelectric power is available.

In 1966 Funk and Reinstorm suggested the use of a multistage cyclic process to produce hydrogen from water, thus overcoming the need for very high temperatures in excess of 2500K for direct water cleavage. This led to the exploration of many different kinds of thermochemical cycles because of the advantage that no electricity is required for the process and thermal energy could be directly transformed into chemical energy.

More than 200 processes have been reported in literature (DeBeni, 1982 and Bamberger, 1978). It is generally accepted that thermochemical cycles are grouped into three families according to the chemicals involved, namely, the iron-chlorine family, sulfur-halogen family and the copper-chlorine family. Additionally the basic reactions taking place may be classified into the hydrogen forming and the oxygen forming reactions.

2.3.1 Thermochemical Cyclic Processes

A good example of a purely thermochemical cycle would be the sulfur-iodine cycle (SI cycle) developed by General Atomics Technologies (Besenburuch, 1980:34). It consists of three steps:

$$I_2 + SO_2 + 2H_2O \leftrightarrow 2HI + H_2SO_4 \qquad T < 100°C \qquad (2.1)$$

$$2HI \leftrightarrow H_2 + I_2 \qquad T \approx 350°C \qquad (2.2)$$

$$H_2SO_4 \leftrightarrow H_2O + SO_2 + \tfrac{1}{2}\,O_2 \qquad T \approx 850°C \qquad (2.3)$$

Reaction (2.1) is the exothermal Bunsen reaction. Reaction (2.2) is the endothermic decomposition of hydrogen iodine in an ideal electro dialysis cell that produces hydrogen, and the third (2.3) is the thermal decomposition of sulfuric acid that is converted to SO_2 and oxygen. The thermal efficiency, as reported by Zhou (Zhou et al, 2006:574), for the process is expected to be between 66.3% and 70.9%. Further development of the process is underway with the JAERI experiments in Japan and SRNL in the USA and others across the world.

2.3.2 Hybrid Cyclic Processes

Thermochemical-Electrochemical hybrid cycle processes are a special form of thermochemical cyclic processes. An electrochemical reaction is included in the process which allows the process to be designed in two stages. The electrochemical reaction is normally run at low temperatures and replaces either the hydrogen or oxygen producing reaction. The energy needed for the electrochemical reaction should be less than that required for direct water electrolysis. Some examples of hybrid cycles include the sulfur hybrid cycle, sulfur-halogen cycle, alkali metal hydride-hybrid cycle and the hydrocarbon-hybrid cycle. Of these, the most promising industrial processes are the hybrid sulfur and a hydrocarbon-hybrid cycle also called the Methane-Methanol-Methanal process (MMM Process).

2.3.2.1 Hybrid Sulfur Process (HYS)

The development of the Hybrid Sulfur Cycle for the production of hydrogen was developed by Westinghouse Electric Corporation in early 1970. The development of the process was curtailed in 1983 due to the abundance of hydrogen being produced through steam methane reforming and the lack of advanced nuclear reactors. The basic process components were already demonstrated on laboratory and bench scale at that time. The three basic steps in the HYS cycle can be seen in Figure 2-1. They are the decomposition reactor linked to the high temperature PBMR, the electrolyzer and the SO_2/O_2 separation unit (Summers, 2005:6).

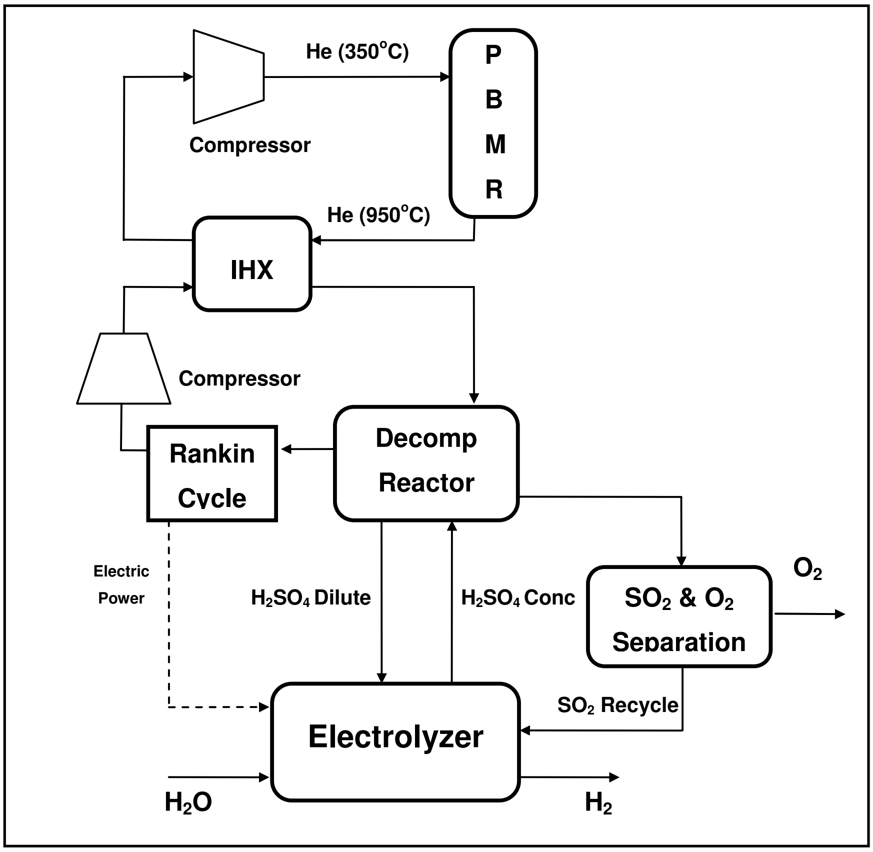

Figure 2-1: Diagram of the PBMR linked to a HYS [adapted from Summers (2005:3)]

As can be seen from Figure 2-1 the decomposition reactor is linked to the PBMR through an intermediate heat exchanger. This is done to separate the helium loop of the PBMR from that of the HYS process. The high temperature process heat is used thermochemically to drive the high temperature endothermic decomposition of sulfuric acid reactions and the low temperature heat is used to supply electricity to the electrolyzer. The hydrogen is produced in the electrolizer according to the following reaction:

$$SO_2 + 2H_2O \leftrightarrow H_2 + H_2SO_4 \qquad (2.4)$$

The reaction is similar to water electrolysis and operates electrochemically at 80-120°C and a pressure of 20 bar.

In the decomposition reactor, sulfur dioxide is generated by the reduction of SO_3 to SO_2 according to the following reaction:

$$H_2SO_4 \leftrightarrow H_2O + SO_3 \leftrightarrow H_2O + \frac{1}{2}O_2 + SO_2 \qquad (2.5)$$

This reaction is a thermochemical reaction and takes place at 800 to 900 °C in the presence of a catalyst. The SO_2 is continually recycled to the electrolyzer after separation from the oxygen in order to produce hydrogen.

Operating at a temperature of 900°C and based on the higher heating value of hydrogen, Summers (2005: 3) reported that a thermal efficiency of 48.8% could be achieved for the HYS process. Based on future developments in process optimization, predictions are made that the efficiency could be increased to above 50%, provided that a higher operating temperature could be achieved (Summers, 2005:4).

It should be noted that this process is still being developed and the original design did not include a PBMR reactor. The effect on the process however, is irrelevant.

The HYS is a two stage cyclic process and holds promise for future development. It might be possible to use the oxygen and allow it to react with methane to produce synthesis gas in order to increase hydrogen production. One such process that is proven on industrial scale for the production of synthesis gas that utilizes oxygen, is the partial oxidation of methane (POX). It is not so widely applied due to the cost of large scale oxygen production and the domination of the steam methane process. In the case of the HYS process oxygen is a by-product and available at a low cost. Synthesis gas is a valuable substance that may be used for a range of chemical processes but can also be further processed to produce hydrogen. The next section will provide an overview of the different POX processes that are available in the market place.

2.4 Different Types of Commercial POX Processes

2.4.1 Introduction

Technology development in partial oxidation of hydrocarbons was started in the 1940s by Texaco and in the 1950s Shell also entered the market. These two companies dominated the market until recently when Lurgi introduced their multi purpose gasification process (MPG). Lurgi had to develop the MPG process in order to handle the tars produced in coal gasification. Other technologies were also developed by companies like Montecatini and GIAP but never acquired great commercial exposure.

The three mentioned commercial processes do not differ in basic design. Entrained flow reactors, top mounted burners in down flow refractory lined reactor vessels with operating temperatures ranging from 1250°C and 1600°C are all similarities the three processes have in common. The differences are mainly in burner design, the method of synthesis gas cooling and soot handling.

2.4.2 Basic Principals of POX Reactor Behaviour

Partial oxidation is, in principal, the reaction of hydrocarbons with an amount of oxygen insufficient for complete combustion at temperatures between 1250°C to 1600°C and pressures of up to 15MPa depending on the feedstock. It operates as a continuous process and the basic reactions involved are the following:

$$C_nH_m + n/2\ O_2 \leftrightarrow nCO + m/2\ H_2 \qquad (2.6)$$

$$C_nH_m + nH_2O \leftrightarrow nCO + (m/2+n)\ H_2 \qquad (2.7)$$

$$C_nH_m + nO_2 \leftrightarrow nCO_2 + m/2\ H_2 \qquad (2.8)$$

The minimum amount of oxygen required for complete conversion of all the hydrocarbons present in the feedstock is indicated by (2.6), 0.5 mol of oxygen is required for every mol of carbon.

Carbon monoxide and hydrogen are the main products. Only when all the hydrocarbons have been completely converted will carbon dioxide and water be formed (Mungen, 1951:5). Opinions differ on the reaction sequence. Some test results indicate that carbon dioxide and water are the primary reaction products (Ter Haar, 1968:9).

It is generally accepted that the elements of the hydrocarbon mixture: carbon, hydrogen, oxygen and sulfur are converted to the thermodynamically stable compounds: carbon monoxide, carbon dioxide, hydrogen, water, methane, hydrogen sulfide, carbonyl sulfide.

To prevent excessive temperature increase, steam is usually added, which reacts endothermically with the hydrocarbons according to equation (2.7). This leads to the formation of more hydrogen than would be expected from conversion according to (2.6).

Equilibrium determines the proportions of various components, such as the shift conversion for example:

$$C + H_2O \leftrightarrow CO_2 + H_2 \qquad (2.9)$$

the methane equilibrium:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad (2.10)$$

the hydrogen sulfide-carbonyl sulfide equilibrium:

$$H_2S + CO_2 \leftrightarrow H_2O + COS \tag{2.11}$$

and:

$$CO + \tfrac{1}{2} O_2 \leftrightarrow CO_2 \tag{2.12}$$

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \tag{2.13}$$

These equilibria are largely established in the reactor at about 1350°C to 1500°C. They remain practically unchanged during very rapid quenching with water or by indirect heat transfer to water boiling at a comparatively low temperature.

Under the conditions prevailing in the reaction zone, no free carbon should be present, according to the Boudouard equilibrium:

$$C + CO_2 \leftrightarrow 2CO \tag{2.14}$$

or the reaction:

$$C + H_2O \leftrightarrow H_2 + CO \tag{2.15}$$

Practically zero soot is produced during partial oxidation of methane.

Sulfur components in the gas mixture are largely hydrogenated according to equation (2.11). Under normal reaction conditions, approximately 95% of the sulfur is converted to hydrogen sulphide and the remaining 5% to carbonyl sulphide. No sulfur dioxide or trioxide is detectable in the raw gas from oxidation.

A natural gas feedstock consisting mainly of methane will have the proposed reaction mechanism:

$$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O \tag{2.16}$$

$$3CH_4 + CO_2 + 2H_2O \leftrightarrow 4CO + 8H_2 \tag{2.17}$$

$$\text{Net Reaction} \quad 4CH_4 + 2O_2 \leftrightarrow 4CO + 8H_2 \tag{2.18}$$

$$\text{Or} \quad CH_4 + \tfrac{1}{2} O_2 \leftrightarrow CO + 2H_2 \tag{2.19}$$

The simplified mechanism corresponds to the one proposed by Mungen (Mungen, 1951:6). The mechanism suggests that combustion of methane (2.16) takes place, providing heat to drive the reforming reaction (2.17).

Research done by Montgomery et al. in 1948 and Mayland & Hays in 1949 on the thermodynamical aspects of partial methane combustion along with the experiments of Mungen et al. in 1951 provided preliminary understanding of the mechanism of methane combustion. Recently several research groups collaborated on the development of a comprehensive methane kinetic mechanism. This mechanism is known as the GRI Mech and the 1998 Version 2.11. It considers 277 elementary reactions involving 49 different species (Bowman et al, 2009). Major chemical pathways in the mechanism are illustrated in Figure 2-2.

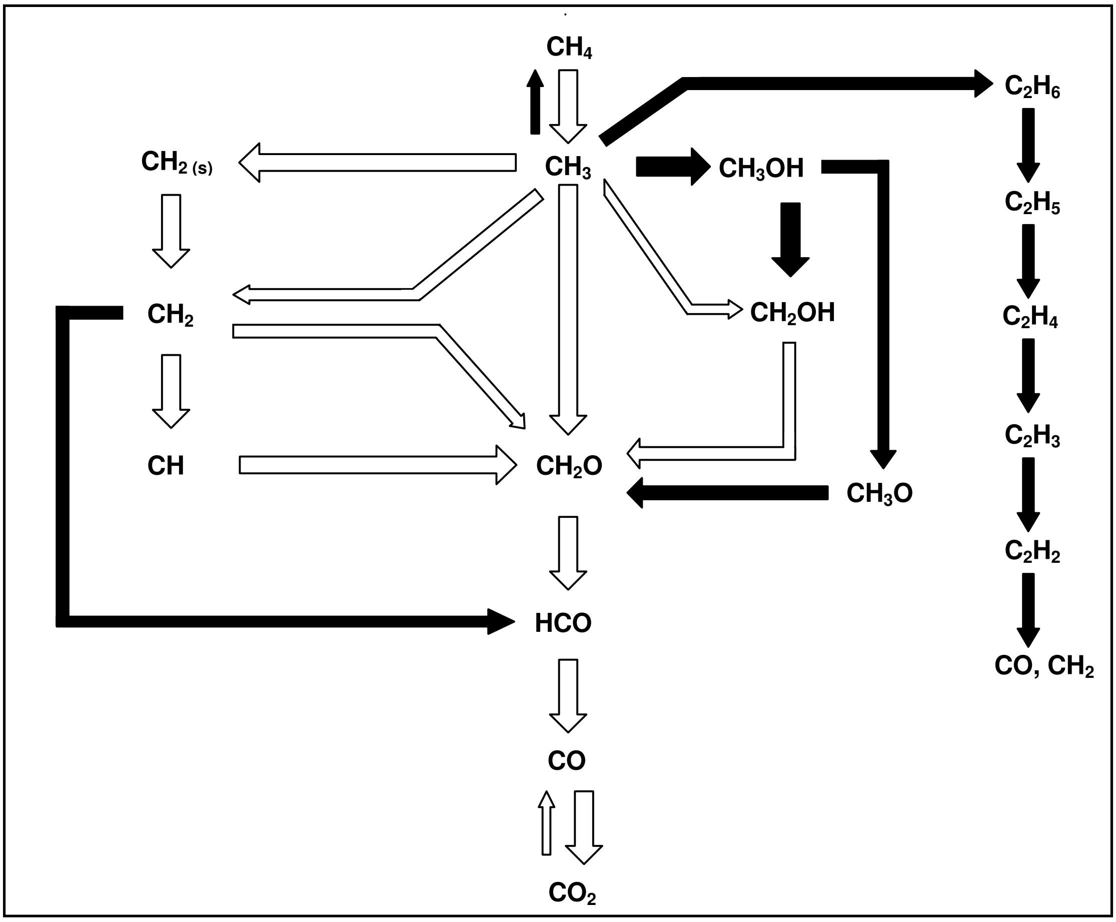

Figure 2-2: Reaction pathway for methane combustion (Turns, 2000:167)

Each arrow in Figure 2-2 represents an elementary reaction, or set of reactions, with the primary reactant species at the tail and the product species at the head. The width of an arrow gives an indication of the relative importance of a specific reaction path. Above a temperature of 2200K the pathways indicated by the black arrows are insignificant. Below a temperature of 1500K black arrow pathways become increasingly important and will complement the high temperature reactions. The mechanism undergoes continuous development. Reductions in the complexity have been suggested by Peters and Smooke with promising results. (Peters, 1987:18 and Smooke, 1991:192)

2.4.3 Partial Oxidation of Gaseous Feed

The Texaco, Shell and Lurgi processes were developed for liquid or gaseous feedstock. Converting to gaseous feed, like natural gas, is possible with small adjustments to the design and process variables. The notable design differences are found in the feed pre-heat train and burner design. Prominent process differences include very little carbon formation (±100 ppm compared to 0.5-1.0% mass) and the carbon is also metal free allowing simplicity in soot capture and management. The gas quality is notably different due to the C/H ratio in the feed. When any sulfur free gas is encountered, corrosion in the form of metal dusting might occur.

2.4.4 Texaco Process

Developed in the late 1940s, the Texaco process had been developed for natural gas, oil as well as coal slurry feedstock. Early versions of the technology were implemented in the manufacturing of liquid hydrocarbons via Fischer-Tropsch utilising natural gas as feedstock. The 1950s saw the first commercial implementation in the manufacturing of ammonia from natural gas. In 1956 the first commercial oil based process went into operation and coal development commenced at approximately the same time. With the oil and gas development established, 1970s research efforts focused on coal gasification (Weisman and Thone, 1995:18).

In the last 50 years, more than 100 reactors for oil and gas feedstock were licensed to produce nearly 100 million Nm^3/d synthesis gas. Commercial plants have been constructed to pressures of up to 80 bar and unit reactor sizes of up to 3.5 million Nm^3/d synthesis gas is now available. The feedstock is mixed with moderating steam and preheated in a fired heater. The Texaco burner is of the water cooled design in which steam and feedstock are fed together through an annular slit surrounding the central oxygen pipe. Mixing is ensured by imparting a counter rotating vortex motion to the two streams. The reactor itself is an empty, refractory lined vessel (Perofsky, 1977:17).

2.4.5 Shell Gasification Process (SPG)

Shell's implementation of the Shell Gasification Process (SPG) in 1956 utilising fuel oil as feedstock was the result of research conducted from 1950 at the Amsterdam research centre. The purpose of this new technology was to produce synthesis gas.

Up to 150 units have been installed worldwide and the combined processing capacity is approximately 7 million tons of residue per year. A single unit reactor size of up to 1.8 million Nm^3/day synthesis gas is possible as well as pressures of about 65 bar.

The non-catalytic partial oxidation of hydrocarbons takes place in a refractory lined reactor fitted with a specially designed burner. In the SGP Figure 2-3, the oxidant is pre-heated and mixed with steam before fed to the burner. The burner and reactor geometry is specifically designed to allow for thorough mixing of the steam and oxygen mixture and the pre-heated hydrocarbon feedstock. The improved co-annular burner followed the pressure atomising design in the 1980s and was considered a significant improvement (Weigner et al, 2002:121).

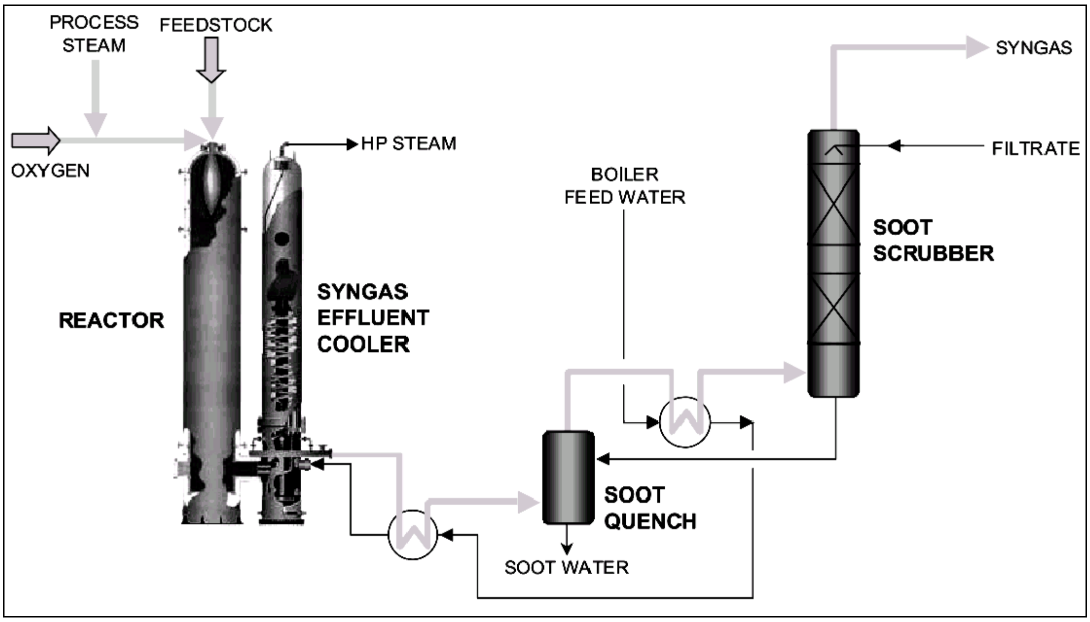

Figure 2-3: Residual oil based SPG from Shell (UHDE, 2008:6)

2.4.6 LURGI Multi Purpose Gasification (MPG)

Since the 1930s, Lurgi maintained the leading position in coal gasification and for years employed as contractor and licensing agent for the Shell SPG process in the gas and liquid partial oxidation industry. In 1998 Lurgi announced a new marketing strategy, in which the technology would be marketed under the name of LurgiSVZ multipurpose gasification (Figure 2-4, Figure 2-5). This technology existed since 1969, when it was developed to process tars from twenty three of Lurgi's gasifiers at SVZ Schwarze Pumpe (Hirschfelder et al, 1997:17).

The technology was developed in a coal gasification environment and appears to be more robust than the technology derived from a refinery background.

Recently an existing reactor operating at 60 bar with a capacity of 16 ton asphalt/hour was started up after a revamp (Erdmann et al, 2002:110).

The Lurgi MPG unit consists of a refractory lined gasification reactor with a top mounted burner. The burner has the capability to accept separate feed streams due to the multiple nozzle design.

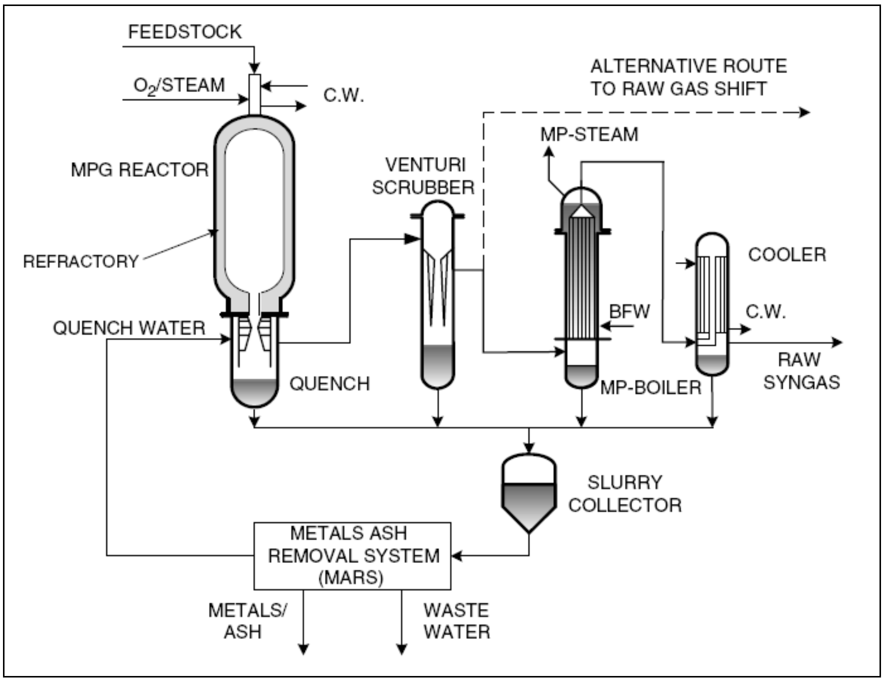

Figure 2-4: Lurgi's quench configuration (Libner, 1998:3)

In the synthesis gas cooler configuration the raw gas leaves the reactor at about 1350°C and enters the heat recovery boiler directly where 10-14MPa steam is generated, simultaneously cooling the gas to a few degrees above saturated steam temperature. The boiler is specifically designed for high gas inlet temperatures and particulates charged gas at high velocities. A small portion of the steam generated is used for oxidant and feedstock pre-heating while the bulk is superheated for use in steam turbine drives or even a combined cycle power plant. The balance of the heat is recovered by the boiler feed water economizer.

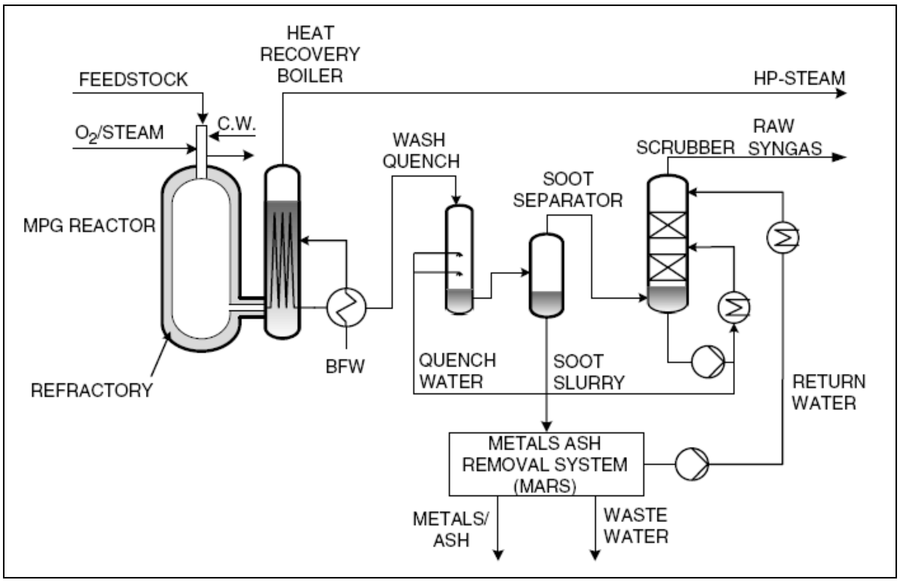

Figure 2-5: Lurgi's Synthesis gas cooler configuration (Libner, 1998:5)

2.4.7 Process Comparison and Evaluation

Table 2-1 shows a comparison of the process performance when natural gas is used as feedstock for the different processes, as discussed. At first glance, the figures appear to be similar. Consumption figures and product gas composition do not differ considerably. Note that the performance figures are given for the production of 1000Nm^3 synthesis gas.

Table 2-1: Process Comparison

	Texaco	**Shell**	**Lurgi**
Feedstock Composition:			
C/H Ratio (wt)	3.22	3.17	3.01
Sulfur (wt%)	-	-	-
Ash (wt%)	-	-	-
Feedstock Pre-heat (°C)		400	
Oxygen Pre-heat (°C)		260	
Consumption Figures per 1000Nm^3 CO + H_2			
CH_4 (kg)	262	330	286
Oxygen (99.5%) (kg)	358	365	338
Steam	-	-	-
Feed Ratio O_2/CH_4 (wt)	1.37	1.11	1.18
Product Gas			
	@ (25 bar, Quench)	@ (40°C, 56 bar)	
CO_2 (mol%)	2.60	1.71	3.10
CO (mol%)	35.00	34.89	33.50
H_2 (mol%)	61.10	61.40	62.00
CH_4 (mol%)	0.30	1.00	0.80
N_2 + Ar (mol%)	1.00	1.00	0.60
H_2S (mol%)	-	-	-
COS (mol%)	-	-	-
H_2/CO Ratio (mol)	**1.75**	**1.76**	**1.85**
Product Steam (kg)	-	890	755
	@ Quench	@ 92 bar sat'd	@ 90 bar sat'd

One way of comparing the three processes is to calculate the carbon conversion as well as the carbon and oxygen efficiencies as defined by equations (2.20), (2.21) and (2.22). Carbon conversion gives an indication of the feedstock utilization; a higher percentage indicates a superior process.

$$C-Conversion\left(\%\right)=\left(1-\frac{CH_4\,in\ product}{mol\ C\ fed}\right)\times 100 \tag{2.20}$$

Carbon Conversion:	Texaco	99.15%
	Shell	97.75%
	Lurgi	97.90%

The Texaco process has the highest feedstock utilization.

Carbon efficiency measures the amount of carbon remaining in the synthesis gas. In this case a higher number indicates a higher efficiency. The Lurgi process provides the highest carbon efficiency.

$$C-Efficiency=\frac{mol\left(CO+H_2\right)}{mol\ C\ fed} \tag{2.21}$$

Carbon Efficiency:	Texaco	2.231
	Shell	2.168
	Lurgi	2.502

Oxygen is generally an expensive raw material and any oxygen lost to carbon dioxide or any other by-product is undesired. The oxygen efficiency indicates the amount of oxygen eventually present in the synthesis gas; a higher number indicates better efficiency.

$$O_2-Efficiency=\frac{mol\left(CO+H_2\right)}{mol\ O_2\ fed} \tag{2.22}$$

The Lurgi process has the most efficient oxygen usage of the three processes.

Oxygen Efficiency:	Texaco	3.988
	Shell	3.911
	Lurgi	4.224

From the performance figures mentioned above it appears that the Lurgi process is the better option. Even with a slight disadvantage in carbon conversion, the carbon and oxygen efficiencies are the highest of the three processes.

2.5 General conclusions

This chapter outlined the role that nuclear hydrogen production could play on a global scale. Mention was made of the different ways that hydrogen could be produced by making use of a nuclear reactor, with the emphasis on high temperature gas cooled reactors, like the PBMR. Thermochemical cycles were introduced and analyzed. The HYS process showed potential for improvement in the form of downstream oxygen utilization. A possible improvement to the process was suggested in the form of a partial methane oxidation process. Three commercial processes, namely, the Shell, Lurgi and Texaco, were presented and analyzed. The governing principals, mentioned in literature, for a POX reactor were presented and evaluated. The history of the basic reaction mechanism was discussed followed by the advance kinetic mechanism in use today. On the grounds of carbon utilization as well as carbon and oxygen efficiency of each process, it was concluded that the Lurgi process was the superior process. Following the literature review, Chapter 3 will present the detailed description of the proposed combination for a PBMR reactor, HYS, POX process as well as the water gas shift process with pressure swing adsorption for the production of synthesis gas and hydrogen.

Chapter 3 - Proposed Process Combination

3.1 Introduction

Chapter 3 introduces the proposed process that is under investigation, a combination of the nuclear island, HYS cycle and additional processes. A general description is provided in the first section to give a global view of the process and the proposed integration of the different sections. The possibility of producing hydrogen and synthesis gas is discussed in section 3.3.1 and the conversion of the synthesis gas to produce additional hydrogen is illustrated in section 3.3.2. Some interaction limitations are also provided.

3.2 The Proposed Process Combination

The coupling of the nuclear reactor to a chemical process will be accomplished by the introduction of an intermediate heat exchanger. This will separate the nuclear island from the chemical facility allowing for safe operation of the entire facility.

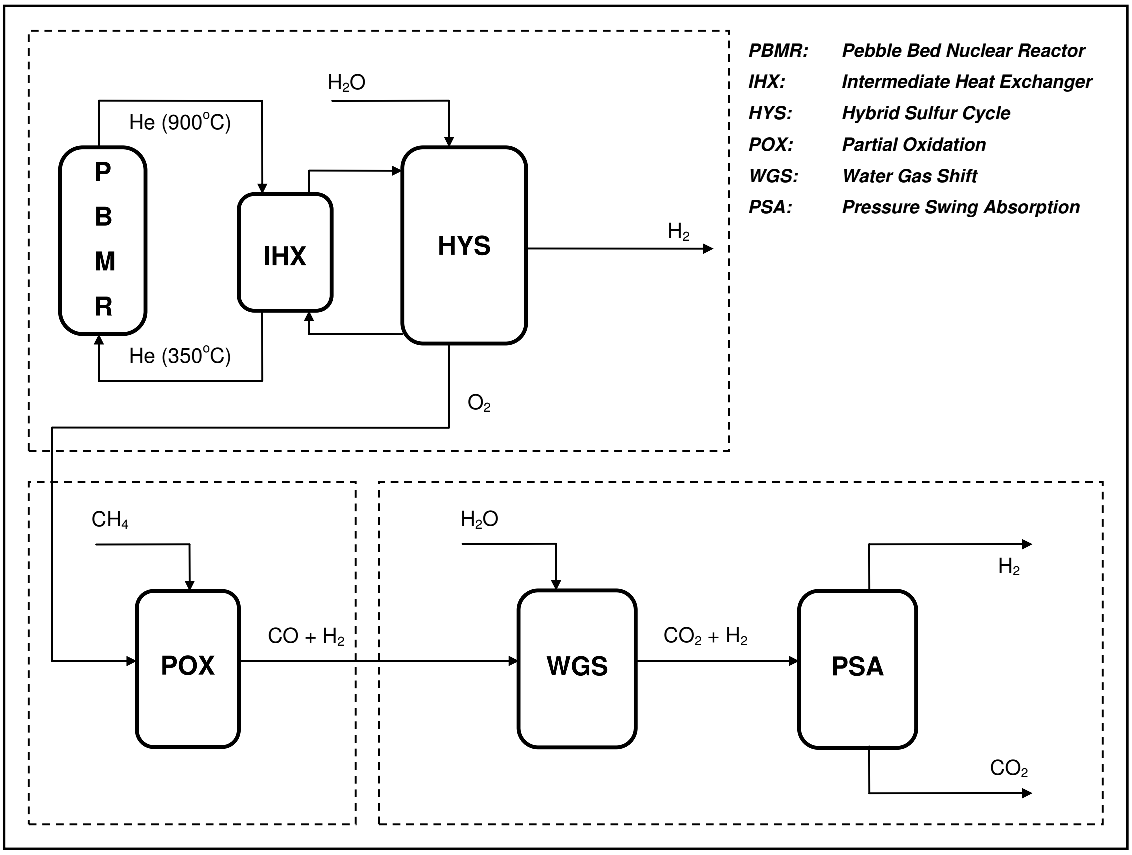

Figure 3-1: The proposed process combination; including PBMR, HYS, POX, WGS and PSA

The Helium heated by the PBMR will exit the reactor at a temperature of 900°C to provide heating to the secondary loop, and recycled back to the reactor at 350°C, as illustrated in Figure 3-1.

Water entering the HYS will be separated into hydrogen and oxygen using the high temperature heat and electricity produced. The hydrogen will be send to storage while the oxygen will be directed to a POX process. In the POX process methane reacts with the oxygen in a flame reactor to produce synthesis gas. Synthesis gas mainly consists of hydrogen, carbon monoxide, carbon dioxide, water and some methane. Synthesis gas is a versatile gas used for the synthesis of many industrial products.

In the case depicted in Figure 3-1 the synthesis gas is allowed to react with steam in a so-called water gas shift reactor (WGS). The WGS process converts the carbon monoxide into additional hydrogen and carbon dioxide. The subsequent process is a pressure swing adsorption (PSA) unit, a very efficient option for the separation of hydrogen from impurities. It is a semi-batch process but with a sufficient number of units, continuity of production is achieved. The product hydrogen from the PSA is of very good quality at 99.99% purity and the waste stream from the PSA unit will contain all the carbon dioxide, carbon monoxide, residue methane, and some hydrogen.

3.3 Process Operating Conditions and Limitations

The process described in Figure 3-1 represents the basic block flow diagram for the production of two important products. Firstly, synthesis gas could be produced by installing a POX process and secondly hydrogen production could be increased by the addition of a WGS and PSA unit. The research conducted will focus in the separate processes for the technical design and economic evaluation but will also consider the process in its entirety. This will allow a global view of the impact the addition of each extra process unit might have on the HYS cycle technically as well as economically.

A version of the HYS based on a 4 times 600MWt modular reactors was proposed by Summers (2005:4), a scaled down version based on the 500 MWt thermal power of a PBMR reactor will be implemented. In this analysis, the amount of hydrogen and oxygen produced by the HYS when a 500MWt PBMR is used, will be calculated.

This will allow the calculation of the capacity of a POX process based on the amount of oxygen produced by the HYS. Once the capacity is calculated an evaluation can be carried out on the first product, synthesis gas, in order to judge its usefulness on both technical and economic basis. Part two of the proposed process will require data from part one, the amount of carbon monoxide in the synthesis gas produced by the POX will determine the capacity of the WGS process and in turn the size of the PSA unit required. This will allow an analysis of the second product, namely, hydrogen. The process will be evaluated, like in part one, on both the technical and economic basis.

The basic flow of each process will be discussed in the subsequent sections. First the synthesis gas production process, followed by the second product, hydrogen. The focus will be to provide insight into the two different processes allowing an understanding of the basic technologies involved in the proposed process integration.

3.3.1 Alternative 1: Synthesis Gas Production

The process for synthesis gas and hydrogen production can be seen in Figure 3-2. The process can be separated into 3 distinct sections; the nuclear island, the HYS cycle and the POX process. The nuclear island will consist of a single 500MWt PBMR unit. The primary helium loop will provide helium at 900°C to the intermediate heat exchanger and will be recycled to the reactor with a temperature of approximately 350°C by means of a circulating compressor. The intermediate heat exchanger (IHX) will separate the nuclear island from the HYS cycle. This will ensure that no nuclear contamination will reach the rest of the process.

The secondary helium loop has a twofold use in as much as it provides heating for the sulfuric acid decomposition reactor and also drives a Rankin cycle to produce electricity. The electricity produced by the Rankin cycle is used in the SO_2 anode depolarized electrolysis. Sulfur dioxide is dissolved in concentrated sulfuric acid and is used to depolarize the anode of the cell producing oxygen, while hydrogen is produced at the cathode.

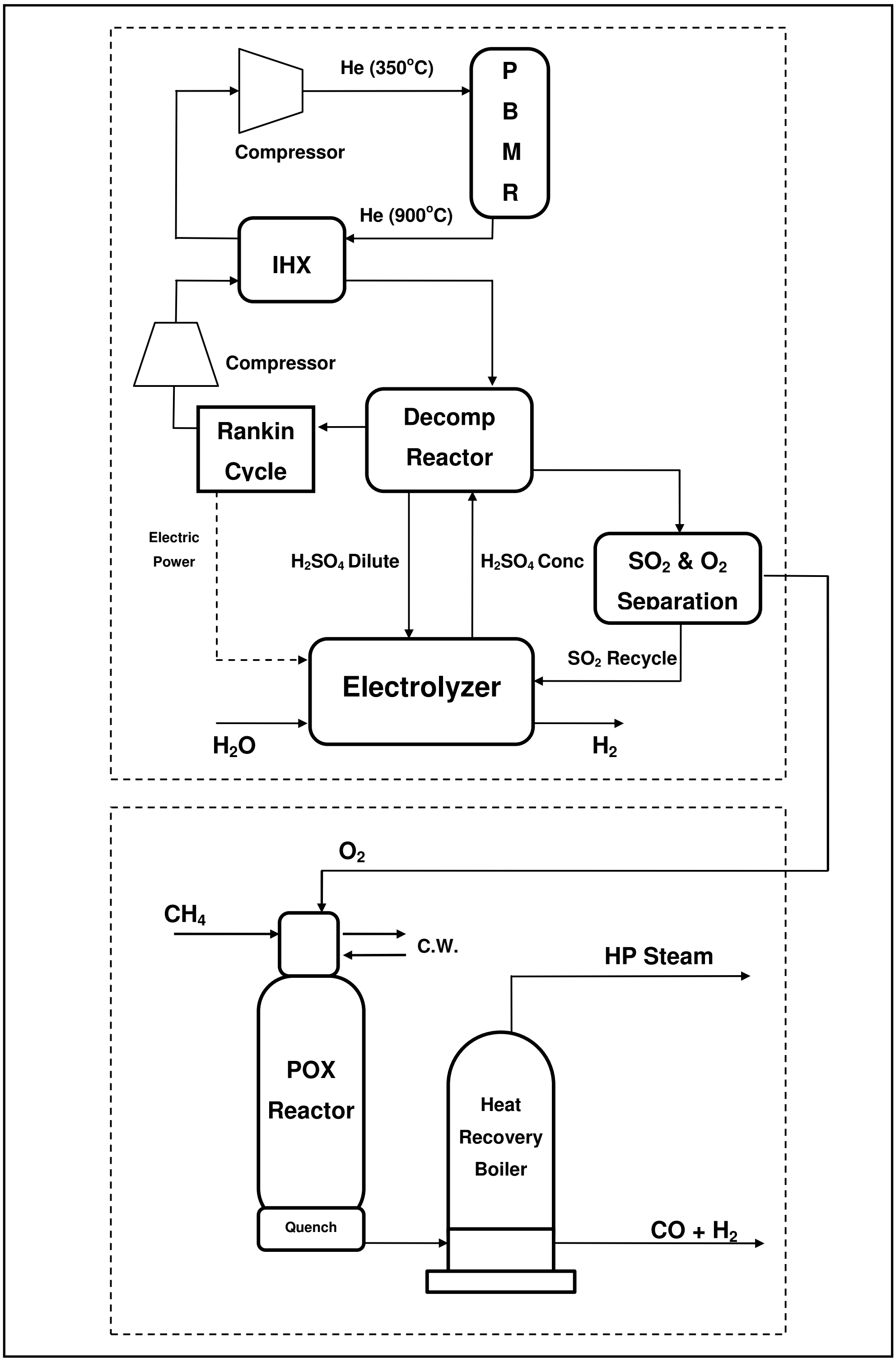

Figure 3-2: HYS in combination with POX for synthesis gas production

The sulfur dioxide is regenerated in the decomposition reactor; the thermochemical step completes the two step HYS process by producing oxygen. After separation from the oxygen, SO_2 is recycled to the electrolyzer and oxygen is exported as a product.

The exported oxygen product could be used as suggested in Figure 3-2 and the oxygen source for the POX process. In the POX process natural gas consisting mostly of methane is mixed with the oxygen and combusted in a refractory lined reactor. The mixture is mixed in the burner of the reactor to mitigate the possibility of premature combustion. The combustion reaction takes place at a temperature of approximately 1350°C; the gas is passed through the quench section of the reactor for initial cooling. Synthesis gas is produced in the reactor and consists mainly of carbon monoxide and hydrogen. Heat from the product gas is recovered with a heat recovery boiler and used to produce steam.

At this stage two products are produced by the process; hydrogen is produced by the HYS cycle and the oxygen is used to produce synthesis gas. This completes the synthesis production part. Alternative two will follow, explaining the additional hydrogen production.

3.3.2 Alternative 2: Hydrogen Production

Synthesis gas could be used for the production of hydrogen as shown in Figure 3-3. The POX process produces synthesis gas containing carbon monoxide and hydrogen. In the water gas shift process the equilibrium is shifted to convert carbon monoxide and water into hydrogen and carbon dioxide. The synthesis gas from the POX is fed into a saturator to saturate the gas mixture with as much steam as possible. The gas mixture is send to the first high temperature shift reactor where conversion of the CO into CO_2 takes place. The reaction is exothermic and heats the gas allowing a recycle stream to heat the incoming gas mixture. The catalyst used in the high temperature shift reactor is iron based and the maximum temperature should not exceed 500-510°C. The temperature limitation suggests the use of a secondary low temperature shift reactor. The catalyst used in the low temperature shift reactor is copper based and is sometimes mixed with zinc. Typical entry temperature for the gas mixture is in the order of 180°C. The gas exits the reactor at approximately 270°C.

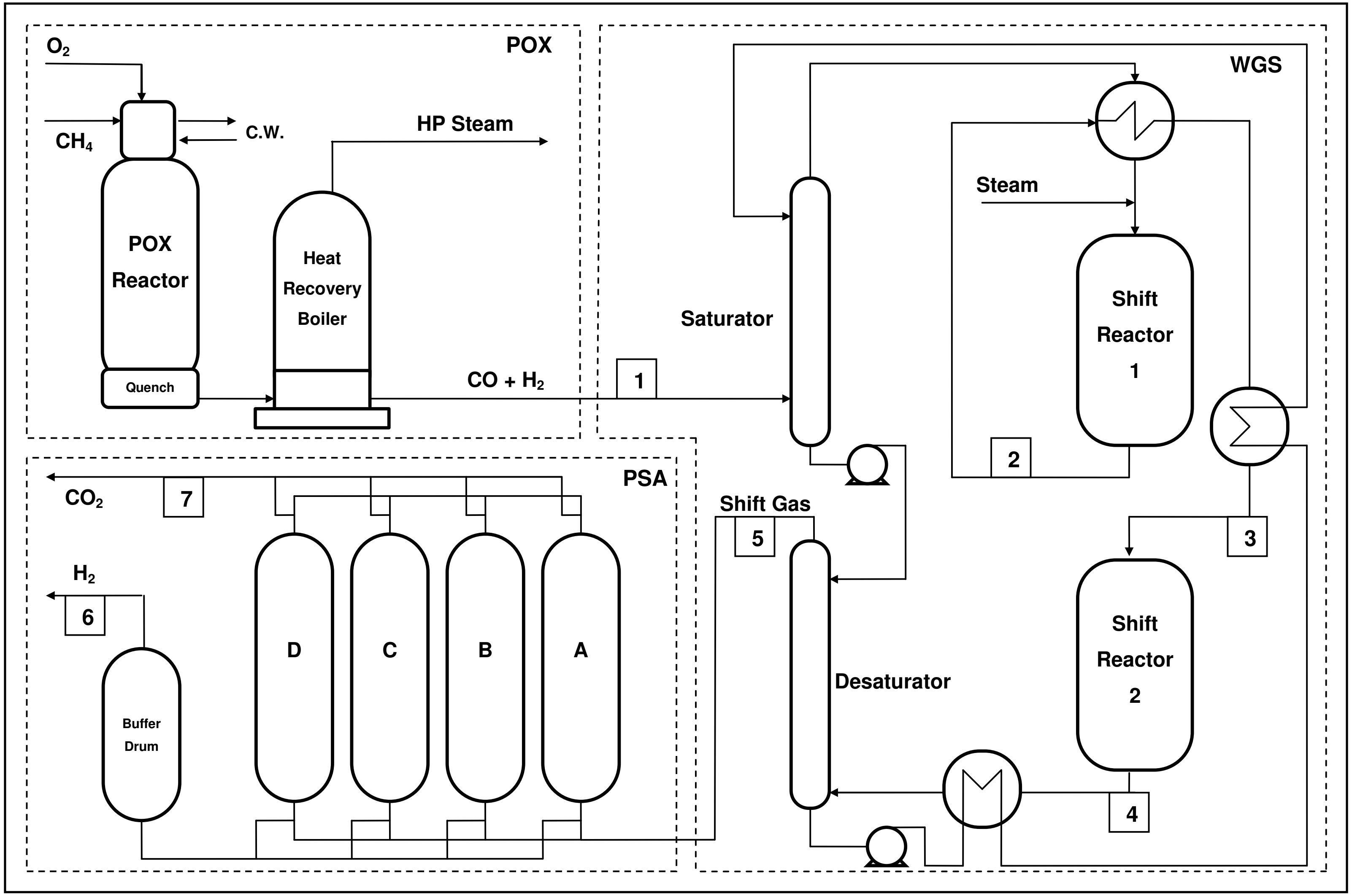

Figure 3-3: POX combined with WGS and PSA for additional Hydrogen production

At this stage in the process almost all of the carbon monoxide has been converted to hydrogen and carbon dioxide. The gas is cooled and water is removed in a desaturator before the gas is allowed to enter the PSA unit. As illustrated in Figure 3-3 the PSA consists of a series of separate absorbers, each performing, in turn, part of the cyclic process required to purify the hydrogen. Typical cycle times are in the order of 3 to 10 minutes. In the PSA unit pressurized adsorption separates the hydrogen from the rest of the mixture and a high quality hydrogen product is obtained. Roughly 90% of the hydrogen is recovered at a purity of 99.99%.

3.4 Process Description Summary

The chapter outlined the proposed process integration. The proposed system consisted of two possibilities; firstly the synthesis gas production that will bring about the integration of a PBMR, HYS cycle and also the POX process. Secondly the production of additional hydrogen by the conversion of the synthesis gas produced in the POX section. This will require the addition of two process steps, namely, the WSG and PSA. Technical integration was proposed for both of the two possibilities and some limitations were discussed. Chapter 4 will present the technical results obtained for the research conducted on both synthesis gas and hydrogen production possibilities.

Chapter 4 - Results Presentation and Discussion: Technical

4.1 Introduction

The general process description was presented in Chapter 3. A more detailed explanation of each process step including the PBMR, HYS, POX, WGS and the PSA will be discussed separately in Chapter 4. The technical results for each individual process will be presented in turn. Material and energy balances were carried out, technical performance indicators are calculated as well as evaluated, and equipment sizes are determined. This chapter forms the foundation on which the economical study of Chapter 5 is based.

4.2 Pebble Bed Modular Reactor

Instead of making use of the standard MEDUL (Mehrfach & Durchlauf) cycle, allowing fuel pebbles passing multiple times through the core, an OTTO fuel cycle can be used in the PBMR.

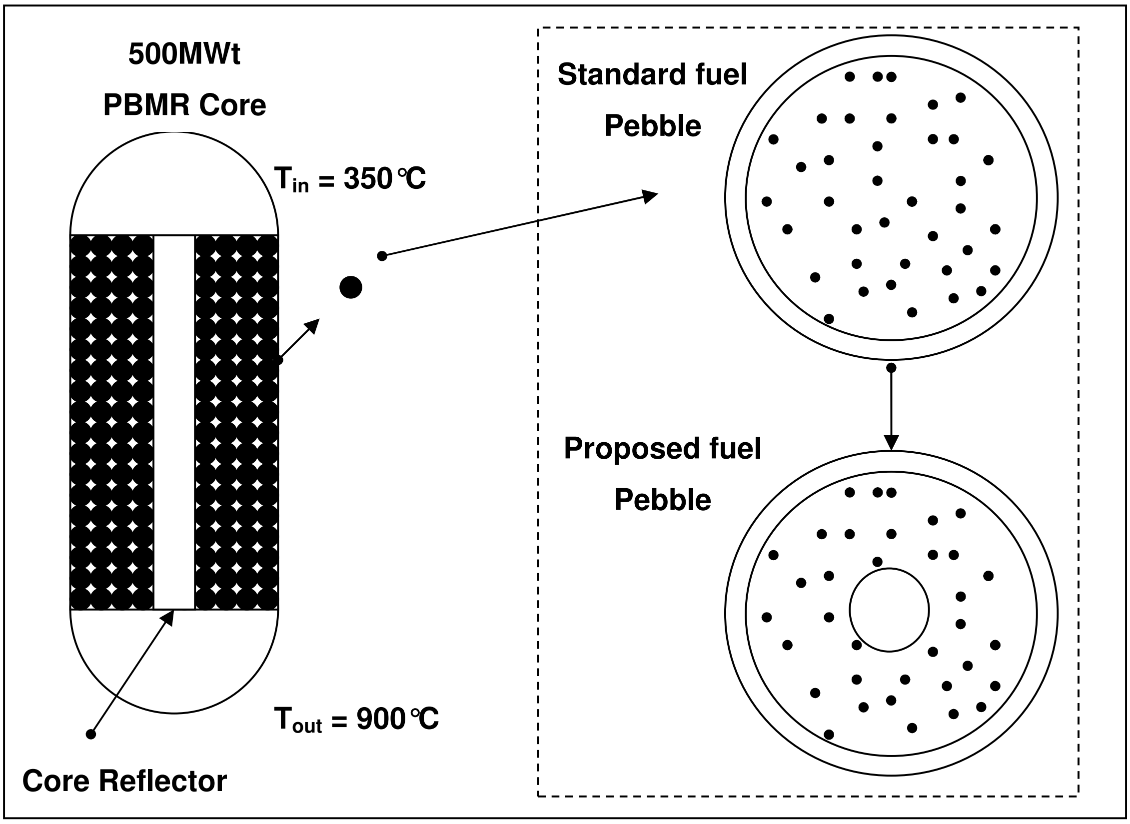

Figure 4-1: Some proposed differences in the PBMR core

The OTTO cycle is a **O**nce **T**hrough **T**hen **O**ut cycle. In this cycle, fuel is passed once through the core and in this single pass obtains full burn-up. The concentration of fissile material and flux, and therefore the power density, are high in the upper part of the core, but small in the lower part. Consequently, the temperature differences between the gas and the fuel are very small at the core exit.

As a result the peak factor of power density distribution is higher than in a MEDUL cycle as a result. The conditions for self acting decay heat removal are altered and the maximum thermal power is reduced by approximately 10% compared to that of a MEDUL cycle. To achieve the average fuel temperature of 950°C, the maximum gas temperature must not be higher that 1000°C (Kugler, 2005:14).

To keep the power per pebble acceptable, the center of the pebble will not have any fuel (Figure 4-1). This will ensure that the maximum fuel temperature does not exceed 1600°C and the fuel integrity does not get affected. A central reflector is also suggested, ensuring that no control issues deter the operation of the PBMR and guarantees that the reactor could be shut down at any time (Mulder, 2004:2).

4.3 Hybrid Sulfur Cycle

The design of the HYS proposed by Summers (2005:1) presents the large scale production of hydrogen based on a 4 times 600MWt high temperature gas cooled nuclear reactors. The amount of hydrogen produced is in the order of 580 TPD with the assumption that the peak thermal input temperature is 900°C.

The thermal energy consumed by the HYS is 1950MWt and 445MWt is available to generate 178MWe of electricity, if it is assumed that the PCU has an efficiency of 40%.

A summary of the basic data for the operation of a HYS cycle is shown in Table 4-1. In the event that a 500MWt PBMR reactor is used, the HYS is scaled down. The data for this scaled down version of the HYS cycle is provided in Table 4-1.

Table 4-1: Basic Operating Conditions for HYS Linked to 500MWt PBMR

		Summers 2005	**PBMR**
Nuclear Reactor Thermal Power	*[MWt]*	2400	500
Peak Thermal input Temperature	*[°C]*	900	900
Thermal energy Consumed by HYS	*[MWt]*	1950	406
Thermal Energy Consumed by PCU	*[MWt]*	445	94
Efficiency of PCU		40%	40%
Electricity Generated	*[MWe]*	178	38
Cooling Water Temperature	*[°C]*	25	25
Hydrogen Produced	*[TPD]*	580	121
Oxygen Produced	*[TPD]*	4603	959

If assumed that the ratio of thermal power used stays proportionally the same, the proposed scaled down version of the HYS will produce 121 tons hydrogen per day and 959 tons of oxygen. If the assumed PCU efficiency and cooling water inlet temperature are unchanged, the thermal power consumed by the HYS will be 406 MWt and that for electricity production will be 94 MWt. The thermal efficiency of the HYS cycle is in the order of 50% (Summers, 2005:2).

An important factor to consider is the mass ratio of oxygen to hydrogen produced. For every 1 kg of hydrogen produced, 8 kg of oxygen is produced as a by-product. This is one of the motivating factors for the downstream utilization of oxygen in, for instance, a POX process.

4.4 Partial Oxidation of Methane

The process diagram presented in Figure 3-2 (p.28) and Figure 3-3 (p.30) is a simplification of the POX process and a more detailed flow diagram is presented in Figure 4-2.

The process makes use of oxygen (1), natural gas (2) and water (3) as raw materials. The POX process operating pressure is in the order of 46 bar, the oxygen produced in the HYS process is supplied at 20 bar, a compressor (K-100) increases the oxygen pressure to 46 bar. The oxygen is pre-heated to 260°C and enters the burner of the reactor (5).
The natural gas supply is assumed to be at 46 bar and after pre-heating to 400°C, it enters the burner of the reactor (4). Steam is required to moderate the reaction and is supplied at 300°C (6). The reactor is represented by R-100 and the waste heat recovery system is represented by the two heat exchangers E-105 (heat recovery boiler) and E-102 (steam super heater).

The hot product gas from the reactor is recycled to pre-heat the incoming oxygen and methane feed streams and is exported as synthesis gas at a temperature of 350°C. Enough steam is produced in the system to allow superheating for electricity generation in the turbine K-101. The electricity produced is used on site to limit the dependence on external electricity supply. Low quality steam is also produced and could be exported (10).
The process flow diagram (PFD) shown in Figure 4-2 is adapted from the PFD used in a SINTEF report on the technical and economical evaluation of natural gas based synthesis gas production technologies (SINTEF, 1994:57). The process was simulated using HYSYS, a Gibbs reactor was used to simulate the POX reactor. A study by Khoshnoodi & Lim (1997:288) demonstrated the capability of a computer simulation package to simulate the Shell GTL plant's POX reactor in Bintulu, East Malaysia. The results presented here for the POX simulation correspond well with that of the Shell GTL plant.

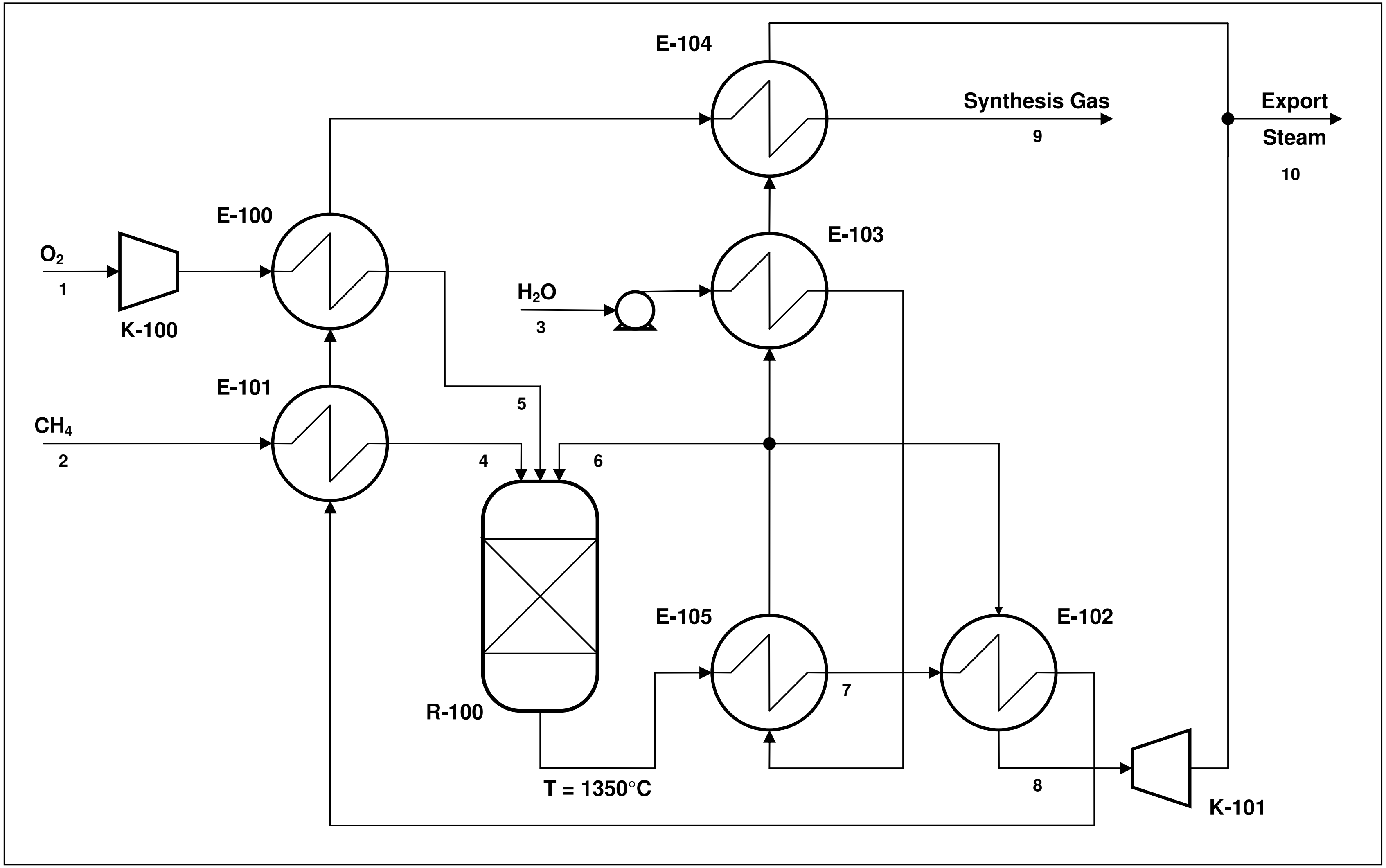

Figure 4-2: Detailed process flow diagram for the POX process

A primary equipment list for the POX process is given in Table 4-2. Calculated sizes for each of the process units are also listed. The equipment was sized based on the synthesis gas production rate of 76697 kg synthesis gas/h.

Table 4-2: Basic Equipment List for POX Process

Equipment:	#	Size	Unit
Oxygen Pre-heater	E-100	542	m^2
Methane Pre-heater	E-101	2758	m^2
Water Pre-heater	E-103	1018	m^2
Product Gas Cooler	E-104	702	m^2
Oxygen Compressor	K-100	1130	kW
Turbine	K-101	4915	kW
Feed Water Pump	P-100	93	kW
Steam Super Heater	E-102	632	m^2
Synthesis Gas Cooler	E-105	1310	m^2
POX Reactor	R-100	83.83	m^3

The reactor system was considered as a whole, including the refractory lined vessel, synthesis gas cooler and the steam superheater. The list provides the opportunity to estimate the capital cost of the system. The two most expensive components of the system, neglecting the reactor system, are the turbine and the oxygen compressor.

A summary of a material balance is given in Table 4-3 for streams one through 10, with reference to Figure 4-2. Essential information like temperature (°C), pressure (kPa), mol and mass flows (kmol/h & kg/h) as well as the molar composition is provided.

Note that the natural gas feed stream (2) consists mainly of methane, but ethane, propane and butane are also present in minute quantities. The fact that the feed consists of additional hydrocarbons does not influence the operational performance of the POX. Note that almost all of the hydrocarbons fed to the reactor are consumed and only a small amount of methane is left in the product gas (9), resulting in a high methane conversion of 99.5%.

Stream (6) represents the steam required for the POX reactor. The steam is produced on site by heat recovery from the synthesis gas. To promote efficiency, the feed water (3) is pre-heated before it is sent to the heat recovery boiler (E-105) by the heat exchanger E-103. This practice improves the efficiency and economy of the system.

The product gas (9) contains approximately 13.5 mol% water. It is in the form of steam and will assist the WGS process by already providing some steam in the feed gas.

Table 4-3: Material Balance on POX Process

	Stream #	*1*	2	3	4	5	6	7	8	9	10
Temperature	°C	40	25	19	400	260	300	689.5	510	350	99.96
Pressure	kPa	2000	4630	101.3	4600	4600	4600	4600	4570	4600	101.3
Molar Flow	kmol/h	1249	1586	3134	1586	1249	344.6	6038	1464	6038	2789
Mass Flow	kg/h	39960	31090	56460	31090	39960	6208	76697	26380	76697	50250
Composition:											
Mol Fraction											
CH_4		0	0.8435	0	0.8435	0	0	0.0009	0	0.0009	0
C_2H_6		0	0.0883	0	0.0883	0	0	0	0	0	0
C_3H_8		0	0.039	0	0.0390	0	0	0	0	0	0
C_4H_8		0	0.0292	0	0.0292	0	0	0	0	0	0
O_2		1	0	0	0	1	0	0	0	0	0
H_2O		0	0	1	0	0	1	0.1346	1	0.1346	1
CO		0	0	0	0	0	0	0.2913	0	0.2913	0
CO_2		0	0	0	0	0	0	0.0226	0	0.0226	0
H_2		0	0	0	0	0	0	0.5507	0	0.5507	0

The export steam is of very low quality, roughly 1 bar and 100°C. The quality of the steam suggests that it can not be used for significant process applications. The stream could be exported to the WGS process and used as initial steam feed. Less energy will be spent on the production of steam for the WGS process.

The technical performance of the system could be evaluated as indicated in section 2.4.7, by comparing the carbon conversion, carbon and oxygen efficiencies as well as the thermal efficiency with that of commercially available processes.

As mentioned in section 2.4.7, the carbon conversion of a typical POX process is in the range of 97.75% to 99.15% and the carbon conversion for the simulated POX process is found to be 99.72% (see Appendix A for calculation). This value is slightly out of range, but appears to be acceptable.

The carbon efficiency of the process is calculated to be 2.556 (see Appendix A). The carbon efficiency for normal POX processes is in the order of 2.168 to 2.502. The considerably high value for the calculated value in the simulated process could be explained by the fact that the system was modeled as an ideal system. Similar results were obtained by Montgomery et al. in 1948 and Mayland and Hays in 1949 in their attempt to solve the POX reactor problem with a thermo dynamical approach.

The oxygen efficiency for normal POX processes ranges from 3.911 to 4.224. The value calculated (Appendix A) corresponds with the range and is in the order of 4.070.

Table 4-4 provides a summary of the important performance indicators including the thermal efficiency of the POX process. It also gives the range for each value obtained from literature.

Table 4-4: POX Technical Performance Indicators

	Calculated	*Literature*
C - Conversion	99.72%	97.75% to 99.15%
C - Efficiency	2.556	2.168 to 2.502
O - Efficiency	4.070	3.911 to 4.224
Thermal Efficiency	81.02%	81.86%

The thermal efficiency is slightly lower, at 81.02%, than suggested by literature, 81.86%, but still within reasonable range. Thermal efficiency is also referred to as cold gas efficiency. "*The heating value of the Synthesis gas in the cold product expressed as a percentage of the heating value of the fuel fed*" (Eastman, 1956:1121).

The performance of the simulated POX process corresponds well with the range found in literature for commercial POX processes. The consumption figures for the simulated POX unit are summarized in Table 4-5. Raw materials consumed in the POX unit is natural gas (methane) and oxygen. Methane consumption is 293.1 kg per 1000Nm^3 synthesis gas produced. When compared with the values from literature the methane consumption is within the range of 262 to 330 kg per 1000Nm^3. The oxygen consumption of 376.7 kg per 1000Nm^3 synthesis gas is approximately 3% larger that the maximum in the range suggested by literature, 365 kg per 1000Nm^3 synthesis gas.

Table 4-5: POX Raw Material & Utility Consumption

	Unit	Unit/1000 Nm^3 Synthesis Gas
Raw Material:		
CH_4	kg	293.1
O_2	kg	376.7
Utilities:		
H_2O	kg	532.3
Steam	kg	473.8
Electricity	kWh	30.2

The necessary utility consumption is also specified in Table 4-5. Water, steam and electricity consumption is provided per 1000Nm^3 of synthesis gas produced.

The hydrogen present in the synthesis gas is 160 TPD. This amount of hydrogen is high compared to that produced by the HYS process (121 TPD). The carbon monoxide in the product gas (9) could be converted to even more hydrogen and will be discussed in the following section.

4.5 Water Gas Shift & Pressure Swing Adsorption

The process described in section 3.3.2 (Figure 3-3) shows the addition of the WGS process to the POX process. The WGS process comprises of four main components, namely, the saturator, high temperature shift reactor, low temperature shift reactor and the desaturator, and additional three heat exchangers and two circulating pumps. The PSA process equipment includes different absorbers and a buffer drum to ensure continuous flow of the hydrogen product.

A summary of the material balance for the WGS and PSA process are given in Table 4-6 (Ngeleka, 2008:37). The stream numbers refer to the numbers provided in Figure 3-3. The synthesis gas from the POX process enters the WGS system at 350°C and has a carbon monoxide molar fraction of 0.2913 (1). The gas mixture is saturated with steam in the saturator before allowed to enter the high temperature shift reactor. The aim at this stage is to convert as much of the carbon monoxide to hydrogen as possible. In the first shift reactor approximately 82.8% (mol%) of the carbon monoxide is converted to hydrogen (2). The low temperature shift reactor converts most of the carbon monoxide to hydrogen. At the exit of the second reactor 98.1 mol% of all the initial carbon monoxide is converted (4).

Table 4-6: Material Balance on WGS & PSA Process (Ngeleka, 2008:37)

	Stream #	*1*	*2*	*3*	*4*	*5*	*6*	*7*
Temperature	°C	350	450	200	380	210	25	25
Pressure	kPa	4540	3000	3000	3000	3000	2000	2000
Molar Flow	kmol/h	6038	11610	11610	20983	6968	4552	2416
Mass Flow	kg/h	76697	177121	177121	346012	93291	9195	84095
Composition:								
Comp Mol Fraction								
H_2		0.5507	0.4152	0.4152	0.2410	0.7258	0.9999	0.2092
CO		0.2913	0.0227	0.0227	0.0013	0.0038	0	0.0109
CO_2		0.0226	0.1405	0.1405	0.0891	0.2682	0	0.7737
H_2O		0.1346	0.4211	0.4211	0.6684	0.0014	0	0.0040
CH_4		0.0009	0.0005	0.0005	0.0003	0.0008	0	0.0022

Before the hydrogen could be separated from the mixture in the PSA unit, the excess water needs to be removed with a desaturator. Note that the water content of stream 5 is extremely low. The hydrogen production at this step in the process has increased by a factor of 1.52 (mol hydrogen in stream (5)/mol hydrogen fed (1)), almost doubling the initial hydrogen production.

As can be seen from Table 4-6 the recovery of hydrogen is in the order of 90% and the purity of the final hydrogen product is 99.99% (mol%).

The raw material consumption of the WGS and PSA unit is provided in Table 4-7. Note that the synthesis gas referred to in Table 4-7 has the composition of that produced by the POX process.

Table 4-7: WGS & PSA Raw Material & Utility Consumption

	Unit	Unit/kg Hydrogen
Raw Material:		
Synthesis Gas	kg	8.34
HTS catalyst	kg	8.69E-05
LTS catalyst	kg	2.41E-04
Utilities:		
H_2O	kg	1.23
Steam	kg	0.308
Electricity	kWh	1.32

Adapted from Ngeleka, 2008:37

The consumption figures for water, steam and electricity are calculated as unit per kg hydrogen in the final product (7).

Due to the fact that there is some loss of hydrogen in the PSA, the total amount of hydrogen produced by the addition of the WGS and the PSA unit, is in the order of 221 TPD. This implies that for every 1 kg of hydrogen produced by the HYS an additional 1.83 kg of hydrogen is produced by the addition of two process units, namely, POX and WGS with a PSA.

4.6 Thermal Efficiency Comparison

In order to compare production pathways the thermal efficiency can give an indication of the performance of each different process. The thermal efficiency of three comparative processes has been calculated and is presented. First the POX process for the production of synthesis gas and the efficiency is compared with an industrial SMR process. Details of thermal efficiency calculations are provided in Appendix B.

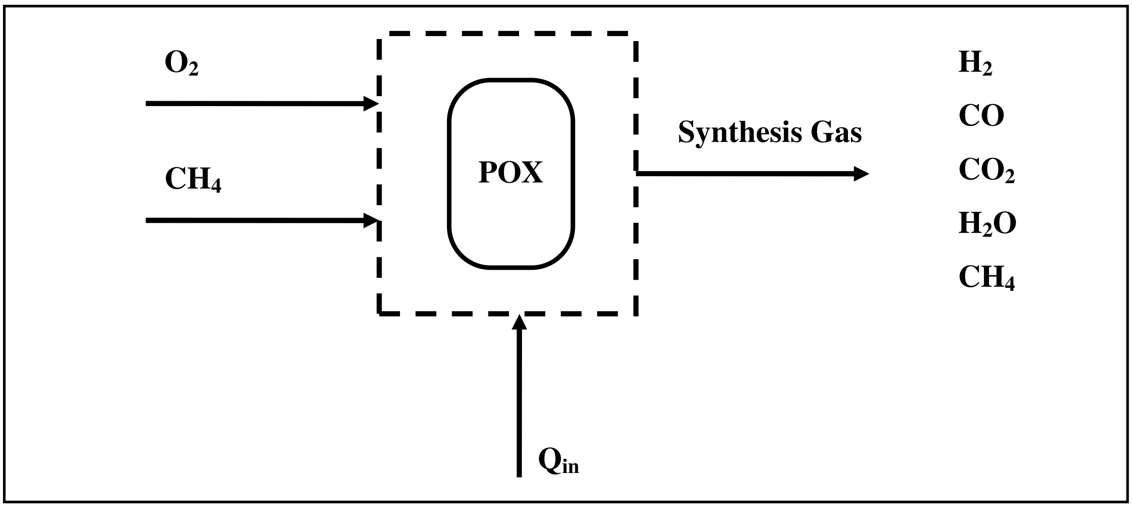

Figure 4-3: Schematic of the energy control volume used to define thermal efficiency for synthesis gas production with POX

Thermal Efficiency POX Synthesis Gas=

$$\left(\frac{\left(n_{co}\times LHV_{co}\right)+\left(n_{H_2}\times LHV_{H_2}\right)+\left(n_{CH_4}\times LHV_{CH_4}\right)_{\text{in product}}}{\left(n_{CH_4}\times LHV_{CH_4}\right)_{\text{in feed}}+\left(n_{C_2H_6}\times LHV_{C_2H_6}\right)+\left(n_{C_3H_8}\times LHV_{C_3H_8}\right)+\left(n_{C_4H_8}\times LHV_{C_4H_8}\right)+Q}\right)\times 100$$

$$=81.02\%$$

$$\begin{aligned}\text{With } Q &= Q_{\text{Electric}} \text{ Converted to Thermal}\\ &= 1223\text{kW}_e\times\left(\frac{100}{35}\right)\\ &= 3494\text{kW}_t\end{aligned}$$

If it is assumed that the conversion efficiency of the PCU is 35%. Comparing this value to that obtained from literature, 81.86%, a good comparison was made (Eastman, 1956:1121).

The following representation of a SMR process for hydrogen production is adapted from Seo et al (2002: 221).

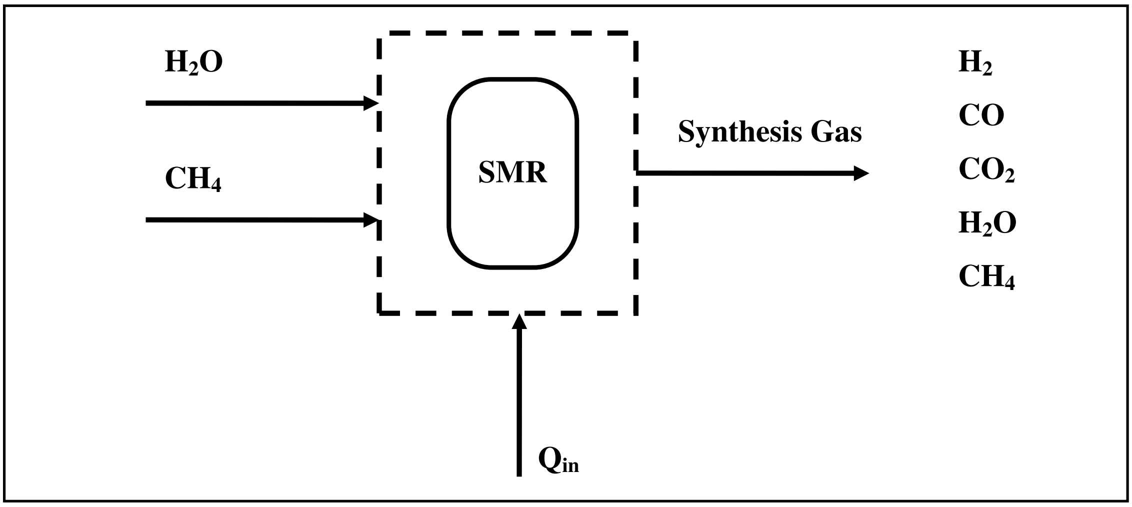

Figure 4-4: Schematic of the energy control volume used to define thermal efficiency for synthesis gas production with SMR

Proven technology for the production of hydrogen is the steam methane reforming of methane. To compare the POX process with SMR for synthesis gas production, note the following calculations:

Thermal Efficiency SMR Synthesis Gas=

$$\left(\frac{\left(n_{co}\times LHV_{co}\right)+\left(n_{H_2}\times LHV_{H_2}\right)+\left(n_{CH_4}\times LHV_{CH_4}\right)_{\text{in product}}}{\left(n_{CH_4}\times LHV_{CH_4}\right)_{\text{in feed}}+Q}\right)\times 100$$

$=79.81\%$

$$\begin{aligned} \text{With Q} \quad &= Q_{\text{Heating}} \\ &= 101.3\,kW_t \end{aligned}$$

The thermal efficiency of synthesis gas production with SMR is comparable to the POX process.

In order to produce hydrogen with the process combination of a POX and WGS with PSA, the following energy control volume was used to define the thermal efficiency.

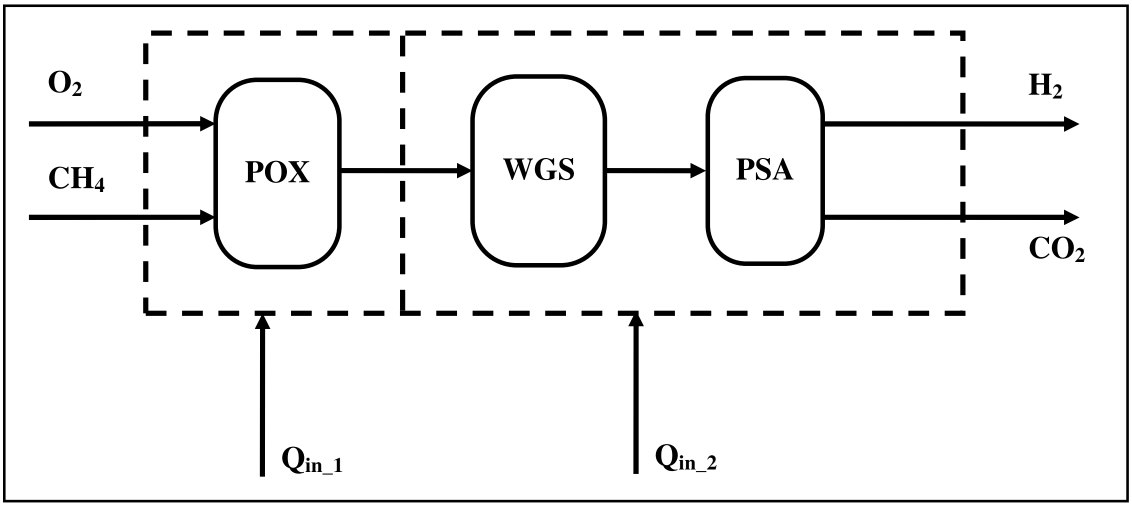

Figure 4-5: Schematic of the energy control volume used to define thermal efficiency for Hydrogen production with POX and WGS with PSA

Thermal Efficiency POX and WGS with PSA for Hydrogen production=

$$\left(\frac{\left(n_{H_2}\times LHV_{H_2}\right)}{\left(n_{CH_4}\times LHV_{CH_4}\right)_{in\,feed}+\left(n_{C_2H_6}\times LHV_{C_2H_6}\right)+\left(n_{C_3H_8}\times LHV_{C_3H_8}\right)+\left(n_{C_4H_8}\times LHV_{C_4H_8}\right)+Q_{in\_1}+Q_{in\_2}}\right)\times 100$$

$$=69.68\%$$

$$\begin{aligned}\text{With } Q_{in\_1} &= Q_{Electric} \text{ Converted to Thermal}\\ &=1223kW_e\times\left(\frac{100}{35}\right)\\ &=3057.5kW_t\end{aligned}$$

If it is assumed, as before, that the conversion efficiency of the PCU is 35% and

$$\begin{aligned}\text{With } Q_{in\_2} &= Q_{Electric} \text{ Converted to Thermal}\\ &=1.32kWe/kg\,H_2\times 9195kg\,H_2/h\\ &=12137kW_t\end{aligned}$$

Mchugh (2005) reported the thermal efficiency of a POX process to be in the order of 70% while that of an industrial SMR process is in the order of 83%. Contadini et al (2000:5) summarized 8 different hydrogen production SMR processes with efficiencies ranging from 80.9% to 89.0%, depending on the production volume, heating values used and estimated steam export and efficiency definition.

4.7 Technical Results General Conclusions

The aim of Chapter 4 was to provide a technical evaluation of the proposed process integration. The HYS proposed by Summers (2005:2) was scaled down to accommodate the 500MWt PBMR and it was found that 121TPD hydrogen and 959 TPD oxygen could be produced. A detailed process flow diagram was provided for the POX process and material and energy calculations were carried out. Technical performance indicators were presented and found to be comparable with industrial POX processes. The thermal efficiencies of the POX synthesis gas and hydrogen production was calculated and found to be 81.0% and 69.7% under given assumptions. The WGS and PSA flow diagram was analyzed and material and energy balances presented. It has been found that by the addition of the three process units, namely, the POX, WGS and the PSA the hydrogen production could be increased to a total of 342 TPD. Consumption of raw materials and utilities were provided for both the POX and WGS & PSA process additions. These consumption figures form the base of the economic study to be presented in Chapter 5.

Chapter 5 - Results Presentation and Discussion: Economic

5.1 Economic Case Results Introduction

Any design, be it chemical or nuclear, in its nature should answer to economic feasibility. Initially in the project life, sufficient capital should be available for the construction of all aspects of the facility to deliver an operational plant.

The net profit of the project is the sum of all possible income minus all expenses and it is essential that the plant generate positive profits for all stakeholders involved. The aim of this section is to present and analyze the initial investment of each process step involved. The section will also present and evaluate the predicted production cost of each process, because this is directly related to the profit of the given process.

Evaluating the initial investment and production cost alone is not adequate to deem a project economically superior or inferior. A profitability analysis will be presented based on the net present value and on the internal rate of return (IRR) method. Both of these methods consider the time value of money, taxes, interest rate as well as fixed charges.

The profitability analysis will be carried out on the POX process for synthesis gas production and on the combination of the POX, WGS and PSA for hydrogen production. Firstly, economic data for synthesis gas production in section 5.1.1 is presented followed by an economic evaluation of hydrogen production in section 5.1.2.

5.1.1 Synthesis Gas Production

The following section is divided into four categories, namely, the capital investment, production cost, sensitivity and profitability analysis. In the first section, the total capital investment cost is estimated for the synthesis gas production unit as depicted in Figure 4-2. The production cost and sensitivity analysis on the production cost is presented, followed by a profitability analysis of the process. Due to the global nature of the project the currency chosen for the economic analysis is the 2008 US dollar.

5.1.1.1 Total Estimated Capital Investment

The total capital investment is based on the total installed equipment cost as suggested by Peters et al (2003: 250). The total delivered equipment cost includes all the equipment listed in Table 4-2. Note that the estimation presented in Table 5-1 is separated into direct cost, for example, the equipment, buildings, piping, etc. and the indirect cost items, such as engineering, legal expenses contractor's fee, etc.

Table 5-1: Total Capital Investment for Synthesis Gas Production

	Fraction of delivered equipment cost	Calculated Value, $
Direct Cost		
Purchased equipment*	1.00	$14,600,000
Delivery, percent of purchased equipment	0.10	$1,460,000
Subtotal: delivered equipment		$16,000,000
Purchased equipment installation	0.47	$7,540,000
Instrumentation and controls (installed)	0.36	$5,780,000
Piping (installed)	0.68	$10,900,000
Electrical systems (installed)	0.11	$1,760,000
Buildings (including services)	0.18	$2,890,000
Yard improvements	0.10	$1,600,000
Service facilities (installed)	0.70	$11,200,000
Total direct cost:		$57,800,000
Indirect Cost		
Engineering and supervision	0.33	$5,290,000
Construction expenses	0.41	$6,580,000
Legal expenses	0.04	$642,000
Contractor's fee	0.22	$3,530,000
Contingency	0.44	$7,060,000
Total indirect cost:		$23,100,000
Fixed capital investment:		$80,900,000
Working capital	0.89	$14,300,000
Total capital investment		$104,000,000

**See Appendix D for equipment cost calculations*

The total direct cost amounts to $57.8 million, the indirect cost is approximately $23.1 million and the working capital is $14.3 million. This results in a total initial investment cost of $104 million for the design, manufacture, delivery, construction and startup of the POX plant.

5.1.1.2 Predicted Production Cost

The production cost of synthesis gas based on the POX process is outlined in Table 5-2. The maintenance cost was assumed to be 7% of the fixed capital investment and it will be a yearly expense resulting in the value of $0.55 per GJ synthesis gas produced. Operating labor was calculated on the basis of total process steps involved and amounts to $0.47 per GJ synthesis gas produced. A general variable referred to as "other" was assigned to rent, insurance, property taxes, plant overhead cost, administration, laboratory charges and operating supplies.

Table 5-2: Production Cost for Synthesis Gas Production

	$/GJ Synthesis Gas
Fixed charges:	
Maintenance	$0.55
Operating Labor	$0.47
Other	$1.00
Total:	**$2.02**
Variable production cost	
Raw Materials	
Natural Gas	$9.42
Oxygen	$0.00
Utilities:	
Water	$0.035
Electricity	$0.043
Steam	$0.036
Total:	**$9.54**
Total Production Cost:	**$11.56**

The raw material cost was based on the results obtained in the technical analysis and summarized in Table 4-5, it was assumed that the cost of natural gas was sold per energy unit and was $8 per GJ. The assumption was made that oxygen could be obtained free of charge directly from the HYS cycle. Utility prices were assumed to be $0.87/ton water, $7.50/ton steam and $0.045/kWh electricity (www.hydrogen.energy.gov, 2008). From Table 5-2 it can clearly be seen that the largest contributing factor to the production cost of synthesis gas is the natural gas consumed. A sensitivity analysis on the production cost will follow.

5.1.1.3 Production Cost Sensitivity and Variation

As stated previously, the most influential component to the production cost of synthesis gas is the natural gas used in the process. Under the assumption that oxygen could be obtained free of charge or at a very low cost, the relevance of the oxygen cost was not considered. The next step is to analyze the possible change in production cost due to the change in raw material cost. The raw materials consumed by the process are mainly natural gas and oxygen. A sensitivity analysis was conducted on the effect that the raw material cost might have on the total production of synthesis gas. Table 5-3 presents the data for synthesis gas production cost with the variation of both natural gas and oxygen cost.

Table 5-3: Synthesis Gas Production Cost Variation

Synthesis Gas Price $/GJ					
		O2 Price $/ton			
		0	30	60	100
Natural Gas Price $/GJ	6	$9.21	$10.13	$11.06	$12.29
	8	$11.56	$12.49	$13.41	$14.65
	10	$13.92	$14.84	$15.77	$17.01
	12	$16.27	$17.20	$18.13	$19.36

The lowest possible production cost for synthesis gas was $9.21/GJ with natural gas cost at $6/GJ and oxygen free of charge. Table 5-3 shows the oxygen cost variation in the horizontal direction and the natural gas cost variation on the vertical direction.

The production cost of synthesis gas varies from $9.21/GJ to $19.36/GJ in the extreme case of an oxygen cost of $100/ton and a natural gas cost of $12/GJ. The possibility of production cost entering the high range of $19.36/GJ is not impossible with the current energy market and should therefore be considered.

A graphic representation of the cost variation can be seen in Figure 5-1 for constant oxygen cost.

Consider the production cost variation of synthesis gas as depicted in Figure 5-1. The synthesis gas production cost is plotted on the vertical (Y) axis while the variation of natural gas cost is presented on the horizontal (X) axis in $ per GJ.

Note the presence of four distinct lines; the four represents an oxygen cost kept constant at $0, $30, $60 and $100 per ton oxygen. As expected an increase in natural gas cost brings about an increase in the production cost.

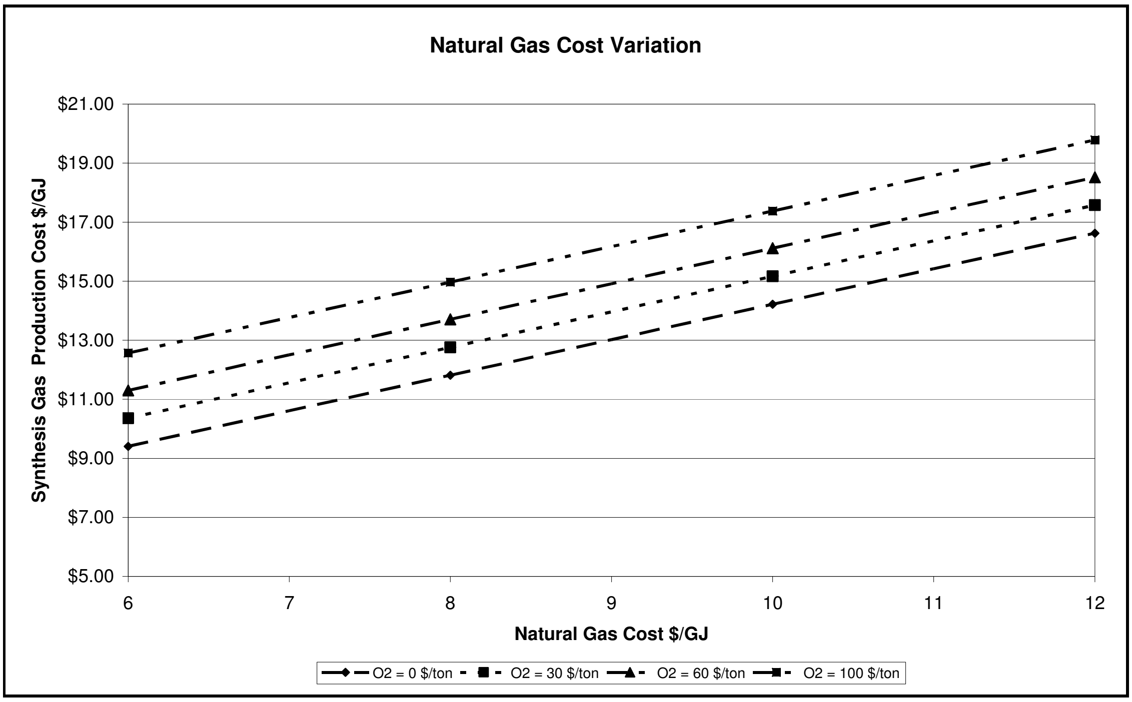

Figure 5-1: The Synthesis gas production cost variation with change in natural gas cost

Also note that the slope of the lines represents a rapid increase in the production cost if a small change is introduced in the natural gas cost. Take for instance the variation of the production cost when the oxygen cost is assumed to be $0/ton, the production cost varies from $9.21/GJ to $16.27/GJ. And if the oxygen cost is $100/ton the production cost varies from $12.29/GJ to $19.36/GJ.

A graphic representation of the cost variation as a function of oxygen cost can be seen in Figure 5-2 for constant natural gas cost.

Consider the production cost variation of synthesis gas as depicted in Figure 5-2. The synthesis gas production cost is plotted on the vertical axis while the variation of oxygen cost is presented on the horizontal axis in $ per ton oxygen.

As before note the presence of four distinct lines; the four represents a natural gas cost kept constant at $6, $8, $10 and $12 per GJ natural gas. As expected, an increase in oxygen cost brings about an increase in the production cost.

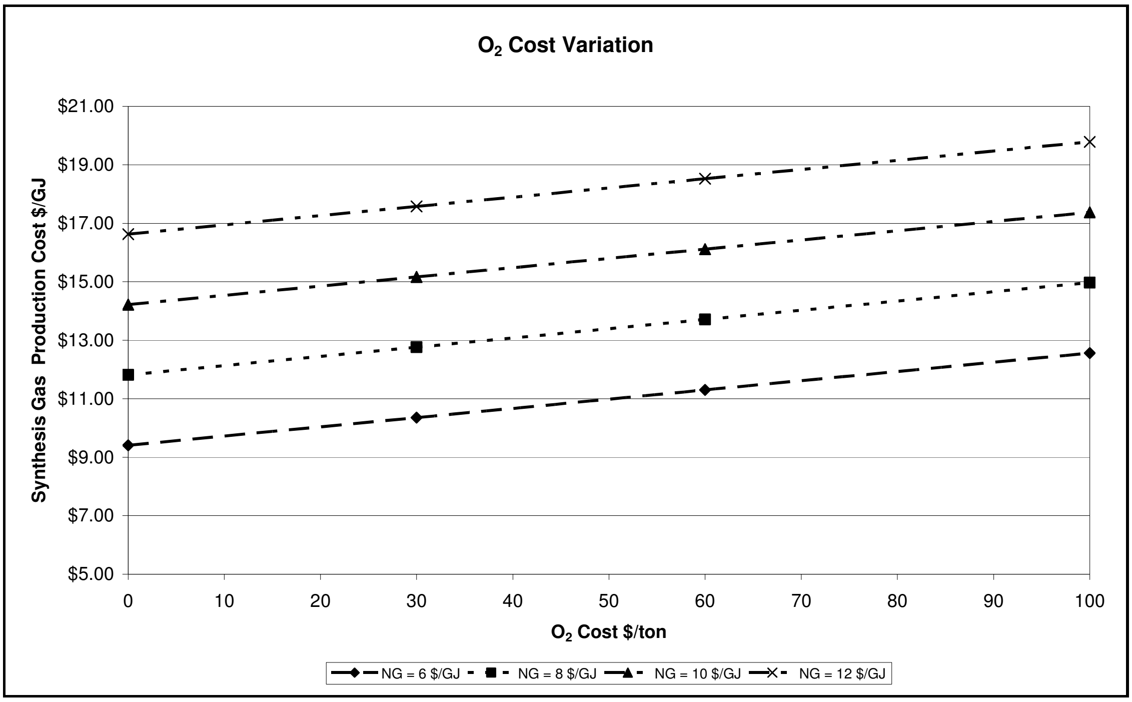

Figure 5-2: The synthesis gas production cost variation with change in oxygen cost

The dependence of the production cost of synthesis gas on the oxygen cost variation resembles the same linear appearance as in Figure 5-1. Take into consideration the variation of the production cost when the natural gas cost is assumed to be $6/GJ, the production cost varies from $9.21/GJ to $12.29/GJ. If the natural gas cost is $12/GJ, the production cost varies from $16.27/GJ to $19.36/GJ.

The extent of the influence of both the oxygen and the natural gas cost is presented in Figure 5-3.

The sensitivity analysis was based on the base case of a natural gas cost of \$6/GJ and an oxygen cost of \$0/ton, making the base case production cost of synthesis gas \$9.21/GJ. The variation of the synthesis gas production cost was recorded for the change in raw material cost as shown in Table 5-3. The percentage change undergone by the synthesis gas production cost was recorded and plotted on the vertical axis of Figure 5-3. The change in the raw material cost was also recorded and converted to percentage value. The percentage variation in raw material cost is shown on the horizontal (X) axis of the following figure.

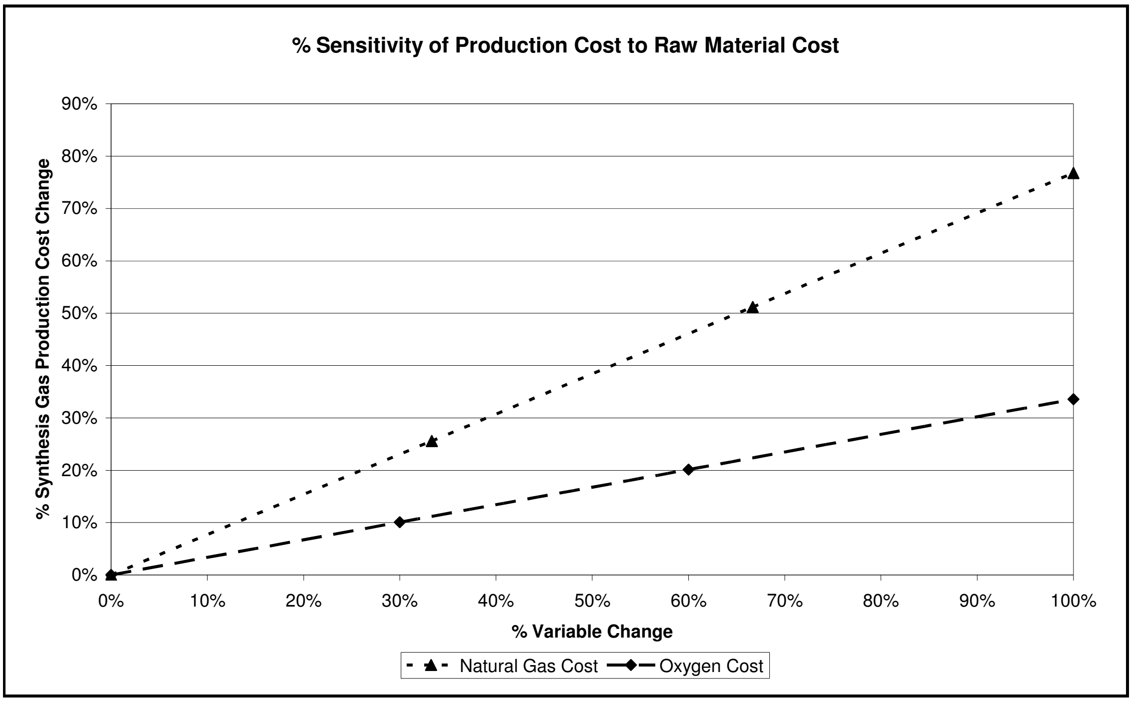

Figure 5-3: Sensitivity of production cost influenced by raw material cost

As suspected, the natural gas cost variation (top line) represents a greater influence on the production cost than the oxygen cost (bottom line). The influence of the oxygen cost can not be ignored however as it still has a large influence on the production cost of synthesis gas.

5.1.1.4 Profitability Analysis

Assumptions on which the profitability analysis for the POX process is based are summarized in Table 5-4. Oxygen cost was taken as \$0/ton and natural gas cost was taken at \$8/GJ.

Table 5-4: Assumptions Made for the Profitability Analysis of Synthesis Gas Production

Total capital investment:	104	$ million
Synthesis gas production tempo:	10 026 264	GJ/year
Synthesis gas selling price:	15	$/GJ
Labor cost:	4 217 119	$/year
Maintenance:	7%	of total capital investment
Raw material cost:		
Natural gas:	8	$/GJ
Oxygen:	0	$/ton
Utilities:		
Water:	0.045	$/GJ synthesis gas
Electricity:	0.966	$/GJ synthesis gas
Steam:	0.005	$/GJ synthesis gas
Discount rate:	10%	
Working capital:	13%	of the total capital investment
Taxes:	35%	

The assumption was made that the construction of the POX plant will take only 2 years implying that all the initial capital will be spent at the end of the first year. The duration of operation was taken to be 20 years.

The tax rate was taken to be 35% and the discount rate used to calculate the net present value was taken as 10%. Utility prices were assumed as before to be \$0.87/ton water, \$7.50/ton steam and \$0.045/kWh electricity.

The calculated NPV for the cash flow of the project is in the order of $87 million after operation for 20 years. (See CD: Synthesis_Gas_Profitability_Analysis_1.xls for calculation of NPV) The positive NPV indicates that the rate of return on investment is larger than the discount rate of 10% and that the project is profitable.

The calculated internal rate of return over a 20 year period is 19.5%. The high rate of return may be explained by the fact that the oxygen was assumed to be free of charge.

A sensitivity analysis was conducted on the IRR for the process over 20 year period and the results are presented in Table 5-5. The blank spaces in the table indicate a negative rate of return which is not acceptable and is hence not displayed.

The sensitivity analysis was performed on four distinct variables, namely, the capital expenditure (Capex), operational cost (Opex), amount of product produced (Volume) and the selling price of the synthesis gas (Sell Price).

These four variables were varied between the ranges -40% and +40% and the calculated IRRs are summarized in Table 5-5. Note that the base case scenario returns a 19.5% IRR.

Table 5-5: IRR Sensitivity, 20 Years of Operation

% Change	Capex	Opex	Volume	Sell Price
-40%	30.0	38.7	8.4	
-30%	26.5	34.2	11.6	
-20%	23.7	29.6	14.4	1.2
-10%	21.4	24.7	17.0	11.7
0%	19.5	19.5	19.5	19.5
+10%	17.9	13.8	21.8	26.3
+20%	16.4	7.2	24.1	32.5
+30%	15.2	-2.1	26.2	38.3
+40%	14.0		28.3	43.9

From the table one could observe that the lowest IRR is recorded at 1.2% when the selling price of synthesis gas drops by 20% and all the other variables are kept constant. The highest IRR recorded is at 43.9% when the selling price is increased by 40%. It appears that the selling price and operating cost has the largest influence on the profitability of the process when compared to the other variables. The capital investment appears to have the least influence on the IRR of all the variables analyzed, as expected.

The results are presented graphically in Figure 5-4. The value of the IRRs is given on the vertical (Y) axis in the scale of percentage and the percentage change in variables is given on the horizontal (X) axis in percentage change.

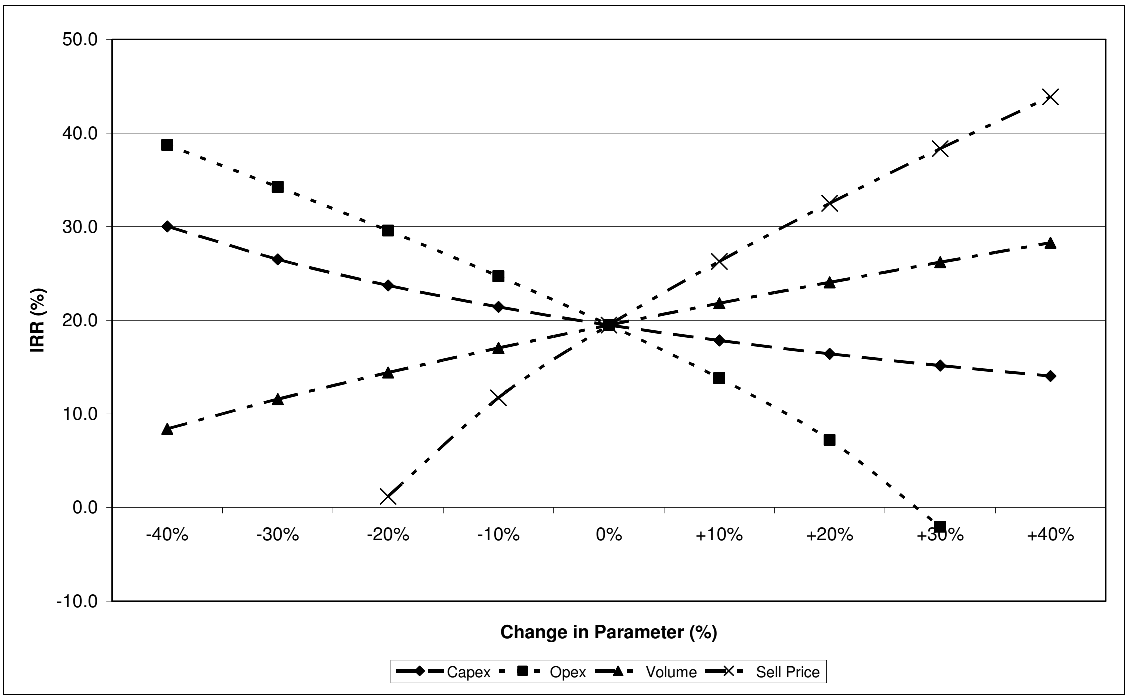

Figure 5-4: IRR sensitivity, 20 years of operation

The selling price appears to be a very sensitive variable. In the case of a 20% drop in selling price the IRR drops from 19.5% to just 1.2%. The operational cost appears to be the second most sensitive variable as, could be expected. Take for example the case when the operational cost increase by 20%, the IRR drops from 19.5% to 7.2%. The least sensitive variable appears to be the production volume, with an IRR increase of only 4.6% for an increase of 20% in production volume. The initial capital investment also has only minor effect on the profitability when compared to the other variables.

According to the profitability analysis it could be concluded that making use of such a plant could have significant economic benefits. It should be remembered that the profitability analysis was only carried out on the POX addition to the process and the HYS capital cost was not considered at all in the profitability analysis. The objective of the profitability analysis was to determine whether or not it would be profitable to couple a POX process to the HYS and to use the by-product, oxygen, to produce a profitable product such as synthesis gas. As a result of the analysis, it could be concluded that the process could be viable under the assumed operating conditions.

5.1.2 Hydrogen Production

The following section is dedicated to hydrogen production and is separated into four categories, exactly like the POX process, namely, the capital investment, production cost, sensitivity and profitability analysis. For the process depicted in Figure 3-3 the total capital investment is estimated, this will include the POX, WGS as well as the PSA.

5.1.2.1 Total Estimated Capital Investment

The capital investment for the hydrogen production plant (Figure 3-3) includes the capital investment of the partial oxidation plant (POX) as well as the capital investment of the WGS and PSA. The capital investment required for the POX, as summarized in Table 5-1, was $104 million. The total capital investment for the WGS and PSA, as reported by Ngeleka, is approximately $50 million (Ngeleka, 2008:38). This includes equipment manufacturing and installation costs. This brings the initial investment to a total of $154 million for the design, manufacture, delivery, construction and startup of the POX, WGS and PSA plant sections.

5.1.2.2 Predicted Production Cost

The production cost for hydrogen based on the proposed process is outlined in Table 5-6. The maintenance cost is \$0.35 per kg while the operating labor is low at only \$0.02 per kilogram hydrogen. The variable operational cost, for synthesis gas, water, electricity and catalyst, of the WGS and PSA was obtained from Ngeleka (Ngeleka, 2008:38). The general variable "other", divined previously, was calculated to be \$0.56 per kg of hydrogen. In this production cost sample calculation Table 5-6, synthesis gas cost was based on the assumption that natural gas could be obtained at \$8/GJ and oxygen at \$0/ton from the HYS.

Table 5-6: Production Cost for Hydrogen Production

			$/kg Hydrogen
Fixed charges:			
Maintenance			\$0.35
Operating Labor			\$0.02
Other			\$0.56
		Total:	**\$0.93**
Variable production cost			
Raw Materials			
Synthesis Gas*			\$1.60
Utilities:			
Water			\$0.03
Electricity			\$0.06
Steam			\$0.04
Catalyst			
	HTS		\$0.001
	LTS		\$0.007
		Total:	**\$1.73**
	Total Production Cost		**\$2.67**

**See appendix F for example calculation*

Table 4-5 and Table 4-7 provide the technical results on which the raw material cost was calculated. Utility prices were assumed to be the same as in section 5.1.1. Synthesis gas is the largest contributing factor in the production of the hydrogen and makes up 60% of the total hydrogen production cost. To evaluate the production cost a sensitivity analysis is carried out in the following section.

5.1.2.3 Production Cost Sensitivity and Variation

As stated in section 5.1.2.2, the most influential component to the production cost of hydrogen is the synthesis gas consumed in the process. The synthesis gas price is directly influenced by the oxygen and natural gas cost as mentioned in section 5.1.1.3 and will thus influence the hydrogen cost significantly. To evaluate the effect that a change in raw material cost could have on the production cost of hydrogen a sensitivity analysis was conducted on the natural gas and oxygen cost. The results are summarized in Table 5-7.

Table 5-7: Hydrogen Production Cost Variation

Hydrogen Price $/kg					
		O2 Price $/ton			
		0	30	60	100
Natural Gas $/GJ	6	$2.34	$2.47	$2.60	$2.77
	8	$2.67	$2.80	$2.93	$3.10
	10	$3.00	$3.13	$3.26	$3.43
	12	$3.33	$3.46	$3.58	$3.76

The lowest possible production cost for hydrogen of $2.34/kg was obtained with natural gas cost at $6/GJ and oxygen $0/ton. Note that Table 5-7 gives the oxygen cost variation in the horizontal direction and the natural gas cost variation on the vertical direction.

The production cost of hydrogen varies from $2.34/kg to the most expensive case of $3.76/kg with oxygen cost at $100/ton and a natural gas obtained at $12/GJ.

Figure 5-5 provides a graphical representation of the results. The hydrogen cost varation is presented in $/kg hydrogen on the vertical (Y) axis. The cost of natural gas is varied along the horizontal (X) axis from $6 to $12 per GJ while the oxygen cost is kept constant at $0, $30, $60 and $100 per ton.

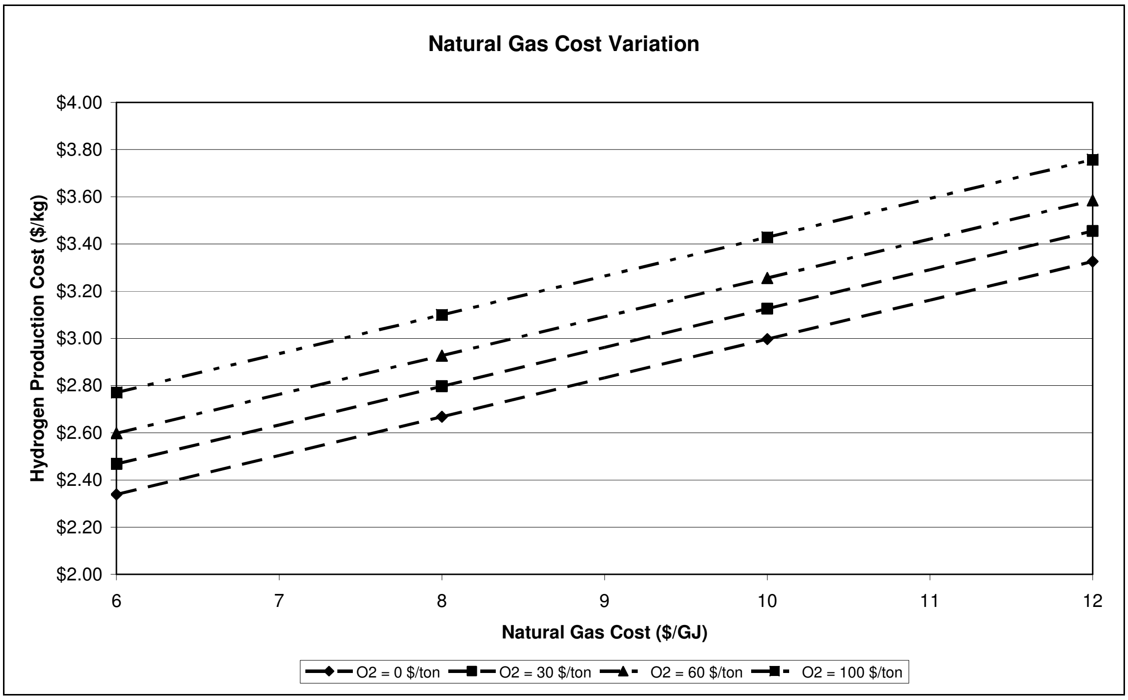

Figure 5-5: Hydrogen Production Cost Variation with Change in Natural Gas Cost

If the oxygen cost is kept constant at $100 per ton the hydrogen cost varies from $2.77 to $3.76 per kg. Doubling the natural gas cost will thus result in a 36% increase in the cost of hydrogen.

Figure 5-6 provides a graphical representation of the oxygen cost variation. The hydrogen cost variation is presented in $/kg hydrogen vertical (Y) axis. The cost of oxygen is varied along the horizontal (X) axis from $0 to $100 per ton while the natural gas cost is kept constant at $6, $8, $10 and $12 per GJ

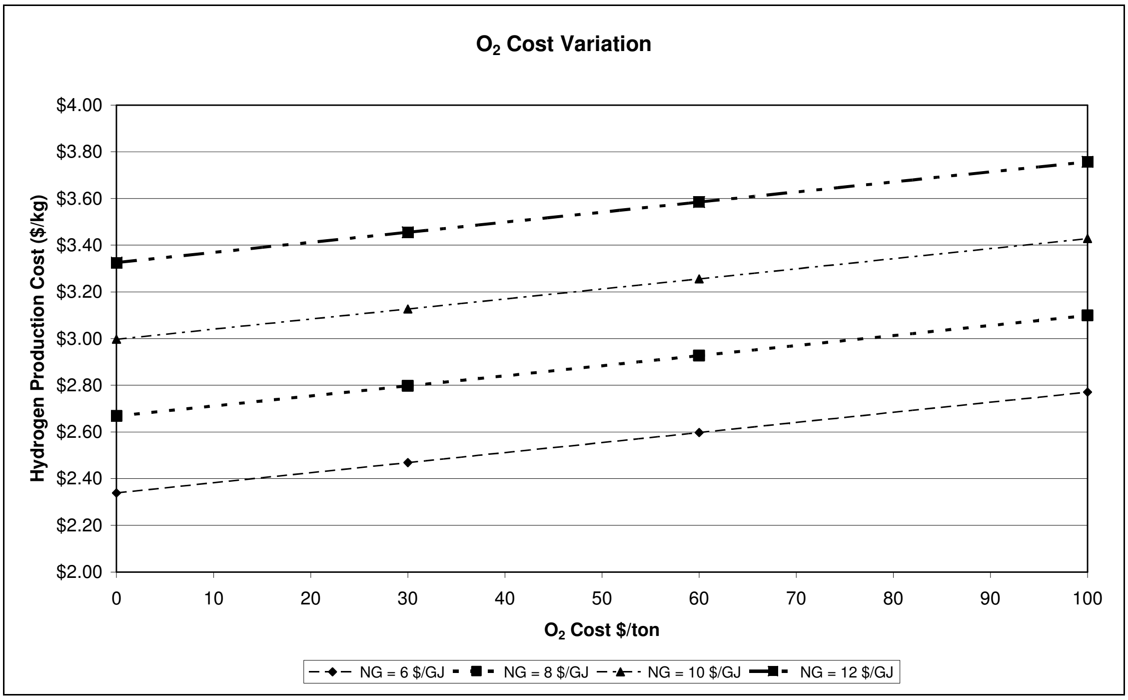

Figure 5-6: Hydrogen production cost variation with variation in oxygen cost

If the natural gas cost is kept constant at $12 per GJ the hydrogen cost varies from $3.33 to $3.76 per kg. Increasing the oxygen cost by 100% will result in a 13% increase in the cost of hydrogen.

The extent of the influence that both the oxygen and the natural gas cost have on the hydrogen cost is presented in Figure 5-7.

The variation of the hydrogen production cost was recorded for the change in raw material cost, as shown in Table 5-7. The percentage change undergone by the hydrogen production cost was recorded and plotted on the vertical (Y) axis of Figure 5-7. The change in the raw material cost was also recorded and converted to percentage value.
The percentage variation in raw material cost is shown on the horizontal axis of the following figure.

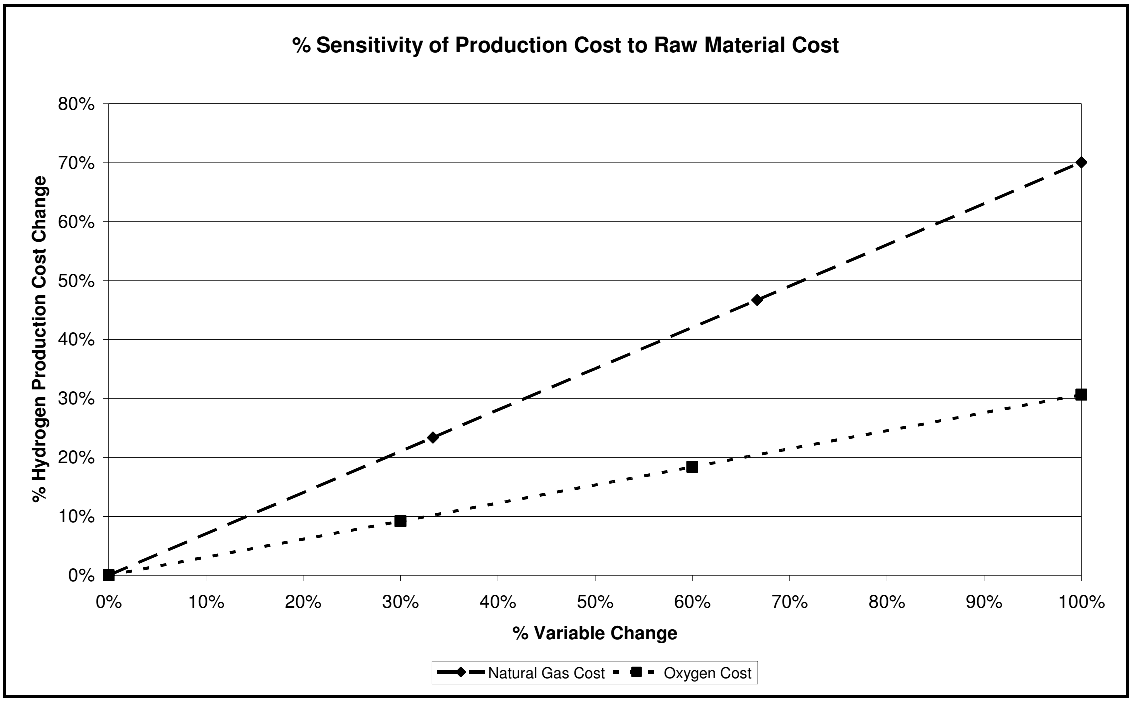

Figure 5-7: Sensitivity of hydrogen production cost to the influence of raw material cost

As suspected, the natural gas cost variation (top line) represents a greater influence on the production cost than does the oxygen cost (bottom line). The gradient of the two variations indicates that a change of for example 30% in the cost of natural gas results in a 22% increase in the cost of hydrogen while the same increase in oxygen cost only gives a 9% increase in hydrogen production cost. The influence of the oxygen cost can not be ignored however as it still has a large influence on the production cost of synthesis gas which in turn has an influence on the hydrogen production cost.

5.1.2.4 Profitability Analysis

The assumptions made for the profitability analysis of hydrogen production is summarized in Table 5-8. The oxygen cost was taken to be $0/ton to bring about maximum profitability and the natural gas cost was taken to be $8/GJ, giving the synthesis gas production cost of $0.194/kg synthesis gas.

Table 5-8: Assumptions Made for the Profitabllity Analysis of Hyrogen Production

Total capital investment:	154	$ million
Hydrogen production tempo:	72 824 400	kg/year
Hydrogen selling price:	3	$/kg
Labor cost:	5 673 607	$/year
Maintenance:	7%	of total capital investment
Raw material cost:		
Synthesis gas cost:	0.194	$/kg
Catalyst	0.008	$/kg H_2
Utilities:		
Water:	1.23	kg/kg H_2
Electricity:	1.32	kWh/kg H_2
Steam:	0.308	kg/kg H_2
Discount rate:	10%	
Working capital:	13%	of the total capital investment
Taxes:	35%	

The construction of the plant was assumed to be 2 years and operation will last for 20 years.

A market survey conducted on the cost of hydrogen showed the average cost varying from $2.5/kg up to as high as $7/kg, thus the assumed selling price ($3/kg) appears appropriate (Mueller-Langer, 2007:3799)

The tax rate was taken to be 35% and the discount rate used to calculate the net present worth was 10%. Utility prices were as before fixed at $0.87/ton water, $7.50/ton steam and $0.045/kWh electricity.

The calculated NPV for the cash flow of the combined process is in the order of $206 million after 20 years of operation. The positive NPV indicates that the rate of return on investment is larger than the discount rate of 10% and that the project is profitable. (See CD: Hydrogen_Profitability_Analysis_1.xls for calculation of NPV)

The assumption that oxygen could be obtained free of charge could explain a high calculated internal rate of return of 23% obtained from the analysis.

A sensitivity analysis was conducted on the IRR for the process for 20 years of operation and the results are presented in Table 5-9. The blank spaces in the table indicate a negative rate of return which is impossible and is hence not displayed.

As in the sensitivity analysis in the synthesis gas profitability study, four distinct variables, namely, the capital expenditure (Capex), operational cost (Opex), amount of product produced (Volume) and the selling price of hydrogen (Sell Price) was considered. The four variables were varied between -40% and +40%.

Table 5-9: IRR Sensitivity, 20 Years of Operation

% Change	Capex	Opex	Volume	Sell Price
-40%	35.0	41.1	11.3	
-30%	30.9	36.9	14.6	
-20%	27.8	32.4	17.5	6.4
-10%	25.2	27.8	20.3	15.5
0%	23.0	23.0	23.0	23.0
+10%	21.1	17.8	25.5	29.7
+20%	19.5	12.1	27.9	35.9
+30%	18.1	5.2	30.3	41.7
+40%	16.9		32.5	47.2

The lowest IRR is recorded at 6.4% when the selling price of hydrogen drops by 20% and all the other variables are kept constant. The highest IRR recorded is at 47.2%, when the selling price is increased by 40%. As with the synthesis gas study it appears that the selling price and the operating expenses has the largest influence on the profitability of the process when compared to the other variables. The capital investment appears to have the least influence on the IRR of all the variables analyzed, as expected.

The results of the sensitivity analysis are presented graphically in Figure 5-8. The value of the IRRs is given on the vertical (Y) axis in the scale of percentage and the percentage change in variables is given on the horizontal (X) axis in percentage change.

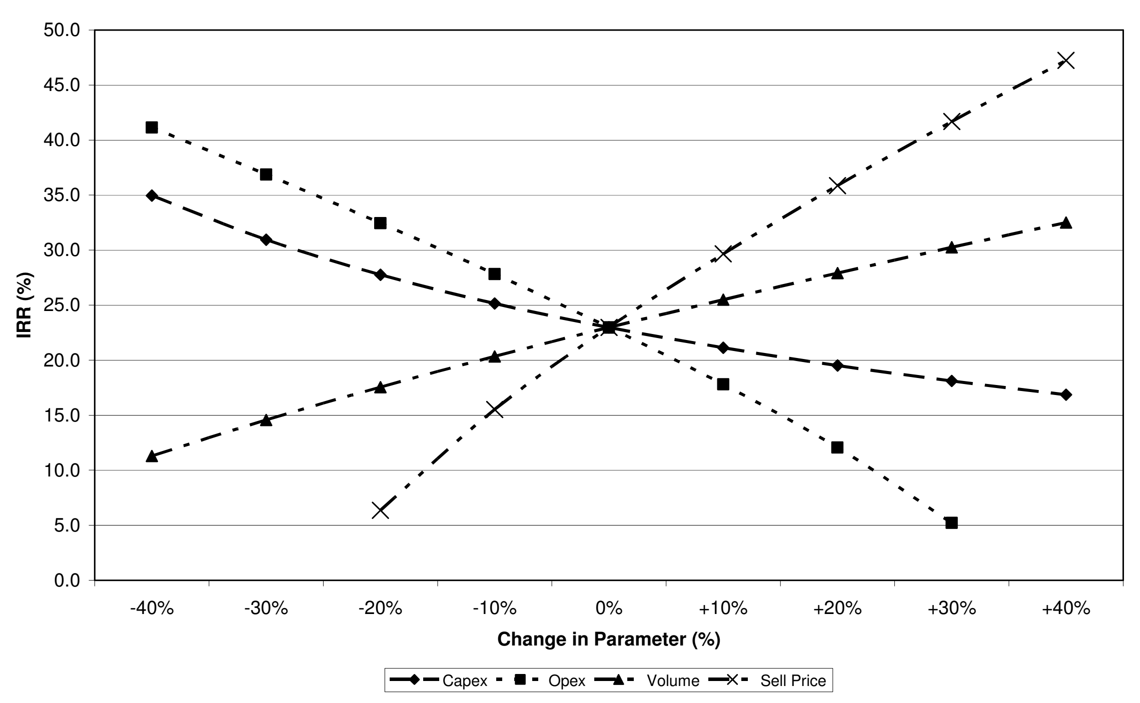

Figure 5-8: IRR sensitivity, 20 years of operation

The selling price appears to be a very sensitive variable. In the case of a 20% drop in selling price the IRR drops from 23.0% to just 6.4%. The operational cost appears to be the second most sensitive variable, as could be expected. Take for example the case when the operational cost increase by 20%, the IRR drops from 23.0% to 12.1%. The least sensitive variable appears to be the production volume, with an IRR increase of only 4.9% for an increase of 20% in production volume.

According to the profitability analysis it could be concluded that operation of such a hydrogen plant could have significant economic benefits. It should be remembered that the profitability analysis was only carried out on the POX, WGS and PSA addition to the process and the HYS capital cost was not considered at all in the profitability analysis. The objective of the profitability analysis was to determine whether or not it would be profitable to couple a POX, WGS and PSA to the HYS and produce additional hydrogen. As a result of the analysis it could be concluded that the process could be viable under the assumed operating conditions.

5.1.3 Economic Contribution of Each Process

With the design based on a 500MWt PBMR reactor, the HYS produced 121TPD of hydrogen and 959TPD of oxygen. When the oxygen is used in a POX process to produce synthesis gas, the hydrogen produced is 160TPD. If the synthesis gas is processed in a WGS reactor to produce additional hydrogen and a PSA unit is used to separate the hydrogen from the gas mixture an additional 61TPD (Ngeleka, 2008:35) could be produced. This implies that for every kilogram of hydrogen produced by the HYS cycle an additional 1.83 kg of hydrogen is produced by including a POX, WGS and PSA.

The production cost for the HYS is in the order of \$6.83/kg hydrogen (Bolthrunis et al., 2009:4-18). The proposed process addition could produce hydrogen at \$2.34/kg hydrogen to a high of \$3.76/kg. If the two hydrogen product streams are combined, the production cost will be in the range of \$3.93/kg hydrogen to \$4.85/kg.

The summary of hydrogen production cost is presented in Table 5-10.

Table 5-10: Contribution of Each Process to the Global Hydrogen Production

	Capital Investment **$\$ \times 10^6$**	**Hydrogen Produced** ***(TPD)***	**Cost of Hydrogen** ***($/kg)***
HYS	600	121	6.83
POX	104	160	2.34 to 3.76
WGS & PSA	50	61	
		342	3.93 to 4.85

The capital investment of the HYS is in the order of \$600 million (Bolthrunis et al., 2009:4-16) and the addition of the POX, WGS and PSA should be in the order of \$154 million. This implies that with the additional capital of less than one fourth of that of the HYS, hydrogen production can increase by a factor of 1.83. This implies that the 1 kilogram of hydrogen produced by the HYS, initially, has now increased to 2.83 kilogram.

5.2 Comparison with Existing Industrial Processes

An evaluation should be made to compare the values obtained from the economic study to other industrial processes. This will provide a bench mark for the economic study.

An array of different processes exist for the production of hydrogen, like coal gasification to natural gas steam reforming, biomass gasification, water electrolysis and even other nuclear based thermochemical cycles, like the SI cycle. A summary of the production cost for each process is given in Table 5-11. According to Bolthrunis et al (2009:4-18) the cost of energy supply from a typical next generation nuclear plant like the PBMR is included in the production cost of the SI, HYS and high temperature steam electrolysis. Depending on the location of the facility and the availability of natural resources the cost might vary from process to process. A very popular process currently used world-wide is the steam reforming of natural gas (SMR), the production cost of SMR is in the order of \$0.60 to \$1.00 per kg of hydrogen. One of the advantages that the SMR process leans on is the ability to export steam; this brings down the production cost significantly.

Table 5-11: Hydrogen Production Options

Hydrogen Production Options	**Current Production Cost** ***(\$/kg H_2)***
Coal Gasification	0.90 to 1.80
Natural Gas Reforming	0.60 to 1.00
Biomass Gasification	2.00 to 4.00
High Temperature Steam Electrolysis	6.04
SI Cycle	10.71
HYS	6.83
HYS + POX + WGS + PSA	3.93 to 4.85

As mentioned earlier, the production cost of a process is not necessarily the best way to determine the profitability. The capital investment should also be considered. The proposed process however appears to compete in the category of \$3.93 to \$4.85/kg hydrogen which would make it a good counterpart for biomass gasification, water electrolysis the SI cycle. The production cost can however not compete with the SMR process.

5.3 Economic Results Conclusions

All economic results for two different processes were presented in Chapter 5. Firstly, the synthesis gas production as depicted in Figure 4-2 and secondly, hydrogen production as shown in Figure 3-3. For both of the two processes, capital investment was estimated and found to be in the order of $104million and $154million respectively. The production cost for each was calculated and a sensitivity analysis was carried out on the influence that raw material cost might have on the production cost. A profitability analysis was carried out on the two processes and both were profitable under the given assumptions. The contribution of each additional process step was evaluated on economic grounds and it could be concluded that the addition of the processes will be of value to the HYS economically. Lastly, a comparison of the production cost of industrial processes was given and the production cost was found to be competitive with most of the possible alternatives with the exception of steam methane reforming.

Chapter 6 - Conclusions and Recommendations

6.1 Summary

An overview of the motivating factors for the proposed hydrogen economy along with possible technological solutions to this new economy was presented in Chapter 1. A possible enhancement to one of the thermochemical cycles (HYS) was suggested and possible plant design considerations, integration and design limitations were given.

In Chapter 2 the possibility of coupling a chemical plant to a high temperature gas cooled nuclear reactor was explored with the focus on thermochemical cycles. The possibility of synthesis gas production was discussed and technologies in the form of partial oxidation of methane was presented and evaluated on technical grounds. The governing principals for partial oxidation were explained to provide insight into the process.

To enhance the HYS cycle, two possible improvement configurations were suggested in Chapter 3. Firstly, the production of synthesis gas with a POX process, by using the by-product oxygen was presented, and secondly, the production of hydrogen with the addition of a WGS and PSA unit to the POX.

A technical evaluation was conducted on the two possible configurations in Chapter 4. The technical analysis was conducted on a scaled down HYS cycle, based on the energy input of a 500MWt PBMR. A limitation on the POX process was imposed by the oxygen supplied by the HYS cycle. With this constraint the total volume of synthesis gas was calculated. With the addition of a WGS and PSA unit an increase in the hydrogen production of the entire process was noted, as expected. Hydrogen production increased by a factor of 1.83, this implies that for every 1 kilogram of hydrogen produced by the HYS an additional 1.83 kg of hydrogen could be produced by the additional process units.

The two proposed process configurations were evaluated on economic grounds in chapter 5. The analysis included capital investment, production cost, the sensitivity of production cost to raw material cost and lastly, a profitability analysis. The profitability analysis indicated that both the process configurations could be profitable under the given assumptions. The production costs were compared to other industrial processes production cost and were found to be comparable.

6.2 Conclusions

On technological grounds it was found that the synthesis gas as well as hydrogen production is possible with the two processes presented. The suggested process addition to the HYS is proven by years of industrial experience in the fossil fuel industry. The additional process units were found to be efficient when compared to other industrial processes, as was expected. From a technical point of view it can thus be concluded that the coupling of the two different fields of technology, a nuclear based thermochemical cycle and a traditionally fossil fuel based POX process, is plausible and technologically possible. Moreover, the integration of the HYS and POX, WGS and PSA processes could provide an elegant technical opportunity for the utilization of the by-product oxygen produced by the HYS for both synthesis gas and hydrogen production.

With technical inputs considered, the financial evaluation was conducted. The production cost for both synthesis gas as well as hydrogen was calculated and was compared to other industrial processes. A profitability analysis based on the internal rate of return and net present worth was completed and from this analysis it was concluded that both the synthesis gas and hydrogen production processes are profitable, under the assumed technical and economic conditions. The combination of a HYS thermochemical cycle and the synthesis gas production process (POX) or the hydrogen production process presented can therefore both improve the financial appeal of the HYS.

6.3 Recommendations for Future Investigation

The following recommendations based on the results of this investigation are proposed for further investigation, which can contribute to the expansion of the knowledge of the integration of traditional fossil fuel based technologies with that of innovative nuclear based technologies.

Technically and economically the proposed process integration could be justified. The nuclear industry is however heavily legislated, for numerous reasons, and a study on the safety of the integration of a nuclear reactor with that of a thermochemical cycle and the POX, WGS and PSA process units could be conducted to explore a safety case for the integration.

The POX process could accommodate a range of feedstock. This study focused on the use on natural gas or methane. The possibility of a different hydrocarbon feedstock like fuel oil, vacuum residue, propane asphalt and orimulsion could have a noticeable effect on the economics of the entire process. Thus a study could be undertaken to evaluate the effectiveness of different feeds to the POX process.

The possibility for using an auto thermal reactor could be considered. An auto thermal reactor is a combination of the partial oxidation reactor and a steam methane reforming reactor. The efficiencies of the system could increase and provide a technically superior process. The technical evaluation could lead to economic advantages and could be investigated.

Instead of making hydrogen, the synthesis gas could be used to produce other valuable products. Based on the Fischer-Tropsch synthesis process many possible products could be made. More profitable products could bring about even more attractive economic incentives and could be investigated.

The steel industry relies on hydrogen for the production of direct reduced iron and hot briquetted iron. Using hydrogen, produced from a CO_2 free source such as in the proposed process, as a reductant can assist the steel industry in cutting CO_2 emissions to a great extent. An investigation could be undertaken to explore the degree of the effect that this could have on the steel industry in general.

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Appendix A: POX Technical Performance Indicators

Carbon Conversion:

$$C-Conversion(\%)=\left(1-\frac{CH_4\ in\ product}{mol\ C\ fed}\right)\times 100 \qquad (2.20)$$

$$=\left(1-\frac{mol\,CH_4\ in\ product}{\left(mol\ C_1+mol\ C_2+mol\ C_3+mol\ C_4\right)fed}\right)\times 100$$

$$=\left(1-\frac{0.0009\times 6038}{\left(0.8435\times 1586\right)+2\left(0.0883\times 1586\right)+3\left(0.039\times 1586\right)+4\left(0.0292\times 1586\right)}\right)\times 100$$

$$=99.72\%$$

Carbon Efficiency:

$$C-Efficiency=\frac{mol\left(CO+H_2\right)}{mol\ C\ fed} \qquad (2.21)$$

$$=\left(\frac{mol\,CO+H_2}{\left(mol\ C_1+mol\ C_2+mol\ C_3+mol\ C_4\right)fed}\right)$$

$$=\left(\frac{\left(0.2913\times 6038\right)+\left(0.5507\times 6038\right)}{\left(0.8435\times 1586\right)+2\left(0.0883\times 1586\right)+3\left(0.039\times 1586\right)+4\left(0.0292\times 1586\right)}\right)$$

$$=2.556$$

Oxygen Efficiency:

$$O_2-Efficiency=\frac{mol\left(CO+H_2\right)}{mol\ O_2\ fed} \qquad (2.22)$$

$$=\left(\frac{mol\,CO+H_2}{mol\ O_2\ fed}\right)\times 100$$

$$=\left(\frac{\left(0.2913\times 6038\right)+\left(0.5507\times 6038\right)}{\left(1\times 1249\right)}\right)$$

$$=4.070$$

Appendix B: Thermal Efficiency Calculations

Table B 1: Thermal Efficiency of POX producing Synthesis Gas

POX Synthesis Gas			
Product			
	mol frac	kJ/mol	kJ/mol
Methane	0.0053	821.95	4.4
CO	0.3071	273.3	83.9
H_2	0.5363	232.3	124.6
	Total		345649 kJ/s
Input			
	mol frac	kJ/mol	kJ/mol
Methane	0.8435	802.6	676.99
Ethane	0.0883	1428.6	126.15
Propane	0.039	2043.1	79.68
n-Butane	0.0292	2657.3	77.59
	Total		423115 kJ/s
Q			
	3494 kWt from electric		
		Thermal Efficiency	**81.02%**

Table B 2: Typical example of thermal efficiency calculation of SMR synthesis gas production

SMR Synthesis Gas			
Input			
	Mol/s	kJ/mol	kW
Methane	0.2526	802.6	202.7
Heating (kWt)			101.3
	Total In:		304.0
Pruduct			
	Mol/s		
Methane	2.28E-03	802.6	1.8
Hydrogen	0.8002	232.3	185.9
CO	0.201	273.3	54.9
	Total Out:		242.7
	Thermal Efficiency		**79.81%**

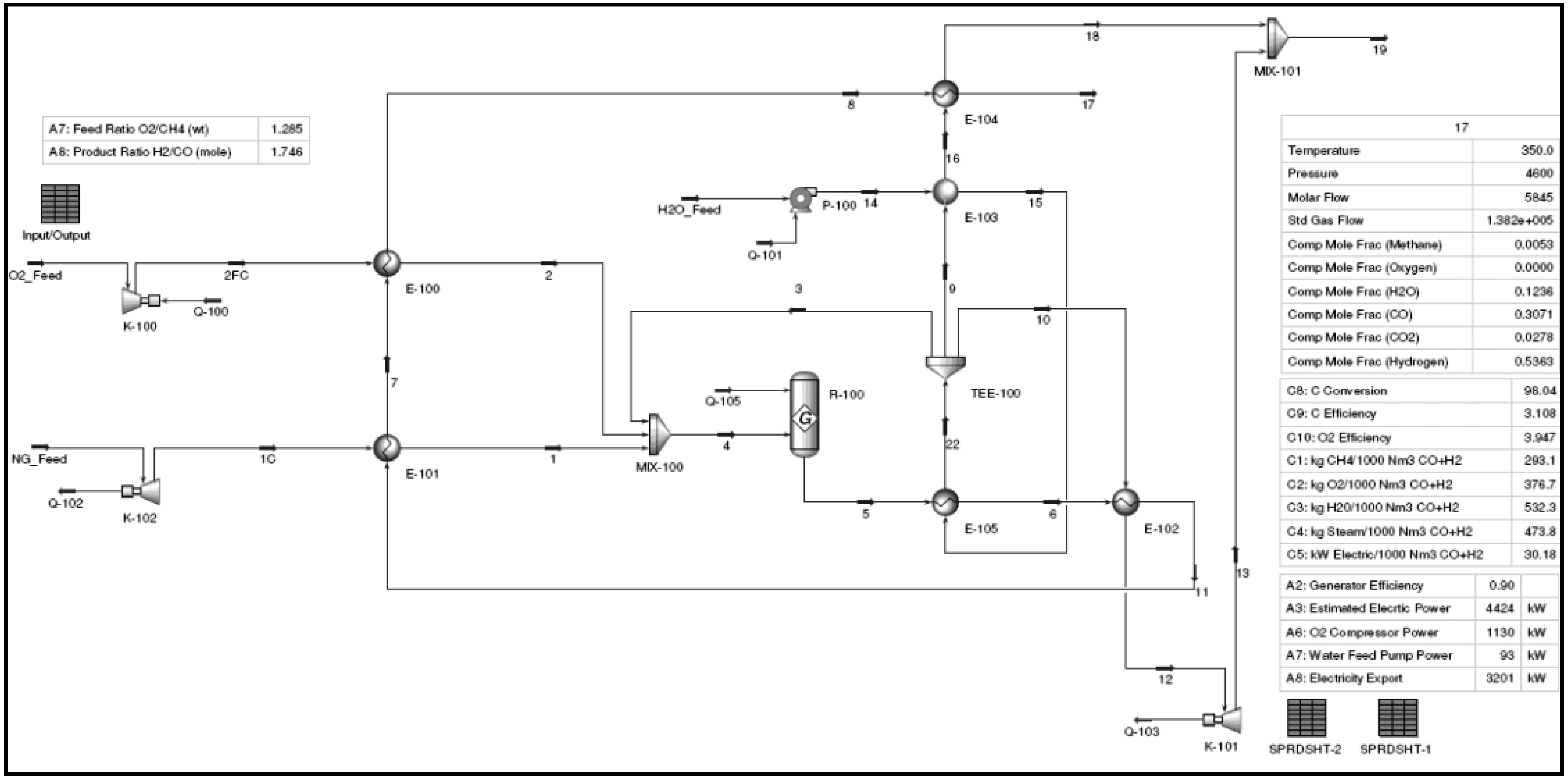
Seo. Y.S et al:2002,221

Table B 3: POX and WGS with PSA thermal efficiency for hydrogen production

POX WGS PSA Hydrogen					
Product	molfrac	kmol/h	mol/s	kJ/mol	kJ/s
H2	0.9999	4552	1264	241.8	305712
Input					
Same as POX					423115
Q	kWh/kgH2		kgH2/h		
	1.32		9195		15632
					438747
				Thermal Efficiency (inc electric)	**69.68%**

Appendix C: HYSYS Simulation results

The following POX PFD was simulated on HYSYS.



A7: Feed Ratio O2/CH4 (wt)	1.285
A8: Product Ratio H2/CO (mole)	1.746

17	
Temperature	350.0
Pressure	4600
Molar Flow	5845
Std Gas Flow	1.382e+005
Comp Mole Frac (Methane)	0.0053
Comp Mole Frac (Oxygen)	0.0000
Comp Mole Frac (H2O)	0.1236
Comp Mole Frac (CO)	0.3071
Comp Mole Frac (CO2)	0.0278
Comp Mole Frac (Hydrogen)	0.5363

C8: C Conversion	98.04
C9: C Efficiency	3.108
C10: O2 Efficiency	3.947
C1: kg CH4/1000 Nm3 CO+H2	293.1
C2: kg O2/1000 Nm3 CO+H2	376.7
C3: kg H20/1000 Nm3 CO+H2	532.3
C4: kg Steam/1000 Nm3 CO+H2	473.8
C5: kW Electric/1000 Nm3 CO+H2	30.18

A2: Generator Efficiency	0.90	
A3: Estimated Elecrtic Power	4424	kW
A6: O2 Compressor Power	1130	kW
A7: Water Feed Pump Power	93	kW
A8: Electricity Export	3201	kW

Figure C 1: HYSYS simulation PDF of POX process

Table C 1: Stream condition data from HYSYS simulation

Name	O2_Feed	NG_Feed	2FC	2	1C	1	4	5	LIQ
Vapour Fraction	1.00	1.00	1.00	1.00	0.90	1.00	1.00	1.00	0.00
Temperature (°C)	40.0	4.0	150.5	260.0	-31.2	400.0	353.2	1204.0	1204.0
Pressure (kPa)	2000.0	10000.0	4630.0	4600.0	4630.0	4600.0	4600.0	4600.0	4600.0
Molar Flow (kgmol/h)	1248.6	1585.7	1248.6	1248.6	1585.7	1585.7	3178.9	5844.7	0.0
Mass Flow (kg/h)	39956.6	31086.2	39956.6	39956.6	31086.2	31086.2	77251.1	77250.5	0.0

Name	6	22	7	8	9	3	10	11	12
Vapour Fraction	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Temperature (°C)	689.5	300.0	416.2	393.0	300.0	300.0	300.0	623.7	510.0
Pressure (kPa)	4600.0	4600.0	4600.0	4600.0	4600.0	4600.0	4600.0	4600.0	4570.0
Molar Flow (kgmol/h)	5844.7	3134.0	5844.7	5844.7	1325.1	344.6	1464.3	5844.7	1464.3
Mass Flow (kg/h)	77250.5	56459.3	77250.5	77250.5	23871.9	6208.3	26379.2	77250.5	26379.2

Name	H2O_Feed	14	15	16	17	18	13	19
Vapour Fraction	0.00	0.00	0.00	0.00	1.00	0.00	1.00	0.63
Temperature (°C)	19.0	19.4	249.9	110.8	350.0	184.3	153.9	100.0
Pressure (kPa)	101.3	4600.0	4600.0	4570.0	4600.0	4540.0	101.3	101.3
Molar Flow (kgmol/h)	3134.0	3134.0	3134.0	1325.1	5844.7	1325.1	1464.3	2789.4
Mass Flow (kg/h)	56459.3	56459.3	56459.3	23871.9	77250.5	23871.9	26379.2	50251.1

Table C 2: Stream composition data from HYSYS POX simulation

Name	**O2_Feed**	**NG_Feed**	**2FC**	**2**	**1C**	**1**	**4**	**5**	**LIQ**
Comp Mol Frac (Methane)	0.00000	0.84350	0.00000	0.00000	0.84350	0.84350	0.42074	0.00531	0.00531
Comp Mol Frac (Ethane)	0.00000	0.08830	0.00000	0.00000	0.08830	0.08830	0.04404	0.00000	0.00000
Comp Mol Frac (Propane)	0.00000	0.03900	0.00000	0.00000	0.03900	0.03900	0.01945	0.00000	0.00000
Comp Mol Frac (n-Butane)	0.00000	0.02920	0.00000	0.00000	0.02920	0.02920	0.01457	0.00000	0.00000
Comp Mol Frac (Oxygen)	1.00000	0.00000	1.00000	1.00000	0.00000	0.00000	0.39279	0.00000	0.00000
Comp Mol Frac (H_2O)	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.10841	0.12356	0.12356
Comp Mol Frac (CO)	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.30707	0.30707
Comp Mol Frac (CO_2)	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.02780	0.02780
Comp Mol Frac (Hydrogen)	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.53625	0.53625

Name	**6**	**22**	**7**	**8**	**9**	**3**	**10**	**11**	**12**
Comp Mol Frac (Methane)	0.00531	0.00000	0.00531	0.00531	0.00000	0.00000	0.00000	0.00531	0.00000
Comp Mol Frac (Ethane)	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
Comp Mol Frac (Propane)	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
Comp Mol Frac (n-Butane)	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
Comp Mol Frac (Oxygen)	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
Comp Mol Frac (H_2O)	0.12356	1.00000	0.12356	0.12356	1.00000	1.00000	1.00000	0.12356	1.00000
Comp Mol Frac (CO)	0.30707	0.00000	0.30707	0.30707	0.00000	0.00000	0.00000	0.30707	0.00000
Comp Mol Frac (CO_2)	0.02780	0.00000	0.02780	0.02780	0.00000	0.00000	0.00000	0.02780	0.00000
Comp Mol Frac (Hydrogen)	0.53625	0.00000	0.53625	0.53625	0.00000	0.00000	0.00000	0.53625	0.00000

Table C 3: Stream composition data from HYSYS POX simulation continue

Name	H2O_Feed	14	15	16	17	18	13	19
Comp Mol Frac (Methane)	0.00000	0.00000	0.00000	0.00000	0.00531	0.00000	0.00000	0.00000
Comp Mol Frac (Ethane)	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
Comp Mol Frac (Propane)	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
Comp Mol Frac (n-Butane)	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
Comp Mol Frac (Oxygen)	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
Comp Mol Frac (H_2O)	1.00000	1.00000	1.00000	1.00000	0.12356	1.00000	1.00000	1.00000
Comp Mol Frac (CO)	0.00000	0.00000	0.00000	0.00000	0.30707	0.00000	0.00000	0.00000
Comp Mol Frac (CO_2)	0.00000	0.00000	0.00000	0.00000	0.02780	0.00000	0.00000	0.00000
Comp Mol Frac (Hydrogen)	0.00000	0.00000	0.00000	0.00000	0.53625	0.00000	0.00000	0.00000

Find attached to the back cover a dvd containing the simulation file (*Figure_4_2_ Detailed Process Flow Diagram for the POX process.HSC).* The pump efficiency was assumed to be 85%, the heat transfer efficiency was assumed to be 80%. Pressure loss in the system was neglected.

Appendix D: POX Equipment Cost Estimation

Heat Exchanger Cost:

$$Purchased\ Cost, \$ = \left(\frac{M\ \&\ S}{280}\right)\left(101.3A^{0.65}F_c\right)_{(Douglas, 1988)}$$

$$F_c = (F_d + F_p)F_m$$

$$F_d = 1.35(boiler), F_d = 1.00(Floating\ Head)$$

$$F_p = 0$$

$$F_m = 3.75(ss/ss)$$

E-100		
Thin	416°C	780.8°F
Thout	393°C	739.4°F
Tcin	150°C	302°F
Tcout	260°C	500°F
ΔT1	478.8	
ΔT2	239.4	
ΔTm	345.4	
U	20Btu/hr.ft2.°F	
A	542m^2	
Cost	**$17,768**	

E-101		
Thin	624°C	1155.2°F
Thout	416°C	780.8°F
Tcin	-31°C	-23.8°F
Tcout	400°C	752°F
ΔT1	1179	
ΔT2	28.8	
ΔTm	309.9	
U	10Btu/hr.ft2.°F	
A	2758m^2	
Cost	**$90,493**	

E-103		
Thin	300°C	572°F
Thout	110°C	230°F
Tcin	19°C	66.2°F
Tcout	250°C	482°F
ΔT1	505.8	
ΔT2	252	
ΔTm	364.3	
U	10Btu/hr.ft2.°F	
A	1018m^2	
Cost	**$33,397**	

E-104		
Thin	393°C	739.4°F
Thout	350°C	662°F
Tcin	110°C	230°F
Tcout	185°C	365°F
ΔT1	509.4	
ΔT2	297	
ΔTm	393.7	
U	20Btu/hr.ft2.°F	
A	702m^2	
Cost	**$23,024**	

Compressor Cost:

$$Purchased\ Cost, \$ = \left(\frac{M\ \&\ S}{280}\right)(517.5)(bhp)^{0.82}\ F_c, _{(Douglas, 1988)}$$

$$F_c = F_d,\ F_d = 1.35(centrifugal, turbine)$$

K-100	
Power	1130kW
	1515Hp
Cost	**$608,335**

K-101	
Power	4915kW
	6591Hp
Cost	**$1,971,963**

P-100	
Power	98kW
	131Hp
Cost	**$4,625**

According to the Power Factor method (Peters, 2003:254), applied to plant capacity, the following cost estimation was obtained for the reactor system:

$$C_n = Cf_eR^x$$

$$= \frac{CEI_{2008}}{394.1} \times (\$9'721'411) \times \left(\frac{5845}{9912}\right)^{0.6}$$

$$; \quad \$11'600'000$$

The estimation was made based on the value provided in the SINTEF report (SINTEF, 1994:32). The CEI used was the preliminary value for January 2008 (530.7) (www.che.com).

Appendix E: POX Reactor Sizing

Using an elementary PFR reactor model in HYSYS the POX reactor was sized. The specific reaction rate k as well as the activation energy E used in the simulation was obtained from Dobergo (2008:83).

$$k = 2.17\times10^{8} EXP\left[15.640/T\left(°C\right)\right]$$

$$E = 59\,000\left(J/mol\,CH_4\right)$$

The volume was calculated as 84.82 m^3. Find attached to the back cover a dvd containing the simulation file (*POX Reactor Size.HSH*)

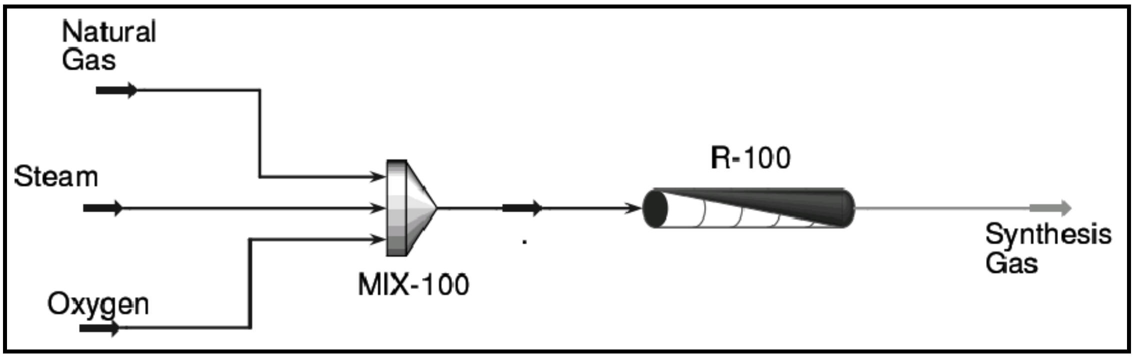


Figure E 1: HYSYS Simulation of POX reactor

Appendix F: Hydrogen Cost Conversion

From Table 4-7 we find the value for synthesis gas consumption by the WGS and PSA to be:

$$\frac{8.34\,\mathrm{kg\,SINTHESIS\,GAS}}{\mathrm{kg\,H_2}}$$

We know from Table 5-3, that the cost of synthesis gas is:

$$\frac{11.56\,\$}{\mathrm{GJ\,SINTHESIS\,GAS}}$$

Thus

$$\frac{8.34\,\mathrm{kg\,SINTHESIS\,GAS}}{\mathrm{kg\,H_2}} \times \frac{11.56\,\$}{\mathrm{GJ\,SINTHESIS\,GAS}} \times \frac{0.01662\,\mathrm{GJ}}{\mathrm{kg\,SINTHESIS\,GAS}}$$

We find the cost of synthesis gas per kilogram hydrogen to be:

$$\frac{1.60\$}{\mathrm{kg\,H_2}}$$