NON-CATALYTIC PLASMA-ARC REFORMING PROCESS OF METHANE WITH CARBON DIOXIDE FOR HYDROGEN PRODUCTION

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Master of Engineering

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A number of people have made the completion of this dissertation possible. To them I wish to express my sincere gratitude:

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TITLE: **NON-CATALYTIC PLASMA-ARC REFORMING PROCESS OF METHANE WITH CARBON DIOXIDE FOR HYDROGEN PRODUCTION**

AUTHOR: **GERT WILHELM BASSON**

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Abstract

The world revolves around energy; it is needed to power industry, move people and products around the world and provide safety and convertibility for everyone. Current technologies produce huge amounts of greenhouse gases. New technologies are needed to produce cleaner energies and save on valuable fossil fuel.

This research project evaluates the Non-catalytic Plasma-arc Reforming Process for the production of synthesis and hydrogen gas. Carbon dioxide was used as the oxidising agent instead of steam that is normally used in the Steam Methane Reforming Process. The Plasma-arc Reforming Unit operates at very high temperatures (2 000-5 000°C) and this enables the reforming reaction to occur stoichiometrically in the unit. A 500 MWt Pebble Bed Modular Reactor can supply 21×8 MW Plasma-arc Reforming Units with electrical power. Synthesis gas can be produced with a hydrogen-to-carbon monoxide ratio of 1:1, which can be varied between 1:1 and 3:1, by adding steam to the inlet gas stream.

The variation in the ratio can be achieved by changing the steam to carbon dioxide feed ratio. A total of 1 435 million Nm^3 synthesis gas can be produced annually at a production cost of $10.43 per GJ. The hydrogen production by the Plasma-arc Reforming Process can be increased by making use of the water-gas-shift reaction. Hydrogen can be produced with a purity of 99.0% using a Pressure Swing Absorption system, in order to separate the hydrogen from the product gas stream.

The annual production of hydrogen is 1 120 million Nm^3 at a production cost of $14.17 per GJ. A sensitivity evaluation was conducted on the process used for the production of synthesis and hydrogen gas. It was observed that natural gas and electrical costs have a significant impact on the production cost and profitability of the plants. The Steam Methane Reforming Process was also compared with the Non-catalytic Plasma-arc Reforming Process, from which it was concluded that Plasma-arc Reforming competes well with Steam Methane Reforming.

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Opsomming

Die wêreld is hoogs afhanklik van energie en dit word benodig om industrieë aan te dryf, mense en produkte oor die wêreld te vervoer en veiligheid en verwisselbaarheid te verseker. Die prosesse wat tans vir die vervaardiging van energie gebruik word, produseer groot hoeveelhede kweekhuisgasse. Daarom word nuwe tegnologieë benodig om skoner energie te produseer en om waardevolle fossielbrandstowwe in die proses te bespaar.

Hierdie navorsingsprojek ondersoek die nie-katalitiese plasmaboog-hervormingsproses vir die vervaardiging van sintese- en waterstofgas. Koolstofdioksied is as oksidasiemiddel gebruik in plaas van stoom wat normaalweg gebruik word in die stoommetaan-hervormingsproses. Hoë temperature (2 000-5 000°C) word in die plasmaboog-hervormingseenheid bereik, en dit voorsien die nodige energie sodat die reaksie stoigiometries kan plaasvind. ’n 500 MWt Korrelbed Modulêre Reaktor (Pebble Bed Modular Reactor) kan 21×8 MW plasmaboog-eenhede elektrisiteit voorsien. Sintesegas met ’n H_2-tot-CO-verhouding van 1:1 kan geproduseer word. Hierdie verhouding kan verder gevarieer word tussen 1:1 en 3:1 deur ’n sekere hoeveelheid stoom by die inlaatgas-stoom te voeg.

Die verandering in die H_2-to-CO-verhouding kan bewerkstellig word deur die voerverhouding van stoom tot koolstofdioksied te varieer. Die produksie van sintesegas is 1 435 miljoen Nm^3 per jaar teen ’n produksiekoste van $10.43 per GJ. Die waterstofproduksie van die plasmaboog-hervormingsproses kan verhoog word deur van die water-gas-skuifreaksie gebruik te maak. Waterstof met ’n suiwerheid van 99.0% kan geproduseer word deur van ’n PSA-sisteem gebruik te maak wat die waterstof van die produk gasstroom skei.

Die totale waterstofproduksie is 1 120 miljoen Nm^3 teen ’n produksiekoste van $14.17 per GJ. ’n Sensitiwiteitsanalise wat uitgevoer is, het getoon dat aardgas en elektrisiteit die produksiekoste en winsgewendheid van die sintese- en waterstofgas produksie merkbaar beïnvloed. Verder is die stoommetaan-hervormingsproses met die nie-katalitiese plasmaboog-hervormingsproses vergelyk, en dit het getoon dat die prosesse ekonomies goed vergelyk.

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Publications and presentations

Basson, G.W. & Blom, P.W.E. 2008. Non-catalytic Plasma-arc Reforming of natural gas with carbon dioxide as the oxidising agent for the production of synthesis gas or hydrogen. Fourth International Topical Meeting on High Temperature Reactor Technology, 28 Sept.–1 Oct. 2008. Washington, D.C. USA.

List of abbreviations and acronyms

ACGLCC	–	Advanced Coal Gasification Large scale with Carbon Capture
BGL	–	Biomass Gasification Large scale
CCGL	–	Conventional Coal Gasification Large scale
CCGLCC	–	Conventional Coal Gasification Large scale with Carbon Capture
DMR	–	Dry Methane Reforming
FCI	–	Fixed Capital Investment
HHV	–	High Heating Value
HTGR	–	High Temperature Gas Reactor
HTS		High Temperature Shift
HTTR	–	High Temperature Test Reactor
HYS	–	Hybrid Sulphur Cycle
IHX		Intermediate Heat Exchanger
IRR	–	Internal Rate of Return
LHV	–	Low Heating Value
NGSRL	–	Natural Gas Steam Reforming Large scale
NGSRLCC	–	Natural Gas Steam Reforming Large scale with Carbon Capture
NPV	–	Net Profit Value
PBMR	–	Pebble Bed Modular Reactor
PBP	–	Payback Period
POX	–	Partial Oxidation
PSA	–	Pressure Swing Adsorption
ROI	–	Return on Investment
SMR	–	Steam Methane Reforming
STP	–	Standard Temperature and Pressure

List of symbols

$C_{p,i}$	−	Heat capacity of component i
ΔH^0_i	−	Enthalpy of component
T	−	Temperature
N_i	−	Number of moles of component
E	−	Energy
ξ	−	Extent of reaction
v_i	−	Stoichiometric coefficient of component

List of units

Nm^3	−	Normal cubic metres
kg	−	Kilogram
°C	−	Degree Celsius
K	−	Kelvin
barg	−	Absolute pressure
GJ	−	Gigajoule
MWe	−	Megawatt electrical
MWt	−	Megawatt thermal
kWh	−	Kilowatt hour
ml	−	Millilitre
wt%	−	Weight percentage

Chapter 1 - Introduction

1.1 Background

The world rotates around energy that is used to power industry, move people and products around the globe and provide safety and convertibility for everyone. Today's energy is supplied by fossil fuels, such as coal, natural gas and petroleum oil. But owing to the world's growing population more energy is needed; thus, more fossil fuels are used to supply the growing population with energy. Because of the increasing use of these fossil fuels, the pollution generated by the conversion of these fuels is a major concern to the world.

New energy solutions are needed to ensure economic growth, a decrease in environmental impacts and energy security through diversity. One simple element has the potential to provide all our energy services, namely hydrogen (H_2). Hydrogen can be produced by various processes, such as Steam Methane Reforming (SMR), Dry Methane Reforming (DMR), Auto Thermal Methane Reforming, Partial Oxidation (POX) of Methane and Electrolytic Hydrogen Production. Except for the last making use of water-splitting, the other methods make use of natural gas as feedstock for the production of synthesis gas and hydrogen.

Energy input is needed for the production of hydrogen from methane (natural gas) or water; thus, energy is needed to create energy. In order to produce the energy needed for the production of hydrogen, fossil fuels are used to supply the energy demand required by these processes. High quantities of fossil fuels are needed for the production of hydrogen and therefore it would be beneficial if hydrogen could be produced by a cleaner energy source, such as nuclear power in order to extend the lifetime of the world's fossil fuels. The two hydrogen production methods are displayed in Figure 1.1.

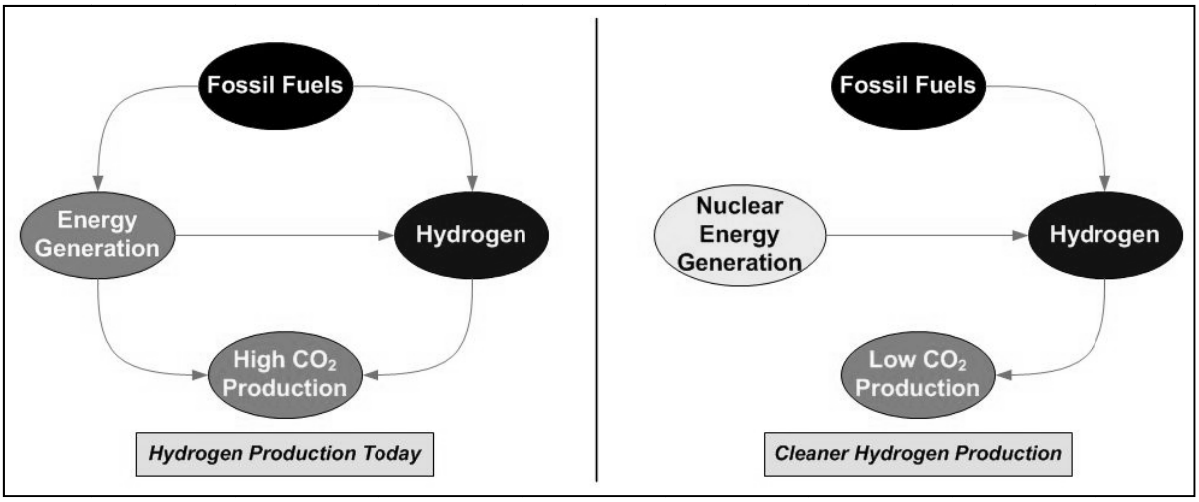

Figure 1.1: Hydrogen production methods

In the following chapter, SMR, DMR and Plasma Methane Reformation are discussed in more detail. Steam Methane Reformation is the most common process used in the industry today for the production of synthesis gas or hydrogen from natural gas. The process conditions under which these processes operate and the positive and negative aspects of each are investigated further.

1.2 Problem statement

This research project seeks to evaluate the feasibility of a Non-catalytic, Carbon Dioxide Methane Reforming process using the energy generated by a Pebble Bed Modular Reactor (PBMR) to power the Plasma-arc System for the production of synthesis gas or hydrogen.

1.3 Need and importance

Hydrogen produced by the above-mentioned processes makes use of fossil energy. An alternative process is therefore needed to produce hydrogen or synthesis gas, depending on the application and global demand. In addition to the global demand for hydrogen, the impact the process has on the environment is a significant concern.

The last two points mentioned form the driving force of the research in hydrogen production from natural gas. Using the process heat and the electricity generated by the nuclear reactor to drive the hydrogen process makes Plasma-arc Reforming a very good process of choice. The process also makes use of carbon dioxide as a reactant for the production of synthesis gas or hydrogen, thereby consuming a greenhouse gas rather than generating greenhouse gases.

1.4 Objectives of the research

The objectives of the research project are to:

- determine the number of 8 MW Plasma-arc Methane Reforming Units that could be powered by a 500 MW PBMR plant. The high temperature helium gas exiting the PBMR is to be used to generate electricity needed by the Plasma-arc units;

- determine the volume of synthesis gas that could be produced and the associated production cost thereof;

- determine the capacity of the water-gas-shift plant that is coupled to the plasma-arc gas reforming plant for the production of hydrogen, based on the available carbon monoxide;

- calculate the hydrogen production output of the plant and the cost of production and conduct a techno-economic evaluation of hydrogen production;

- compare the production cost of hydrogen, making use of the Non-catalytic Plasma-arc Gas Reforming Process with that of the conventional Catalytic Steam Gas Reforming Process; and

- conduct a sensitivity analysis, in order to determine the effect of the following parameters on the production of the synthesis gas/hydrogen:
  - cost of natural gas ($2/GJ – $8/GJ);
  - cost of electricity ($0.02/kWh – $0.06/kWh);
  - capital cost (increases by 5.0%, 10.0%, 15.0% and 20.0%); and
  - varying the H_2/CO ratio between 1:1 and 3:1 of the synthesis gas.

1.5 Benefits of the research

The findings of this research project will benefit many areas of the chemical industry. Several of the industries that will benefit from the results of the investigation are:

- the hydrogen industry – cleaner hydrogen that is produced through Plasma-arc Reforming Technology;
- the liquid fuels industry – through the variation of the synthesis gas ratio without the use of the WGS reaction reduces the cost of synthesis gas; and
- the metallurgical industry – the synthesis gas that is produced is used in the reduction reaction of metal oxides to metallic iron for the production of steel and alloys.

Chapter 2 - Literature survey

2.1 Introduction

In this chapter, the different reformation technologies that can be used for the production of synthesis gas and hydrogen from natural gas (methane) are investigated. The Plasma-arc Reforming Technology that is used in this research project for the production of synthesis gas or hydrogen is also examined.

2.2 Steam Methane Reforming

One of the most studied technologies for the production of hydrogen from fossil based fuels, such as natural gas, is SMR. Steam is reacted with methane over a catalyst to produce synthesis gas (Van Beurden, 2004; Dybkjaer *et al*., 1994).

Steam Methane Reforming consists of the following two reactions: steam reforming reaction is highly endothermic and the water-gas shift reaction that follows is moderately exothermic (Van Beurden, 2004):

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H^0_{298} = +206 \text{ kJ/mol} \qquad (1)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H^0_{298} = -41 \text{ kJ/mol} \qquad (2)$$

Owing to the steam reforming reaction being highly endothermic, it is favoured by high temperature and low pressures because of volume increase with reaction. The water-gas shift in contrast is favoured by low temperature and unaffected by pressure changes (Van Beurden, 2004).

2.3 Process description

A steam to carbon (methane) ratio of between 2.5 and 3.0 is maintained in the industry today. The conversion of methane in the reformer is controlled by the steam to carbon ratio; more steam means a higher conversion of methane, but more energy is required to produce the steam for the reforming process (Van Beurden, 2004; Dybkjaer *et al*., 1994; Gol & Dybkjaer, 1995).

The feed gas to the reformer is heated in a waste heat section of the tubular reformer that is used. The sulphur present in the natural gas is removed over a zinc oxide catalyst because the reforming catalyst is sensitive to sulphur. The cleaned feed gas is mixed with steam and further heated to 535°C before it enters the reformer. The reformed product gas leaves the reformer at a temperature of approximately 820°C (Dybkjaer *et al*., 1994). The conversion of methane in the steam reformer at the operating conditions is approximately 85.0% and the thermal efficiency of the process is 66.7% (Simpson & Lutz, 2007; Sogge Strom & Sundset, 1994).

The reformed gas is cooled before it enters the shift converters. The shift section can be a two-step section, which consists of a high temperature and low temperature shift reactor or only a one-step section, which is a high temperature shift (HTS) or a medium temperature shift reactor (Dybkjaer *et al*., 1994). The HTS reactor uses an iron-based catalyst, whereas the medium and low temperature shift uses a copper-based catalyst (Dybkjaer *et al*., 1994).

The carbon monoxide and steam is converted into carbon dioxide and hydrogen in the shift reactors. The unreacted carbon monoxide concentration in the product gas can be as low as 0.1% (Van Beurden, 2004). The gas is then cooled down to ambient temperature before it enters the Pressure Swing Adsorption (PSA) Init. The efficiency of the PSA Unit can be as high as 90.0% with a feed gas pressure of 30 bar (Dybkjaer *et al*., 1994). A layout of the described process can be seen in Figure 2.1 below.

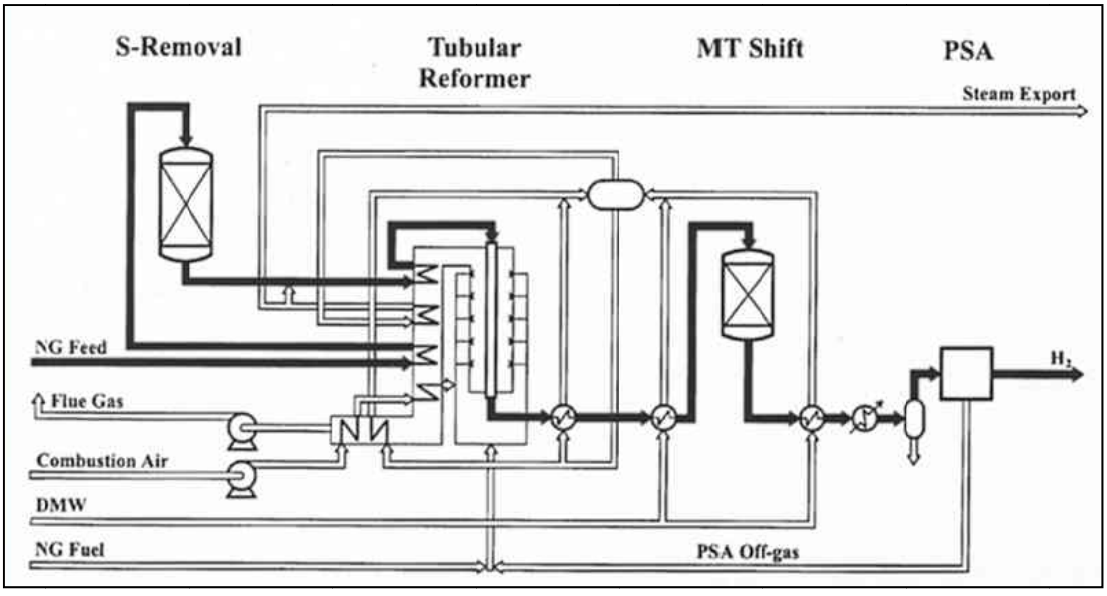

Figure 2.1: Natural gas-based hydrogen plant, typical process layout (Dybkjaer *et al*., 1994)

2.3.1 Negative aspects of steam reforming of methane

The negative aspect of Catalytic Steam Reforming of methane is discussed in this section. One of these negative aspects is the deactivation of the catalyst that is used in the reforming process.

There are four major causes of the deactivation of the catalyst during the reforming process, these causes are (Kirk-Othmer, 2001; Van Beurden, 2004):

- sintering;
- oxidation;
- sulphur poisoning; and
- carbon deposition.

Sintering

Sintering is the process of agglomeration of the crystallites of the active phase of the catalyst. This agglomeration of the crystallites leads to the loss of the active surface of the catalysts, which then results in a decrease in the activity of the catalyst. Ideally, during this process, crystallites are also formed that are less reactive than the crystallites that are lost (Kirk-Othmer, 2001; Van Beurden, 2004). The severity of and rate at which the sintering takes place depends on many factors, namely the metal used in the catalyst, the metal content, initial crystallite size and distribution, the nature of the support used and the conditions under which the reforming reaction takes place (Kirk-Othmer, 2001; Van Beurden, 2004).

Oxidation of the metal catalyst

Oxidation of the catalyst occurs at high steam-to-methane ratios and with low catalyst activities. The nickel catalysts used in the industry today for the reforming processes are prone to oxidation. The catalyst becomes deactivated owing to the oxidation of the metal phase, which is the active phase of the catalysts (Kirk-Othmer, 2001; Van Beurden, 2004).

The nickel catalyst is reduced by a hydrogen-rich gas before the catalyst is used in the SMR Process. At normal SMR operating conditions, sufficient hydrogen is produced to keep most of the active phase during the process reduced (Kirk-Othmer, 2001; Van Beurden, 2004).

Sulphur poisoning of the catalyst

The poisoning of the catalyst blocks the active phase surface area. It may even change the atomic structure of the catalyst used, which then reduces the activity of the catalyst (Kirk-Othmer, 2001; Van Beurden, 2004). Some of these poisons are arsenic, copper, vanadium, lead, sulphur and chlorine.

Sulphur is the most severe poison that affects the steam reforming catalysts. If the feed gas to the reformer contains more than 5 ppm of sulphur at a temperature of 800°C, it becomes poisoned and the activity of the catalysts reduced. The sulphur is present in the form of H_2S (hydrogen sulphide). The sulphur can be removed from the catalyst by oxidation and reduction of the catalyst (Kirk-Othmer, 2001; Van Beurden, 2004).

Carbon deposition on the catalyst

Carbon deposition is a frequently experienced phenomenon with catalytic SMR. At the operation temperature for the reforming process, some of the methane is decomposed and carbon is deposited on the catalyst; this is mainly observed in the first half of the reformer tubes where the methane concentrations are still high (Kirk-Othmer, 2001; Van Beurden, 2004). The deposition of the carbon on the catalysts causes serious operational problems and the deactivation of the catalyst (Kirk-Othmer, 2001).

Because Catalytic Steam Reforming is a highly endothermic reaction, high activity of the catalyst leads to low temperature reaction rates, thus increasing the risk of carbon formation of the catalyst (Kirk-Othmer, 2001). Carbon formation on the noble metal catalysts is far less than on the nickel catalysts used in the industry today (Kirk-Othmer, 2001).

The conclusion regarding the four major causes of catalytic deactivation is that the feed stream needs to be desulphirised and a steam to methane ratio has to be maintained.

The deactivated catalyst needs to be reactivated at a cost and this in turn increases the production cost of hydrogen from methane. The catalyst must also be changed every few years owing to the decreases in the active phases of the catalysts used. Noble metal catalysts can be used owing to their resistance to sulphur poisoning and carbon formation, but these catalysts are more expensive, which will then increase the cost of hydrogen when used.

2.4 Dry Methane Reforming

2.4.1 Process description

Catalytic Dry Reforming of Methane or also known as Catalytic Carbon Dioxide Reforming of Methane is an alternative to Catalytic Steam Reforming of methane for the production of synthesis gas or hydrogen (Ullmann's, 2006; Van Beurden, 2004). In this case, carbon dioxide is used as the oxidising agent instead of steam. The reaction that takes place in the reformer is given by reaction equation (3) and is more endothermic than (1) thus more thermal energy is needed for the reforming process to take place.

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \qquad \Delta H^0_{298} = +247 \text{ kJ/mol} \qquad (3)$$

Dry reforming is more attractive than steam reforming from an environmental point of view because carbon dioxide is consumed as a reactant and not produced as is the case in steam reforming (Van Beurden, 2004). The same catalysts that are used in steam reforming can also be used in the dry reforming process. But this process is not used as widely in industry as steam reforming owing to the risk of high carbon deposition on the catalyst surface. A process flow diagram is given in Figure 2.2 below.

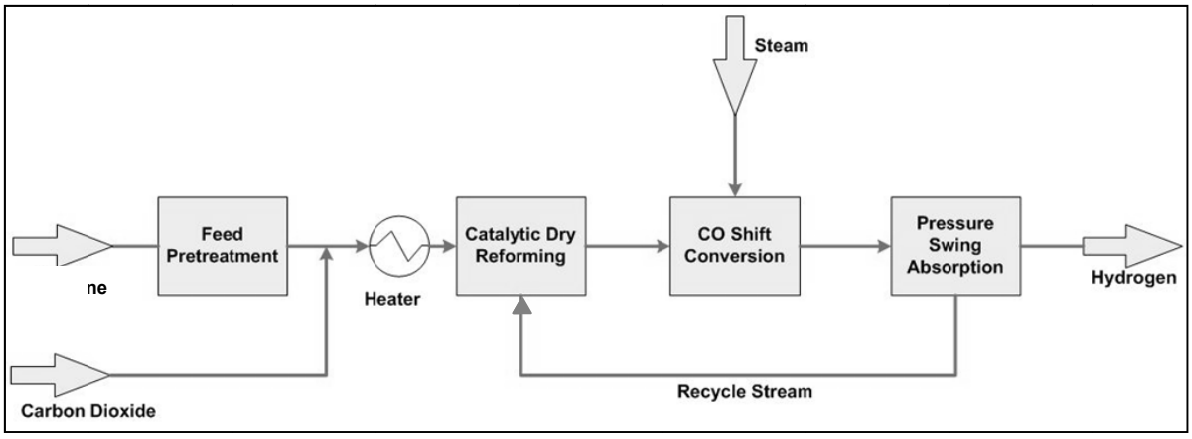

Figure 2.2: Block flow diagram of Catalytic Dry Reforming of Methane

Several attempts have been made to improve the catalyst's performance used in this reforming process, which is discussed in the next section (Van Beurden, 2004). The hydrogen to carbon monoxide present in the synthesis gas has a ratio of 1:1. In order to increase the hydrogen production or to vary the hydrogen to carbon monoxide ratio, the

carbon monoxide can be converted into hydrogen in shift converters by means of the water-gas shift reaction.

2.4.2 Investigation into the different catalysts that can be used in the Dry Reforming of Methane Process

Extensive research has been carried out to attempt to improve the lifetime of the catalysts that are used in the Dry Reforming of Methane Process. Several of the catalysts under investigation are (Roh, Jun, Baek & Park, 2002; Zhang, Tsipouriari, Efstathiou & Verykios, 1996; Lemonidou & Vasalos, 2002; Gokon, Oku, Kaneko & Tamaura, 2002):

- Ni/θ-Al_2O_3;
- Supported Rh;
- 5wt% Ni/CaO-Al_2O_3; and
- FeO catalyst in molten salt.

The catalysts were first pre-treated with hydrogen prior to loading into the reactors for the reforming of methane to synthesis gas.

The operating temperature for these catalysts varied in the range between 600°C and 1 000°C and flow rates between 20ml/min and 200ml/min. The feed ratio of methane to carbon dioxide is controlled at 1:1 (Roh *et al*., 2002; Zhang *et al*., 1996; Lemonidou *et al*., 2002; Gokon *et al*., 2002).

The results of these investigations seemed very promising for the industrial reforming of methane with carbon dioxide as the oxidising agent. The conversions that were achieved varied between 33.0% and 95.0% in the reformer units under the operating conditions mentioned above. Several of these results are given in Figure 2.3 and Figure 2.4 below.

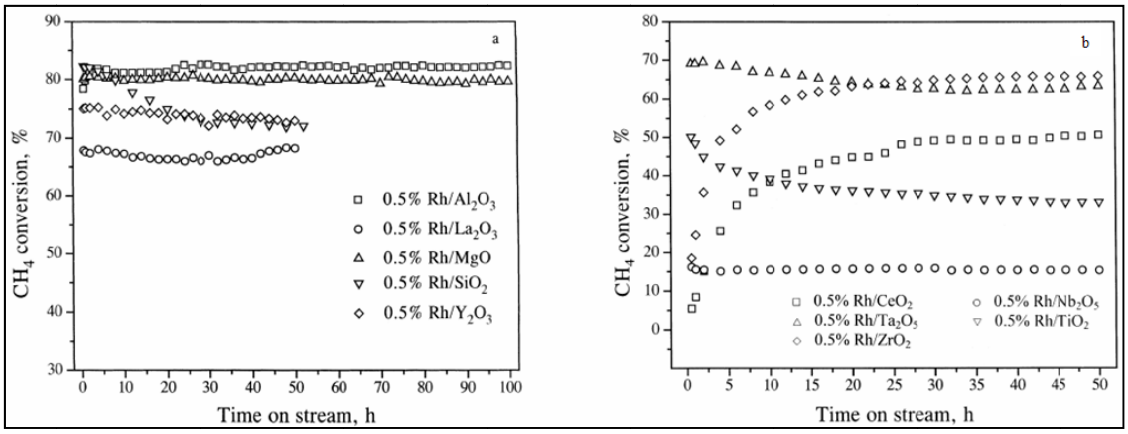

Figure 2.3: Time-dependent conversion of CH_4 over Rh catalyst with irreducible metal oxides (a) and reducible metal oxides (b; Zhang *et al*., 1996)

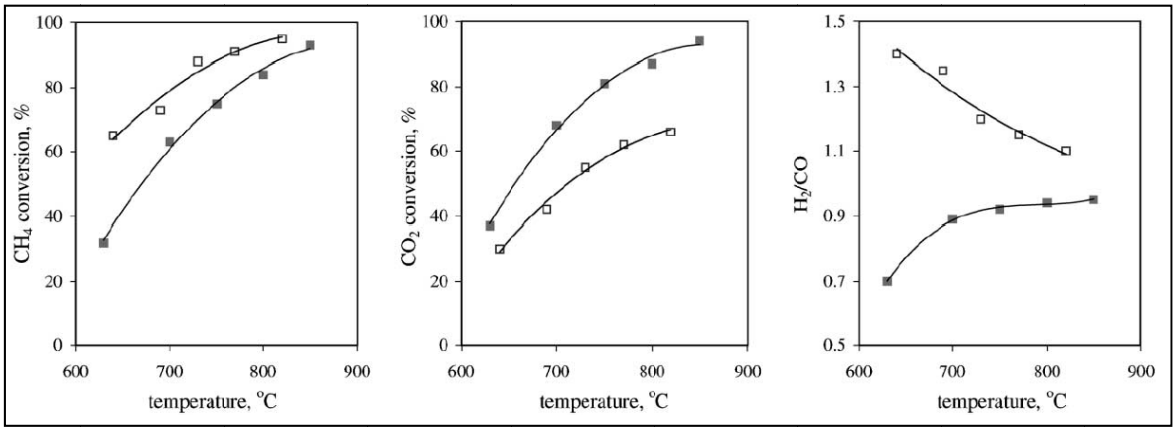

Figure 2.4: The performance if the 5 wt% Ni/CaO-Al2O3 catalyst is plotted against temperature (□ CH_4:CO_2:H_2O, ■ CH_4:CO2; Lemonidou *et al*., 2002)

From these investigations, it was also observed that the time methane and carbon dioxide spent in the presence of the catalysts had a significant effect on the conversion of methane.

2.5 Non-catalytic Partial Oxidation of Methane

The gasification process of heavy oils most commonly used in the industry is POX (Ullmann's, 2006). During the POX Process the hydrocarbon reacts with oxygen to produce synthesis gas, this reaction is shown in reaction equation (4).

$$CH_4 + 0.5O_2 \rightarrow CO + 2H_2 \qquad \Delta H^0_{298} = -37.5 \text{ kJ/mol} \qquad (4)$$

2.5.1 Process description

The POX process can produce a wide range of hydrogen-to-carbon monoxide ratios, by making use of different types of feedstock. Also by the addition of steam or recycling of carbon dioxide to the reactor the ratio can be varied. A flow diagram of the POX Process is shown in Figure 2.5.

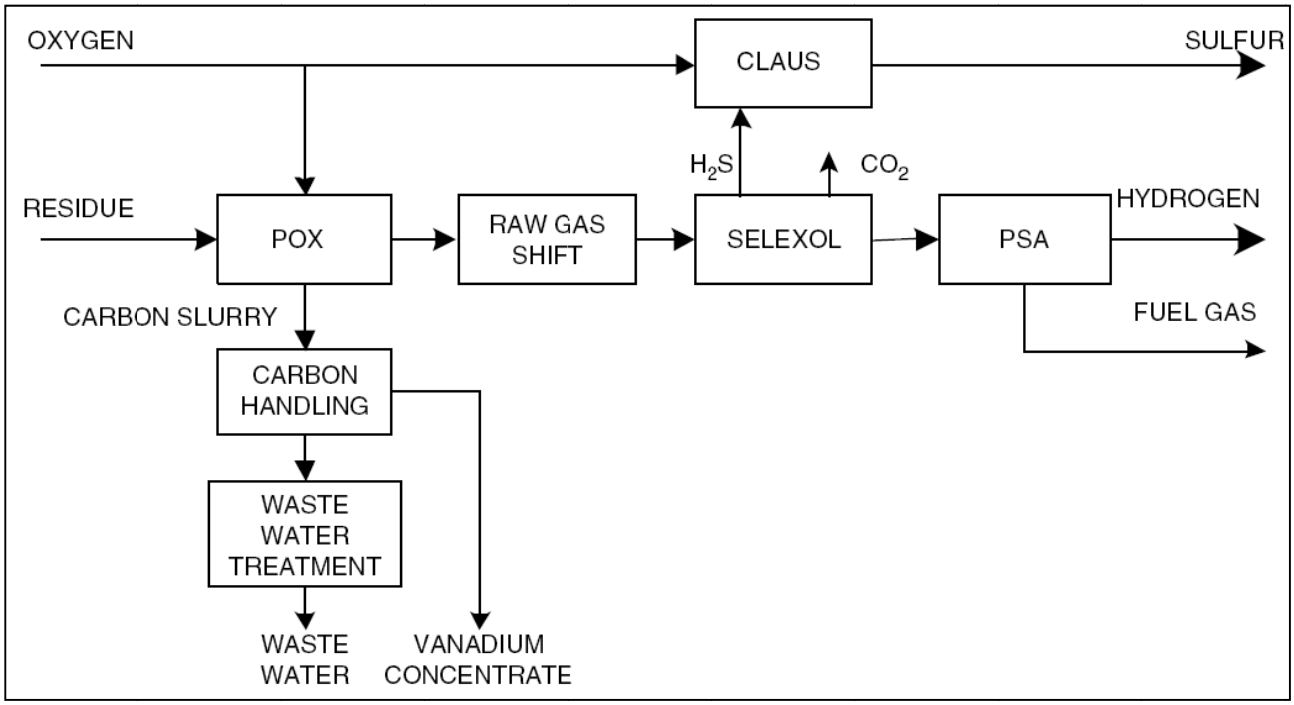

Figure 2.5: Hydrogen production plant making use of the Partial Oxidation Process for synthesis gas production (Higman & Van der Burgt, 2003)

The complete combustion of the hydrocarbons, such as natural gas, takes place between temperatures of 1350°C to 1600°C and pressures as high as 80 bar (Sogge *et al*., 1994; Higman & Van der Burgt, 2003). Hydrogen and carbon monoxide are the main products that form in the reactor until all the hydrocarbons have completely been converted into these two products, only will water and carbon dioxide then be formed from the remaining oxygen in the reactor (Ullmann's, 2006).

The water that is added to the POX process keeps the temperature low, ensuring that there are not extensive temperature increases in the reactor. The conversion of methane at the operating conditions is close to 98.0%. The composition of the feed stream and product stream is given in Table 2.1 (Sogge *et al*., 1994). Carbon is produced as a by-product in the reactor and needs to be removed before the synthesis gas can be used further. A schematic diagram of the Texaco POX Reactor with quench cooling and synthesis gas cooler is given in Figure 2.6 following the table.

Table 2.1: Gas composition of the Partial Oxidation of Methane (Sogge *et al*., 1994)

	Feed gas composition	Product gas composition
Temperature (°C)	331.7	1204.8
Pressure (kPa)	8537.0	8330.0
Molar flow rate (kmol/h)		
CH_4	2644.4	33.1
C_2H_6	273.2	–
C_3H_8	121.9	–
C_4H_{10}	91.3	–
CO_2	55.5	635.8
CO	1.8	3310.4
H_2O	2651.4	3078.0
O_2	2447.7	–
H_2	40.9	6601.6
N_2	32.8	32.8
CH_3OH	0.4	–

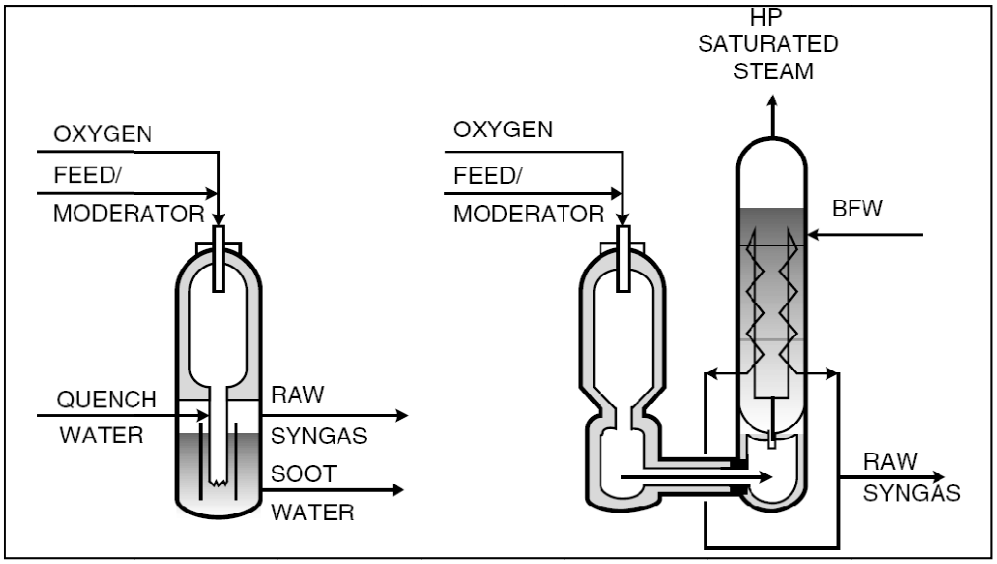

Figure 2.6: Texaco POX Reactors with quench cooling and synthesis gas cooler (Highman & Van der Burgt, 2003)

The raw synthesis gas leaves the reactor and is cooled to a temperature of about 250°C and pressure of 80 bar. The synthesis gas enters the quench, where it is cooled and saturated with water; approximately 2 kg H_2O per Nm^3 of synthesis gas is added (Higman &

Van der Burgt, 2003). This high water loading makes the quenched synthesis gas suitable for the water-gas-shift reaction. The quench removes the bulk of solids (carbon) from the synthesis gas and is extracted from the quench as black water (Higman & Van der Burgt, 2003).

The cooled synthesis gas then enters a scrubber unit, where it is scrubbed with water to remove any final traces of carbon from the gas before the sulphur that may be present in the gas is removed from the system. After the sulphur has been removed, the synthesis gas is fed to the shift reactors, where more hydrogen is produced. Finally, the hydrogen is recovered from the product gas of the shift reactors with a final purity of 99.0% (Higman & Van der Burgt, 2003).

2.6 Plasma-arc Methane Reforming

Hydrogen is mainly produced from natural gas using the conventional SMR process, which has already been discussed in this chapter. A new process would be advantageous for the production of hydrogen from natural gas in the absence of a catalyst, although a catalyst can also be used in Plasma-arc Reforming, depending on the process selection.

The technical application of the Plasma-arc Reformer Units in the chemical industry dates back to the beginning of the twentieth century, where it was used for the production of nitrogen oxides from air, which forms the basis for the production of fertilisers. The technology was also used for the production of acetylene from light hydrocarbons (Müller & Kerker, 1984). Plasma processes can be divided into three categories as shown in Table 2.2 below.

Table 2.2: Plasma processes (Müller & Kerker, 1984)

Process	Temperature (K)	Electrical achievement	Application
Nuclear fusion	> 1 000 000	> 100 MW	Energy production
Thermal plasma	1 000 – 10 000	0.1 – 10 MW	Chemical reactions, Heating of gases
Low pressure plasma	100 – 1 000 (Gas) 1 000 – 100 000 (Electrical)	1 W – 1 kW	Polymerisation, Semiconductor technology corrode (protective layers)

These plasma processes have the following advantages (Müller & Kerker, 1984):

- saving of high-quality fossil raw materials: electricity that is used to produce the heat necessary for the chemical reaction can be generated by an inferior fossil or a non-fossil fuel basis;
- achievement of high temperatures and high power densities; and
- a solution to the technical and ecological problems that arise as a result of conventional technology.

Temperatures above 3 000°C can be generated in the Plasma-arc Reformers using electricity (Bromberg *et al*., 2000). The energy that is generated inside the reformer is independent of chemical reaction taking place, and optimal operation conditions can be maintained over a wide range of flow rates and feed compositions (Bromberg *et al*., 2000). High energy density is created by the plasma reformer and the chemical reaction time is decreased, which results in a short residence time for the reactants to be converted into products (Bromberg *et al*., 2000).

A wide range of hydrocarbons can be used for the production of hydrogen with conversions of the hydrocarbons close to 100.0% with the plasma reformer (Bromberg *et al*., 2000). The plasma reformers accelerate thermodynamically favourable chemical reactions without the use of a catalyst or provide the energy needed by endothermic reactions (Bromberg *et al*., 2000).

Two types of plasma reformers are discussed, namely the Hüls Plasma-arc Furnace (commercialised) and the Glidarc (under development) reformers. Attention is given to the operating conditions, the general functioning of the reformers and the conversion achieved through experimental investigations.

2.6.1 Hüls Plasma-arc Furnace/Torch

2.6.1.1 Operation of the Plasma-arc Furnace

In 1985, the Union Steel Corporation of South Africa and Chemische Werke Hülls constructed the first 3×8 MW Plasma-arc Reforming plant in South Africa. The plasma-arc reactors were designed to convert SASOL gas (GASCOR gas) into synthesis gas. The synthesis gas was used as a reductant to reduce iron oxide into metallic iron for the

production of direct reduced iron. The Plasma-arc Reforming plant was operated successfully and high chemical and thermal efficiencies have been obtained.

The working of the Hüls plasma-arc furnace is discussed, addressing the core arrangement, generator arc stabilisation and efficiency control (Müller & Kerker, 1984).

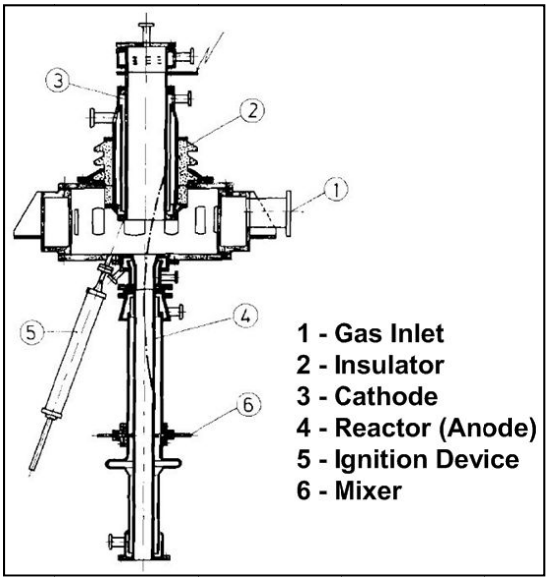

Figure 2.7: Hülls Plasma-arc Furnace (Müller & Kerker, 1984)

Core arrangement: the core arrangement of the Hüls Plasma-arc Furnace is shown in Figure 2.7 above. The stabilisation of the arc in the core is essential for maximum conversion of the feed gases (Müller & Kerker, 1984). Stabilisation is defined as:

- the burning of the elbow in the pre-determined area; and
- the rotation of the elbow starting points on the electrodes, to achieve an even burn-up conversion.

Generator arc stabilisation: in the centrifugal chamber of the furnace, the tangentially attached slots form a gas eddy that stabilises the arc (Müller, 1982; Müller & Kerker, 1984). The Plasma-arc Furnace consists of a cylindrical water-cooled pipe constructed from ordinary carbon steel. The upper cylindrical pipe is the cathode, which is insulated and connected to a direct current potential of 7 to 8 kV (Müller, 1982; Müller & Kerker, 1984). The lower cylindrical pipe is the grounded anode of the furnace.

The gas with a pressure of between 1 – 2 barg enters the plasma chamber tangentially where the gas whirl (vortex) is formed, which makes it almost possible for the arc to be distributed over the entire length of the unit. The lifetime of the anode and the cathode is approximately 800 – 1 000 hours for a 1.2 kA and 8 MW Plasma-arc Furnace unit, owing to

the hydrocarbon atmosphere inside the plasma chamber (Müller, 1982; Müller & Kerker, 1984). The methane gas that is cracked deposits a thin layer of carbon on the cathode surface, which extends the lifetime of the cathode.

Efficiency control: Approximately 80.0% to 90.0% of the energy (power) is transferred from the arc to the gas; the remaining energy is lost owing to the water-cooled anode and cathode (Müller & Kerker, 1984). The gas is heated in the furnace to a temperature range of 2 000°C and 5 000°C (Müller & Kerker, 1984). Part of the gas forms the arc between the cathode and anode. The temperature in the furnace reaches more than 15 000°C in the centre of the arc in a few milliseconds and the gas becomes ionised (Müller, 1982).

2.6.1.2 Experimental investigation of the Plasma-arc Furnace

A Plasma Reforming pilot plant was constructed in the 1980s. Three types of Hüls Plasma-arc Furnaces were used for the experimental investigation of the reforming of methane using steam. The three types were 6.2, 7.8 and 8 MW units (Müller & Kerker, 1984). Figure 2.8 presents a block diagram of the plasma reforming plant for the experimental reforming of methane. The feed gas to the gas-mixing unit consists mainly of natural gas (methane), and the oxidising agent could be either steam or carbon dioxide (Müller & Kerker, 1984).

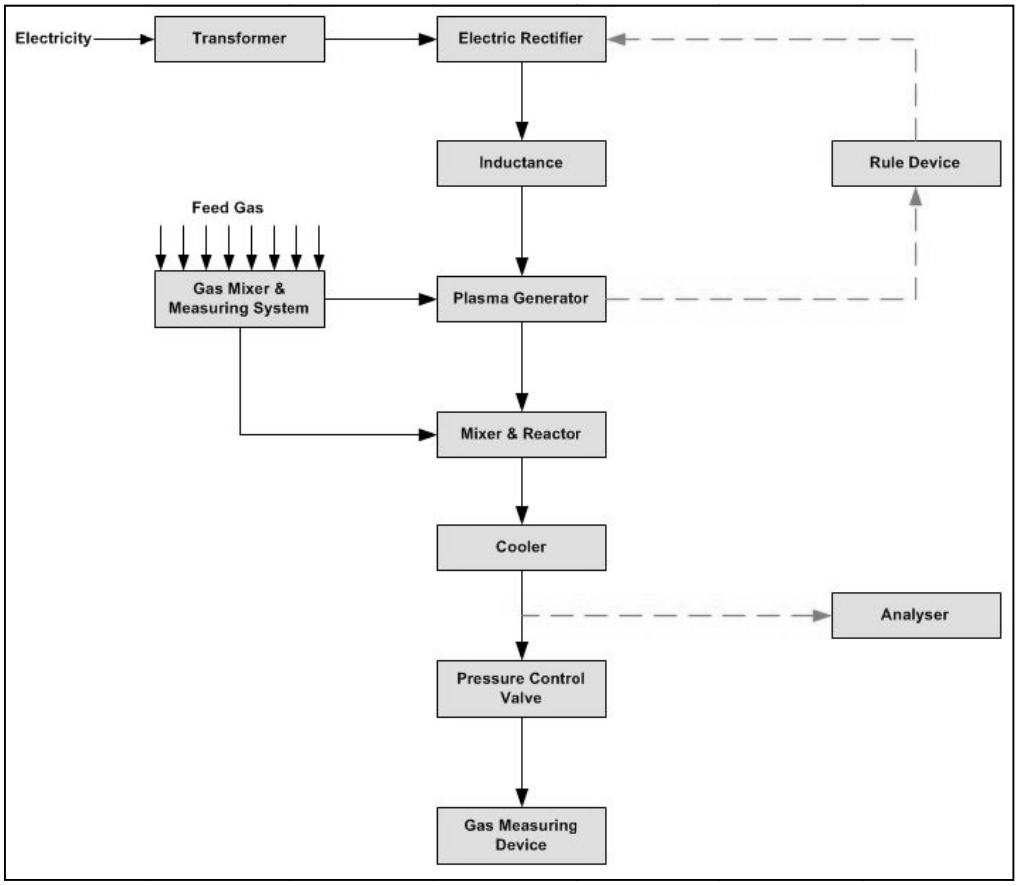

Figure 2.8: Plasma reforming pilot plant (Müller & Kerker, 1984)

By making use of the three types of plasma generator units in the pilot plant setup, the following test results were obtained, which are given in Table 2.3 on the following page.

The Union Steel Corporation used three Plasma-arc Reformer Units of 7 MW each that could be enlarged to 8.5 MW units. The methane-rich gas (SASOL gas) was produced by liquefaction of coal and was used as feed gas with a composition (volume %) of 47.0% H_2, 22.0% CO, 3.0% CO_2, 27.0% CH_4 and 1.0% N_2 (Müller & Kerker, 1984). The methane-rich gas was mixed with steam in a ratio of 1:1 and the mixed gas was pre-heated to 850°C. The reformed gas left the Plasma-arc Reformer Units at a temperature of 1 100°C with a final composition of 70.0% H_2, 25.2% CO, 1.3% CO_2, 0.9% H_2O and 2.4% N_2. The final composition consisted of more than 90.0% hydrogen and carbon monoxide (Müller & Kerker, 1984).

Plasma-arc reforming of natural gas has the following three advantages (Müller & Kerker, 1984; Kaske, Kerke & Muller, 1986):

- The process can be driven at very low ratios of oxidising agents to natural gas (close to stoichiometric values). This results in small amounts of carbon dioxide and steam in the product gas, which causes a high reduction potential of the gas.
- In order to achieve a high conversion of methane in the reactor unit, the exhaust gas from the plasma generator must be higher than 1 000°C. Both the retention time of the gas in the reactor unit and the size of the unit are affected by the feed gas composition.
- Desulphurisation of natural gas is unnecessary when making use of a plasma-reforming process.

Table 2.3: Test results of the plasma reforming pilot plant (Müller & Kerker, 1984)

Measuring range	Unit	Results		
Electrical achievement Plasma-arc Furnace	MW	6.2	7.8	8.0
Gas to plasma reforming	Nm^3/h	7 000	6 300	6 300
Thermal efficiency	%	83	85	92
Hydrogen/methane ratio	mol/mol	1.1	1.26	1.05
Exhaust gas temperature	°C	1 040	1 160	1 250
CH_4-content in exhaust gas	vol%	9.0	3.6	3.0

2.6.2 Glidarc (Gliding arc)

2.6.2.1 Functional working of the Glidarc Plasma Reformer

Experimental investigation of the conversion of natural gas to synthesis gas has been conducted using a bench-scale Gliding-arc Reformer (Czernichowski, 2001). The Glidarc-I has at least two diverging knife-shaped electrodes and is immersed in a fast-flowing gas stream (Czernichowski, 2001). A sketch of the Glidarc-I is shown in Figure 2.9.

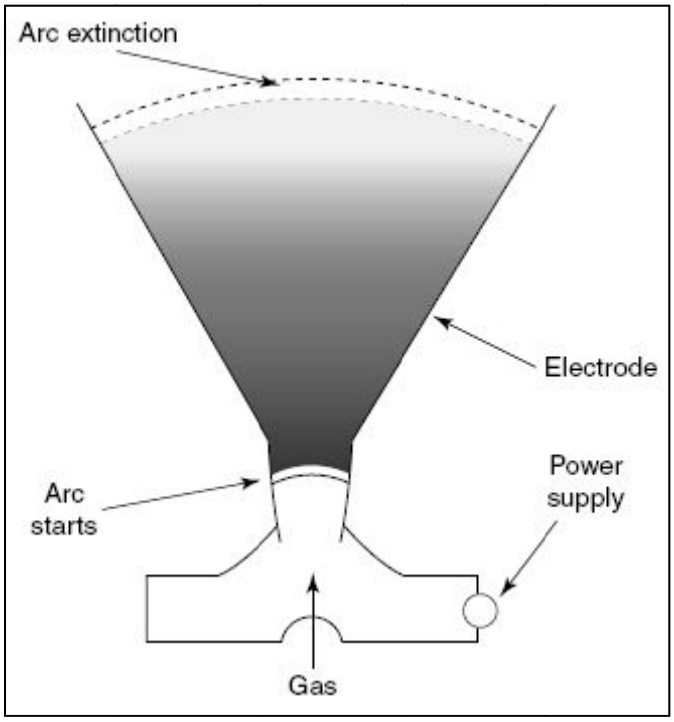

Figure 2.9: A schematic diagram of the Glidarc-I (Czernichowski, 2001)

A high voltage with a low current arc is formed between the electrodes in the gas flow; the arc forms between the closest points and glides along the electrodes and disappears (Czernichowski, 2001). The electrodes do not have to be cooled during the reforming process, which means that the total electrical energy is transferred to the process gas (Czernichowski, 2001). A voltage of 20 kV is used with a current as high as 50 A. The pressure range for the system can vary between 5 kPa and 1.2 MPa (Czernichowski, 2001).

2.6.2.2 Experimental investigation of the Glidarc-I Plasma Reformer

During the experimental investigation of the Glidarc-I Plasma Reformer, natural gas with the following composition was used (volume percentages): 91.0% methane, 6.7% ethane, 1.1% propane, 0.3% butane and 0.9% nitrogen (Czernichowski, 2001). The results of the experimental investigation are given in Table 2.4.

Table 2.4: Steam, dry and mixed steam/CO_2 reforming of natural gas (Czernichowski, 2001)

Example		G1	G2	G3	G11	G12	G21
Input (L(n)/h)	Hydrocarbon	424	424	424	328	328	495
	CO_2	0	0	0	438	438	52
	Steam	473	606	785	0	0	332
Specific energy input	kWh/m^3(n)	1.1	1.0	0.9	0.75	1.4	1.2
Temperature (°C)	Preheat	220	215	215	140	165	240
	Reaction	630	590	560	290	380	665
H_2/CO	mol/mol	3.9	3.8	3.8	0.84	0.82	3.3
Specific energy requirements							
H_2 + CO	kWh/m^3(n)	3.0	3.2	3.2	2.6	3.6	2.9
CO	kWh/kg	12	12	12	3.9	5.3	9.9
Carbon converted	%	25	24	24	17	23	23

As can be observed from the table above, the energy input varied between 1.4 and 0.7 kWh/m^3. The conversions achieved are expected to be low owing to the very low operating temperatures but can be increased with increasing energy input to the system (Czernichowski, 2001).

2.7 Combined methane reforming

A simultaneous reforming process has recently been studied owing to the increase of the greenhouse gases, such as carbon dioxide. Investigations that have been conducted suggest that such a process is possible and has great advantages. During the simultaneous reforming process, the following two reactions take place with methane:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H^0_{298} = +206 \text{ kJ/mol} \qquad (5)$$

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \qquad \Delta H^0_{298} = +247 \text{ kJ/mol} \qquad (6)$$

A feed mixture consisting of CO_2, CH_4 and steam is fed over a $NdCoO_3$ perovskite-type mixed metal-oxide catalyst (Gesser, Hunter, Shigapov & Januati, 1994). The CO_2/H_2O ratio is controlled between 0.0 and 2.4, whilst the $(H_2O + CO_2)/CH_4$ ratio is kept constant at 1.06. Changing the ratio of the CO_2/H_2O has been shown to have an effect on the conversion of methane, hence the H_2/CO ratio (Gesser *et al*., 1994).

The results obtained indicate that the conversion of both CO_2 and H_2O was kept above zero, there was no net formation of side products and the selectivity for both the desired products formed was 100.0% (Gesser *et al*., 1994).

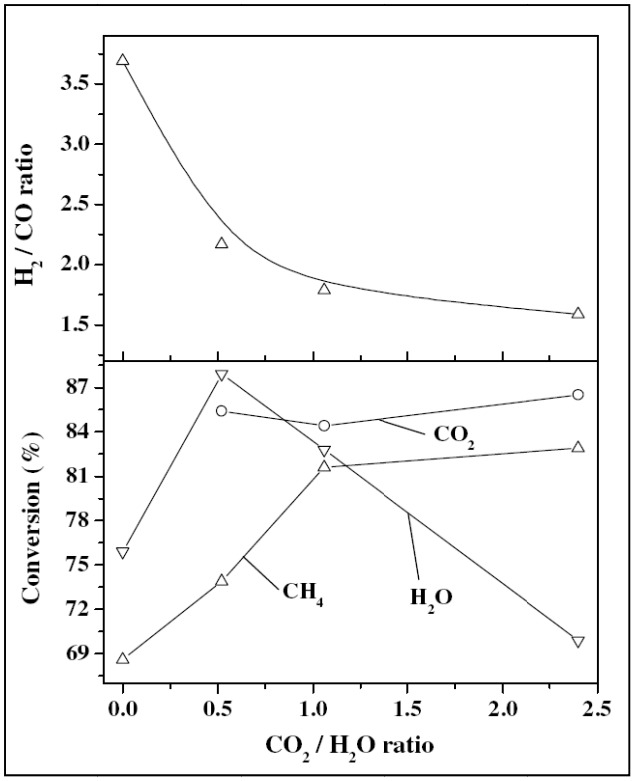

Figure 2.10: The effect of CO_2/H_2O ratio on the conversion of methane and the H_2/CO ratio (Gesser *et al*., 1994)

By changing the feed ratio of the CO_2/H_2O, the production ratio of H_2/CO can be controlled, as seen in Figure 2.10 above. Through this investigation, it can be seen that by controlling the feed ratio of the reactants, the ratio of the products can be controlled. This shows that simultaneous CO_2 and steam reforming is a viable option for the chemical industry because the preferred ratio of H_2/CO can be obtained to satisfy needs of the chemical and petrochemical industry.

2.8 The water-gas-shift reaction

The water-gas shift reaction is used with the SMR, DMR and POX process for the additional production of hydrogen or variation of the synthesis gas ratio. This reaction is an exothermic reversible reaction that makes use of a catalyst. The water-gas-shift reaction is the reaction between water and carbon monoxide for the production of hydrogen and carbon dioxide, the reaction equation is given as:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H^0_{298} = -41 \text{ kJ/mol} \qquad (7)$$

The water-gas-shift reaction can be seen as an example of equilibrium controlled chemical reaction. The equilibrium constant (K_p) of the water-gas-shift reaction can be calculated using the following expression, which is valid for the temperature range 315 to 480°C (Newsome, 1980):

$$K_P = \exp\left[\left(\frac{4577.8}{T}\right) - 4.33\right], \text{ where T is in K.}$$

In order to reduce the CO to 1.0% for a feed gas with a ratio 1 for CO/H_2 at a temperature of 370°C, a steam-to-gas ratio of 3.5 is needed, and for a temperature of 500°C the steam-to-gas ratio has to be 10.5 (Newsome, 1980). Thus, it is desirable for the reaction to take place at a lower temperature, as less steam is needed.

The water-gas-shift reaction is not dependent on the pressure of the system, as the amount of moles of material in the shift reaction does not change during the reaction. Two types of catalyst are used in the industry for the conversion of carbon monoxide in the reactors. The first catalyst is an iron-based catalyst that operates at a temperature of between 320°C and 450°C (Newsome, 1980). This catalyst is mainly used in the HTS reactor, and it can tolerate small amount of sulphur. The second catalyst is a copper-based catalyst that operates at lower temperatures, between 200°C and 250°C (Newsome, 1980).

2.9 Hydrogen economy

The hydrogen economy is driven by concerns about oil dependence, the impact of greenhouse gases on the environment and the recognition of the benefits of hydrogen (Kirk-Othmer, 2001; Mueller-Langer, Tzimas, Kaltschmitt & Peteves, 2007). At present 77.0% of the hydrogen produced in the industry is produced from natural gas, 18.0% from coal, 4.0% by electrolysis and 1.0% from other sources (Ullmann's, 2006). Hydrogen offers the following significant advantages (Mueller-Langer *et al*., 2007):

- It can be used in any sector where energy is required, such as transport, households, services and in industry.
- It can be stored in small or large quantities for long periods with small losses, unlike electricity.

- Hydrogen is almost free of emissions, such as CO_2, acid gases and other greenhouse gases. The only by-product is water vapour.
- It can be produced from a wide range of raw materials, as stated above.

There are three points that are crucial for the production of hydrogen in a growing hydrogen economy: the production of hydrogen efficiently, at a minimum cost and in an environmentally friendly manner (Mueller-Langer *et al*., 2007). Approximately 95.0% (54 million tons) of hydrogen produced in the world today is captive; only 3 million tons are traded. Hydrogen is mainly produced from fossil fuels, making use of the processes discussed in the previous section (Mueller-Langer *et al*., 2007). Other processes that are also used for the production of hydrogen are coal gasification, biomass gasification and electrolysis of water (Mueller-Langer *et al*., 2007).

Table 2.5: Hydrogen production and CO_2 mitigation costs (Mueller-Langer *et al*., 2007)

Concepts	**Steam-reforming concepts**		**Gasification concepts**			
	NGSRL	NGSRLCC	CCGL	CCGLCC	ACGLCC	BGL
Hydrogen production cost ($/GJ)	13.40	15.60	13.40	18.86	16.36	18.70
CO_2 mitigation costs ($/$t_{CO2}$)	-	40.21	-	30.70	21.05	-

From Table 2.5, it can be seen that the hydrogen production cost is lower using steam reforming of natural gas technologies than the gasification of coal for the production of hydrogen. The production cost of hydrogen in steam reforming plants depends mainly on the price of natural gas (Mueller-Langer *et al*., 2007). Capital cost has a high impact on the total hydrogen production cost when using a coal gasification process, as can be seen from Table 2.6. Should the plant output decrease by 20.0%, the hydrogen production cost in the case of steam reforming plants will increase by 5%, and that for coal gasification by 18.0% (Mueller-Langer *et al*., 2007).

Table 2.6: Technical and base data for economical analysis (Meuller-Langer *et al*., 2007)

Concept	Large scale					
	Natural gas steam reforming		Coal gasification			Biomass gasification
	Conventional	Conventional with carbon capture	Conventional	Conventional with carbon capture	Advanced with carbon capture	
Abbreviation	NGSRL	NGSRLCC	CCGL	CGLCC	ACGLCC	BGL
Technical data						
Production rate (1000 Nm^3/h)	20 – 250	20 – 250	>100	>100	>100	20 – 150
Energy content (MWt)	60 – 750	60 – 750	>300	>300	>300	60 – 450
System characteristics	Refinery-type reformer	Refinery-type reformer	EF gasifier, cold gas cleaning	EF gasifier, cold gas cleaning, physical scrubbing	EF gasifier, hot gas cleaning, O_2 combustor	CFB gasifier, cold gas cleaning
Annual load (h/a)	7 884	7 884	7 008	7 008	7 008	7 008
Overall efficiencies (%)	70 – 80	-	49 – 53	-	-	-
Database for the economic analysis						
Mass and energy flow – base case						
Feedstock input (unit/h)	65 000 Nm^3	60 000Nm^3	120 t	118 t	91 t	203 t
Auxiliary electricity input (MWe)	5	13	36	65	66	40
Net by-products (MW_{unit})	140 MWt	40	43 MWe	13 MWe	6 MWe	-
Separated CO_2 (t/h)	-	88	-	291	230	-
Cost data – base case						
Total capital investment (1000$/MWt)	234 000	267 000	585 000	671 000	523 033	653 480
Specific total capital investment (1000$/MWt)	519	592	1 300	1 491	1 161	1 453
Operation & maintenance costs (1000$/a)	12 359	30 297	26 978	69 900	55 732	27 087
Specific O & M (1000$/MWt)	28	67	59	156	123	61
Feedstock costs ($/GJ)	8.4	8.4	3.27	3.27	3.27	6.65

Chapter 3 - Nuclear energy for synthesis gas or hydrogen production

3.1 Introduction

Nuclear energy has become an important energy source over the last fifty years and approximately thirty countries make use of nuclear-generated energy for the production of electricity. A total of 440 nuclear reactors are used to produce a total capacity of 360 GW(e) (Verfondern & Nishihara, 2005). Nuclear-generated energy is such a viable energy source because the energy created is carbon dioxide free.

The energy that is generated is not only limited to the production of electricity, but the thermal energy use is an added advantage for use in the chemical and petroleum industry. The production of synthesis gas or hydrogen using nuclear heat and electrical energy has become more important over the past few years. Many processes have been considered for the production of hydrogen using nuclear energy. One such process is SMR, which was discussed in Chapter 2. This chapter considers the combination of the SMR with a nuclear facility.

3.2 Nuclear-type reactor

A High Temperature Gas Reactor (HTGR) is used for the production of synthesis gas or hydrogen because of the following characteristics (Verfondern, 2005):

- low power modular unit;
- low power density;
- graphite core structures;
- coated particle fuel; and
- helium gas coolant.

Many new promising nuclear-reactor concepts were presented in 2002 for the next generation in nuclear-type reactors. The aim of these concepts is to deliver electrical and heat energy, hydrogen and clean water (Verfondern, 2007).

These new and even revolutionary nuclear-reactor technologies are expected to give convincing answers to the challenges that are now faced in the industry namely, improved safety, reduced cost, minimised waste and enhanced resistance against sabotage and proliferation (Verfondern, 2007).

A HTGR makes use of UO_2 kernels that are embedded in a graphite matrix to form the fuel elements for either a block-type or pebble-type HTGR (Verfondern, 2005). Helium gas is used as the cooling medium because it is an inert gas and no phase changes will occur during the high operating temperatures. The gas is heated to 950°C, which reduces the heat transfer area and improves efficiency (Verfondern, 2007).

The fuel temperature should stay below 1 300°C, in order to avoid larger release rates of fission products. The OTTO (Once through then out) loading scheme that is used by pebble bed reactor will enable the reactor to produce high helium exit temperatures with low fuel temperatures (Verfondern, 2007). The maximum difference in temperatures between the coolant and fuel temperature will be around 100°C. This continues reloading of fuel elements, which is suitable for the industrial market because refineries that employ this heat source do not have to shut down for decades and the heat market requires smaller units (Verfondern, 2007).

The nuclear reactor and the hydrogen plant will be separated from each other. The heat produced by the nuclear reactor will transfer to the hydrogen plant through an intermediate heat exchanger (IHX; Verfondern 2005; Verfondern, 2007). All applications with IHX require helium exit temperatures of 900°C or higher, in order to realise a compact IHX (Verfondern, 2007).

The HTGR is the most desired nuclear reactor for the chemical industry owing to the following conditions:

- It offers a high degree of safety at a comparatively low risk owing to the low power density and an inherent limitation of the thermal load on the fuel to a non-dangerous level (Verfondern, 2005).
- Low enrichment with fissile uranium and difficult reprocessing avoids problems of proliferation of nuclear materials (Verfondern, 2005).
- The high temperature heat can be used for endothermal reaction process application (Verfondern, 2005).

Various designs of nuclear process heat HTGRs of different sizes have been proposed. Some of these proposed designs are the PNP-3000, PR-500, as well as modified HTR-Module and AVR reactors (Verfondern, 2005). The main downstream components of a high temperature process reactor are the steam reformer linked to a steam generator in series or a He/He IHX.

When comparing an electrical generating nuclear reactor with a process heat reactor, various modifications are needed (Verfondern, 2005). Several of these modifications are the following:

- reduced power and power density because of the high core outlet temperature (3 → 2.55 MW/m^3 or 200 → 170 MW(t) for the same core volume);
- reduced system pressure: the pressure ranges between the high pressure for the nuclear reactor and the low pressure of the chemical process;
- two fuel zones in the pebble bed, in order to minimise the occurrence of hot/cold gas strains in the core to achieve a radial temperature profile as uniform as possible; and
- ceramic liner to replace the metallic liner because of the higher temperature.

3.2.1 Pebble Bed Modular Reactor

The PBMR is under development by PBMR Pty (Ltd), Eskom and partners around the world and has been under development since 1994 (Elder & Allen, 2009). The reactor consists of a fixed graphite central column, which could be replaced in mid-life. The core has a diameter of 3.7 m with an inner diameter of 2 m. About 452 000 spherical TRISO-coated fuel elements are encased in spherical graphite matrix (Elder & Allen, 2009).

Helium with a flow rate of 160 kg/s is used as the cooling medium for the PBMR. The PBMR consists of an online refuelling system, which means that the reactor does not have to be shut down for refuelling and the fuel elements are recycled on average six times through the core before they are depleted (Elder & Allen, 2009). This feature makes the PBMR very desirable for the production of hydrogen or other chemical processes that need high temperatures. The PBMR will make use of a direct Brayton Cycle for the production of electricity (Elder & Allen, 2009). A schematic diagram of the PBMR is given in Figure 3.1.

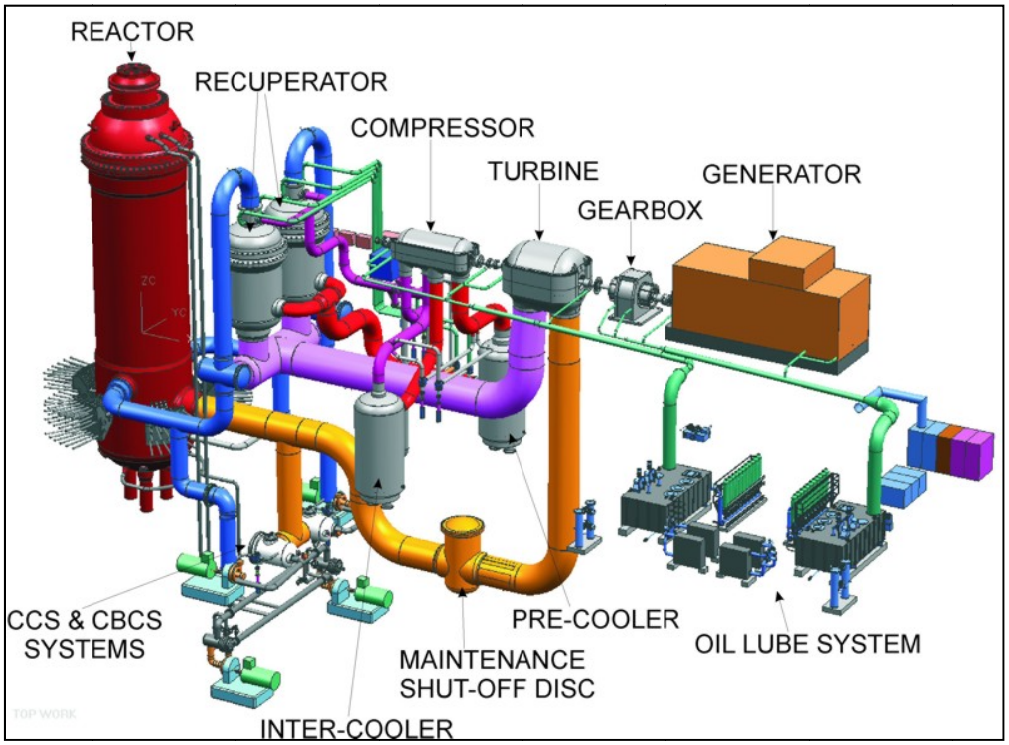

Figure 3.1: Schematic diagram of the Pebble Bed Modular Reactor (http://www.pbmr.com)

3.3 Nuclear Steam Methane Reforming

Certain changes are required in the case of nuclear SMR, since the operational conditions are not as flexible as a fossil-fuel fired furnace (Verfondern, 2007). In addition, the safety regulations are stricter for the nuclear system than for the fossil fuel system. A large hydrogen production rate can be achieved when the process feed gas rate and conversions are high. The feed gas rate depends on the amount of heat input into the process and the temperature of the feed gas, whereas the conversion depends on the temperature and pressure of the process gas (Verfondern, 2007).

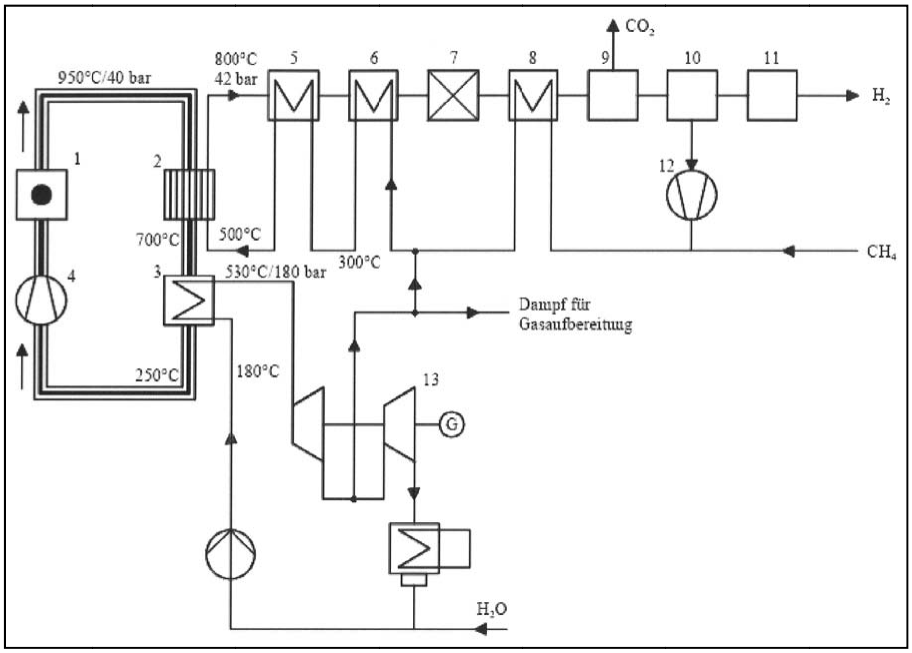

Figure 3.2: Process flow sheet of High Temperature Gas Reactor with steam reforming (Verfondern, 2007)

The steam reformer uses the high temperature helium at a temperature between 950°C and 700°C, in order to drive the endothermic chemical reactions, whilst the steam generator, which is in series with the steam reformer, uses the helium at 700°C and 250°C to produce steam (Verfondern, 2007). The feed gas with a ratio of steam to methane of 3:1 and a pressure of 40 bar is preheated to a temperature of 500°C. It is then further heated to a temperature of 800°C while the reforming reaction takes place (Verfondern, 2007).

The conversion of methane to synthesis gas in the reformer is 85.0%. Reformed gas is used for preheating the feed gas to the reformer to the water-gas-shift reaction and the methanation, which are all unit operations that follow the steam-reforming step in the production of hydrogen (Verfondern, 2007).

A feed rate of 25 000 Nm^3/h methane, 170 MWt produces approximately 100 000 Nm^3/h of hydrogen (Verfondern, 2007). The methane is completely converted to hydrogen; the total efficiency of the chemical combined with the nuclear heat is approximately 65.0%. Because nuclear heat is used as the heat source for the reforming process and depending on the operation conditions, a 40.0% saving of methane is achieved compared with the conventional reforming process, which makes use of burning methane as the heat source (Verfondern, 2007).

Germany and Japan have conducted further investigations into nuclear SMR. Germany's approach was to install the steam reformer directly in the primary circuit and not make use of an IHX (Verfondern, 2007). This resulted in a simplified design of a process heat HTGR.

Steam reforming was investigated by Germany using the EVA, a single tube-splitting test facility and the EVA-II. A methanation plant ADAM was also investigated, where the product gas was reconverted into methane and steam, creating a closed cycle without any carbon dioxide emissions. The EVA-II and ADAM are shown in Figure 3.3 below.

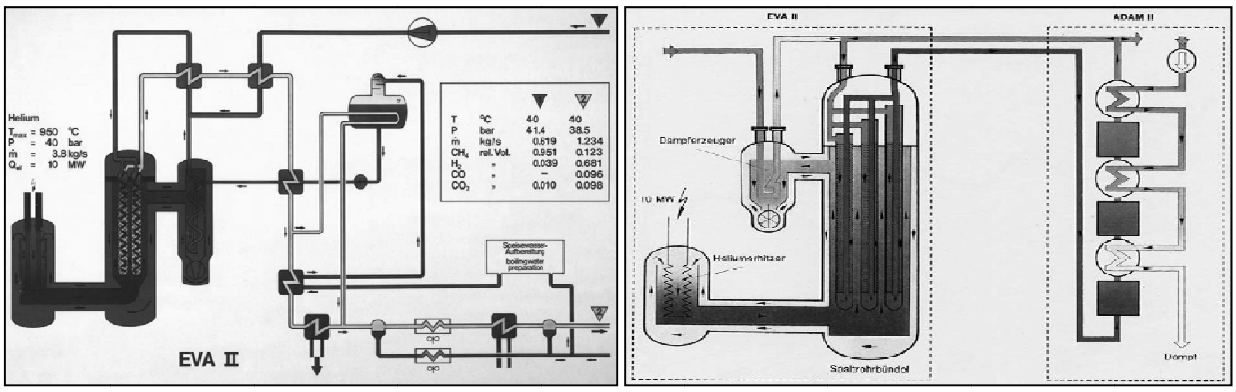

Figure 3.3: Flow sheet of the steam reforming test facility EVA-II (left) and the combined test facilities EVA-II and ADAM-II (right; Verfondern, 2007)

Japan's approach was different to that of Germany. They coupled the steam methane reformer to the HTGR using an IHX (Verfondern, 2007). A flow diagram of the hydrogen production system is displayed in Figure 3.4.

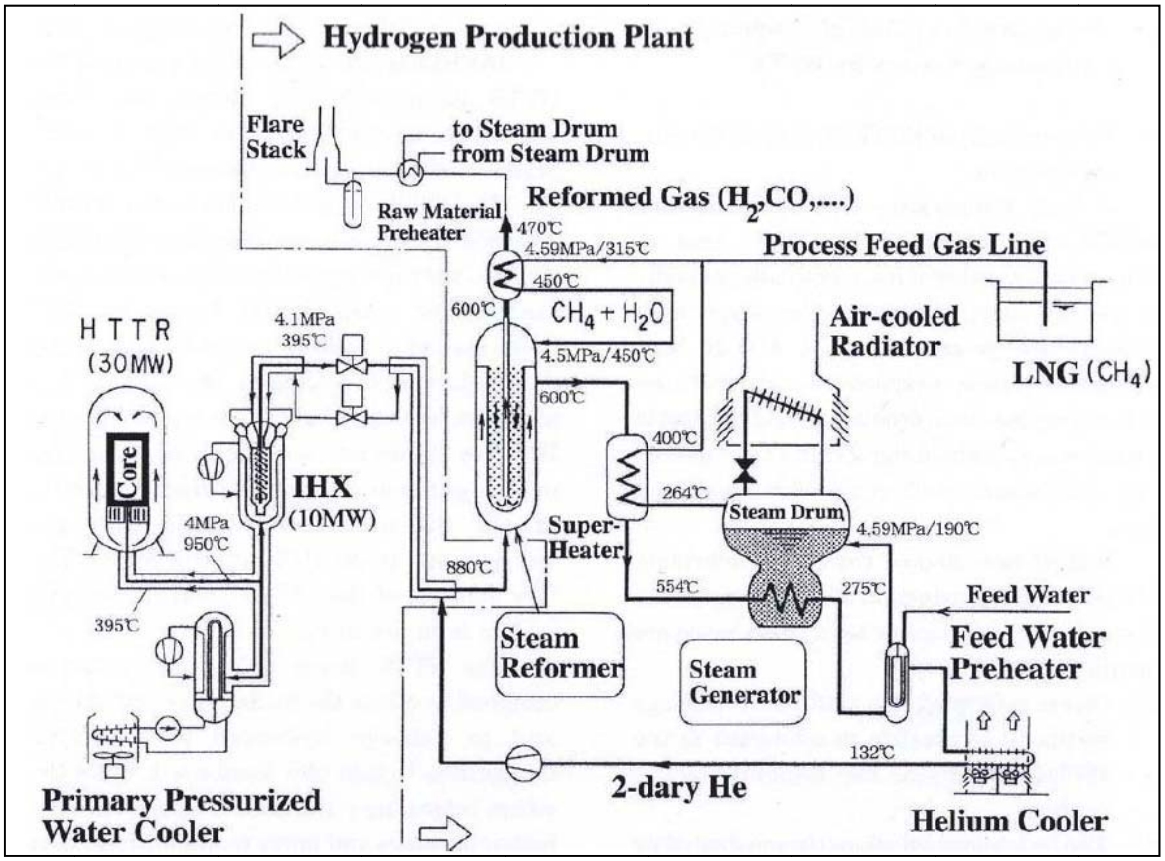

Figure 3.4: High Temperature Test Reactor coupled to a hydrogen production plant based on Steam Methane Reforming (Verfondern, 2007)

Because the chemical circuit is separated from the nuclear circuit, it avoids contamination in the steam reformer and it reduces the permeation rates of hydrogen and tritium to negligible values (Verfondern, 2007). The High Temperature Test Reactor (HTTR) has been designed to produce 4 200 Nm^3/h of hydrogen in a steam reformer, using a Ni-based catalyst with 10 MW thermal energy. The 73.0% of the heat produced is used in the reforming process, which makes it competitive with the conventional steam reforming system, which has a heat utilisation of 80.0% (Verfondern, 2007). Design specifications of a steam reformer for the HTTR facility are given in Table 3.1.

Table 3.1: Design specifications of the steam reformer for High Temperature Test Reactor (Verfondern, 2007)

Parameter	Steam reformer in HTTR
Nuclear electrical input	3.6 MW (plus 1.3 MW from product gas)
Material: Tubes	Hastelloy XR
Catalyst	Ni/Al_2O_3
Size: Shell diameter (m)	1.19
Shell height (m)	14.0
Catalyst tube	Bayonet type, concentric double-walled tube
Outer diameter (mm)	153.8
Wall thickness (mm)	13.0
Length (mm)	7.9
Inner tube diameter (mm)	60.5
Wall thickness (mm)	3.9
Length (mm)	on none
Number of tubes	37
Secondary helium	
Inlet temperature (°C)	880
Outlet temperature (°C)	585
Pressure (MPa)	4.1
Flow rate (kg/s)	2.5
Process feed gas	
Inlet temperature (°C)	450
Outlet temperature (°C)	580 (max. 800)
Pressure (MPa)	4.5
Raw gas flow rate (kg/s)	0.39
Raw gas conversion (%)	64.2
Steam-methane ratio	3.5
Hydrogen production rate (Nm^3/h)	4 240

The proposed design of the nuclear steam reformer for the hydrogen production facility is given in Figure 3.5.

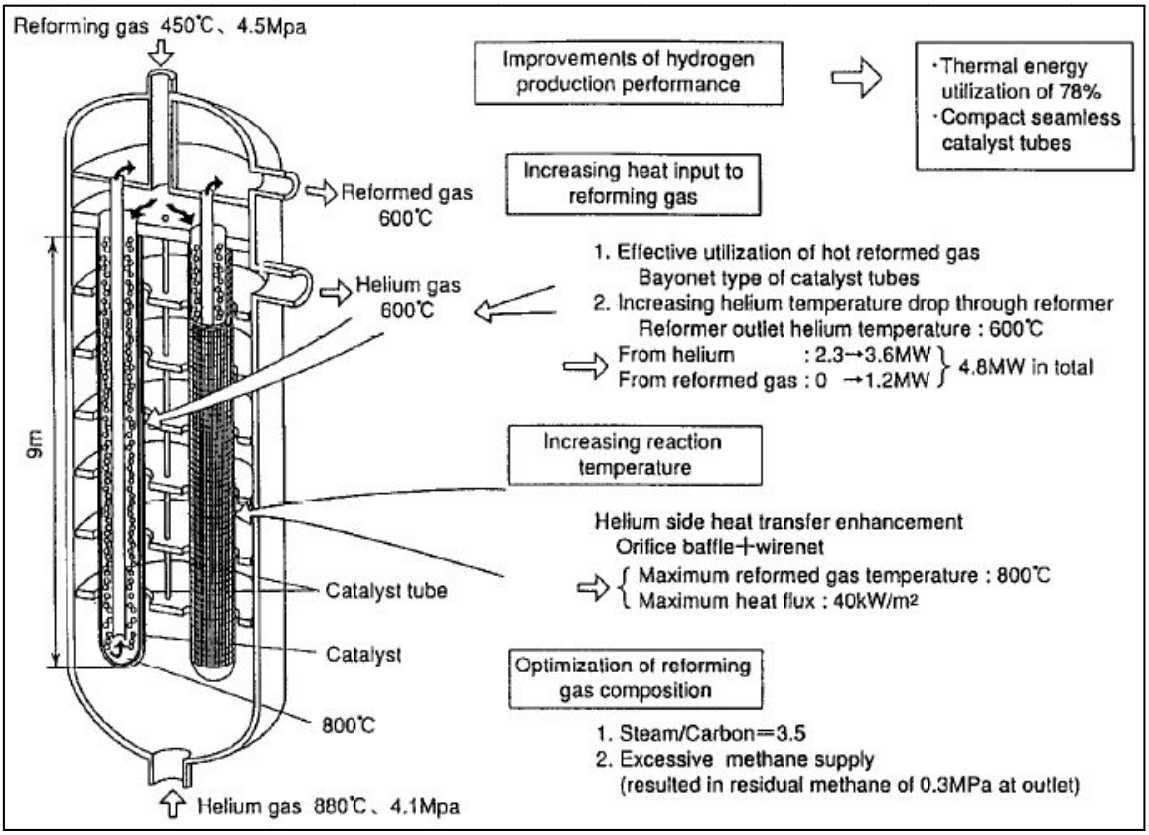

Figure 3.5: New concept of helium-heated steam reformer (Verfondern, 2007)

3.4 Thermo-chemical water-splitting using nuclear energy

In 1973 to 1983, Westinghouse developed the hybrid-sulphur (HYS) process. This is a two-step sulphuric acid hybrid process (Verfondern 2007, Summers, Gorensek, & Buckner, 2005). This process produces hydrogen from water-splitting and oxygen as a by-product. The reactions that take place in the process are given by reaction equations (8) and (9) (Verfondern 2007, Summers *et al*., 2005).

$$H_2SO_4 \rightarrow H_2O + SO_3 \rightarrow H_2O + SO_2 + \tfrac{1}{2}O_2 \quad \text{(Thermo-chemical, 800 – 900°C)} \quad (8)$$

$$SO_2 + 2H_2O \rightarrow H_2 + H_2SO_4 \quad \text{(Electro-chemical, 80 – 120°C)} \quad (9)$$

The sulphur used in the process is regenerated and recycled as process intermediates. A schematic block diagram of the process is given in Figure 3.6. Reaction (9) takes place in the electro-chemical cell; here sulphur dioxide (SO_2) is dissolved in concentrated sulphuric acid (H_2SO_4) and is used to depolarise the anode of the cell (Summers *et al*., 2005). This produces sulphuric acid at the anode, and not oxygen as with the water electrolyser, and hydrogen is produced at the cathode.

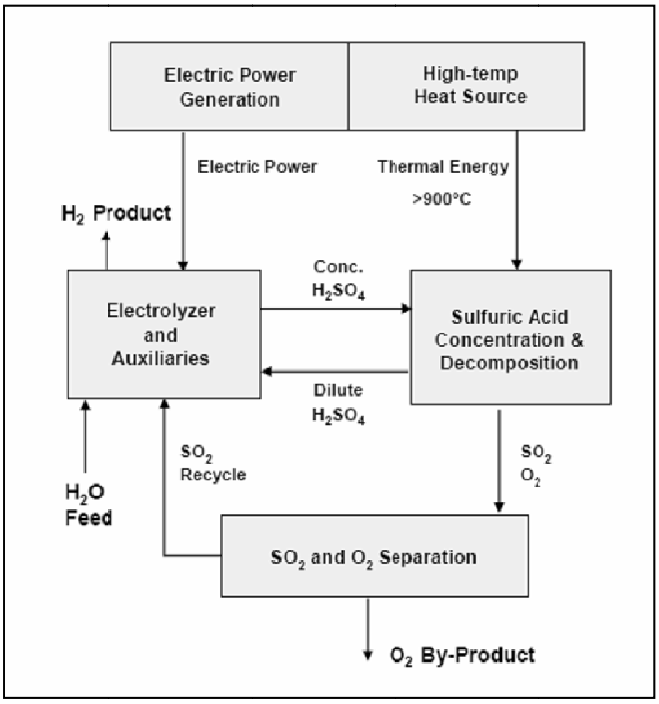

Figure 3.6: Schematic block diagram of the Hybrid Sulphur Cycle (Summers *et al*., 2005)

The sulphur dioxide is regenerated in the thermo-chemical section of the process and oxygen is then produced as a by-product of the process (Summers *et al*., 2005). The HYS process has an overall thermal efficiency of 48.8%, which is based on a peak thermal temperature of 900°C produced by a HTGR (Verfondern 2007, Summers *et al*., 2005). Table 3.2 below presents the design parameters of the investigation.

Table 3.2: Hybrid sulphur design parameters (Summers *et al*., 2005)

SO_2-depolarised electrolyser	**Unit**	
Operating temperature	°C	100
Operating pressure	bar	20
H_2SO_4 concentration	wt%	65
SO_2 inlet concentration	wt%	8.95
Conversion per pass	%	50
Current efficiency	%	99
Average cell voltage	mV	525
Peak thermal input temperature	°C	900
Cooling water temperature	°C	24
Heat-to-electric efficiency for auxiliary power requirements (Brayton cycle)	%	48

The HYS cycle can produce approximately 174 tons of hydrogen per day, at a cost of $1.60 per kilogram. The cost of hydrogen is further reduced when the oxygen is also sold at $1.31 per kilogram (Summers *et al*., 2005).

3.5 Safety aspects of combined Nuclear Steam Reforming

Many safety aspects have to be considered when combining a hydrogen production facility with a nuclear energy facility. There are three areas of concern when using nuclear energy for the production of hydrogen, namely:

- The hydrogen production system is the final heat sink of the nuclear reactor.
- Flammable substances are present in the system.
- Hydrogen is handled outside the nuclear plant.

A safety-related issue is the operability of the production process system during a nuclear reactor scram (Verfondern *et al*, 2005; Verfondern, 2007). According to the safety regulations, the heat sink of the nuclear power plant is limited to water and cannot be that of electricity or chemical energy as the result of a conversion process. Therefore, the production system is not designed to take over the safety functions of the nuclear power plant (Verfondern *et al*, 2005; Verfondern, 2007).

In the case of a reactor scram, the power output of the reactor decreases to a level where the reactor shuts down safely and remains in a sub-critical state. When the heat input to the production process is abrupt, the process feedstock supply is stopped and the production system is filled with nitrogen gas, to prevent carbon deposition on the catalyst (Verfondern *et al*, 2005; Verfondern, 2007). In order to prevent the scramming of the nuclear reactor and meet the safety requirement, the temperature in the secondary helium loop must not be allowed to increase by 15°C.

Should the feedstock supply system suddenly be halted owing to electric power or control system malfunction, this would induce an increase in the helium temperature at the steam reformer outlet. The steam generator that is installed downstream will cool down the hot helium gas to the saturation temperature of steam, providing a stable controllability for any disturbance at the steam reformer (Verfondern *et al*, 2005; Verfondern, 2007).

Chapter 4 - Process description

4.1 Introduction

In the previous chapters, the different types of reforming technologies and other synthesis/hydrogen gas production processes have been considered. In this chapter, the different processes used for the production of synthesis gas and hydrogen are described, using Plasma-arc Technology for the reforming of methane with carbon dioxide as the oxidising agent.

4.2 Assumptions applied for material balance calculations

The following assumptions were made as basis for the material balance equations:

- Methane and carbon dioxide gas inlet temperature is 25°C.
- Process water is fed at 25°C.
- Cooling water inlet temperature is 25°C.
- The maximum flow rate of feed gas to a Plasma-arc Reformer is 4 000 Nm^3/h.
- The PBMR produces hot helium at 950°C at a flow rate of 160 kg/s.
- The PBMR produces 500 MWt energy.
- A Rankine cycle is used to produce electrical energy at an efficiency of 35.0%.
- The thermal efficiency of the Plasma-arc Reformer is 88.0%.
- Each Plasma-arc Reformer has a capacity of 8 MW.
- A chemical conversion of 95.0% is achieved and varying the conversion between 90.0% and 100.0% for sensitivity evaluation.
- The reference temperature is taken as 25°C.

The conversion of methane increases with increasing temperature, as was observed in the Chapter 2. A conversion of 85.0% at a temperature of 850°C is achieved in the SMR, 98.0% at a temperature of 1350°C for the POX and a conversion close to 100.0% at temperatures above 3000°C for the Plasma-arc Reforming process. Figure 4.1 shows a graph of methane conversion as a function of temperature and pressure. It can be seen that a higher methane conversion is directly influenced by the pressure of the system; thus, if a high conversion of methane is to be achieved at a high pressure, more energy is required by the system. As expected, the increase in temperature results in a significant

increase in the methane conversion that can be achieved. Therefore, it is realistic to assume a methane conversion of 95.0% for the Plasma-arc Reforming process investigated in this research project. It is also known that hydrocarbons, such as acetylene and ethylene, are not formed in the presence of an oxidant at these high temperatures.

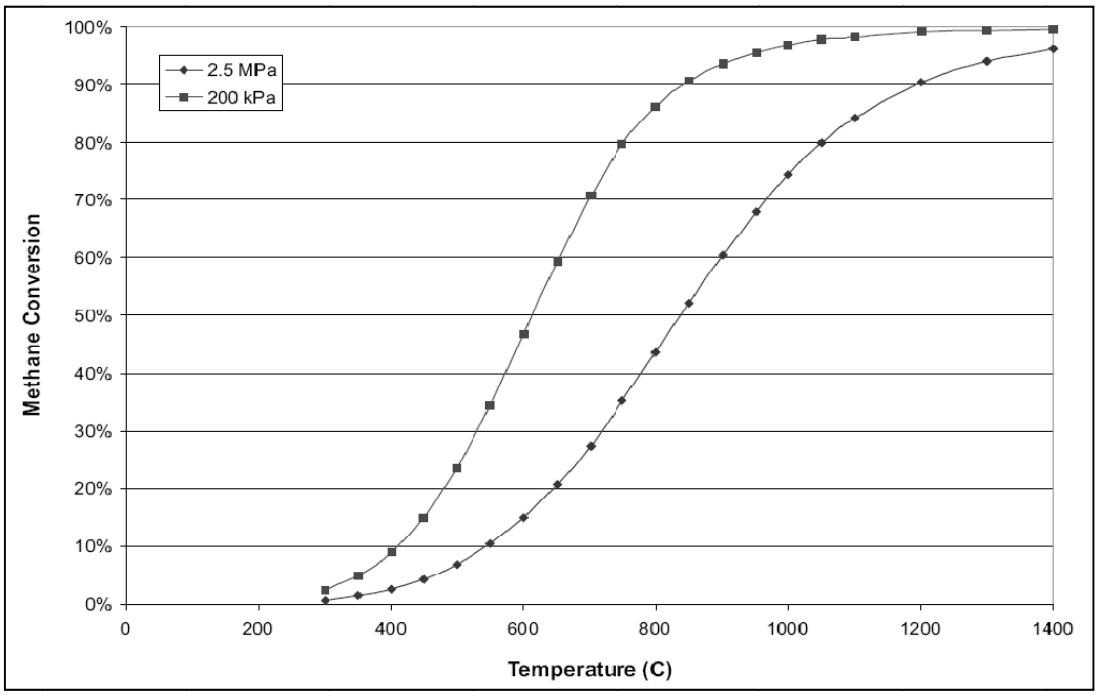

Figure 4.1: Methane conversion as a function of operating temperature (Lane & Spath, 2001)

Methane is used as the basis for all the calculations, but natural gas can also be used for the production of synthesis gas or hydrogen. Due to the endothermic nature of the dry methane reforming process, the thermal energy that is required by the process is very high as given in reaction equation (3) in Chapter 2. The plasma-arc units have the ability to provide the large amount of energy, which is required without the aid of a catalyst, due to the high temperatures (2 000°C – 5 000°C) produced in the units. The PBMR provides the thermal energy for the generation of electrical energy, which is in turn used by the plasma-arc units and converted back into a higher thermal energy output that is required by the process.

The plasma-arc units is operated at low pressures between 1 to 2 barg and low flow rates. If the pressure/flow rate to the units is to high the arc which is formed in the unit will be extinguished and if the pressure/flow rate is to low the arc will become unstable and unit will be difficult to operate. Microsoft Excel was used for the calculation of the mass and energy calculations, making use of the equations given in Appendix A. The results were correlated using the ASPEN HYSYS simulation package, and the results of the calculations are presented in Appendix C.

4.3 Synthesis gas production using Plasma-arc Technology

The production of synthesis gas can be categorised into two processes using Plasma-arc Technology. The one process only uses carbon dioxide as the oxidising agent in the Plasma-arc Reformer. The second process makes use of a mixture of carbon dioxide and steam, which acts as the oxidising agent. These two processes are discussed in the following sections.

4.3.1 Methane Reforming using CO_2 for the production of synthesis gas

4.3.1.1 Process description of synthesis gas production using CO_2 as the oxidising agent

In Figure 4.2, a simplified process flow diagram is given for the production of synthesis gas, using only carbon dioxide as the oxidising agent. The feed gas to the heat exchanger consists of methane and carbon dioxide, which is mixed at a 1:1 molar ratio. The mixed feed gas is then heated to 850°C at 1 barg in the heat exchanger. The heated feed gas then enters the Plasma-arc Reformer Units, where it is reformed into synthesis gas containing mainly hydrogen and carbon monoxide.

The reaction in the Plasma-arc Reformer takes place stoichiometrically according to reaction (4). The reformed gas leaves the Plasma-arc Reformer at a temperature of approximately 1 197°C. This high temperature gas is then used to pre-heat the feed gas to the reformer to maximise thermal energy utilisation. The reformed gas leaves the heat exchanger at a temperature of approximately 430°C.

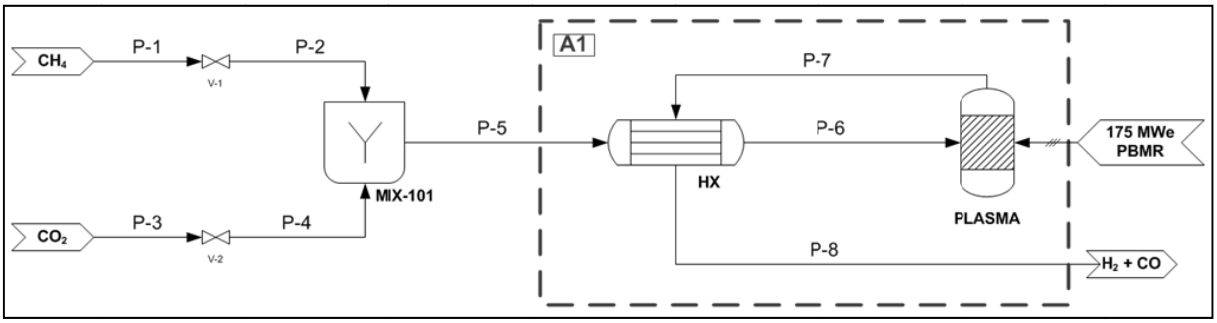

Figure 4.2: Simplified process flow diagram using Plasma-arc Technology for synthesis gas production, using CO_2 as the oxidising agent

As mentioned in the assumptions, a 500 MWt PBMR is used for the production of electrical energy requirements, making use of a Rankine Cycle. A 500 MWt PBMR is capable of producing 175 MWe energy, which can supply 21×8 MW Plasma-arc Reformer Units of electricity. Three Plasma-arc Reformers are grouped together with a single heat exchanger and seven of these combined groups are proposed.

4.3.1.2 Material and energy balance

A complete mass and energy balance for the production of synthesis gas, using carbon dioxide as the oxidising agent is given in Table 4.1.

Table 4.1: Complete mass and energy balance of synthesis gas production, using CO_2 as the oxidising agent

Component	P-1/P-2	P-3/P-4	P-5	P-6	P-7	P-8
Mass flow rate (kg/h)						
CH_4	30 060.5	-	30 060.5	30 060.5	1 503.0	1 503.0
CO_2	-	82 461.7	82 461.7	82 461.7	4 123.1	4 123.1
H_2	-	-	-	-	7 176.5	7 176.5
CO	-	-	-	-	99 718.8	99 718.8
Total	**30 060.5**	**82 461.7**	**112 522.2**	**112 522.2**	**112 522.2**	**112 522.2**
Volumetric flow rate (Nm^3/h)						
CH_4	42 000.0	-	42 000.0	42 000.0	2 100.0	2 100.0
CO_2	-	42 000.0	42 000.0	42 000.0	2 100.0	2 100.0
H_2	-	-	-	-	79 800.0	79 800.0
CO	-	-	-	-	79 800.0	79 800.0
Total	**42 000.0**	**42 000.0**	**84 000.0**	**84 000.0**	**163 800.0**	**163 800.0**
Temperature (°C)	25.0	25.0	25.0	850.0	1 197.0	430.0
Pressure (barg)	1	1	1	1	1	1
Energy (MW)	-	-	-	53.0	78.7	25.7

The feed gas is divided into seven streams, which are fed to the seven heat exchangers used for heating the feed gas from 25°C to 850°C. Once the gas streams to the heat exchangers have been heated, the gas is again divided into three streams, which are then introduced into the three Plasma-arc Reformers. The reformed gas from the Plasma-arc Reformers is then combined to produce a single reformed product gas stream, which is used for heating the feed gas stream to the reformers.

The process configuration is illustrated in Figure 4.3. The incoming feed gas is used to supply seven heat exchangers with cold feed gas, which then supplies twenty-one Plasma-arc Reformers with hot reactant gas at 850°C. The mass and energy balance values for the different streams as indicated in Figure 4.3 are given in Table 4.2 that follows.

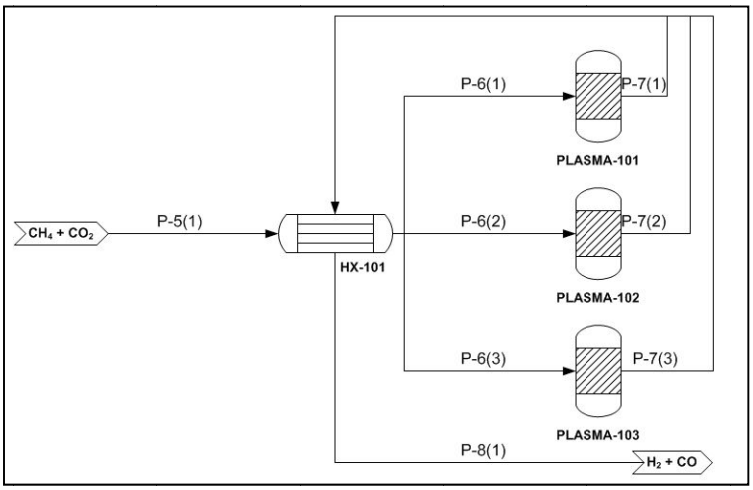

Figure 4.3: A single group of three Plasma-arc Reformers per single heat exchanger

Table 4.2: Mass and energy balance for a single group of three Plasma-arc Reformers per one heat exchanger

Component	P-5(1)	P-6(1)	P6-(2)	P6(3)	P-7(1)	P-7(2)	P-7(3)	P-8
Mass flow rate (kg/h)								
CH_4	4 294.4	1 431.5	1 431.5	1 431.5	71.6	71.6	71.6	214.7
CO_2	11 780.2	3 926.7	3 926.7	3 926.7	196.3	196.3	196.3	589.0
H_2	-	-	-	-	341.7	341.7	341.7	1 025.2
CO	-	-	-	-	4 748.5	4 748.5	4 748.5	14 245.5
Total	**16 074.6**	**5 358.2**	**5 358.2**	**5 358.2**	**5 358.2**	**5 358.2**	**5 358.2**	**16 074.6**
Volumetric flow rate (Nm^3/h)								
CH_4	6 000.0	2 000.0	2 000.0	2 000.0	100.0	100.0	100.0	300.0
CO_2	6 000.0	2 000.0	2 000.0	2 000.0	100.0	100.0	100.0	300.0
H_2	-	-	-	-	3 800.0	3 800.0	3 800.0	11 400.0
CO	-	-	-	-	3 800.0	3 800.0	3 800.0	11 400.0
Total	**12 000.0**	**4 000.0**	**4 000.0**	**4 000.0**	**7 800.0**	**7 800.0**	**7 800.0**	**23 400.0**
Temperature (°C)	25.0	850.0	850.0	850.0	1 197.0	1 197.0	1 197.0	430.0
Pressure (barg)	1	1	1	1	1	1	1	1
Energy (MW)	-	2.5	2.5	2.5	3.7	3.7	3.7	3.7
Total energy (MW)	7.5				11.1			

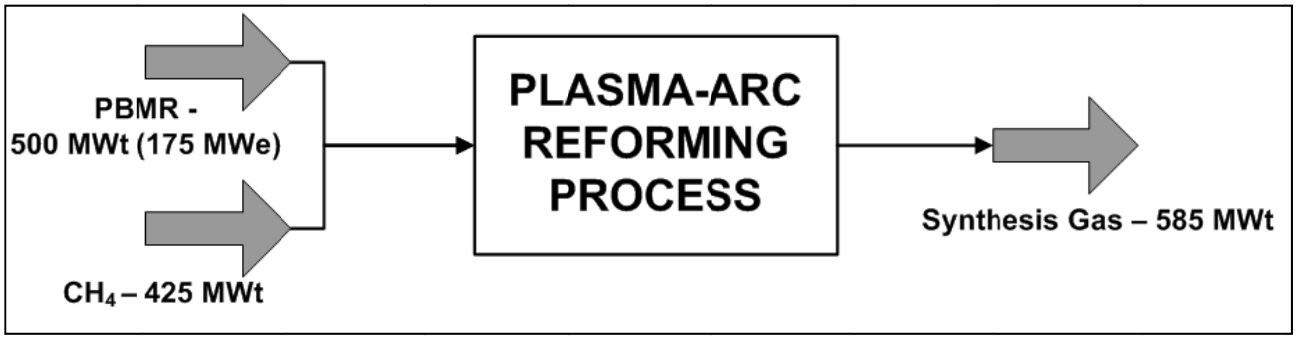

Figure 4.4: The in-and-out flow of the thermal energy for the process

In Figure 4.4, the thermal energy that enters the process and the energy of the synthesis gas that leaves the process can be seen. Below is the calculation of the total thermal energy of the process. Thus, for a 500 MWt PBMR combined with the Plasma-arc Reforming plant, the thermal efficiency is 63.0%.

$$Natural\ Gas\ Energy = Flow\ Rate\ CH_4 \times Calorific\ Value$$
$$= 0.56\ {}^{Nm^3}/_{s} \times 36.4\ {}^{MJ}/_{Nm^3}$$
$$= 425\ MW$$

$$\eta_{thermal} = \frac{\text{Synthesis Gas}}{\text{Nuclear Energy} + \text{Natural Gas}}$$
$$= \frac{585}{500 + 425}$$
$$= 63\%$$

4.3.1.3 Sensitivity evaluation of the process

A sensitivity evaluation of the process was conducted, in order to determine how the process would react if lower or higher conversion of methane was achieved in the Plasma-arc Reformer than the investigated conversion and if an alternative electricity generation cycle was used.

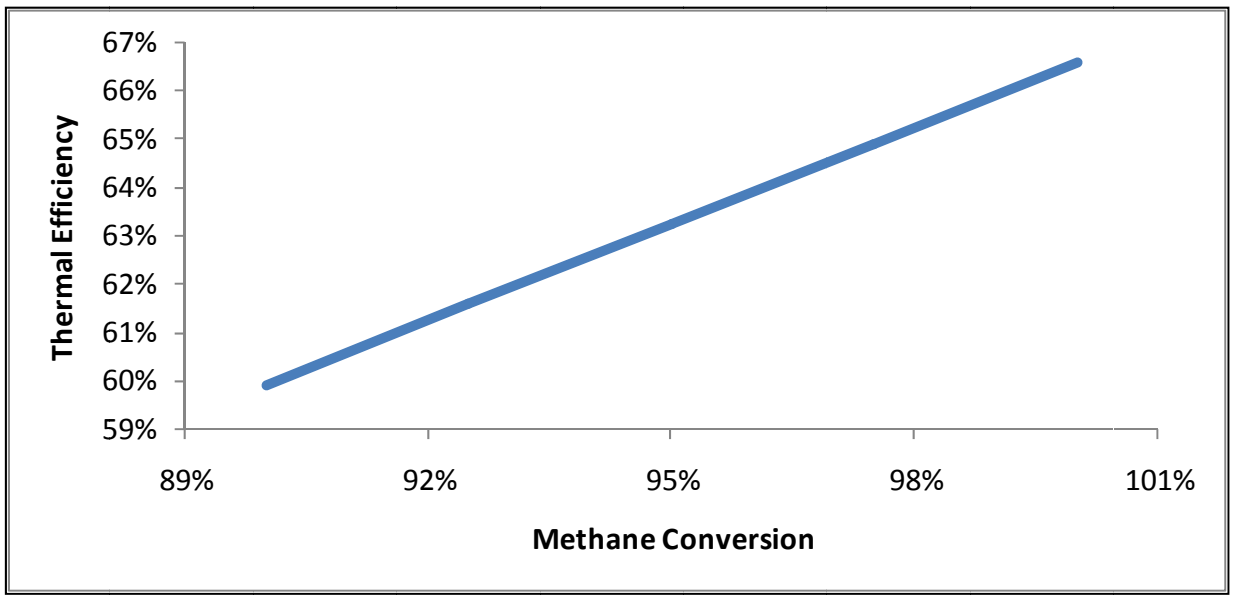

Figure 4.5: Thermal efficiency as a function of methane conversion in Plasma-arc Reformer Unit

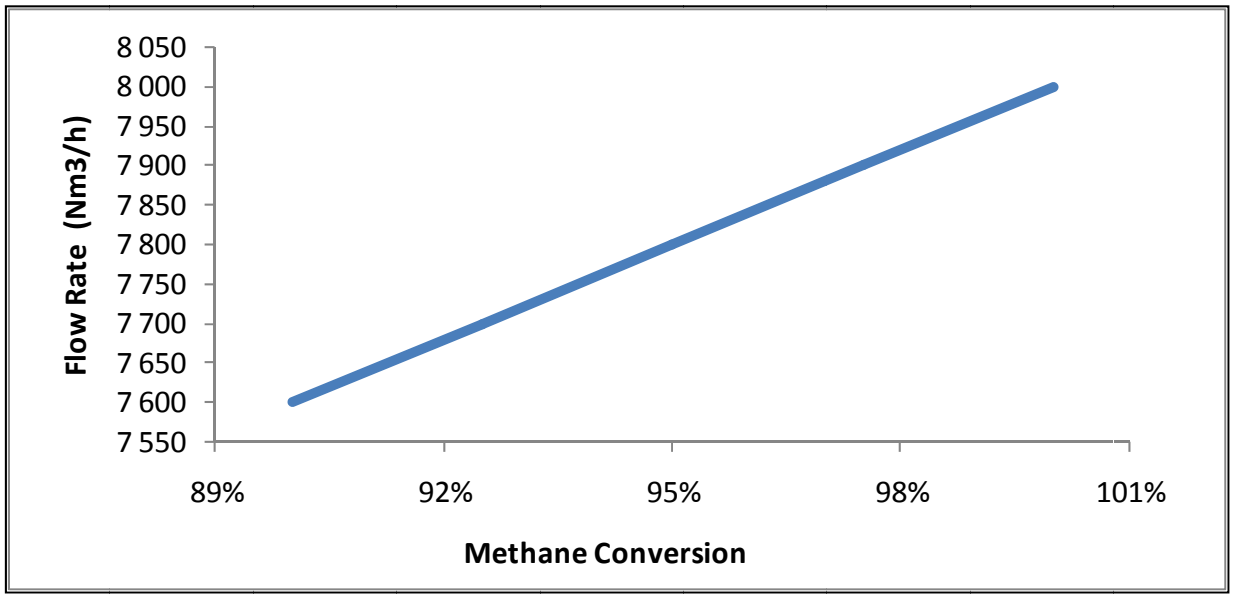

Figure 4.6: Synthesis gas flow rate and outlet temperature of the Plasma-arc Reformer Unit as functions of methane conversion

From Figure 4.5 and Figure 4.6, it can be seen that conversion of methane plays a vital role in the thermal efficiency and production of synthesis gas by the Plasma-arc Reformer Units. As expected, the thermal efficiency and production of synthesis gas increase with increasing methane conversion. The methane conversion that is achieved in the Plasma-arc Reformer also influences the outlet temperature – it varies between 1 100°C to 1 300°C. With increasing methane conversion, the outlet temperature from the Plasma-arc Reformer Unit decreases owing to the endothermic nature of the reaction that takes place.

The electricity generation cycle also plays a vital role in the production of synthesis gas. If the Brayton Cycle, which has an efficiency of 40.0%, is used rather than the Rankine Cycle, the number of Plasma-arc Reformer Units that could be used increases to 25. Also the thermal efficiency of the process increases to 69.2% with a production of 1 173 million kg per year of synthesis gas.

The conclusion can be drawn that the methane conversion that is achieved in the units and the generation cycle has a major impact on the process.

4.3.2 Methane reforming using a mixture of CO_2 and steam for the production of synthesis gas

4.3.2.1 Process description of synthesis gas production using steam and CO_2 as the oxidising agent

A simplified process flow diagram of the combined steam and carbon dioxide process is given in Figure 4.7. In the combined process, both steam and carbon dioxide are used to reform methane in the Plasma-arc Reformer. The combined reaction is given in equation (10) which is a combination of steam and carbon dioxide reforming.

$$2CH_4 + H_2O + CO_2 \rightarrow 3CO + 5H_2 \qquad \Delta H^0_{298} = +\ 453\ kJ/mol \qquad (10)$$

The feed gas to the reformer consists of a mixture of methane, carbon dioxide and steam, with methane in a molar ratio of 1:1 with steam and carbon dioxide. The ratio between carbon dioxide and steam is varied so that the molar concentration of hydrogen to carbon monoxide can be varied between 3:1 and 1:1. Methane and carbon dioxide are mixed together and fed into a heat exchanger, where they are heated from 25°C to 850°C. The steam is generated through the evaporation of water from 25°C in its liquid phase to 850°C in its gaseous phase.

Superheated steam and the pre-heated carbon dioxide and methane streams are then mixed together to form the hot reactant gas, which is fed into the Plasma-arc Reformers. The reactant gas is reformed in the Plasma-arc Reformer according to reaction (10). The outlet temperature of the reformed gas from the reformer is approximately 1 313°C. This temperature varies according to the steam and carbon dioxide ratio in the inlet gas stream to the Plasma-arc Reformer.

The high temperature gas is used to heat the gas mixture of carbon dioxide and methane to 850°C and to generate steam at 850°C, which is needed for the process. The product gas from the Plasma-arc Reformer leaves the first heat exchanger at a temperature of approximately 700°C and the second heat exchanger at 390°C. These temperatures are dependent on the ratio of carbon dioxide and steam that are present in the inlet gas. The H_2-to-CO ratio in the product gas can be varied between 3:1 and 1:1, depending on the required product gas composition.

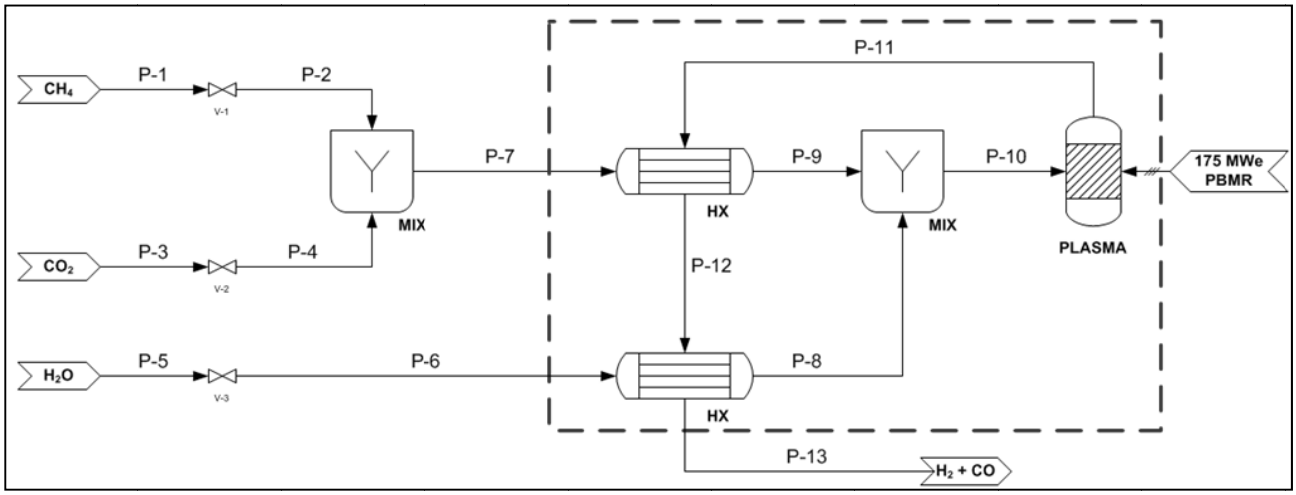

Figure 4.7: Combined steam and CO_2 oxidising agents for the production of synthesis gas

As mentioned in the previous process, a 500 MWt PBMR power plant is used to generate electricity needed to power the 21×8 MW Plasma-arc Reformer Units. Three Plasma-arc Reformers are grouped together with a single heat exchanger. There are seven of these group configurations. The reformed gas from all these groups is mixed together before it is sent through the second heat exchanger (boiler) where the steam is generated. Only a single boiler is used for the production of steam that is needed for the process.

4.3.2.2 Material and energy balances

The following H_2-to-CO ratios were investigated: 1:1, 1.5:1, 2:1, 2.5:1 and 3:1.

Table 4.3: Mass and energy balance for a H_2-to-CO ratio of 1:1 ($CH_4 + CO_2 \rightarrow 2CO + 2H_2$)

Component	P-1/P-2	P-3/P-4	P-5/P-6	P-7	P-8	P-9	P-10	P-11	P-12	P-13
Mass flow rate (kg/h)										
CH_4	30 060.5	-	-	30 060.5	-	30 060.5	30 060.5	1 503.0	1 503.0	1 503.0
CO_2	-	82 461.6	-	82 461.6	-	82 461.6	82 461.6	4 123.1	4 123.1	4 123.1
H_2O	-	-	0.0	-	0.0	-	0.0	0.0	0.0	0.0
H_2	-	-	-	-	-	-	-	7 176.5	7 176.5	7 176.5
CO	-	-	-	-	-	-	-	99 718.8	99 718.8	99 718.8
Total	**30 060.5**	**82 461.6**	**0.0**	**112 522.1**	**0.0**	**112 522.2**	**112 522.1**	**112 521.4**	**112 521.4**	**112 521.4**
Volumetric flow rate (Nm^3/h)										
CH_4	42 000.0	-	-	42 000.0	-	42 000.0	42 000.0	2 100.0	2 100.0	2 100.0
CO_2	-	42 000.0	-	42 000.0	-	42 000.0	42 000.0	2 100.0	2 100.0	2 100.0
H_2O	-	-	0.0	-	0.0	-	0.0	0.0	0.0	0.0
H_2	-	-	-	-	-	-	-	79 800.0	79 800.0	79 800.0
CO	-	-	-	-	-	-	-	79 800.0	79 800.0	79 800.0
Total	**42 000.0**	**42 000.0**	**0.0**	**84 000.0**	**0.0**	**84 000.0**	**84 000.0**	**163 800.0**	**163 800.0**	**163 800.0**
Temperature (°C)	25.0	25.0	25.0	25.0	850.0	850.0	850.0	1 196.6	430.0	430.1
Pressure (barg)	1	1	1	1	1	1	1	1	1	1
Energy (MW)	-	-	-	-	-	53.0	53.0	78.7	25.7	25.7

Table 4.4: Mass and energy balance for a H_2-to-CO ratio of 1.5:1 ($CH_4 + 0.6CO_2 + 0.4H_2O \rightarrow 1.6CO + 2.4H_2$)

Component	P-1/P-2	P-3/P-4	P-5/P-6	P-7	P-8	P-9	P-10	P-11	P-12	P-13
Mass flow rate (kg/h)										
CH_4	30 060.5	-	-	30 060.5	-	30 060.5	30 060.5	1 503.0	1 503.0	1 503.0
CO_2	-	49 477.0	-	49 477.0	-	49 477.0	49 477.0	2 473.8	2 473.8	2 473.8
H_2O	-	-	13 503.0	-	13 503.0	-	13 503.0	675.1	675.1	675.1
H_2	-	-	-	-	-	-	-	8 611.8	8 611.8	8 611.8
CO	-	-	-	-	-	-	-	79 775.1	79 775.1	79 775.1
Total	**30 060.5**	**49 477.0**	**13 503.0**	**79 537.5**	**13 503.0**	**79 537.5**	**93 040.4**	**93 038.9**	**93 038.9**	**93 038.9**
Volumetric flow rate (Nm^3/h)										
CH_4	42 000.0	-	-	42 000.0	-	42 000.0	42 000.0	2 100.0	2 100.0	2 100.0
CO_2	-	25 200.0	-	25 200.0	-	25 200.0	25 200.0	1 260.0	1 260.0	1 260.0
H_2O	-	-	16 800.0	-	16 800.0	-	16 800.0	840.0	840.0	840.0
H_2	-	-	-	-	-	-	-	95 760.0	95 760.0	95 760.0
CO	-	-	-	-	-	-	-	63 840.0	63 840.0	63 840.0
Total	**42 000.0**	**25 200.0**	**16 800.0**	**67 200.0**	**16 800.0**	**67 200.0**	**84 000.0**	**163 800.0**	**163 800.0**	**163 800.0**
Temperature (°C)	25.0	25.0	25.0	25.0	850.0	850.0	850.0	1 289.8	662.2	409.8
Pressure (barg)	1	1	1	1	1	1	1	1	1	1
Energy (MW)	-	-	-	-	16.7	43.8	50.9	84.7	40.8	24.2

Table 4.5: Mass and energy balance for a H_2-to-CO ratio of 2:1 ($CH_4 + 0.33CO_2 + 0.67H_2O \rightarrow 1.33CO + 2.67H_2$)

Component	P-1/P-2	P-3/P-4	P-5/P-6	P-7	P-8	P-9	P-10	P-11	P-12	P-13
Mass flow rate (kg/h)										
CH_4	30 060.5	-	-	30 060.5	-	30 060.5	30 060.5	1 503.0	1 503.0	1 503.0
CO_2	-	27 487.2	-	27 487.2	-	27 487.2	27 487.2	1 374.4	1 374.4	1 374.4
H_2O	-	-	22 504.9	-	22 504.9	-	22 504.9	1 125.2	1 125.2	1 125.2
H_2	-	-	-	-	-	-	-	9 568.6	9 568.6	9 568.6
CO	-	-	-	-	-	-	-	66 479.2	66 479.2	66 479.2
Total	**30 060.5**	**27 487.2**	**22 504.9**	**57 547.7**	**22 504.9**	**57 547.7**	**80 052.6**	**80 050.5**	**80 050.5**	**80 050.5**
Volumetric flow rate (Nm^3/h)										
CH_4	42 000.0	-	-	42 000.0	-	42 000.0	42 000.0	2 100.0	2 100.0	2 100.0
CO_2	-	14 000.0	-	14 000.0	-	14 000.0	14 000.0	700.0	700.0	700.0
H_2O	-	-	28 000.0	-	28 000.0	-	28 000.0	1 400.0	1 400.0	1 400.0
H_2	-	-	-	-	-	-	-	106 400.0	106 400.0	106 400.0
CO	-	-	-	-	-	-	-	53 200.0	53 200.0	53 200.0
Total	**42 000.0**	**14 000.0**	**28 000.0**	**56 000.0**	**28 000.0**	**56 000.0**	**84 000.0**	**163 800.0**	**163 800.0**	**163 800.0**
Temperature (°C)	25.0	25.0	25.0	25.0	850.0	850.0	850.0	1 352.5	815.4	396.0
Pressure (barg)	1	1	1	1	1	1	1	1	1	1
Energy (MW)	-	-	-	-	27.8	37.7	49.4	88.6	50.9	23.2

Table 4.6: Mass and energy balance for a H_2-to-CO ratio of 2.5:1 ($CH_4 + 0.14CO_2 + 0.86H_2O \rightarrow 1.14CO + 2.86H_2$)

Component	P-1/P-2	P-3/P-4	P-5/P-6	P-7	P-8	P-9	P-10	P-11	P-12	P-13
Mass flow rate (kg/h)										
CH_4	30 060.5	-	-	30 060.5	-	30 060.5	30 060.5	1 503.0	1 503.0	1 503.0
CO_2	-	11 780.2	-	11 780.2	-	11 780.2	11 780.2	589.0	589.0	589.0
H_2O	-	-	28 934.9	-	28 934.9	-	28 934.9	1 446.7	1 446.7	1446.7
H_2	-	-	-	-	-	-	-	10 252.1	10 252.1	10 252.1
CO	-	-	-	-	-	-	-	56 982.2	56 982.2	56 982.2
Total	**30 060.5**	**11 780.2**	**28 934.9**	**41 840.7**	**28 934.9**	**41 840.7**	**70 775.6**	**70 773.1**	**70 773.1**	**70 773.1**
Volumetric flow rate (Nm^3/h)										
CH_4	42 000.0	-	-	42 000.0	-	42 000.0	42 000.0	2 100.0	2 100.0	2 100.0
CO_2	-	6 000.0	-	6 000.0	-	6 000.0	6 000.0	300.0	300.0	300.0
H_2O	-	-	36 000.0	-	36 000.0	-	36 000.0	1 800.0	1 800.0	1 800.0
H_2	-	-	-	-	-	-	-	114 000.0	114 000.0	114 000.0
CO	-	-	-	-	-	-	-	45 600.0	45 600.0	45 600.0
Total	**42 000.0**	**6 000.0**	**36 000.0**	**48 000.0**	**36 000.0**	**48 000.0**	**84 000.0**	**163 800.0**	**163 800.0**	**163 800.0**
Temperature (°C)	25.0	25.0	25.0	25.0	850.0	850.0	850.0	1 397.4	924.3	386.0
Pressure (barg)	1	1	1	1	1	1	1	1	1	1
Energy (MW)	-	-	-	-	35.7	33.3	48.4	91.5	58.1	22.4

Table 4.7: Mass and energy balance for a H_2-to-CO ratio of 3:1 ($CH_4 + H_2O \rightarrow CO + 3H_2$)

Component	P-1/P-2	P-3/P-4	P-5/P-6	P-7	P-8	P-9	P-10	P-11	P-12	P-13
Mass flow rate (kg/h)										
CH_4	30 060.5	-	-	30 060.5	-	30 060.5	30 060.5	1 503.0	1 503.0	1 503.0
CO_2	-	0.0	-	0.0	-	0.0	0.0	0.0	0.0	0.0
H_2O	-	-	33 757.4	-	33 757.4	-	33 757.4	1 687.9	1 687.9	1 687.9
H_2	-	-	-	-	-	-	-	10 764.7	10 764.7	10 764.7
CO	-	-	-	-	-	-	-	49 859.4	49 859.4	49 859.4
Total	**30 060.5**	**0.0**	**33 757.4**	**30 060.5**	**33 757.4**	**30 060.5**	**63 817.9**	**63 815.0**	**63 815.0**	**63 815.0**
Volumetric flow rate (Nm^3/h)										
CH_4	42 000.0	-	-	42 000.0	-	42 000.0	42 000.0	2 100.0	2 100.0	2 100.0
CO_2	-	0.0	-	0.0	-	0.0	0.0	0.0	0.0	0.0
H_2O	-	-	42 000.0	-	42 000.0	-	42 000.0	2 100.0	2 100.0	2 100.0
H_2	-	-	-	-	-	-	-	119 700.0	119 700.0	119 700.0
CO	-	-	-	-	-	-	-	39 900.0	39 900.0	39 900.0
Total	**42 000.0**	**0.0**	**42 000.0**	**42 000.0**	**42 000.0**	**42 000.0**	**84 000.0**	**163 800.0**	**163 800.0**	**163 800.0**
Temperature (°C)	25.0	25.0	25.0	25.0	850.0	850.0	850.0	1 431.2	1 005.7	378.5
Pressure (barg)	1	1	1	1	1	1	1	1	1	1
Energy (MW)	-	-	-	-	41.6	30.0	47.6	93.6	63.5	21.9

From Table 4.3 to Table 4.7, it can be seen that the volumetric flow ratio of the process is unchanged, but the mass flow rate decreases owing to the decrease in carbon monoxide production in the reforming process. The exit temperature of the reformed product gas increases from approximately 1 200°C for a H_2-to-CO ratio of 1 to 1 431°C for a ratio of 3. This is due to the decrease in energy that is needed for the reforming reaction that takes place.

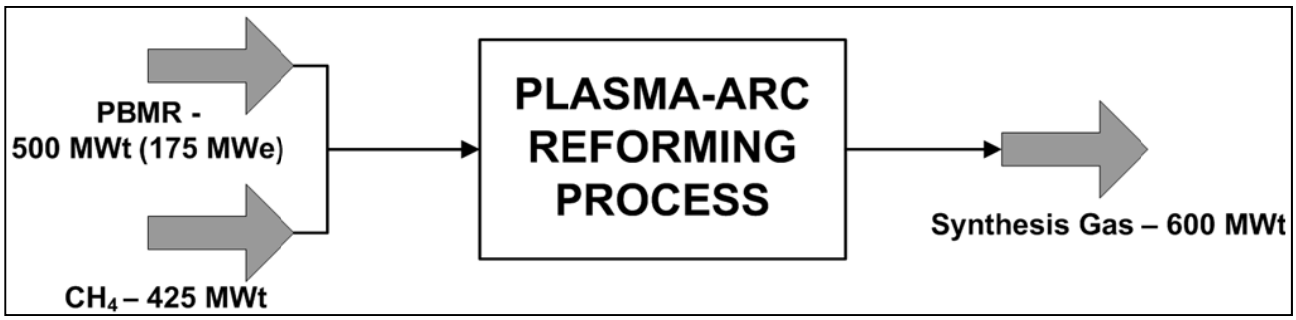

Figure 4.8: The total thermal energy of the process

In Figure 4.8, the thermal energy that enters and leaves the process can be seen. Below is the calculation of the total thermal energy of the process. Thus, for a 500 MWt PBMR combined with the Plasma-arc Reforming plant, the thermal efficiency is 65.0%.

$$\eta_{thermal} = \frac{\text{Synthesis Gas}}{\text{Nuclear Energy} + \text{Natural Gas}}$$
$$= \frac{600}{500 + 425}$$
$$= 65\%$$

4.3.2.3 Sensitivity evaluation of the process

As in the previous process, a sensitivity evaluation was conducted, in order to determine what effect the methane conversion and electricity generation cycle would have on this process, which makes use of both water and carbon dioxide as the oxidising agents.

The conversion of methane in the Plasma-arc Reformer Unit has a major impact on the outlet temperature of the Plasma-arc Reformer Units as seen in Figure 4.9. As the conversion increases, the temperature decreases because more energy is required for the conversion of methane due to the endothermic nature of the reactions. It is also

evident that the synthesis gas ratio has an impact on the outlet temperature, as the ratio increases there is also an increase in the temperature depending on the conversion.

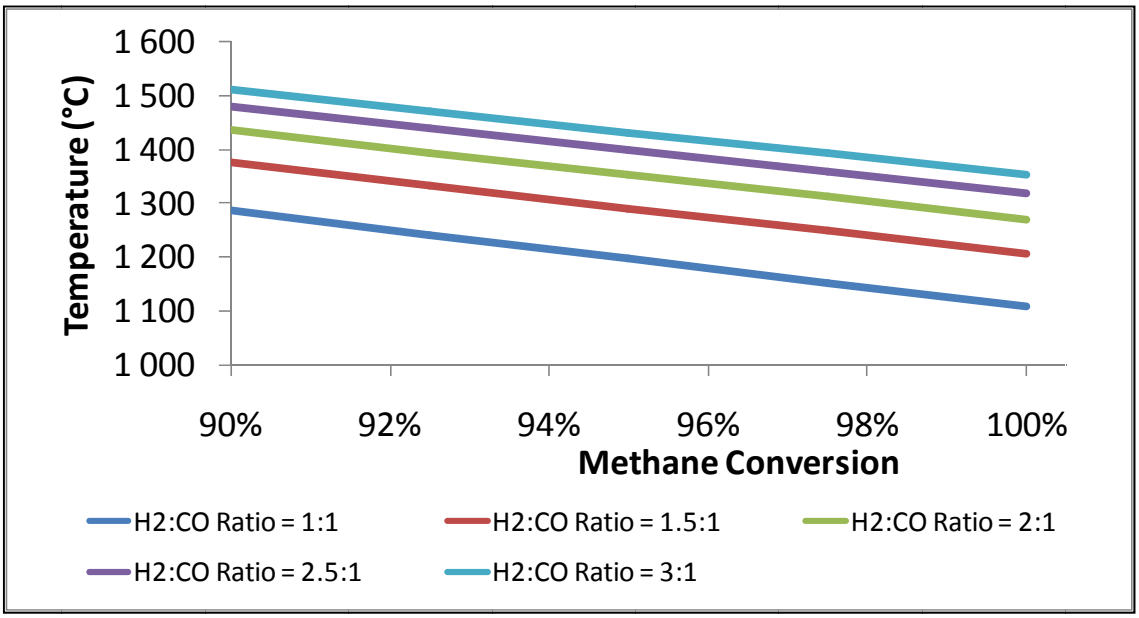

Figure 4.9: Synthesis gas outlet temperature as a function of methane conversion in the Plasma-arc Reformer Units

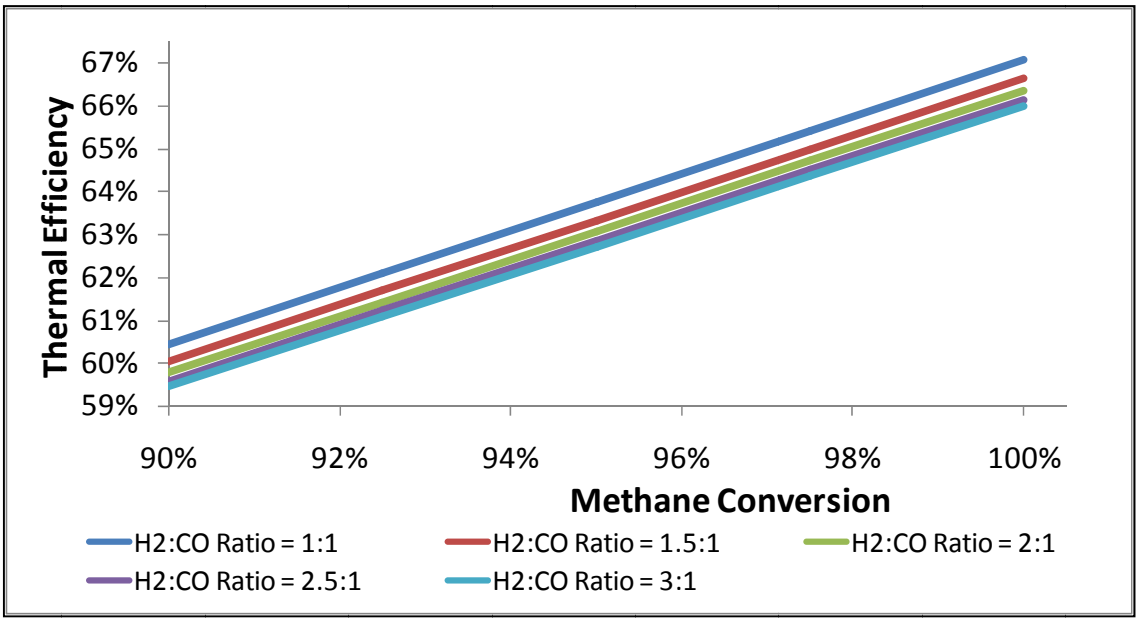

Figure 4.10: Thermal efficiency of the process as a function of methane conversion in the Plasma-arc Reformer Units

From Figure 4.10, it can be clearly seen that the thermal efficiency of the process is directly influenced by the methane conversion that is achieved in the Plasma-arc Reformer Units. Also, the synthesis gas ratio influences the thermal efficiency of the process greatly.

The electricity generation cycle also influences the production of synthesis gas greatly. As in the previous process, the Brayton Cycle was used, which has a higher efficiency than the Rankine Cycle. Using this cycle, the number of Plasma-arc Reformer Units that can be supported by 500MWt PBMR reactor increases to twenty-five, which results in the production of 1 173 million kg per year of synthesis gas. The thermal efficiency of the process also increases and is close to 70.0%, depending on the synthesis gas ratio produced.

The conclusion can be drawn that the methane conversion that is achieved in the units and the generation cycle has a major impact on the process.

4.4 Hydrogen production using Plasma-arc Technology

The production of hydrogen with carbon dioxide as the oxidising agent and using Plasma-arc Reformers can be grouped into two processes. The first process makes use of the total electrical energy that can be generated by a 500 MWt PBMR, and the second process uses both the thermal and the electrical energy that can be generated by a 500 MWt PBMR. These two processes are discussed in the next sections.

4.4.1 Methane Reforming with CO_2 for the production of hydrogen, utilising the electrical energy supplied by a PBMR

4.4.1.1 Process description of hydrogen production using CO_2 as the oxidising agent

A simplified process flow diagram of the Hydrogen Production Process can be seen in Figure 4.11. A 500 MWt PBMR is used for the production of 175 MWe, using the Rankine Cycle. All the thermal energy supplied by the PBMR is converted into electrical energy and used for the production of hydrogen, through reforming methane with carbon dioxide. It supplies electrical energy to 21×8 MW Plasma-arc Reformer Units.

Methane and carbon dioxide are introduced into the reforming process at a molar ratio of 1:1. The reactant gas is firstly heated from 25°C to 850°C in a heat exchanger identical to that of the case was for the production of synthesis gas. The heated gas then enters the Plasma-arc Reformers according to reaction equation (4) where it is reformed to produce

synthesis gas at a temperature of approximately 1 197°C. The high temperature reformed gas is then used to pre-heat the cold incoming reactant gas and the reformed gas leaves the heat exchanger at a temperature of approximately 450°C.

The sensible heat of the reformed gas is further utilised, by heating the feed gas to the water-gas-shift reactors to 350°C. The water-gas-shift reactors operate at a pressure of 10 bar, which means that the reformed gas pressure has to be increased from 1 bar to 10 bar by making use of a series of compressors and coolers. The gas is firstly cooled down to 100°C before it is compressed. After compression, the gas is mixed with steam, which is at a temperature of 350°C and 10 barg. The volumetric ratio of steam to carbon monoxide in the synthesis gas stream is 1.9, which is necessary for the shift reaction to proceed (Newsome, 1980).

After the mixing of the reformed gas and steam, the temperature of the mixer is approximately 280°C. It is heated in a heat exchanger to a temperature of 350°C, using the remaining heat available in the reformed gas.

The mixed gas, which at this point consists of hydrogen, carbon monoxide and water, is fed into a high-temperature shift reactor. The reaction that takes place in the water-gas-shift reactor is given by reaction (2). The high temperature reaction takes place in the presence of an iron-based catalyst. A conversion of approximately 70.0% is obtained in the high temperature reactor (Newsome, 1980). The product gas leaves the reactor at a temperature of approximately 555°C.

The product gas from the HTS reactor is cooled down to 230°C in a cooler. The cooled down product gas becomes the feed to a low temperature shift reactor. The low temperature shift reaction further takes place in the presence of a copper-based catalyst (Newsome, 1980). The conversion in the low temperature reactor is also approximately 70.0% (Newsome, 1980). The product gas leaves the reactor at a temperature of approximately 285°C. The reaction rate is favoured by high temperatures, whilst maximum conversion is obtained at low temperatures.

The product gas from the low temperature shift reactor is fed into a temperature flash vessel, where the temperature is lowered to 25°C at a pressure of 10 bar and water is separated from the product stream. Further purification of the product stream is done by using a PSA system. The hydrogen-rich stream is purified to 99.0% with an efficiency of 85.0%. The waste stream leaving the PSA plant mainly consists of carbon dioxide and could be recycled in the process, making it self-sustainable on carbon dioxide.

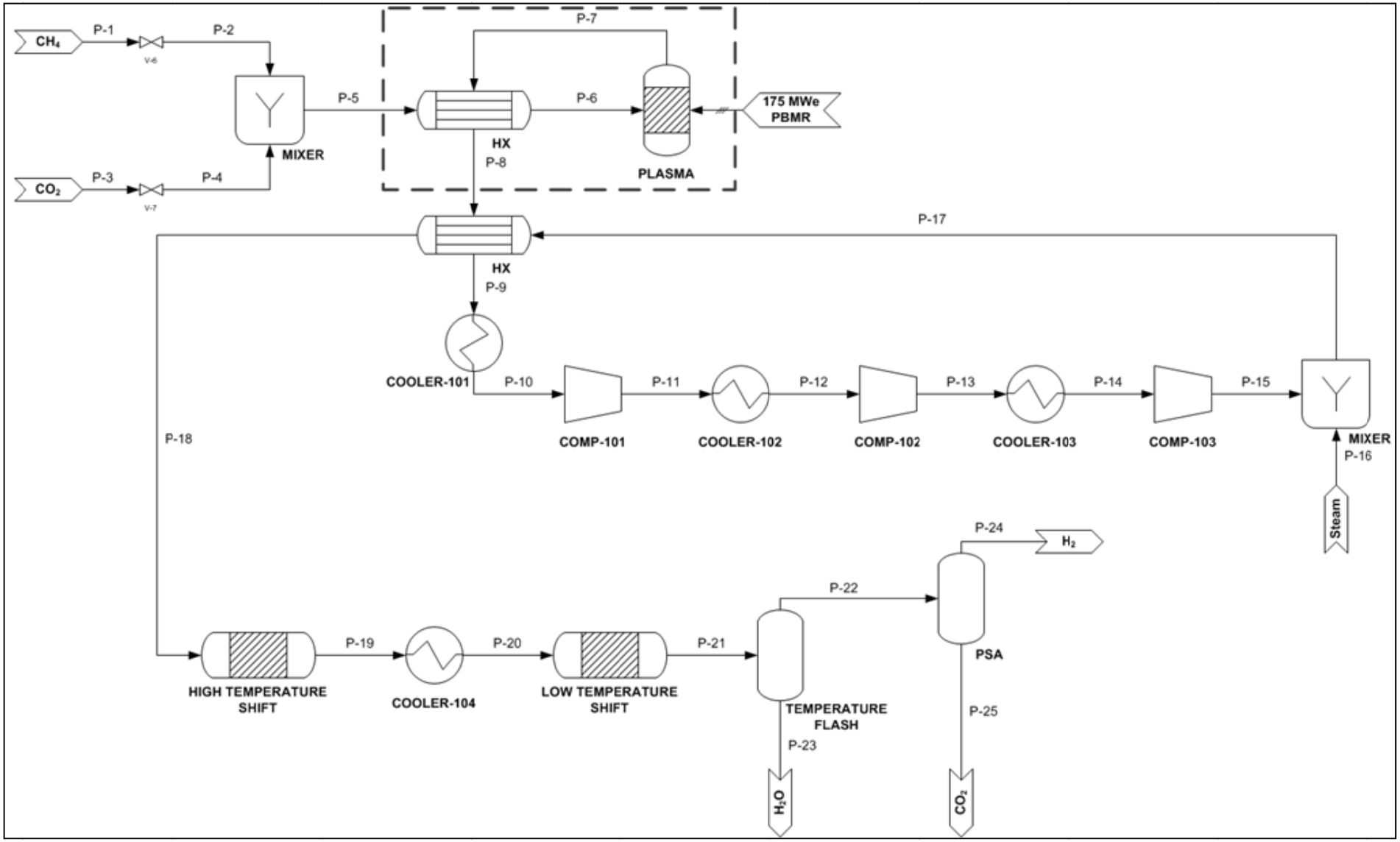

Figure 4.11: Simplified process flow diagram for the production of hydrogen using Plasma-arc Technology, making use of the electrical energy generated by a PBMR

4.4.1.2 Material and energy balances

The Hydrogen Production Process can be divided into four sections, namely:

- Plasma-arc Reforming section;
- compression section;
- water-gas-shift reaction section; and
- purification section.

Table 4.8: Mass and energy balance for the Plasma-arc Reforming section of the Hydrogen Production Process

Component	P-1/P-2	P-3/P-4	P-5	P-6	P-7	P-8
Mass flow rate (kg/h)						
CH_4	30 060.5	-	30 060.5	30 060.5	1 503.0	1 503.0
CO_2	-	82 461.7	82 461.7	82 461.7	4 123.1	4 123.1
H_2	-	-	-	-	7 176.5	7 176.5
CO	-	-	-	-	99 718.8	99 718.8
Total	**30 060.5**	**82 461.7**	**112 522.2**	**112 522.2**	**112 522.2**	**112 522.2**
Volumetric flow rate (Nm^3/h)						
CH_4	42 000.0	-	42 000.0	42 000.0	2 100.0	2 100.0
CO_2	-	42 000.0	42 000.0	42 000.0	2 100.0	2 100.0
H_2	-	-	-	-	79 800.0	79 800.0
CO	-	-	-	-	79 800.0	79 800.0
Total	**42 000.0**	**42 000.0**	**84 000.0**	**84 000.0**	**163 800.0**	**163 800.0**
Temperature (°C)	25.0	25.0	25.0	850.0	1 197.0	430.0
Pressure (barg)	1	1	1	1	1	1
Energy (MW)	-	-	-	53.0	78.7	25.7

Table 4.9: Mass and energy balance for the compression section of the Hydrogen Production Process

Component	P-9	P-10	P-11	P-12	P-13	P-14	P-15
Mass flow rate (kg/h)							
CH_4	1 503.0	1 503.0	1 503.0	1 503.0	1 503.0	1 503.0	1 503.0
CO_2	4 123.1	4 123.1	4 123.1	4 123.1	4 123.1	4 123.1	4 123.1
H_2	7 176.5	7 176.5	7 176.5	7 176.5	7 176.5	7 176.5	7 176.5
CO	99 718.8	99 718.8	99 718.8	99 718.8	99 718.8	99 718.8	99 718.8
Total	**112 522.2**	**112 522.2**	**112 522.2**	**112 522.2**	**112 522.2**	**112 522.2**	**112 522.2**
Volumetric flow rate (Nm^3/h)							
CH_4	2 100.0	2 100.0	2 100.0	2 100.0	2 100.0	2 100.0	2 100.0
CO_2	2 100.0	2 100.0	2 100.0	2 100.0	2 100.0	2 100.0	2 100.0
H_2	79 800.0	79 800.0	79 800.0	79 800.0	79 800.0	79 800.0	79 800.0
CO	79 800.0	79 800.0	79 800.0	79 800.0	79 800.0	79 800.0	79 800.0
Total	**163 800.0**	**163 800.0**	**163 800.0**	**163 800.0**	**163 800.0**	**163 800.0**	**163 800.0**
Temperature (°C)	290.0	99.0	200.0	100.0	200.0	100.0	200.0
Pressure (barg)	1	1	2.2	2.2	4.7	4.7	10
Energy (MW)	16.6	4.6	10.9	4.6	10.9	4.6	10.9

The total conversion of carbon monoxide in the water-gas-shift section of the process is calculated below and the conversion is 91.0%.

$$\text{Conversion} = \frac{CO_{inlet} - CO_{outlet}}{CO_{inlet}}$$
$$= \frac{79800 - 7182}{79800} \times 100$$
$$= 91\%$$

Table 4.10: Mass and energy balance for the water-gas-shift reaction section of the Hydrogen Production Process

Component	P-15	P-16	P-17	P-18	P-19	P-20	P-21
Mass flow rate (kg/h)							
CH_4	1 503.0	-	1 503.0	1 503.0	1 503.0	1 503.0	1 503.0
CO_2	4 123.1	-	4 123.1	4 123.1	113 797.1	113 797.1	146 699.3
H_2O	-	121 864.2	121 864.2	121 864.2	76 966.9	76 966.9	63 497.7
H_2	7 176.5	-	7 176.5	7 176.5	12 200.0	12 200.0	13 707.1
CO	99 718.8	-	99 718.8	99 718.8	29 915.7	29 915.7	8 974.7
Total	**112 522.2**	**121 864.2**	**234 386.4**	**234 386.4**	**234 382.6**	**234 382.6**	**234 381.6**
Volumetric flow rate (Nm^3/h)							
CH_4	2 100.0	-	2 100.0	2 100.0	2 100.0	2 100.0	2 100.0
CO_2	2 100.0	-	2 100.0	2 100.0	57 960.0	57 960.0	74 718.0
H_2O	-	151 620.0	151 620.0	151 620.0	95 760.0	95 760.0	79 002.0
H_2	79 800.0	-	79 800.0	79 800.0	135 660.0	135 660.0	152 418.0
CO	79 800.0	-	79 800.0	79 800.0	23 940.0	23 940.0	7 182.0
Total	**163 800.0**	**151 620.0**	**315 420.0**	**315 420.0**	**315 420.0**	**315 420.0**	**315 420.0**
Temperature (°C)	200.0	350.0	278.0	350.0	523.0	230.0	285.0
Pressure (barg)	10	10	10	10	10	10	10
Energy (MW)	10.9	23.2	33.7	43.7	72.0	28.5	37.1

The hydrogen production for the Plasma-arc Reforming process is 274 tons of hydrogen per day(Table 4.11, stream P24), which is approximately 1.6 times larger than the HYS process, which produces 170 tons of hydrogen per day.

Table 4.11: Mass and energy balance for the purification section of the Hydrogen Production Process

Component	P-21	P-22	P-23	P-24	P-25
Mass flow rate (kg/h)					
CH_4	1 503.0	1 488.0	15.0	14.9	1473.1
CO_2	146 699.3	145 232.3	1 467.0	1 452.3	143 780.0
H_2O	63 497.7	635.0	62 862.7	6.3	628.6
H_2	13 707.1	13 570.0	137.1	11 419.2	2 150.8
CO	8 974.7	8 884.9	89.7	88.8	8 796.1
Total	**234 381.6**	**169 810.2**	**64 571.5**	**12 981.6**	**156 828.7**
Volumetric flow rate (Nm^3/h)					
CH_4	2 100.0	2 079.0	21.0	20.8	2 058.2
CO_2	74 718.0	73 970.8	747.2	739.7	73 231.1
H_2O	79 002.0	790.0	78 212.0	7.9	782.1
H_2	152 418.0	150 893.8	1 524.2	126 977.1	23 916.7
CO	7 182.0	7 110.2	71.8	71.1	7 039.1
Total	**315 420.0**	**234 843.8**	**80 576.2**	**127 816.6**	**107 027.2**
Temperature (°C)	285.0	25.0	25.0	25.0	25.0
Pressure (barg)	10	10	10	10	10
Energy (MW)	37.1	-	-	-	-

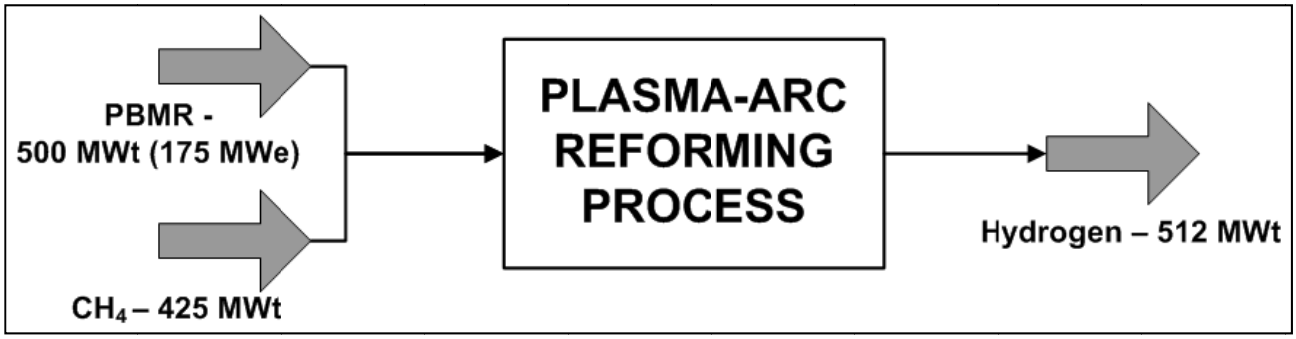

Figure 4.12: Total thermal energy for the Hydrogen Production Process

In Figure 4.12, the thermal energy that enters and leaves the process for the production of hydrogen, using only the electrical energy of a PBMR, can be seen. Below is the calculation of the total thermal energy of the process. Thus, for a 500 MWt PBMR combined with the Plasma-arc Reforming plant, the thermal efficiency is 55.0%.

The compressors and other electrical components in the plant use the remaining electrical energy that is not used by the plasma-arc units.

$$\eta_{thermal} = \frac{\text{Hydrogen Gas}}{\text{Nuclear Energy} + \text{Natural Gas}}$$
$$= \frac{512}{500 + 425}$$
$$= 55\%$$

4.4.1.3 Sensitivity evaluation of the process

A sensitivity evaluation of the process was conducted, in order to determine how the Hydrogen Production Process would be influenced by different methane conversions in the Plasma-arc Reformer Units and different electricity generation cycle.

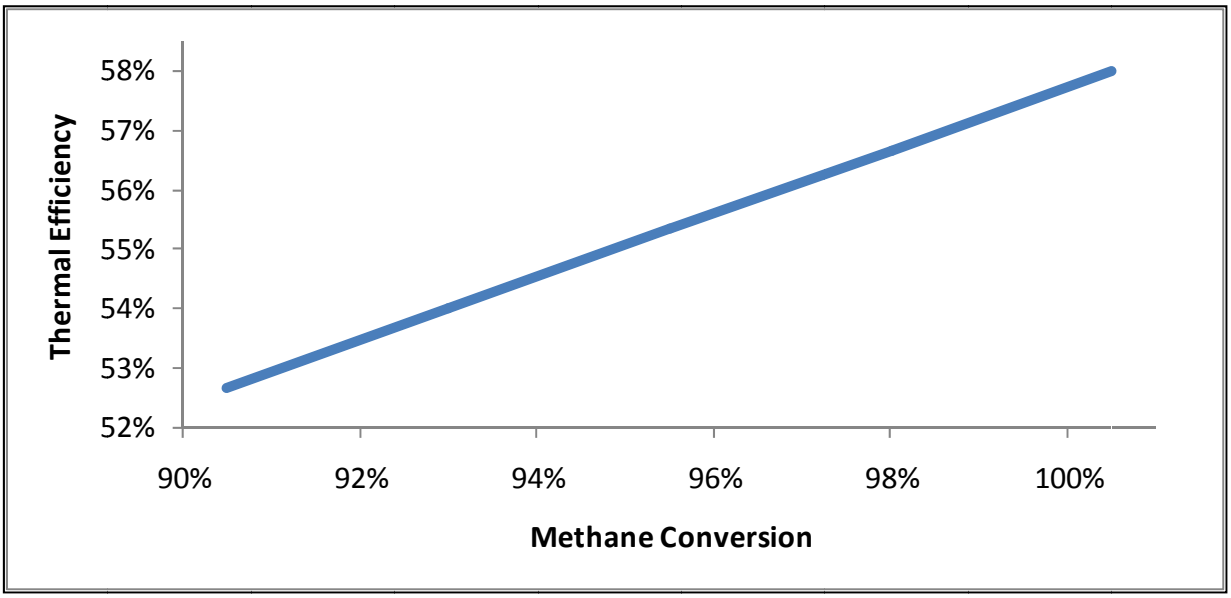

Figure 4.13: Thermal efficiency as a function of methane conversion in the Plasma-arc Reformer Units for the production of hydrogen

Figure 4.13 and Figure 4.14 show how the methane conversion in the Plasma-arc Reformer Units influences the production of hydrogen and the thermal efficiency of the Hydrogen Production Process. The thermal efficiency of the process is directly influenced by the methane conversion, as the conversion of methane in the Plasma-arc Reformer Units increases, the thermal efficiency of the process also increases. The outlet temperature of the process is also influenced by the methane conversion, with increasing conversion the outlet temperature decreases owing to the endothermic nature of the reaction that takes

place in the Plasma-arc Reformer Units. The outlet temperature of the units varies between 1 100°C and 1 300°C. The hydrogen production increases with increasing methane conversion as expected, as more carbon monoxide is produced, which results in a higher additional hydrogen production by the water-gas-shift reaction.

The electricity generation cycle that is used by the process also influences the Hydrogen Production Process. Making use of the assumptions mentioned in section 4.1 and using the Brayton Cycle with an efficiency of 40.0% it was observed that the number of Plasma-arc Reformer Units that can be used increased to twenty-five. The thermal efficiency increases to 60.5% and 135 million kg of hydrogen per year is produced with the Brayton Cycle.

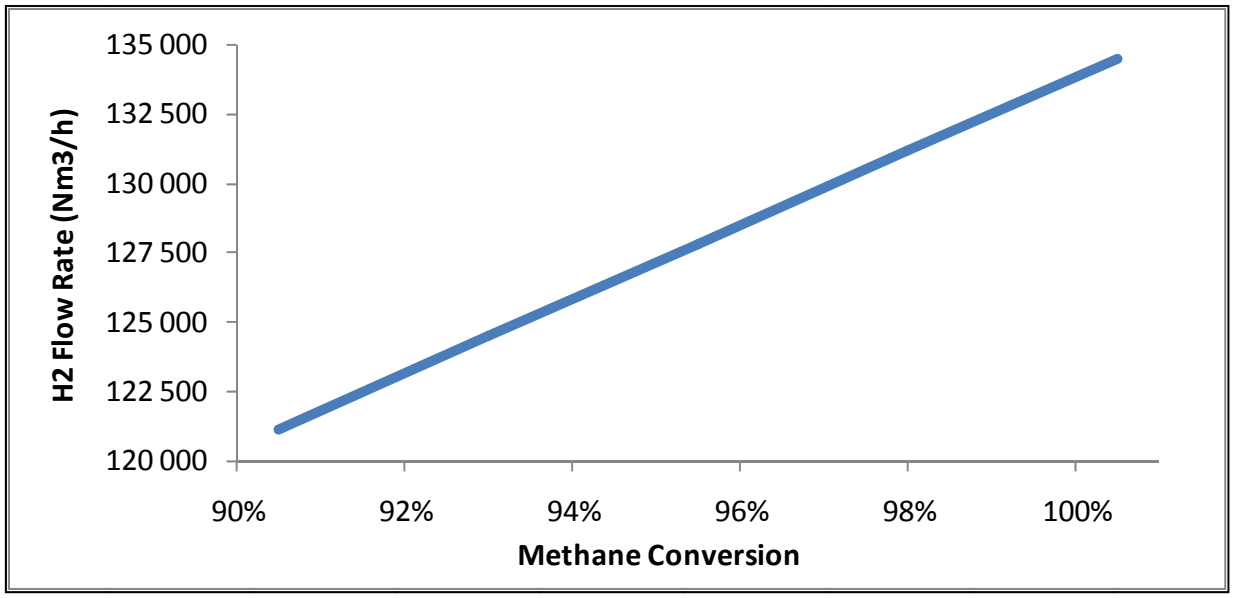

Figure 4.14: Hydrogen flow rate and Plasma-arc outlet temperature as functions of methane conversion in the Plasma-arc Reformer Unit for the Production of Hydrogen

4.4.2 Methane reforming with CO_2 for the production of hydrogen, utilising the electrical and thermal energy of a Pebble Bed Modular Reactor

4.4.2.1 Process description of hydrogen production using CO_2 as the oxidising agent

A simplified process flow diagram of the Hydrogen Production Process can be seen in Figure 4.15. As mentioned in the assumptions made at the beginning of this chapter, a 500 MWt PBMR is used as the source of energy. Both the thermal and the electrical energy generated by a PBMR are used for the production of hydrogen. In this case, it was calculated that only 19×8 MW Plasma-arc Reformer Units could be operated using both energy sources as supplied by the PBMR.

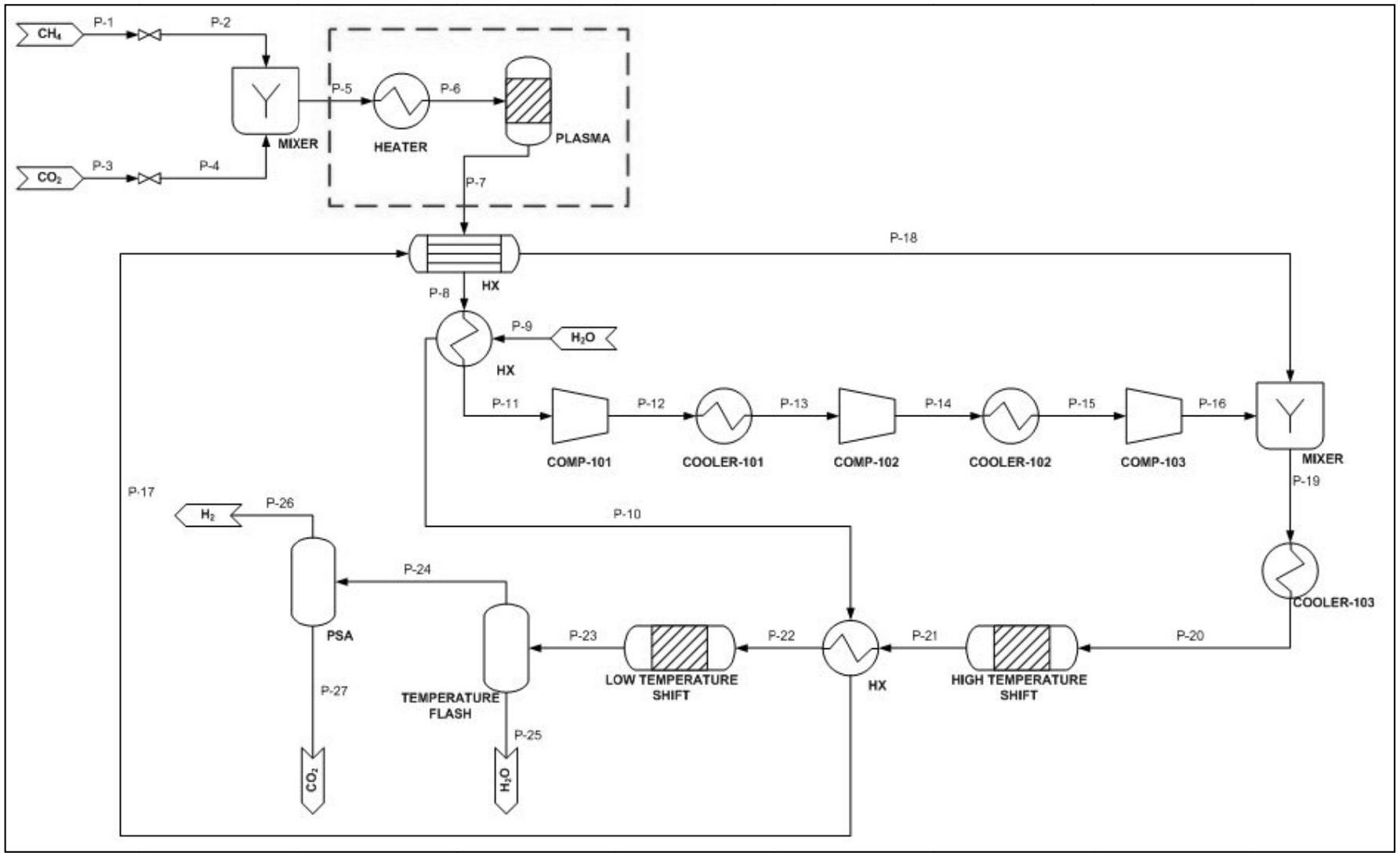

Figure 4.15: Simplified process flow diagram for the production of hydrogen using Plasma-arc Reformer Technology making use of both the electrical and thermal energy generated by a Pebble Bed Modular Reactor

Methane and carbon dioxide are fed at a molar ratio of 1:1 to the reforming process. The reactant gas is first heated from 25°C to 850°C in a heat exchanger as described previously, but in this case the process heat present in the hot helium stream for the PBMR is used for the pre-heating. The pre-heated gas enters the Plasma-arc Reformers according to reaction equation (4), where it is reformed to produce synthesis gas at a temperature of approximately 1 197°C. The remainder of the process is the same as the previous process that has been discussed.

4.4.2.2 Material and energy balances

The Hydrogen Production Process can be divided into four sections, namely:

- Plasma-arc Reforming section;
- compression section;
- water-gas-shift reaction section; and
- purification section.

Table 4.12: Mass and energy balance for the Plasma-arc Reforming section of the Hydrogen Production Process

Component	P-1/P-2	P-3/P-4	P-5	P-6	P-7	P-8
Mass flow rate (kg/h)						
CH_4	27 197.6	-	27 197.6	27 197.6	1 359.9	1 359.9
CO_2		74 608.2	74 608.2	74 608.2	3 730.4	3 730.4
H_2	-	-	-	-	6 493.0	6 493.0
CO	-	-	-	-	90 221.9	90 221.9
Total	**27 197.6**	**74 608.2**	**101 805.8**	**101 805.8**	**101 805.8**	**101 805.8**
Volumetric flow rate (Nm^3/h)						
CH_4	38 000.0		38 000.0	38 000.0	1 900.0	1 900.0
CO_2		38 000.0	38 000.0	38 000.0	1 900.0	1 900.0
H_2	-	-	-	-	72 200.0	72 200.0
CO	-	-	-	-	72 200.0	72 200.0
Total	**38 000.0**	**38 000.0**	**76 000.0**	**76 000.0**	**148 200.0**	**148 200.0**
Temperature (°C)	25.0	25.0	25.0	850.0	1 197.0	200.0
Pressure (bar)	1	1	1	1	1	1
Energy (MW)	-	-	-	48.0	71.2	9.9

Table 4.13: Mass and energy balance for the compression section of the Hydrogen Production Process

Component	P-8	P-11	P-12	P-13	P-14	P-15	P-16
Mass flow rate (kg/h)							
CH_4	1 359.9	1 359.9	1 359.9	1 359.9	1 359.9	1 359.9	1 359.9
CO_2	3 730.4	3 730.4	3 730.4	3 730.4	3 730.4	3 730.4	3 730.4
H_2	6 493.0	6 493.0	6 493.0	6 493.0	6 493.0	6 493.0	6 493.0
CO	90 221.9	90 221.9	90 221.9	90 221.9	90 221.9	90 221.9	90 221.9
Total	**101 805.8**	**101 805.8**	**101 805.8**	**101 805.8**	**101 805.8**	**101 805.8**	**101 805.8**
Volumetric flow rate (Nm^3/h)							
CH_4	1 900.0	1 900.0	1 900.0	1 900.0	1 900.0	1 900.0	1 900.0
CO_2	1 900.0	1 900.0	1 900.0	1 900.0	1 900.0	1 900.0	1 900.0
H_2	72 200.0	72 200.0	72 200.0	72 200.0	72 200.0	72 200.0	72 200.0
CO	72 200.0	72 200.0	72 200.0	72 200.0	72 200.0	72 200.0	72 200.0
Total	**148 200.0**	**148 200.0**	**148 200.0**	**148 200.0**	**148 200.0**	**148 200.0**	**148 200.0**
Temperature (°C)	200.0	99.0	200.0	100.0	200.0	100.0	200.0
Pressure (bar)	1	1	2.2	2.2	4.7	4.7	10
Energy (MW)	9.9	4.1	9.9	4.1	9.9	4.1	9.9

Table 4.14: Mass and energy balance for the water-gas-shift reaction section of the Hydrogen Production Process

Component	P-9	P-10	P-17	P-18	P-19	P-20	P-21	P-22	P-23
Mass flow rate (kg/h)									
CH_4	-	-	-	-	1 359.9	1 359.9	1 359.9	1 359.9	1 359.9
CO_2	-	-	-	-	3 730.4	3 730.4	102 959.3	102 959.3	132 727.9
H_2O	110 258.1	110 258.1	110 258.1	110 258.1	110 258.1	110 258.1	69 636.7	69 636.7	57 450.3
H_2	-	-	-	-	6 493.0	6 493.0	11 038.1	11 038.1	12 401.6
CO	-	-	-	-	90 221.8	90 221.8	27 066.5	27 066.5	8 120.0
Total	**110 258.1**	**110 258.1**	**110 258.1**	**110 258.1**	**212 063.2**	**212 063.2**	**212 060.5**	**212 060.5**	**212 059.7**
Volumetric flow rate (Nm^3/h)									
CH_4	-	-	-	-	1 900.0	1 900.0	1 900.0	1 900.0	1 900.0
CO_2	-	-	-	-	1 900.0	1 900.0	52 440.0	52 440.0	67 602.0
H_2O	137 180.0	137 180.0	137 180.0	137 180.0	137 180.0	137 180.0	86 640.0	86 640.0	71 478.0
H_2	-	-	-	-	72 200.0	72 200.0	122 740.0	122 740.0	137 902.0
CO	-	-	-	-	72 200.0	72 200.0	21 660.0	21 660.0	6 498.0
Total	**137 180.0**	**137 180.0**	**137 180.0**	**137 180.0**	**285 380.0**	**285 380.0**	**285 380.0**	**285 380.0**	**285 380.0**
Temperature (°C)	25.0	67.0	180.0	716.0	482.0	350.0	535.0	230.0	288.0
Pressure (bar)	10	10	10	10	10	10	10	10	10
Energy (MW)	-	5.5	45	118.1	56.4	28.5	65.2	25.8	33.5

Table 4.15: Mass and energy balance for the purification section of the Hydrogen Production Process

Component	P-23	P-24	P-25	P-26	P-27
Mass flow rate (kg/h)					
CH_4	1 359.9	1 346.3	13.6	13.5	1 332.8
CO_2	132 727.9	131 400.6	1 327.3	1 314.0	130 086.6
H_2O	57 450.3	574.5	56 875.8	5.7	568.8
H_2	12 401.6	12 277.6	124.0	10 331.6	1 946.0
CO	8 120.0	8 038.8	81.2	80.4	7 958.4
Total	**212 059.7**	**153 637.8**	**58 421.9**	**11 745.2**	**141 892.6**
Volumetric flow rate (Nm^3/h)					
CH_4	1 900.0	1 881.0	19.0	18.8	1 862.2
CO_2	67 602.0	66 926.0	676.0	669.3	66 256.7
H_2O	71 478.0	714.8	70 763.2	7.1	707.6
H_2	137 902.0	136 523.0	1 379.0	114 884.1	21 638.9
CO	6 498.0	6 433.0	65.0	64.3	6 368.7
Total	**285 380.0**	**212 477.8**	**72 902.2**	**115 643.6**	**96 834.1**
Temperature (°C)	288.0	25.0	25.0	25.0	25.0
Pressure (bar)	10	10	10	10	10
Energy (MW)	33.5	-	-	-	-

The total production of hydrogen for the process is 248 tons per day, which is 1.45 times more than the HYS process, which as mentioned before produces 170 tons of hydrogen per day.

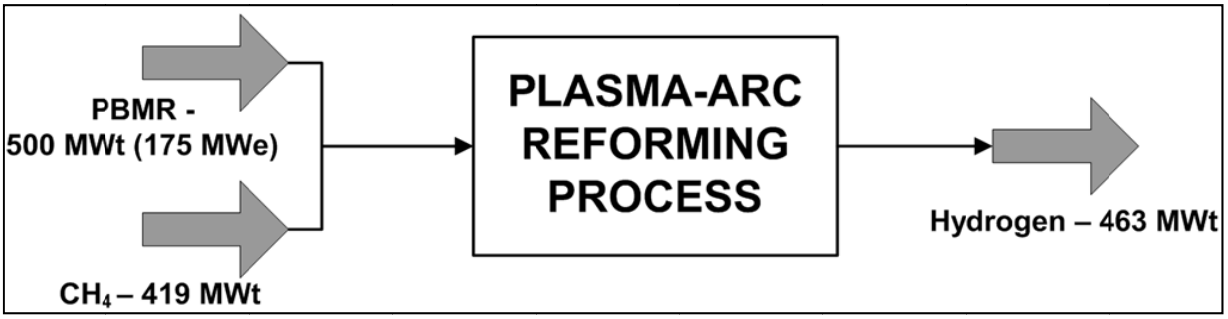

Figure 4.16: The total thermal energy for the Hydrogen Production Process using both the thermal and electrical energy of a Pebble Bed Modular Reactor

In Figure 4.16, the thermal energy that enters and leaves the process for the production of hydrogen, using only the electrical energy of a PBMR, can be seen. Below is the calculation of the total thermal energy of the process. The compressors and other electrical components in the plant use the remaining electrical energy that is not used by the plasma-arc units. Thus, for a 500 MWt PBMR combined with the Plasma-arc Reforming plant, the thermal efficiency is 50.0%.

$$\eta_{thermal} = \frac{\text{Hydrogen Gas}}{\text{Nuclear Energy} + \text{Natural Gas}}$$
$$= \frac{463}{500 + 419}$$
$$= 50\%$$

4.4.2.3 Sensitivity evaluation of the process

A sensitivity evaluation of the process was conducted, in order to determine how the Hydrogen Production Process, which utilises both thermal and electrical energy from the PBMR facility, would be influenced by different methane conversions in the Plasma-arc Reformer Units and different electricity generation cycle.

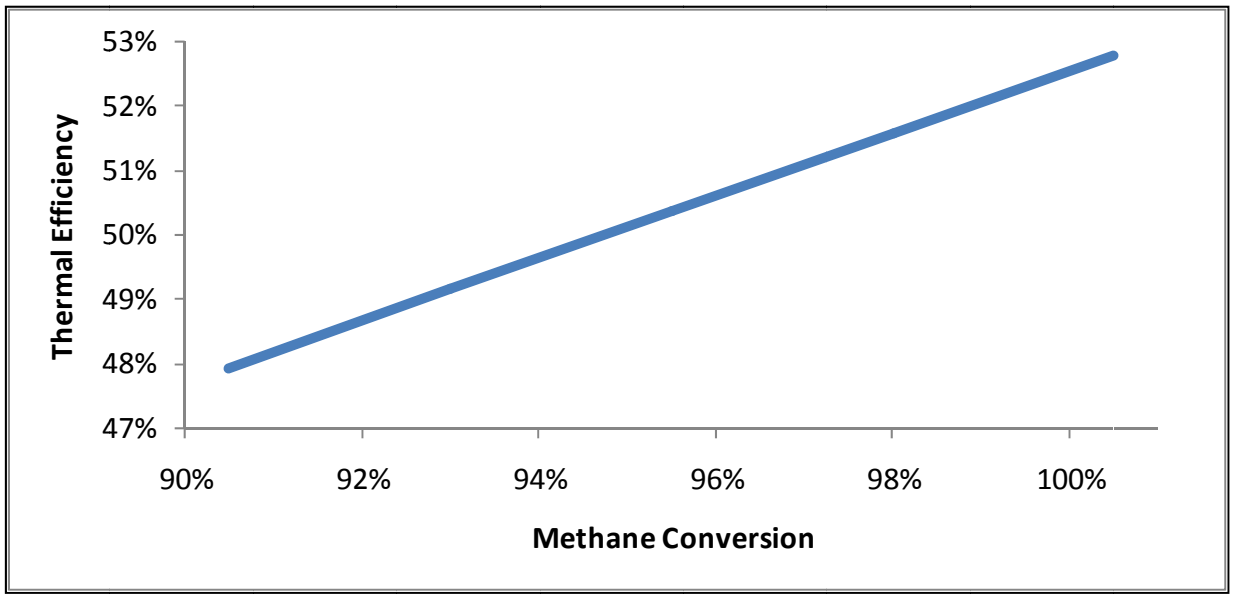

Figure 4.17: Thermal efficiency as a function of methane conversion in the Plasma-arc Reformer Units for the production of hydrogen

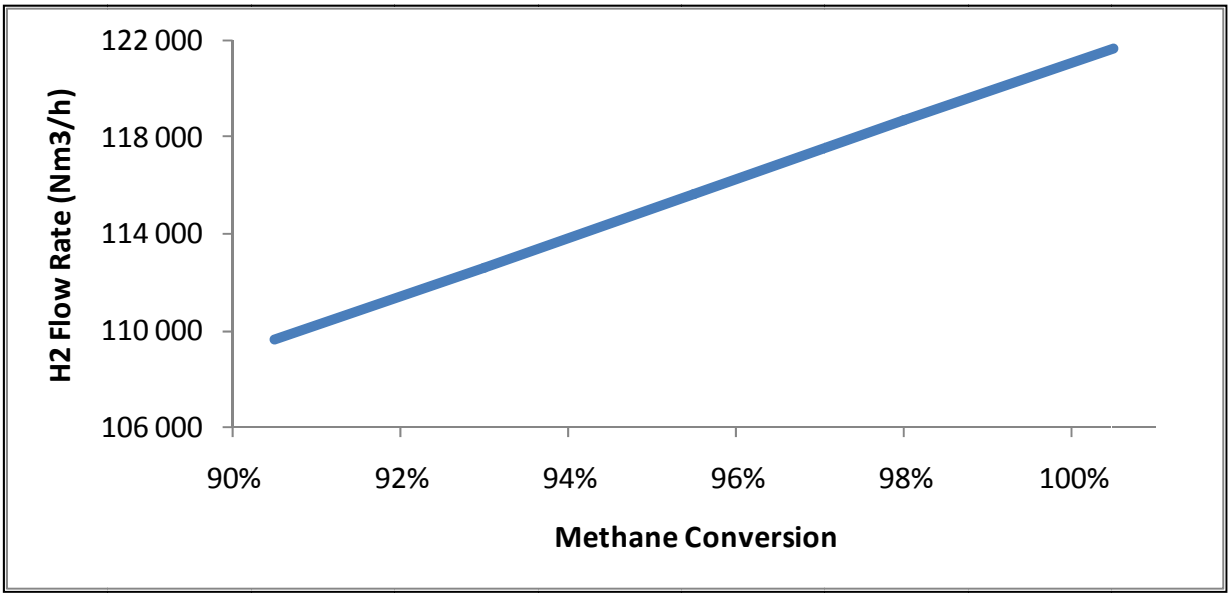

Figure 4.18: Hydrogen flow rate and Plasma-arc outlet temperature as functions of methane conversion in the Plasma-arc Reformer Units for the production of hydrogen

From Figure 4.17 and Figure 4.18, it can be seen that the methane conversion in the Plasma-arc Reformer Units has a major impact on the thermal efficiency and temperature. It is further seen that if the conversion of methane is 90.0%, the thermal efficiency is less than 48.0% and only 107 million kg of hydrogen is produced per year. The temperature decreases with increasing methane conversion, owing to the endothermic nature of the reaction that takes place in the Plasma-arc Reformer Units. This results in an outlet temperature variation of between 1 100°C and 1 300°C as the methane conversion changes.

If the Brayton Cycle with an efficiency of 40.0% is used for the production of electricity, three additional Plasma-arc Reformer Units can be supplied with electricity; thus, a total of twenty-two Plasma-arc Reformer Units can be operated. Using the assumptions stated in section 4.2, the thermal efficiency of the process increases to 54.0% with a production of 119 million kg of hydrogen per year.

4.5 Conclusion

From the data given above, it can be concluded that the hydrogen produced using both the thermal and electrical energy generated by a PBMR is compared to the case where only electrical energy is used. There is approximately a 10.0% decrease in hydrogen production when comparing these two processes.

The thermal efficiency of the process decreases when both the thermal and electrical energy is used for the production of hydrogen; there is a 5% decrease in efficiency when compared with the previous Hydrogen Production Process. Therefore, the conclusion can be drawn that this process is less productive than the first for the production of hydrogen.

For the production of hydrogen where only the electrical energy is used steam from an external source is needed since no excess energy is available compared to the second process where both the thermal and electrical energy is used. From this point of view the second hydrogen production process is better since no external energy source is needed for the supply of high temperature steam.

Chapter 5 - Techno-economic evaluation

5.1 Introduction

In the previous chapter, the various processes using Plasma-arc Reformer Technology for the production of synthesis/hydrogen gas were examined. In this chapter, a techno-economic evaluation is conducted on the different processes that were discussed.

5.2 Assumptions on which the techno-economic evaluation calculations are based

The assumptions as presented in the following table were made for the techno-economic evaluation of the four different processes as discussed in the previous chapter.

Table 5.1: Techno-economic evaluation assumptions

Parameter	Unit	Value/Assumptions
Higher heating value (HHV) of CH_4	MJ/Nm^3	36.4
Higher heating value of synthesis gas	MJ/Nm^3	11.8
Construction time	years	2
Economic lifetime after construction	years	20
Discount rate	per year	9%
Inflation rate	per year	5%
Tax rate	per year	35%
Feedstock costs:		
CH_4	per GJ	\$6.00
CO_2	per ton	\$5.00
Process water	per ton	\$0.53
Steam (10 bar)	per ton	\$15.00
Electricity cost	per kWh	\$0.045
Cooling water	per ton	\$0.08

The values tabulated in Table 5.1 were taken from Peters, Timmerhaus and West (2003) and the Marshall and Swift Index for 2007 was used for the calculations of the equipment costs.

The following assumptions were applied for the sensitivity analysis:

- varying the cost of natural gas between $3 and $10 per gj;
- varying the cost of carbon dioxide between $0 and $20 per ton;
- varying the cost of electricity between $0.03 and $0.1 per kWh; and
- increasing the capital cost of the Plasma-arc Reforming plant by 5.0%, 10.0%, 15.0% and 20.0%.

The transformer and rectifier costs used were obtained through quotation from Siemens. The other equipment costs were calculated using the equations given in Appendix B because not all the companies who supply these equipment are willing to provided the cost information for the purpose of this investigation and the economic model and values as given in Peters *et al*. (2003) were used for the economic evaluation of the process.

5.3 Techno-economic evaluation of the process for the production of synthesis gas

As mentioned in the previous chapter, the production of synthesis gas is categorised into two processes. The first process only uses carbon dioxide and the second is a combined process, where both water and carbon dioxide are used as the oxidising agents for the production of synthesis gas. A techno-economic analysis was conducted for both these processes, in order to determine the production cost of synthesis gas.

5.3.1 Techno-economic evaluation of synthesis gas production using CO_2 as the oxidising agent

5.3.1.1 Production cost and cash flow calculations

The total volumetric flow rate of synthesis gas for the process is 1 435 million Nm^3 for the year over which the techno-economic evaluation was done. The total capital investment cost of the plant can be divided into two sections: firstly, the fixed capital investment cost, which is subdivided into the equipment, direct and indirect costs; and secondly, the working capital cost. The total equipment cost of the process is given in Table 5.2 and the total capital cost of the process in Table 5.3.

Table 5.2: Equipment cost of synthesis gas production utilising CO_2 as the oxidising agent

Equipment type	Amount of units	Cost per unit	Total costs of units
Plasma-arc Unit (Torch)	21	$100 000	$2 100 000
Transformer	21	$540 541	$11 351 351
Rectifier	21	$270 270	$5 675 675
Heat exchanger	7	$95 330	$667 310
Compressors (feed)	2	$939 346	$1 883 692
TOTAL COST			**$21 678 029**

Table 5.3: Estimation of the total capital investment for the production of synthesis gas, using CO_2 as the oxidising agent

Direct cost	**% of Delivered equipment**	
Equipment	100%	$21 678 029
Installation of equipment	39%	$8 454 431
Instrumentation	26%	$5 636 288
Pipes	31%	$6 720 189
Electrical systems	10%	$2 167 803
Buildings	18%	$3 902 045
Yard improvements	12%	$2 601 363
Utilities	55%	$11 922 916
Total direct cost		**$63 083 064**
***Indirect* cost**		
Engineering and supervision	32%	$6 936 969
Construction expenses	34%	$7 370 530
Legal expenses	4%	$867 121
Contractor's fee	19%	$4 118 825
Contingency	37%	$8 020 871
Total indirect cost		**$27 314 316**
Fixed capital investment cost		**$90 397 381**
Working capital cost		**$10 847 686**
TOTAL CAPITAL INVESTMENT COST		**$101 245 066**

All the information required for calculating the production cost of the synthesis gas produced by the plant is given in Table 5.4. The costs of the various items were calculated using the assumptions as stated in section 5.2. The production cost of 1 435 million Nm^3 synthesis gas per year was calculated as \$0.12 per Nm^3 or \$10.43 per GJ.

Table 5.4: Calculation of the production cost of synthesis gas using CO_2 as the oxidising agent

Item	Default percentage	Base	Cost per year
Raw materials: Natural gas Carbon dioxide Total			**\$80 353 728** **\$3 611 821** **\$83 965 549**
Utilities			\$66 571 168
Operating labour			\$4 217 119
Operating supervision	15%	of Operating labour	\$632 568
Maintenance and repairs	7%	of FCI	\$6 327 817
Operating supplies	15%	Maintenance & repairs	\$949 173
Laboratory charges	15%	of Operating labour	\$632 568
Total direct production cost			**\$163 295 960**
Taxes (property)	2%	of FCI	\$1 807 947
Financing (interest)	12%	of FCI	\$10 847 685
Insurance	1%	of FCI	\$903 973.81
Rent	0%	of FCI	\$ -
Total fixed charges			**\$13 559 607**
TOTAL PRODUCT COST			**\$176 855 567**

The profitability of any chemical plant can be calculated, by making use of a cash flow analysis. Figure 5.1 illustrates the cumulative cash flow of the plant over a period of twenty years after two years of construction.

A case study was conducted only to determine the economics of the process. In this case, the selling price of synthesis gas for the given plant was assumed to be \$0.15 per Nm^3 or \$13.00 per GJ. This information was used to generate a cash flow diagram.

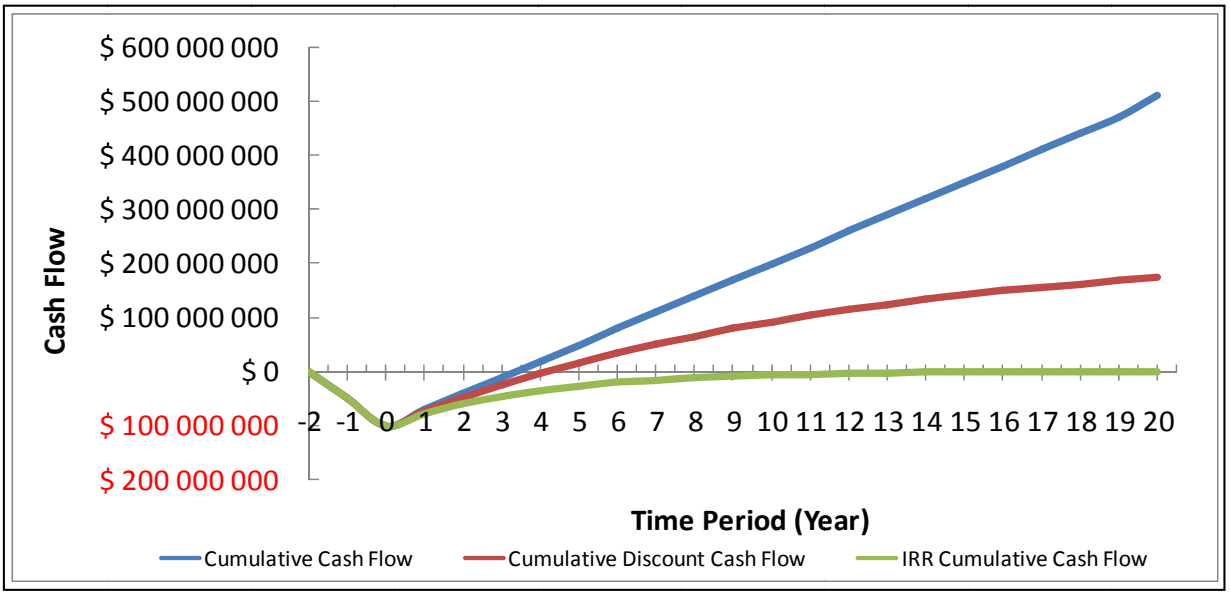

Figure 5.1: Cash flow diagram for the production of synthesis gas using CO_2 as the oxidising agent

From Figure 5.1, it can be observed that the payback period (PBP) of the plant is four years, based on the assumptions made. The net profit value (NPV), the return on investment (ROI) and the internal rate of return (IRR) have also been calculated. The NPV for the given plant is $165 million with a ROI of 45.3% and an IRR of 26.4%, based on the above-mentioned selling price of synthesis gas. Plasma-arc Reforming combined with a nuclear plant offer a profitable option for the production of synthesis gas based on the assumptions made.

5.3.1.2 Sensitivity evaluation

Change in economical parameters

The purpose of the sensitivity evaluation is to investigate how sensitive the profitability of the synthesis gas production process is to changes that might take place over a particular period. The following parameters were evaluated:

- production cost;
- ROI;
- IRR;
- NPV. and
- PBP.

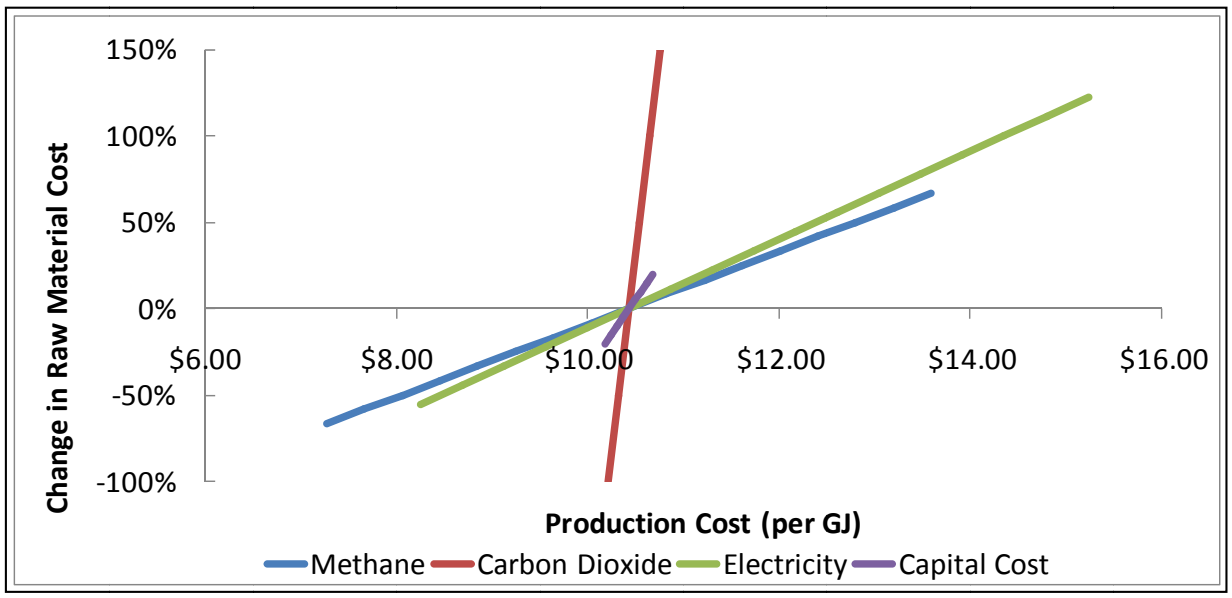

Figure 5.2: **Sensitivity evaluation of the production cost of synthesis gas using CO_2 as the oxidising agent**

From Figure 5.2, it can be seen that the variation in the cost of methane and electricity has the biggest impact on the production cost of synthesis gas compared with that of carbon dioxide. Capital cost also has an impact on the production cost but not to the same extent as that of methane and electricity. The same scenario was observed in the case of the PBP, as can be seen from Figure 5.3. By varying the selling price of the synthesis gas, it is seen that the lower the price of synthesis gas, the longer the PBP of the plant becomes. It is very sensitive to changes in synthesis gas price.

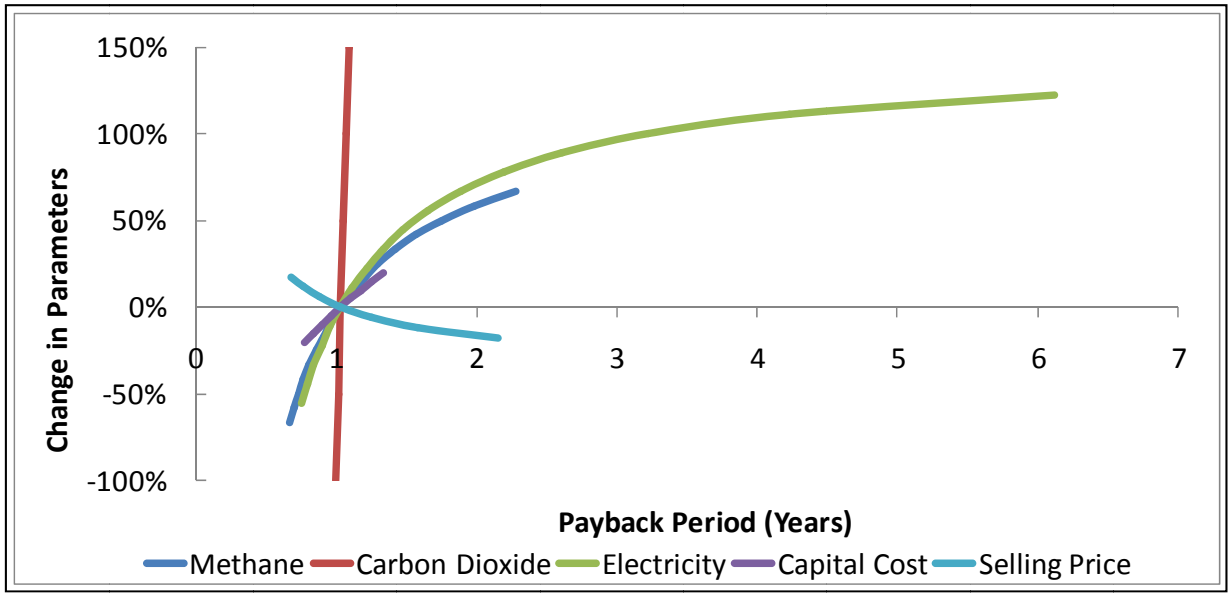

Figure 5.3: **Sensitivity evaluation of the payback period of synthesis gas production using CO_2 as the oxidising agent**

The sensitivity evaluation of the ROI and IRR as a function of the change in parameters, as mentioned, is shown in Figure 5.4 and Figure 5.5. It can be seen from both figures that the change in methane and electricity cost has a major impact on the ROI and IRR values. As the selling price of the synthesis gas increases, a positive increase in both the ROI and IRR values is observed. All the other parameters, such as methane, carbon dioxide, electricity cost, and the capital cost, have a negative impact on the ROI and IRR with an increase in values.

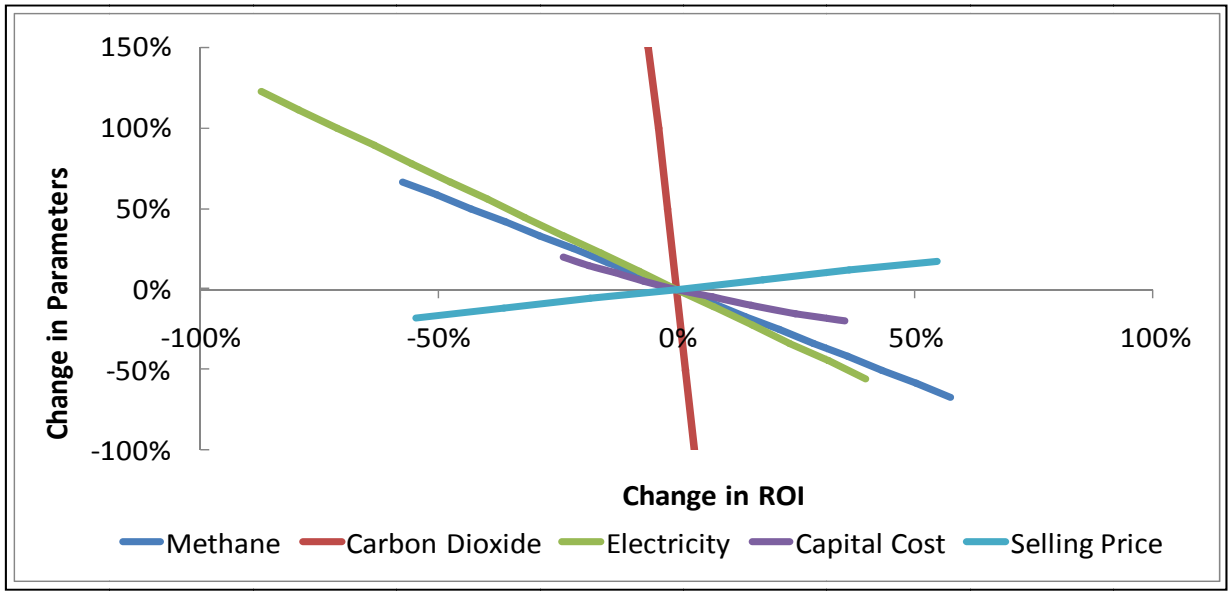

Figure 5.4: Sensitivity evaluation of the return on interest of synthesis gas production using CO_2 as the oxidising agent

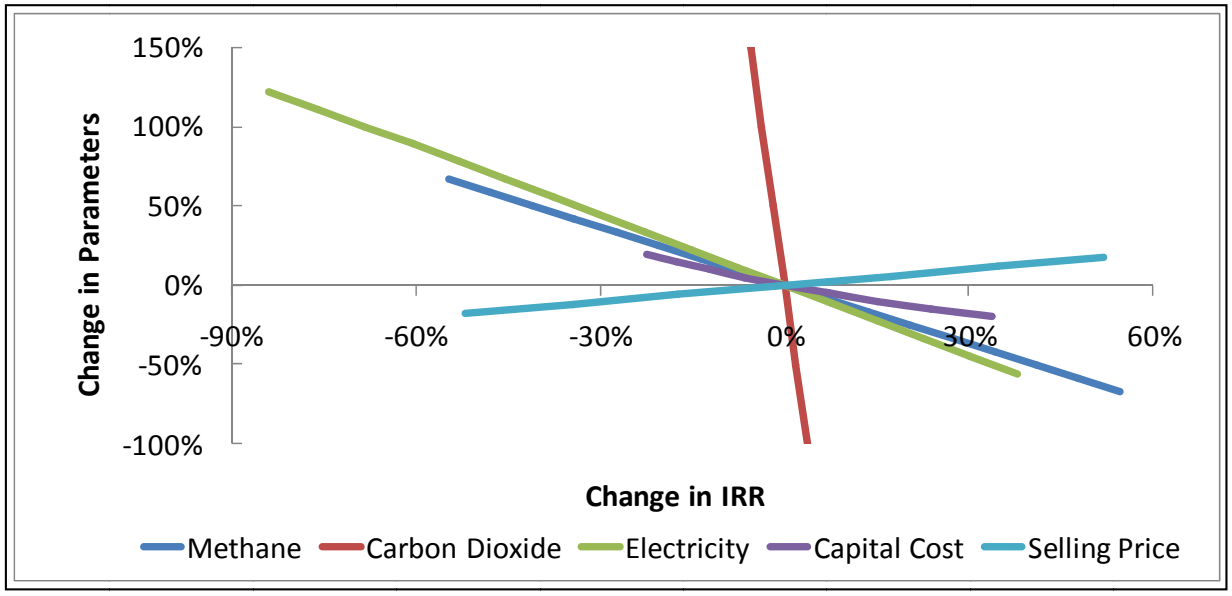

Figure 5.5: Sensitivity evaluation of the internal rate of return of synthesis gas production using CO_2 as the oxidising agent

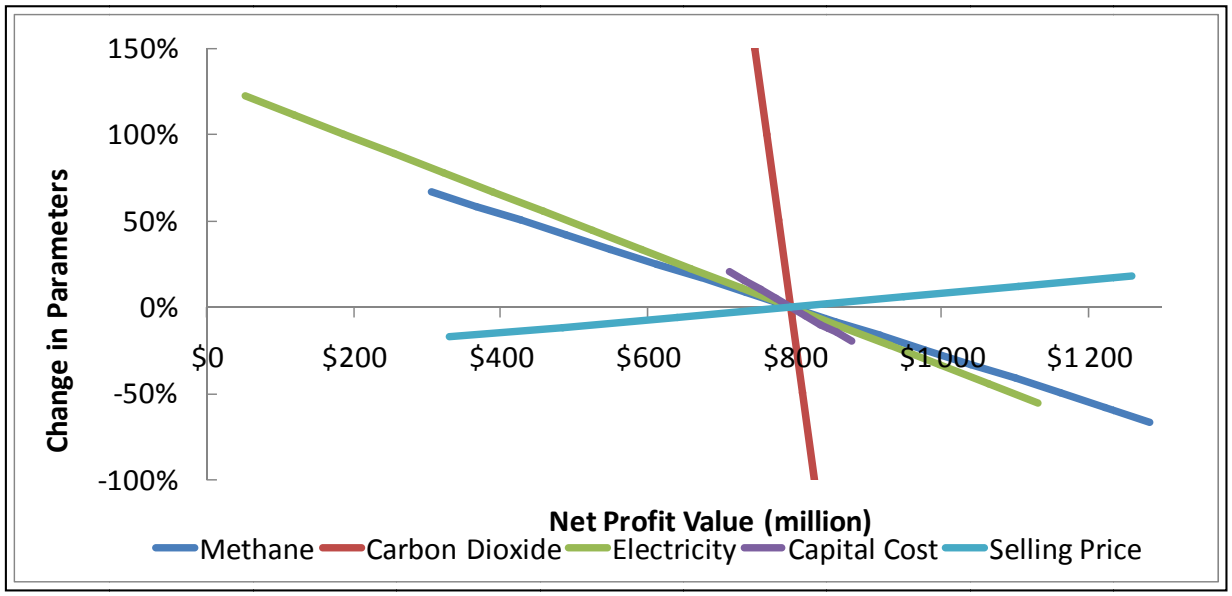

Figure 5.6: Sensitivity evaluation of the net profit value of synthesis gas production using CO_2 as the oxidising agent

As shown, methane and electricity costs have a major impact on the process profitability. The same tendency is observed in Figure 5.6, but in this case the capital cost also has a significant impact on the NPV of the plant. Therefore, by increasing the values of methane, electricity and capital cost, a decrease in the NPV is observed.

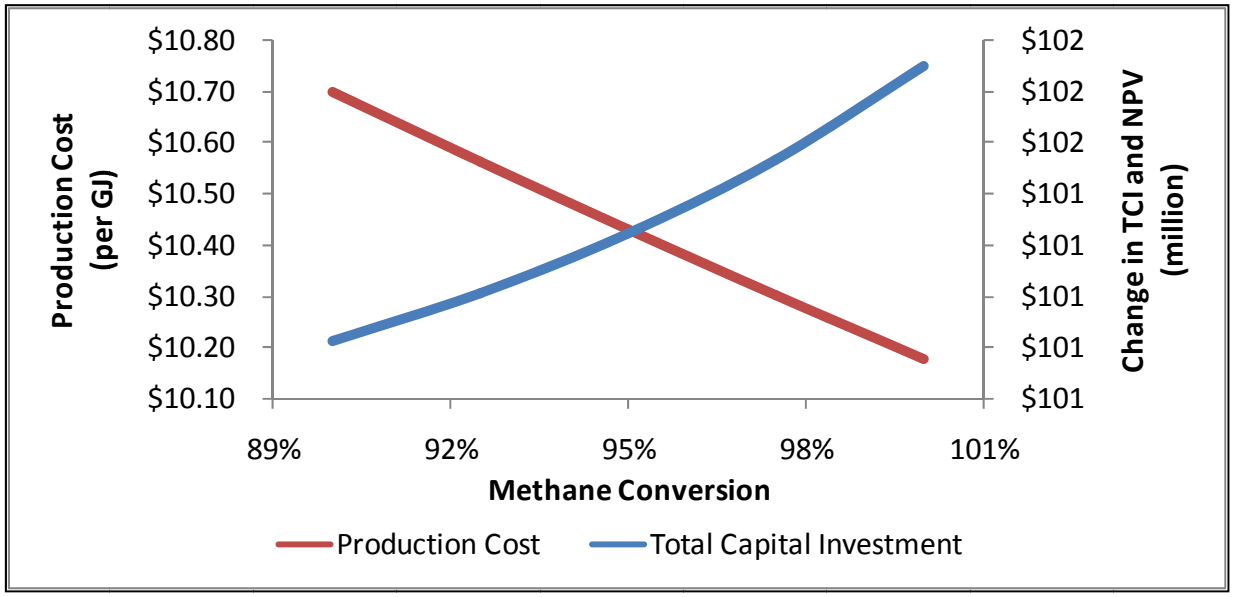

Figure 5.7: Sensitivity evaluation of the production cost and total capital cost at different methane conversions for the production of synthesis gas

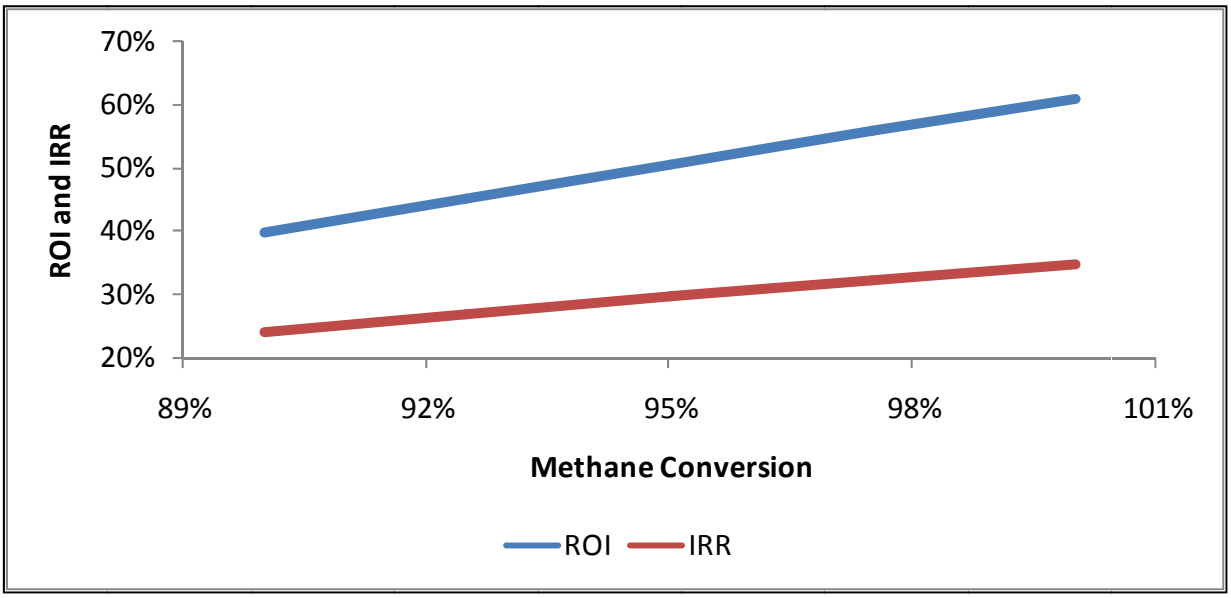

Figure 5.8: Sensitivity evaluation of return on investment and the internal rate of return at different methane conversions during the production of synthesis gas

Change in process parameters

In Chapter 4, a sensitivity evaluation was conducted, in order to determine what effect the methane conversion would have on the production of synthesis gas. Figure 5.7 and Figure 5.8 show the economical effect of the different methane conversions on the process. As expected, the production cost of synthesis gas decreases with the increasing methane conversion in the Plasma-arc Reformer Units, which in turn influences the NPV of the process. The NPV varies between $125 and $224 million as the synthesis gas production cost decreases. A very small, even dismissible change occurs in the total capital cost of the plant.

Variations that occur in the production cost also affect the ROI and IRR of the process. As the production cost decreases owing to increasing methane conversion, the ROI and IRR of the process increases. Thus, it is seen that methane conversion of the process indirectly influences these values and the profitability of the process.

Making use of Brayton Cycle as an alternative means of the required electricity generation also affects the process on an economical level. The affect of this cycle is shown, Table 5.5, where it is compared with the Rankine Cycle for which the economical study was conducted in section 5.3.1.1. From the table, it can be observed that there is an increase of 26.0% in the net profitability and a decrease in the year needed to generate the capital cost of the plant.

Table 5.5: Effect of different electricity generation cycles

Parameters	Rankine Cycle	Brayton Cycle
Production cost (per GJ)	$10.43	$10.37
ROI	45.3%	53.3%
IRR	26.4%	30.9%
NPV	$165 million	$222 million
PBP (years)	4.0	3.2

5.3.2 Techno-economic evaluation of synthesis gas production using CO2 and steam as the oxidising agent

The total production rate of synthesis gas is 1 435 million Nm^3 per year. The total capital investment of the plant can be grouped into two sections; firstly, the fixed capital investment cost, which is subdivided into the equipment, direct and indirect costs; and secondly, the working capital investment cost.

5.3.2.1 Production cost and cash flow evaluations

An economic evaluation was conducted for different feed ratios of carbon monoxide and water as mentioned in Chapter 4 (section 4.3.2.2). The total equipment cost of the process is given in Table 5.6 and the total capital investment cost in Table 5.7.

Table 5.6: Equipment cost of synthesis gas production utilising CO_2 as the oxidising agent

Equipment type	Amount of units	Cost per unit	Total costs of units
Plasma-arc Reformer	21	$100 000	$2 100 000
Transformer	21	$540 541	$11 351 351
Rectifier	21	$270 270	$5 675 676
Heat exchanger (gas to gas)	7	$95 316	$667 214
Heat exchanger (gas to water)	1	$703 617	$703 617
Compressors (feed)	2	$956 846	$1 913 692
TOTAL COST			**$22 411 549**

Table 5.7: Estimation of the total capital investment for the production of synthesis gas using CO_2 as the oxidising agent

Direct cost	% of Delivered equipment	
Equipment	100%	$22 411 549
Installation of equipment	39%	$8 740 504
Instrumentation	26%	$5 827 003
Pipes	31%	$6 947 580
Electrical systems	10%	$2 241 155
Buildings	18%	$4 034 079
Yard improvements	12%	$2 689 386
Utilities	55%	$12 326 352
Total direct cost		**$65 217 607**
Indirect cost		
Engineering and supervision	32%	$7 171 696
Construction expenses	34%	$7 619 927
Legal expenses	4%	$896 462
Contractor's fee	19%	$4 258 194
Contingency	37%	$8 292 273
Total indirect cost		**$28 238 552**
Fixed capital investment cost		**$93 456 159**
Working investment cost		**$11 214 739**
TOTAL CAPITAL INVESTMENT COST		**$116 837 096**

The total capital investment cost that was calculated and given in Table 5.7 is the same for all the different hydrogen-to-carbon monoxide ratios in the product gas. It must be noted that the cost of raw materials will change owing to the variation of steam to carbon dioxide ratio in all the different feed streams as discussed in Chapter 4.

The tabulated values and figures for this process are the same as in the case of the previously discussed process. Thus, Table 5.4 and Figure 5.1 to Figure 5.6 can be used to described this process. The production cost and PBPs for the different synthesis gas ratios are given in Table 5.8. For the comparison of the different synthesis gas ratios, the selling price of the synthesis gas was taken as $13.00 per GJ.

Table 5.8: Production cost, payback period, return on investment and internal rate of return for the different H_2-to-CO ratios

Synthesis gas ratio (H_2:CO)	Production cost (per GJ)	PBP (years)	ROI	IRR
1:1	$10.47	4	41.5%	24.5%
1.5:1	$10.39	4	43.9%	25.7%
2:1	$10.33	3.7	45.5%	26.5%
2.5:1	$10.30	3.7	46.6%	27.0%
3:1	$10.27	3.5	47.5%	27.5%

As is evident from Table 5.8, the production cost of the synthesis gas decreases with an increase in synthesis gas ratio (H_2-to-CO ratio). As the hydrogen in the synthesis gas increases, the higher heating value of the synthesis gas increases, which then results in a decrease in the selling price. The reforming reaction with steam is less endothermic, which means that less energy is required compared with only carbon dioxide reforming.

5.3.2.2 Sensitivity evaluation

Change in economical parameters

A sensitivity evaluation was conducted regarding the production cost of synthesis gas, in order to investigate how sensitive the following parameters are to change: the NPV, PBP, ROI and IRR. It was observed that the sensitivity for the different synthesis gas ratios was the same; therefore, only one ratio is illustrated. The ratio 2.5:1 of H_2-to-CO was chosen to illustrate the sensitivity of the combined process of carbon dioxide and water.

Figure 5.9 and Figure 5.10 reveal that the variation in cost of methane and electricity has a major impact on the production cost and PBP of the synthesis gas produced. The effect of steam on both these parameters is very slight and therefore not shown in the figures. As the synthesis gas ratio varies from 1:1 to 3:1, the effect CO_2 has on the process decreases until it has no effect. The effect of capital cost of the plant on the above-mentioned parameters is minimal.

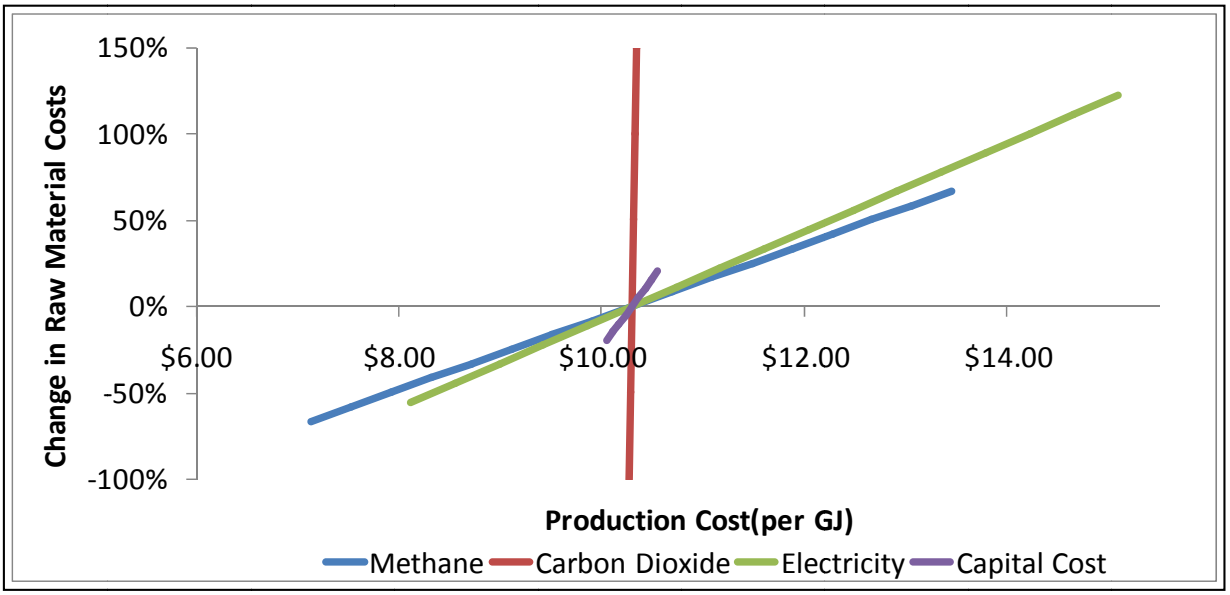

Figure 5.9: Sensitivity evaluation on the production cost of synthesis gas with a H_2-to-CO ratio of 2.5:1, using CO_2 and H_2O as the oxidising agents

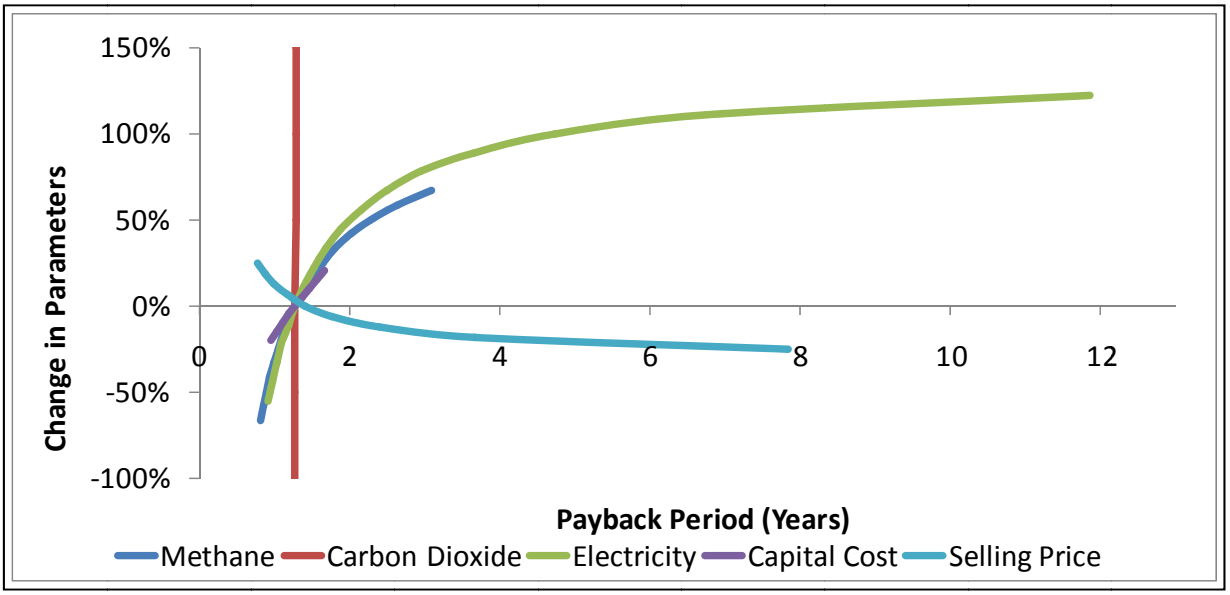

Figure 5.10: Sensitivity evaluation on the payback period of synthesis gas with a H_2-to-CO ratio of 2.5:1, using CO_2 and H_2O as the oxidising agents

As expected from Figure 5.11 and Figure 5.12, the methane and electricity costs have a major impact on the ROI and IRR. It can further be seen that the selling price has a positive effect on ROI and IRR. Thus, the ROI and IRR are strongly influenced by the market that controls the raw material cost and selling price of the synthesis gas.

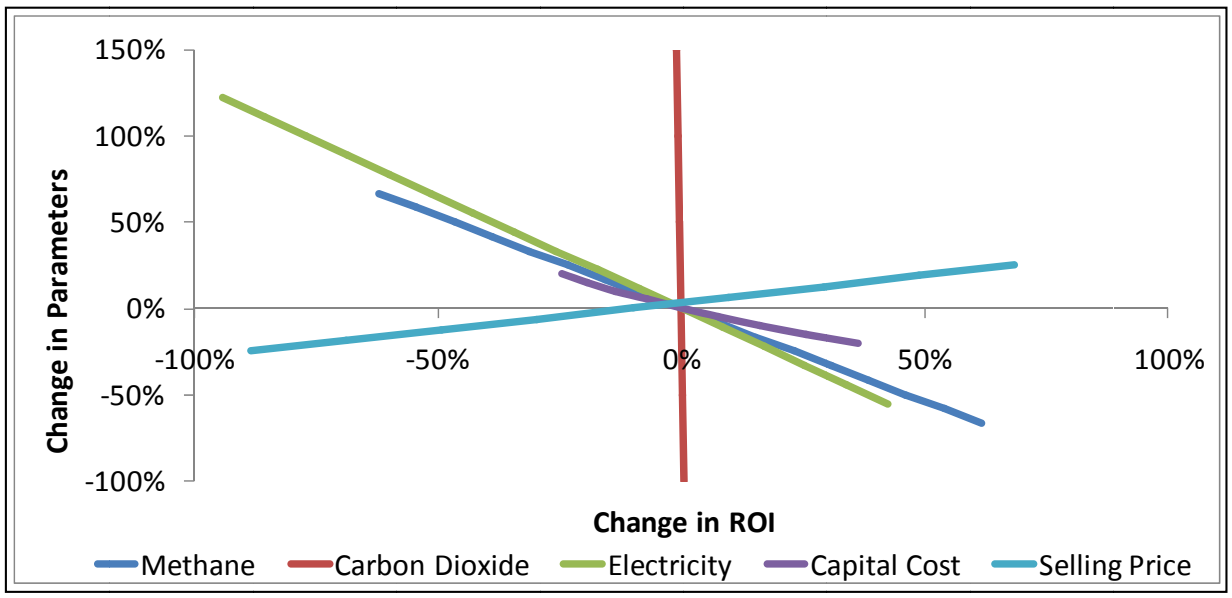

Figure 5.11: Sensitivity evaluation on the return on investment of synthesis gas with a H_2-to-CO ratio of 2.5:1 using CO_2 and H_2O as the oxidising agents

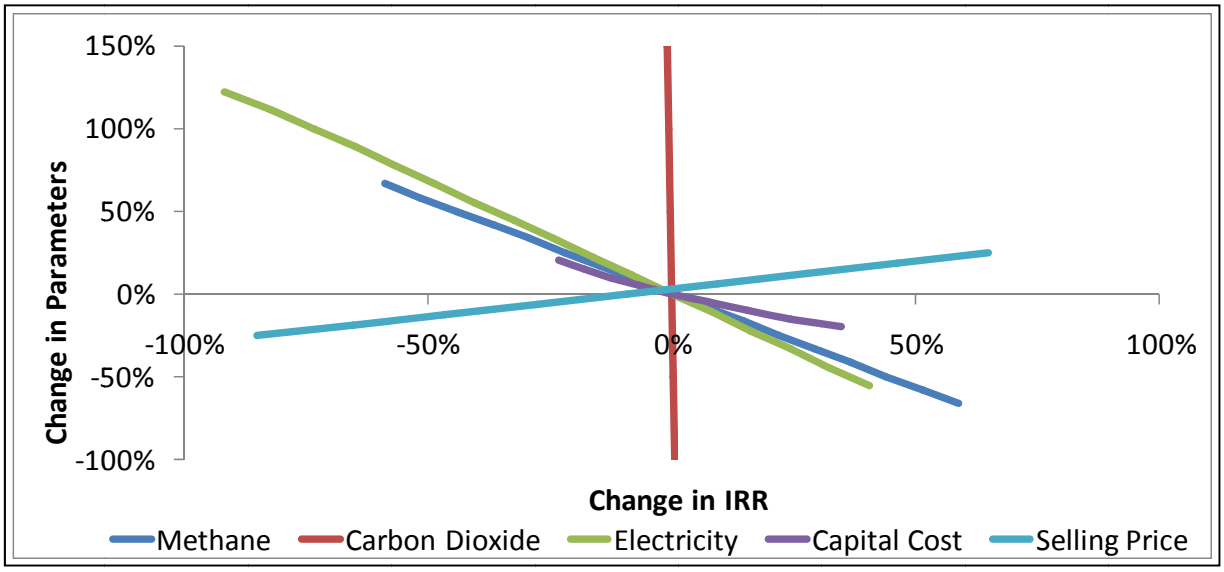

Figure 5.12: Sensitivity evaluation on the internal rate of return of synthesis gas with a H_2-to-CO ratio of 2.5:1 using CO_2 and H_2O as the oxidising agents

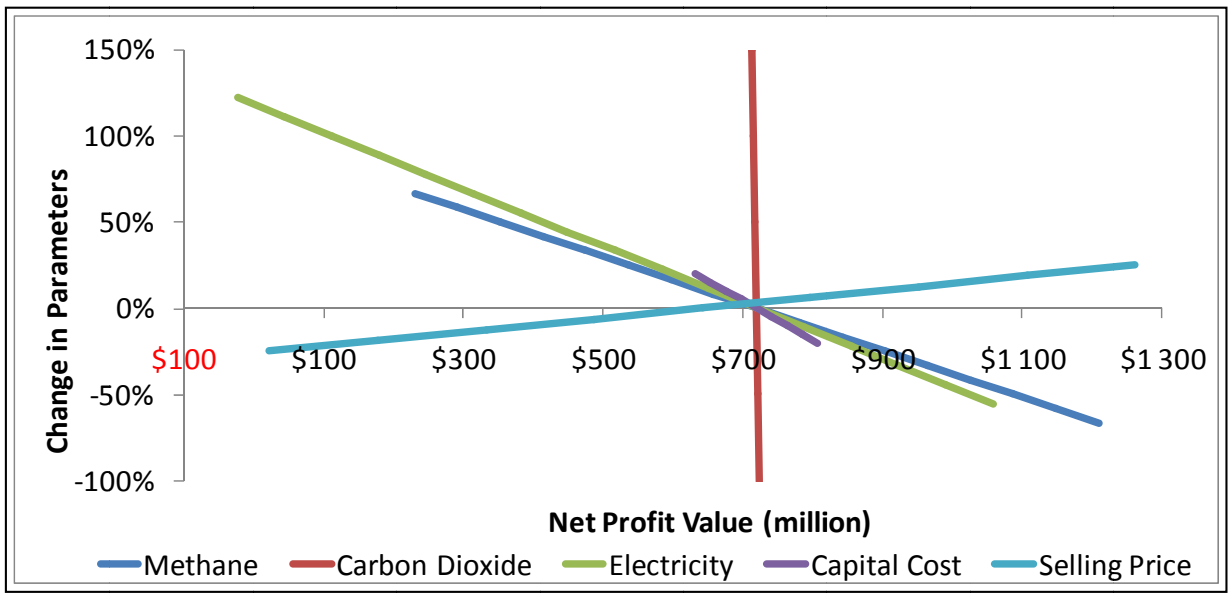

Figure 5.13: Sensitivity evaluation of the net profit value of synthesis gas with a H_2-to-CO ratio of 2.5:1 using CO_2 and H_2O as the oxidising agents

The effect capital cost has on the process is more significant compared with the other parameters, as illustrated in Figure 5.13. The methane and electricity costs are again the major parameters, which will play a significant role in the profit to be generated at the life cycle end of the synthesis gas process plant.

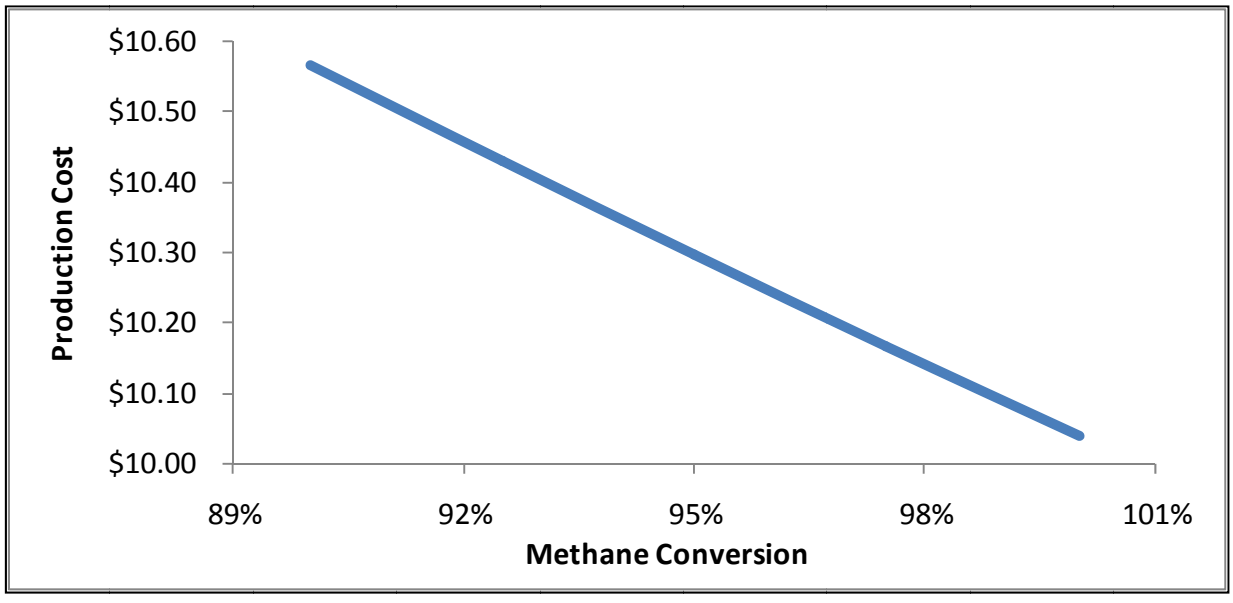

Figure 5.14: Sensitivity evaluation of the production cost at different methane conversions for the production of synthesis gas with a H_2-to-CO ratio of 2.5:1

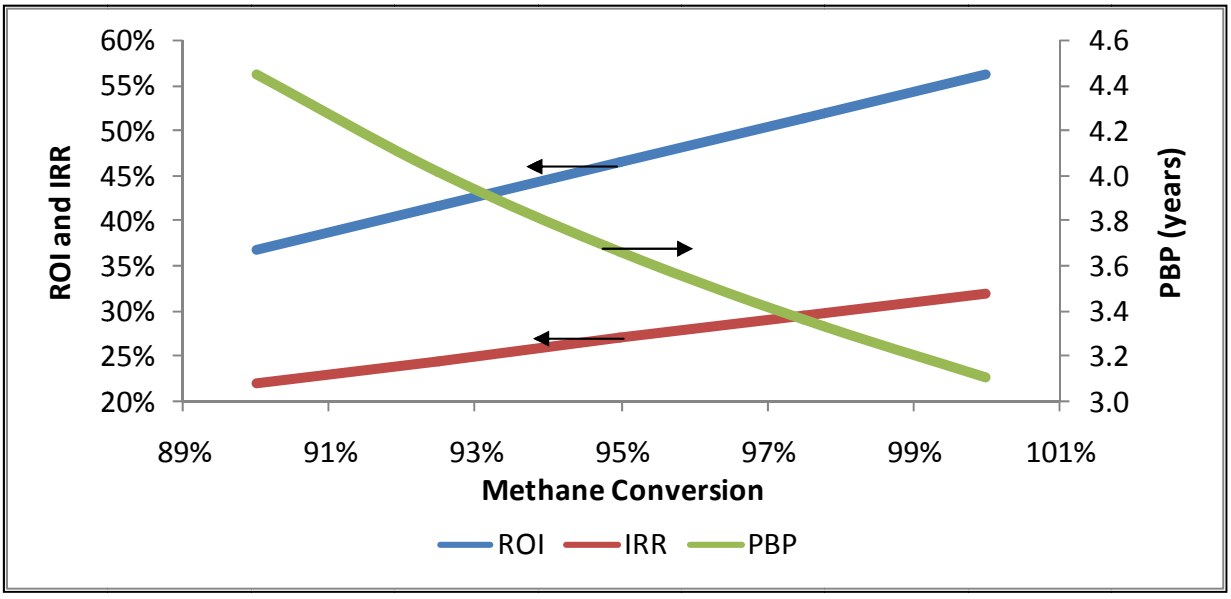

Figure 5.15: Sensitivity evaluation of the return on investment, internal rate of return and payback period at different methane conversions for the production of synthesis gas with a H_2-to-CO ratio of 2.5:1

Change in process parameters

Figure 5.14 andFigure 5.15 show the economical effect of the different methane conversions on the process, and for this sensitivity evaluation the H_2-to-CO ratio was taken as 2.5:1. As expected, the production cost of synthesis gas decreases with the increasing methane conversion in the Plasma-arc Reformer Units, which further results in an increase in the NPV of the process.

Variations that occur in the production cost also affect the ROI and IRR of the process. As the production cost decreases owing to increasing methane conversion, the ROI and IRR of the process increases. As in the previous process, the methane conversion again influences these parameters indirectly through the production cost.

Making use of Brayton Cycle as an alternative means of the needed electricity generation also affects the process on an economical level. The affect of this cycle is shown in Table 5.9, where it is compared with the Rankine Cycle for which the economical study was conducted in section 5.3.1.1. From the Table, it can be observed that there is an increase of 23.0% in the net profitability and a decrease in the year needed to generate the capital cost of the plant.

Table 5.9: Effect of different electricity generation cycles on the combined synthesis gas process

Parameters	Rankine Cycle	Brayton Cycle
Production cost (per GJ)	$10.30	$10.22
ROI	46.6%	50.5%
IRR	27.0%	29.0%
NPV	$178 million	$232 million
PBP (years)	3.7	3.2

5.3.3 Conclusion

The chemical and petrochemical industry needs determine which synthesis gas processing plants will be the better option. Different chemical processes will require different H_2-to-CO ratios. Should a chemical process require a 1:1 ratio of H_2-to-CO, for example, then the first process will be best suited, as the production cost is lower and a higher NPV is generated. In cases where the preferred ratio is between 1:1 and 3:1, the second process is best suited. The higher the H_2-to-CO ratio, the higher the NPV generated and the lower the production cost of the synthesis gas. The electricity generation cycle also influences the production cost and net profitability of the plants.

5.4 Techno-economic evaluation for the production hydrogen

As mentioned in Chapter 4, the production of hydrogen gas can be categorised into two processes. The first process uses only the electrical energy that is generated by a PBMR, whilst the second process makes use of both the thermal and electrical energy for the production of hydrogen gas. A techno-economic evaluation was conducted for both these processes, in order to determine the production cost of hydrogen gas and its profitability. In the case of the second Hydrogen Production Process, the hydrogen production cost varies very little from the first process; therefore, only a techno-economic evaluation was conducted on the first process.

5.4.1 Techno-economic evaluation of the hydrogen production process using the electrical energy from a Pebble Bed Modular Reactor

5.4.1.1 Production cost and cash flow evaluation

The process is capable of producing 1 120 million Nm^3 of hydrogen per year. The total equipment cost of the plant is given in Table 5.10 and the cost of the total capital investment in Table 5.11.

Table 5.10: Equipment cost of hydrogen production using the electrical energy of a Pebble Bed Modular Reactor

Equipment type	Amount of units	Cost per unit	Total costs of units
Plasma-arc Reformer	21	$100 000	$2 100 000
Transformer	21	$540 541	$11 351 351
Rectifier	21	$270 270	$5 675 676
Heat exchanger (Reforming section)	7	$87 890	$615 229
Heat exchangers (cooling)	1	$425 367	$425 367
Compressors (feed)	2	$192 848	$385 696
Compressors (WGS)	1	$15 001 353	$15 001 353
Reactor (HTS)	1	$35 724	$35 724
Reactor (LTS)	1	$35 724	$35 724
PSA	1	$25 922 853	$25 922 853
Flash cooler	1	$200 000	$200 000
TOTAL COST			**$61 748 973**

Table 5.11: Estimation of the total capital investment cost for the production of hydrogen using the electrical energy of a Pebble Bed Modular Reactor

Direct cost	**% of Delivered equipment**	
Equipment	100%	$61 748 973
Installation of equipment	39%	$24 082 100
Instrumentation	26%	$16 054 733
Pipes	31%	$19 142 182
Electrical systems	10%	$6 174 897
Buildings	18%	$11 114 815
Yard improvements	12%	$7 409 877
Utilities	55%	$33 961 935
Total direct cost		**$179 689 512**
Indirect cost		
Engineering and supervision	32%	$19 759 671
Construction expenses	34%	$20 994 651
Legal expenses	4%	$2 469 959
Contractor's fee	19%	$11 732 305
Contingency	37%	$22 847 120
Total indirect cost		**$77 803 706**
Fixed capital investment cost		**$257 493 218**
Working investment cost		**$30 899 186**
TOTAL CAPITAL INVESTMENT COST		**$288 392 405**

The production cost of hydrogen can be calculated making use of the values shown in

Table 5.12. The production cost of hydrogen for a flow rate of 1 120 million Nm^3 per year is calculated as $1.78 per kg or $14.17 per GJ.

Table 5.12: Calculation of the production cost of the hydrogen using the electrical energy of a Pebble Bed Modular Reactor

Item	Default percentage	Base	Cost per year
Raw materials: Natural gas			$80 353 728
Carbon dioxide			$3 611 820
Steam			$16 012 955
Total			**$99 978 504**
Utilities: Electricity			$66 226 956
Cooling water			$1 368 952
Shift catalyst			$640 115
Total			**$68 236 023**
Operating labour			$4 217 119
Operating supervision	15%	of Operating labour	$632 568
Maintenance & repairs	7%	of FCI	$18 024 525
Operating supplies	15%	Maintenance & repairs	$2 703 679
Laboratory charges	15%	of Operating labour	$632 568
Total variable production cost			**$194 424 986**
Taxes (property)	2%	of FCI	$5 149 864
Insurance	1%	of FCI	$2 574 932
Total fixed charges			**$7 724 797**
TOTAL PRODUCT COST			**$202 149 782**

Figure 5.16 illustrates the cash flow of a hydrogen production plant using the electrical energy that is generated by a 500 MWt PBMR nuclear plant. It was assumed that the selling price of hydrogen is $2.50 per kg or $20.00 per GJ. A selling price of $2.50 per kg for hydrogen is generally regarded as acceptable in the industry today. The NPV of the plant is then approximately $380 million with a ROI of 39.0% and an IRR of 23.2%. The PBP of the hydrogen production plant is approximately four years after two years of construction.

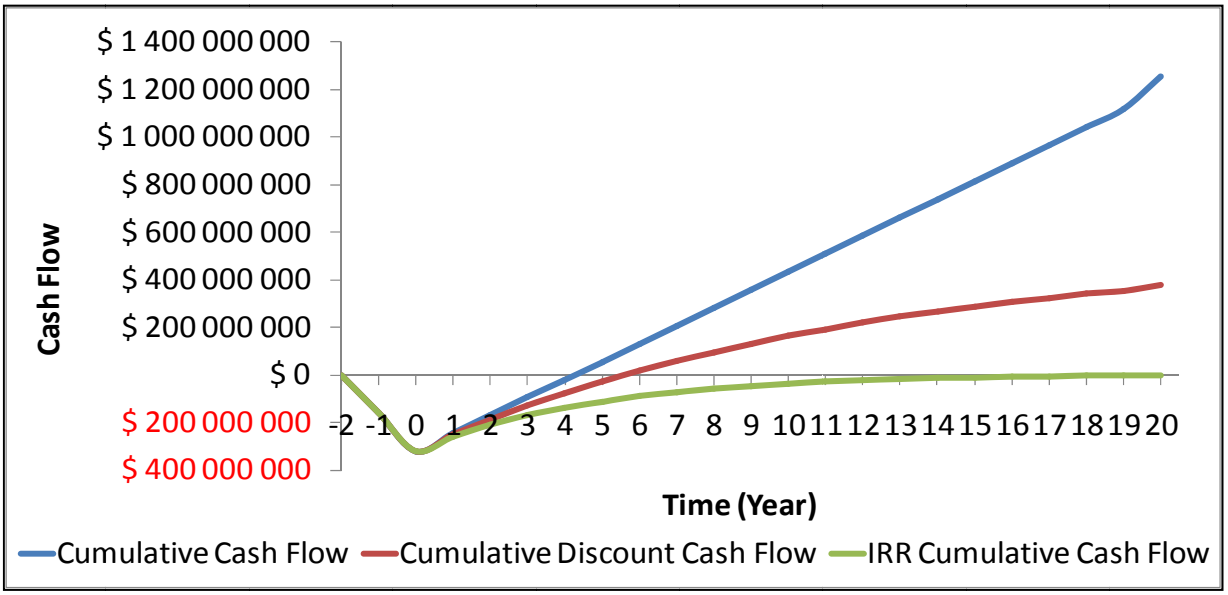

Figure 5.16: **Cash flow diagram for the production of hydrogen using the electrical energy generated by a Pebble Bed Modular Reactor**

5.4.1.2 Sensitivity evaluation of the process

Change in economical parameters

The purpose of the sensitivity evaluation is to investigate how sensitive the process is to changes that may occur in the market place. The parameters that were investigated are the production cost of hydrogen, PBP, ROI, IRR and NPV.

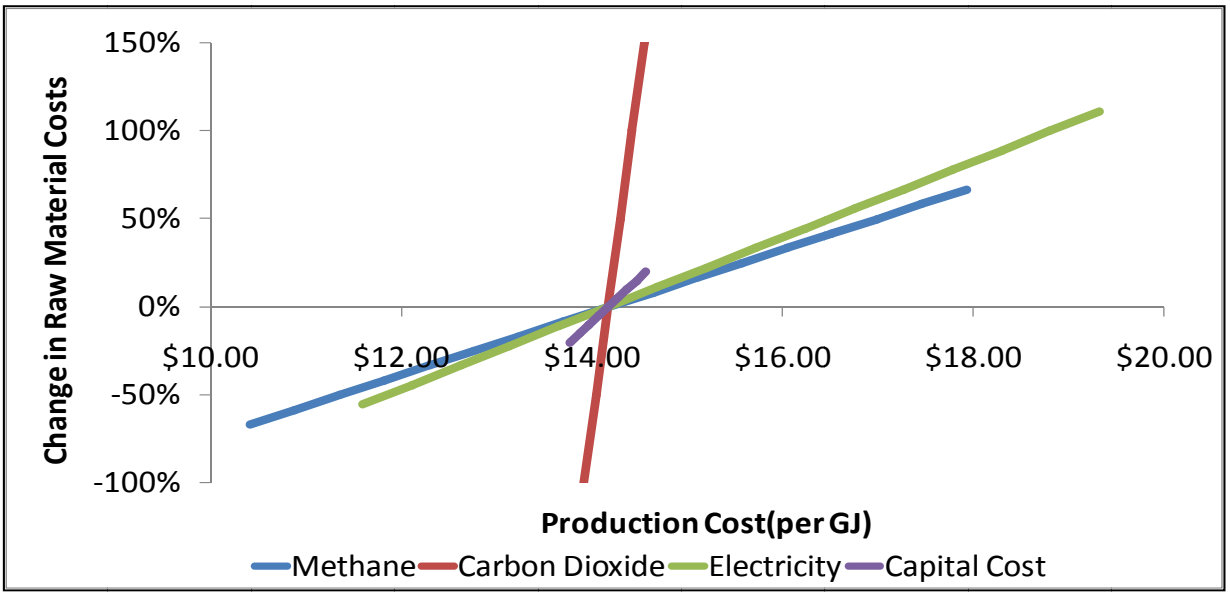

Figure 5.17: **Sensitivity evaluation of the production cost of hydrogen using the electrical energy generated by a Pebble Bed Modular Reactor**

From Figure 5.17 and Figure 5.18, it can be observed that the production cost and PBP are dramatically affected by changes in the methane and electrical costs. The capital cost of the plant has a major impact on the production cost of hydrogen as well as the PBP of the plant. As can be seen from Figure 5.18, an increase in the selling price of hydrogen reduces the PBP of the plant compared with the increases in raw material costs, which increases the PBP of the process plant.

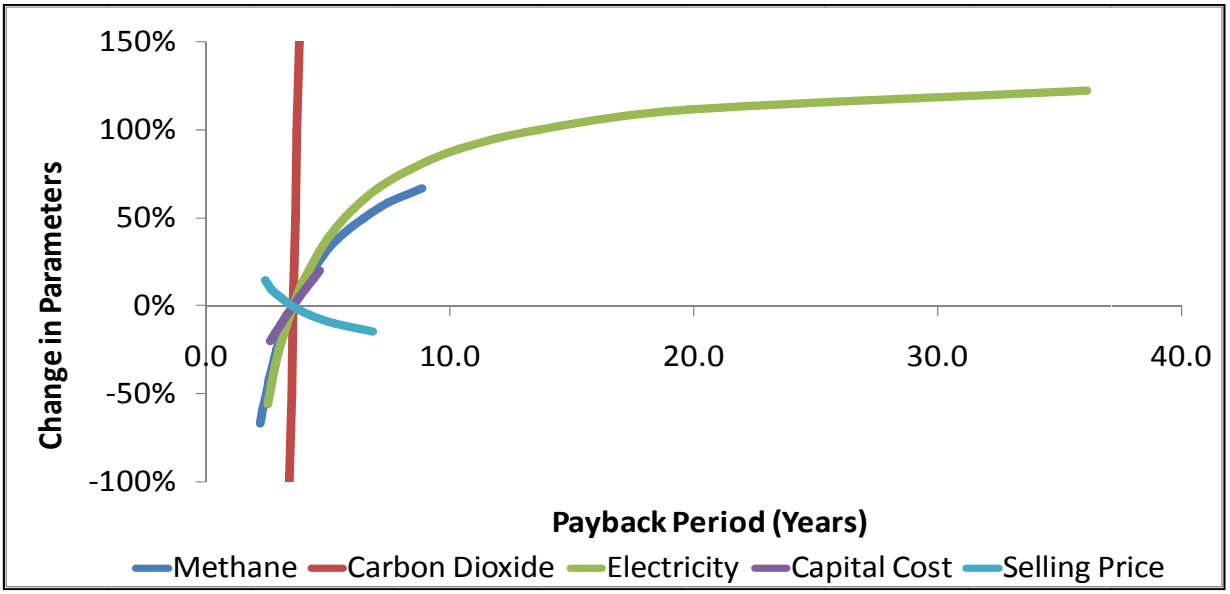

Figure 5.18: Sensitivity evaluation of the payback period of hydrogen using the electrical energy generated by a Pebble Bed Modular Reactor

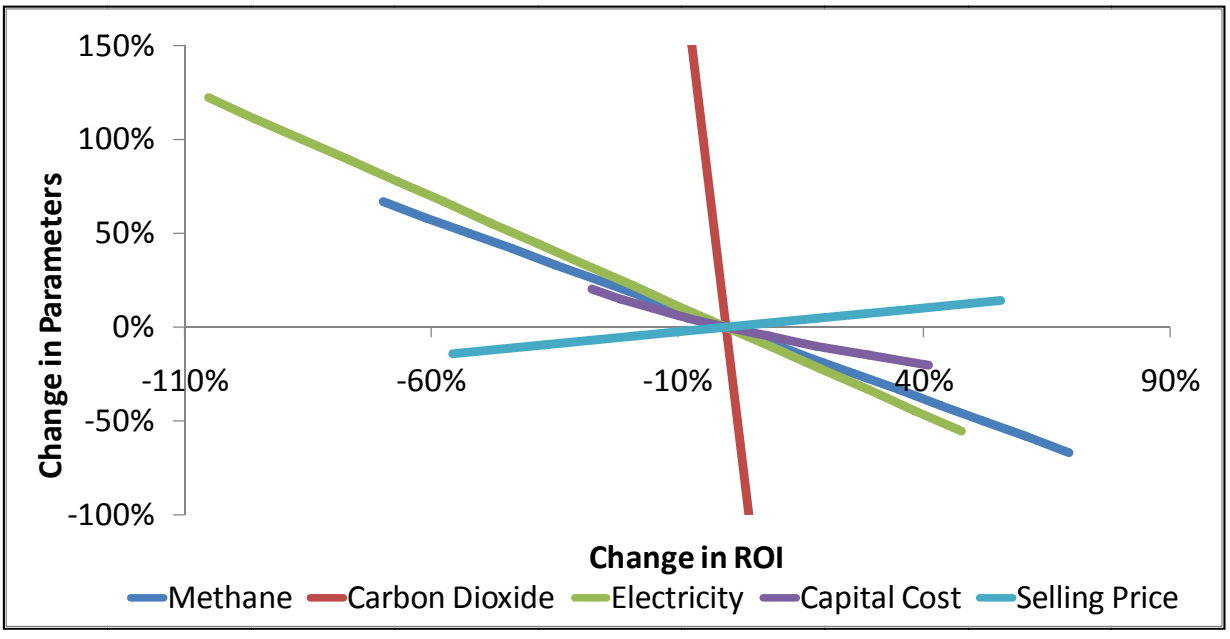

Figure 5.19: Sensitivity evaluation of the return on investment of hydrogen using the electrical energy generated by a Pebble Bed Modular Reactor

The sensitivity of the ROI and IRR is illustrated in Figure 5.19 and Figure 5.20. It is again observed in both these figures that the change in methane and electricity costs has a major impact on the ROI and IRR. As the selling price of the synthesis gas increases, there is a positive increase in the ROI and IRR compared with the methane, carbon dioxide, electricity, and capital costs, which has a negative impact on the ROI and IRR, with increasing values.

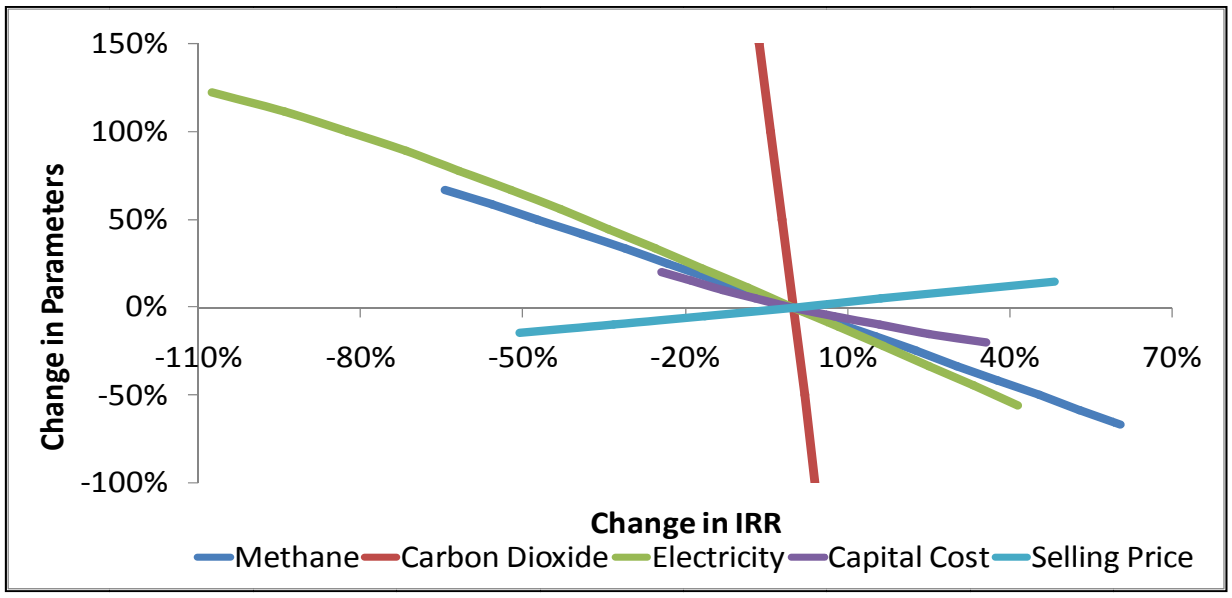

Figure 5.20: **Sensitivity evaluation of the internal rate of return of hydrogen using the electrical energy generated by a Pebble Bed Modular Reactor**

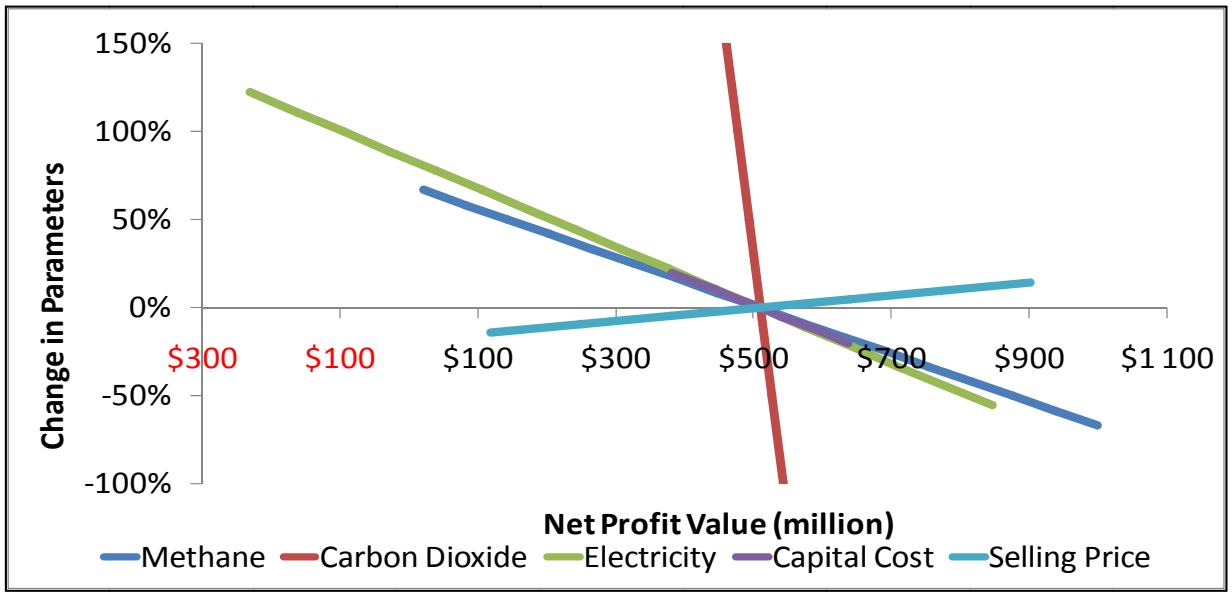

Figure 5.21: **Sensitivity evaluation of the net profit value of hydrogen using the electrical energy generated by a Pebble Bed Modular Reactor**

It is evident that the methane and electricity costs have a major impact on the process profitability. The same is observed in Figure 5.21, but here the capital cost has a major impact on the NPV of the plant. Thus, an increase in the values of methane, electricity and capital costs result in a decrease in the NPV. The carbon dioxide cost has a minor effect on the NPV.

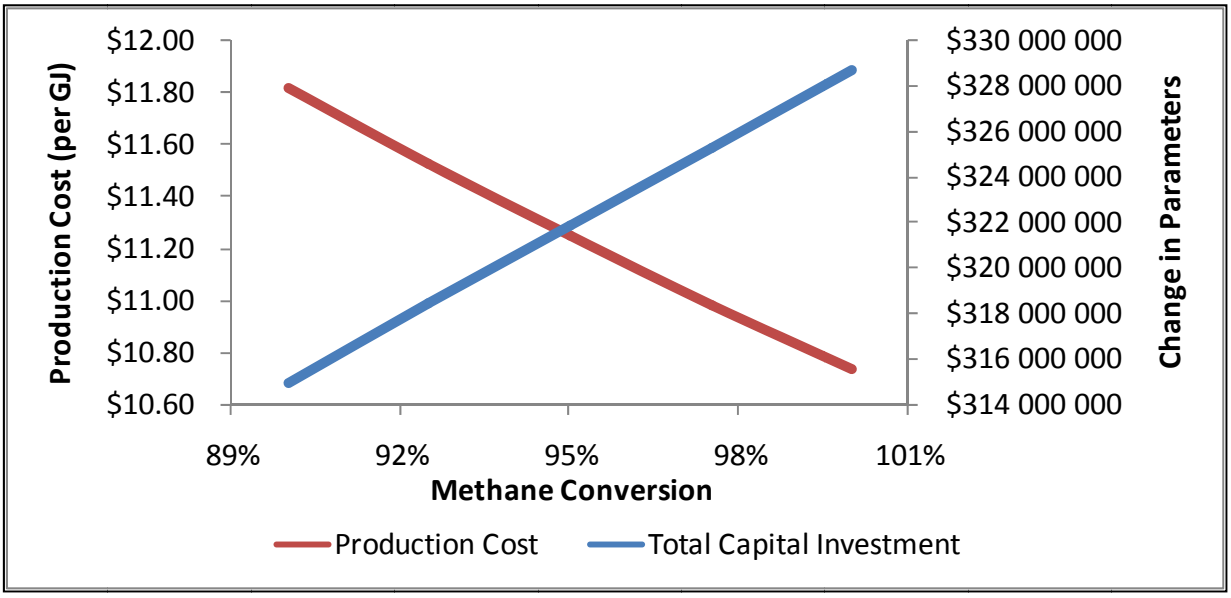

Figure 5.22: Sensitivity evaluation of production cost, total capital cost and net profit value at different methane conversions for the production of hydrogen

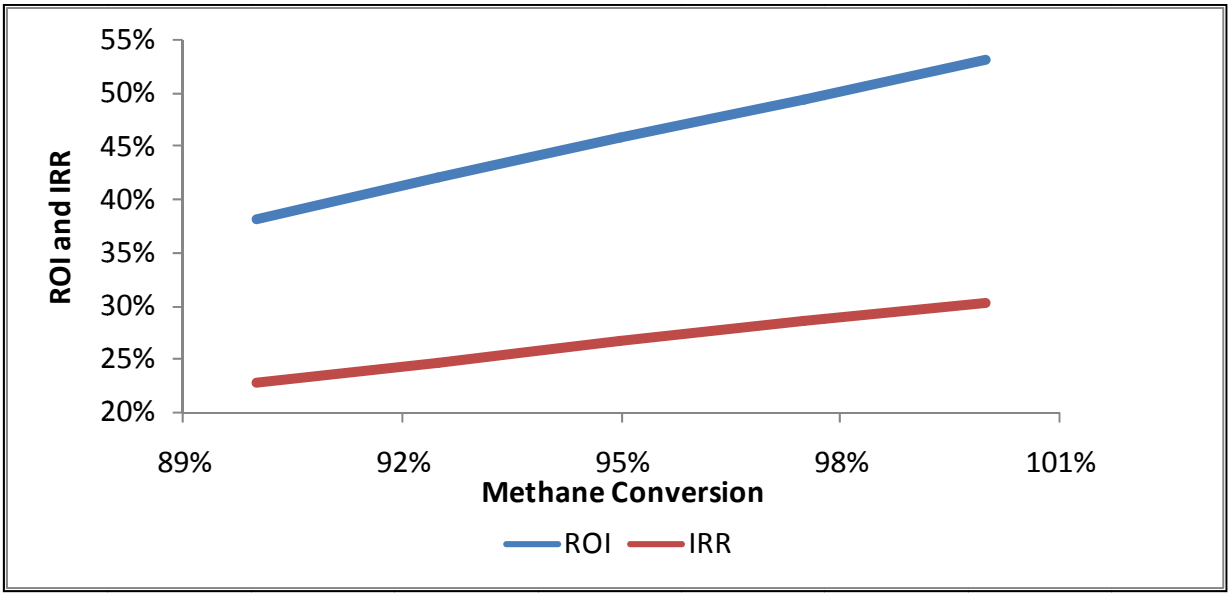

Figure 5.23: Sensitivity evaluation of the return on investment, internal rate of return and payback period at different methane conversions for the production of hydrogen

Change in economical parameters

In Chapter 4, a sensitivity evaluation was conducted, in order to determine what effect the methane conversion would have on the production of hydrogen, using only the electrical energy. Figure 5.22 and Figure 5.23 show the economical effect of the different methane conversions on the process. As expected, the production cost of synthesis gas decreases with the increasing methane conversion in the Plasma-arc Reformer Units, which further results in a NPV. A very small increase in the total capital cost of the plant is seen with the increasing methane conversion achieved by the Plasma-arc Reformer Units.

Variations that occur in the production cost also affect the ROI and IRR of the process. As the production cost decreases owing to increasing methane conversion, the ROI and IRR of the process increase. Thus, it is seen that methane conversion of the process indirectly influences these values.

Making use of Brayton Cycle as an alternative means of the needed electricity generation also affects the process on an economical level. The affect of this cycle is shown Table 5.5, where it is compared with the Rankine Cycle for which the economical study was conducted in section 5.3.1.1. From the table, it can be observed that there is an increase of 22.0% in the net profitability and a decrease in the year needed to generate the capital cost of the plant. There is also a decrease of $0.13 in the production cost of the hydrogen produced by the plant.

Table 5.13: Effect of different electricity generation cycles on the combined synthesis gas process

Parameters	Rankine Cycle	Brayton Cycle
Production cost (per GJ)	$14.17	$14.04
ROI	39.0%	41.8%
IRR	23.2%	24.6%
NPV	$380 million	$485 million
PBP (years)	3.8	3.6

5.4.2 Conclusion

It can be concluded that the cost of methane and electricity has a major impact on the process. The process is very sensitive to any changes that may occur in the market regarding these two parameters. The capital cost only starts playing a vital role in the NPV of the plant, but its effect on the other factors of the process is minor. The second Hydrogen Production Process, which utilises both the thermal and the electrical energies, is \$0.13 per GJ cheaper than the first process, but the production of hydrogen is 100 million Nm^3 less than the first process. Considering this, it is observed that the first process is more desirable than the second process.

Chapter 6 - Comparison of Steam Methane Reforming with Non-catalytic Plasma-arc Reforming

6.1 Introduction

Steam reforming of methane is currently the most widely used process in the industry for the production of synthesis gas and hydrogen. The SMR Process can be categorised into two processes. The first is the conventional process, where fossil fuels are used for the generation of the energy required; and the second, where the thermal energy generated by a HTR nuclear plant is used. Considering the above, it is important to compare a non-catalytic Plasma-arc Reforming process with a SMR Process for the production of synthesis gas and/or hydrogen.

6.2 Comparison of the Steam Methane Reforming and Plasma-arc Methane Reforming Process for the production of synthesis gas

Sogge *et al*. (1994) investigated the following processes: the conventional SMR and pre-reforming SMR Process. The conventional SMR plant under investigation produces approximately 141.6 tons of synthesis gas per hour and the pre-reforming SMR plant produces approximately 136.2 tons of synthesis gas per hour. The capital costs of these plants were $167.99 million and $120.86 million respectively (Sogge *et al*., 1994).

Comparing this information with the two non-catalytic Plasma-arc Reforming processes which have been investigated for the production of synthesis, it was seen that the capital cost of the non-catalytic Plasma-arc Reforming plants are competitive with that of SMR plants. The Plasma-arc Reforming plant produces approximately 112.5 tons of synthesis gas per hour, with the capital cost of the two plants varying between $113 million and $116 million respectively.

6.3 Comparison of the Steam Methane Reforming and Plasma-arc Methane Reforming Process for the production of hydrogen

Many investigations have been conducted regarding the production cost of hydrogen using the SMR Process. Some of the investigations available in the literature combine the SMR Process with a steam cycle or gas turbines for generating electricity. It should be kept in mind that the production cost of hydrogen produced by the SMR Process is influenced by additional income owing to the selling of excess steam and electricity that could be generated.

From Corradetti and Desideri (2007), their reference SMR plant has a capacity of 302.4 tons of H_2 per day and has a capacity similar to the plants that have been investigated in this research project. The capacity of the hydrogen produced by Non-catalytic Plasma-arc Reforming is 321.2 tons of H_2 per day.

The assumptions that wre applied in the investigation by Corradetti and Desideri (2007) are as follows:

- The cost of methane is $4.7 per GJ.
- The cost of electricity is $0.05 per kWh.

Using these assumptions, it was calculated that the cost of hydrogen produced by the SMR plant is $7.89 per GJ. But if carbon taxes are applied, the production cost of hydrogen increases to $9.37 per GJ for a carbon tax of $20 per ton and $10.86 per GJ for a carbon tax of $40 per ton (Corradetti & Desideri, 2007). If these same assumptions are applied to the Non-catalytic Plasma-arc Reforming Process, the cost of hydrogen is $13.42 per GJ without carbon tax.

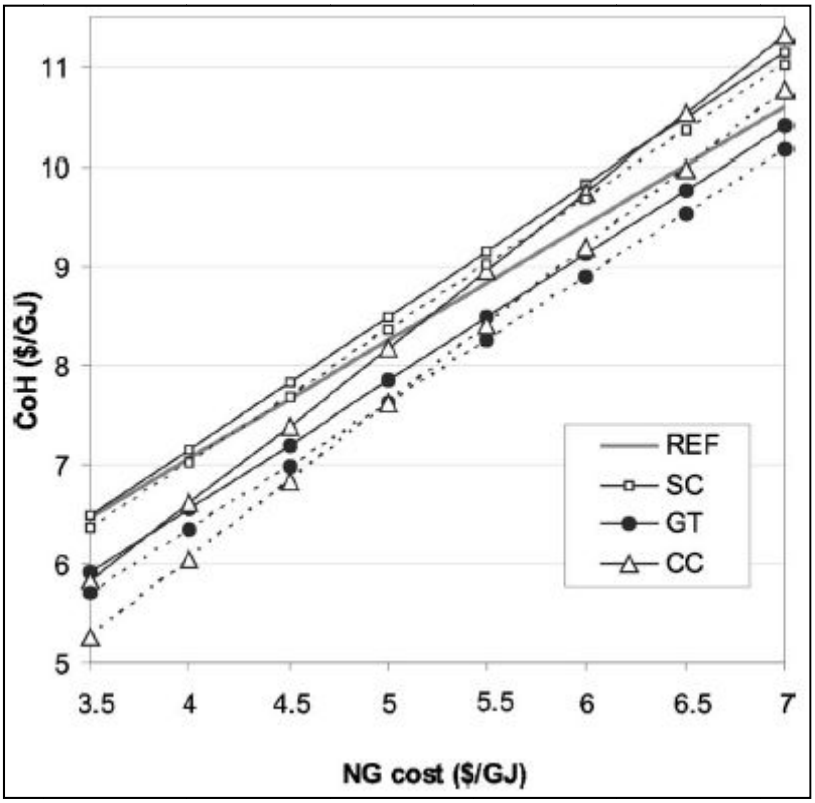

Figure 6.1: Production cost of H_2 versus CH_4 cost for a electricity cost of $0.05/kWh (solid line) and $0.06/kWh (dotted line). [SC – steam cycle, GT – gas turbine cycle, CC – combined cycle] (Corradetti & Desideri, 2007)

Making use of Figure 6.1, the cost of hydrogen could be calculated at a methane cost of $6 per GJ. The production cost of hydrogen with this input cost is approximately $9.50 per GJ. The production costs of hydrogen using Non-catalytic Plasma-arc Reforming for the two investigated processes are $13.19 per GJ and $13.06 per GJ, respectively using the assumptions given in Figure 6.1. Thus, these values are relatively close to those calculated by Corradetti and Desideri (2007), taking into consideration that steam and electricity are produced as by-products.

Mueller-Langer *et al*. (2007) state that a conventional SMR plant with a production of 250 000 Nm^3 hydrogen per hour has a total capital investment cost of $221 million, and for a plant with carbon capture the total capital investment cost is $253 million. The production of hydrogen with a natural gas price of $8 per GJ is $12.70 per GJ without carbon capture and with carbon capture the cost is $14.77 per GJ. Using the $8 per GJ natural gas price in the Non-catalytic Plasma-arc Reforming Process, the production cost of hydrogen is $14.96 per GJ.

The Non-catalytic Plasma-arc Reforming Process only produces 135 000 Nm^3 hydrogen per hour compared with the 250 000 Nm^3 hydrogen per hour given by Mueller-Langer *et al*. (2007) Thus, comparing the production costs of the processes, it can be stated that the production cost making use of the Non-catalytic Plasma-arc Reforming Process is competitive, taking that the production is almost half of that of the SMR plant. The estimated capital investment cost of the Non-catalytic Plasma-arc Reforming plant is $288 million, which is higher than the total capital investment of the SMR plants.

6.4 Conclusion

The production cost of hydrogen using the Non-catalytic Plasma-arc Reforming process is competitive with conventional SMR processes. It was further observed that the carbon tax that was added to the SMR process drastically increased the cost of hydrogen. It should be kept in mind that the Plasma-arc Reforming Process consumes carbon dioxide as an oxidising agent and the carbon dioxide that is produced is recycled in the process.

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Therefore, the carbon tax was not included in the calculations. The production of hydrogen gas using the Non-catalytic Plasma-arc Reforming Process is approximately half of the amount of hydrogen gas produced by the SMR Process with which the comparison was made. By increasing the hydrogen production of the Non-catalytic Plasma-arc Reforming plant, the production cost of hydrogen will decrease, making this process very desirable.

Chapter 7 - Conclusion of investigation

7.1 Conclusion of investigation

Plasma-arc methane reforming using carbon dioxide as the oxidising agent was investigated for the production of synthesis gas and hydrogen. Four different processes were evaluated for the production of synthesis and hydrogen gas. A 500 MWt PBMR produces the thermal and electrical energy that is required by the processes.

21×8 MW Plasma-arc Reformers were used for the conversion of methane and carbon dioxide to synthesis or hydrogen gas. Synthesis gas can be produced with the hydrogen-to-carbon monoxide ratio varying between 1:1 and 3:1. This is achieved by the addition of water (steam) to the synthesis gas production process; by varying the ratio between carbon dioxide and steam, the synthesis gas ratio can be varied between 1:1 and 3:1.

The annual production rate of synthesis gas from both processes was 1 435 million Nm^3, and the maximum thermal efficiency of the processes was 65.0%. The thermal efficiency of the process is dependent on the ratio between carbon dioxide and steam in the feed gas. Using only carbon dioxide as the oxidising agent, the thermal efficiency was 63.0% (H_2-to-CO ratio of 1:1 in the product gas). In the case of the combined process, using both carbon dioxide and steam as the oxidising agents, the efficiency could be as high as 65.0%.

The total capital investment cost of the Plasma-arc Reforming Process, using only carbon dioxide, for the production of synthesis gas is $101 million. Synthesis could be produced at a cost of $10.43 per GJ ($0.12 per Nm^3) for this scenario. The production cost was calculated using a natural gas price of $6 per GJ and electrical cost of $0.045 per kWh.

The total capital investment cost for the Plasma-arc Reforming Process, using both carbon dioxide and water as the oxidising agents, for the production of synthesis gas is $117 million. The production cost of synthesis gas is dependent on the ratio that is produced by the Plasma-arc Reforming Process. The production cost for a ratio of 1:1 for H_2-to-CO was the same as for the first process but as the ratio increased to 3:1 the production cost of synthesis gas decreased to $10.27 per GJ ($0.12 per Nm^3).

It was observed during the economic evaluation that the natural gas and electrical costs have high contributions to the production cost of synthesis gas. Natural gas and electrical

costs contributes to approximately 45.0% and 38.0% of the production cost, respectively. Through the sensitivity evaluation conducted, it was observed that both these costs have a major influence on the production cost and profitability of the plant. Any significant changes in these parameters result in a rapidly increasing production cost of synthesis; thus, the selling price of synthesis gas is indirectly controlled by the market.

The effect of the capital and carbon dioxide costs on the production cost of synthesis gas is negligible but the profitability of the plants is significantly influenced by the capital cost. Assuming a selling price of $13 per GJ, the PBP of the first plant that uses CO_2 as the oxidising agent is four years with a ROI of 45% and IRR of 26%. As discussed earlier, the ratio of synthesis gas that is produced by the second plant that uses both water and CO_2 also influences the PBP, ROI and IRR of the plant.

The maximum PBP of the plant is four years, using the same selling price as the first process, and the maximum ROI is 48% and IRR is 28%. The type of process that could be used in the chemical or petrochemical industry is determined by the further usage of the synthesis gas. If only a low ratio of 1:1 of H_2-to-CO is required by the industry, the first process is the best choice. But if the ratio has to be varied whilst keeping the production cost at a minimum, the second process would be recommended.

The methane conversion achieved by the Plasma-arc Reformer Unit was also investigated, in order to determine how it would effect the production of synthesis gas and the economical viability of the process. For this, the methane conversion was varied between 90.0% and 100.0%, which can be achieved at the very high operation temperatures in the Plasma-arc Reformer Units.

It was seen that the production of synthesis gas varied between 1 398 million and 1 472 million Nm^3 synthesis gas per year. The thermal efficiency of the processes is also affected by the different methane conversions and a thermal efficiency as high as 67.0% can be achieved by the processes.

The economical viability of the processes was also affected by the various methane conversions investigated. At a low methane conversion of 90.0%, the production cost of synthesis gas was $10.70 per GJ and at a high conversion of 100%, it was $10.18 per GJ. Thus, it was seen that methane conversion has a major impact on the process on the production aspect of the synthesis gas and the economical aspect.

For the production of hydrogen, two processes were investigated: the first process uses only the electrical energy from a 500 MWt PBMR ; the second process uses both the thermal and electrical energies that are produced. The Plasma-arc Reforming section of the first process is the same as for the production of synthesis gas, using carbon dioxide as the oxidising agent.

For the production of hydrogen, using both the thermal and electrical energies from a 500 MWt PBMR, only nineteen Plasma-arc Reformer Units could be supplied with power. The total production of hydrogen, using only the electrical energy, is 1 120 million Nm^3 and the total thermal efficiency of the process is 55.0%. The total production of hydrogen for the second Hydrogen Production Process is 1 013 million Nm^3 and the total thermal efficiency for the process is only 50.0%. It is observed that in the case where both the thermal and electrical energies are used, less hydrogen is produced with a lower efficiency than the first Hydrogen Production Process.

The total capital cost for the production of hydrogen, using the first process, is $288 million and the production cost of hydrogen with a final purity of 99.0% is $14.17 per GJ ($0.18 per Nm^3). The second Hydrogen Production Process has a capital cost of $266 million and the production cost of hydrogen is $14.04 per GJ ($0.17 per Nm^3). It was observed that the capital and production cost of hydrogen for the second process is lower compared with the first process. The total volume of hydrogen that is produced per annum is 100 million Nm^3 less than the first process.

The techno-economic evaluation of the Hydrogen Production Process showed that the natural gas price and the electrical costs contribute to 42.0% and 34.0% of the production cost of hydrogen. These contributions are very high, and it was expected that any changes in these costs would result in significant variations of the production cost and the profitability of the plants.

In the same way, the methane conversion was investigated for the production of synthesis gas and the production of hydrogen gas. Again, the methane conversion was varied between 90.0% and 100.0%, which can be achieved at the high operation temperatures of the Plasma-arc Reformer Units.

For the first Hydrogen Production Process, which only uses the electricity generated by a PBMR, the thermal efficiency of the process varies between 52.0% for a 90.0% conversion and 58.0% for 100.0%. For the second process, which make use of both the thermal and

the electrical energies, the thermal energy decreased to 48.0% for a methane conversion of 90%.

The production cost hydrogen varies between $11.80 per GJ for a conversion of 90.0% and $10.80 per GJ for 100.0%. There is a very small change in the capital cost of the plant for the different methane conversions, which was investigated in this research project. Thus, the methane conversion affects the Hydrogen Production Process in terms of both the production and economical aspects of the process.

Through the sensitivity evaluations conducted on the processes, the suspicion regarding the influences of the natural gas and electrical costs was confirmed. The capital cost of the plant influenced the profitability of the plant but had a minor effect on the production cost of hydrogen. A selling price of $20 per GJ resulted in a PBP of 3.7 years with a ROI of 48.0% and IRR of 27.0% for the first process.

When the same selling price was assumed for second process, it was seen that the PBP, ROI and IRR are almost the same with only a 1.0% variation between the values. When comparing the production cost of the Non-catalytic Plasma-arc Reforming Process with the conventional SMR Process, it was shown that the production cost of the Non-catalytic Plasma-arc Reforming process is competitive with that of the SMR. The environmental impact of the Non-catalytic Plasma-arc Reforming process is much lower than the SMR, which makes use of fossil fuels for its energy requirements.

Thus, the following can be stated for the Non-catalytic Plasma-arc Reforming of methane:

- No carbon dioxide is produced for the production of synthesis gas but is rather consumed.
- The carbon dioxide that is produced in the Hydrogen Production Process is less than the conventional SMR Process.
- The natural gas and electrical costs have a major influence on the production cost of synthesis and hydrogen gas.
- The profitability of the synthesis and hydrogen gas plants is significantly influenced by variations in natural gas, electrical and capital costs.
- The synthesis gas ratio can be varied between 1:1 and 3:1 for H_2-to-CO without an increase in production cost.
- Thermal efficiencies of the processes are as high as 65.0% compared with 75.0% in the SMR process.
- The production cost of hydrogen is competitive with the conventional SMR processes used extensively in the industry today.

7.2 Further investigation

Considerations for further investigation of the Non-catalytic Plasma-arc Reforming Process:

- construct a small-scale process plant, to verify the theoretical mass and energy balance values that have been calculated.
- experimental research to evaluate the methane conversion achieved in the plasma-arc units.
- design heat exchangers for a more accurate cost evaluation.
- conduct an economic evaluation of chemical products produced in the industry, using the hydrogen or synthesis gas produced by the Non-catalytic Plasma-arc Reforming Process.
- obtain more accurate figures on the estimated capital cost of the Plasma-arc Reforming Process.

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Appendix A - Equations and constants used for calculations

A.1 *Equations for process calculations*

Heat capacity calculation:

$$\mathrm{Cp_i} = a + bT + cT^2 + dT^3 \qquad \text{(kJ/mol·°C)}$$

Enthalpy calculation:

$$\Delta H_i = \left(\int_{25}^{T} Cp_i \, dT \right) \times 1000 \qquad \text{(kJ/mol)}$$

Energy calculation:

$$E = \frac{\Delta H_i \cdot N_i}{3.6 \times 10^6} \qquad \text{(MW)}$$

Reaction energy calculation:

$$E_{\mathrm{Re}action} = \frac{\Delta H_i \cdot \xi}{3.6 \times 10^6} \qquad \text{(MW)}$$

$$\xi = \frac{N_{i,o} - N_{i,i}}{\nu_i} \qquad \text{(kmol/h)}$$

Plasma-arc Unit calculation:

$$\# = \frac{\text{Thermal Nuclear Energy} \times 0.35}{\text{Plasma-arc Unit Size}}$$

Conversion calculation:

$$N_{H_2} = x \cdot N_i \cdot \xi \qquad \text{(Product produced)}$$

$$N_{i,o} = N_{i,i} - x \cdot N_{i,i} \qquad \text{(Reagents remaining)}$$

Temperature calculation:

$$N_{T,o} \int_{25}^{T} \sum Cp_i dT = N_{T,i} \int_{25}^{850} \sum Cp_i dT + E_{\text{Remaining}}$$

$$E_{\text{Remaining}} = x_{\text{Thermal Efficiency}} \cdot E_{\text{Plasma-arc}} - E_{\text{Reaction}} \qquad \text{(MW)}$$

A.2 *Constants*

Table A.1: Heat capacities used for energy balance calculations

Compound	Formula	State	a $\times 10^3$	b $\times 10^5$	c $\times 10^8$	d $\times 10^{12}$
Carbon dioxide	CO_2	Gas	36.11	4.233	-2.887	7.464
Carbon monoxide	CO	Gas	28.95	0.4110	0.3548	-2.220
Hydrogen	H_2	Gas	28.84	0.00765	0.3288	-0.8698
Methane	CH_4	Gas	34.31	5.469	0.3661	-11.00
Water	H_2O	Liquid	75.4			
		Gas	33.46	0.6880	0.7604	-3.593

Table A.2: Values used for conversion of molar to mass and volumetric at standard conditions

Compound	Molar mass (kg/kmol)	Molar mass (STP) (m^3/kmol)
Carbon dioxide	44.01	22.415
Carbon monoxide	28.01	22.415
Hydrogen	2.016	22.415
Methane	16.04	22.415
Water	18.016	22.415

Appendix B - Equations used for techno-economic evaluation

B.1.1 Equipment cost calculation

Marshall and Swift (M&S) = 1 224.4 (2007)

B.1.2 Heat exchanger cost

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

$$F_c = \left(F_d + F_p\right)F_m$$

F_d = 1.35 (boiler), F_d = 1.00 (Floating head)

F_p = 0

F_m = 3.75 (ss/ss)

B.1.3 Compressor cost

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

$$F_c = F_d$$

F_d = 1.15 (centrifugal, turbine)

B.1.4 Pressure Swing Absorption cost

$$\text{Purchased Cost, \$} = 7.445e^6\left(\frac{\text{s}}{0.294\ \text{kmol/s}}\right)^{0.74}, \text{ (Corradetti \& Desideri, 2007)}$$

B.1.5 Reactor cost

$$\text{Purchased Cost, \$} = \left(\frac{M\&S}{280}\right)\left(101.9D^{1.066}H^{0.82}F_c\right), \text{ (Douglas, 1988)}$$

$$F_c = F_m F_p$$

F_m = 3.67 (ss)

F_p = 1.15

Appendix C - HYSYS simulations of processes

C.1 *Methane Reforming using CO_2 for the production of synthesis gas*

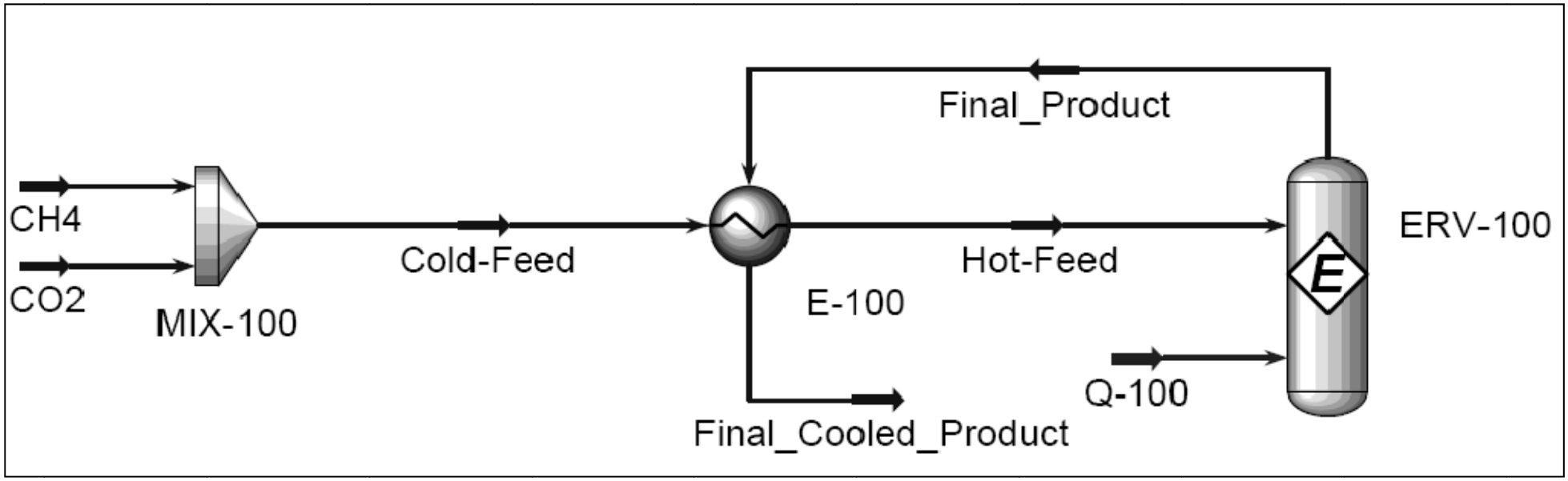

Figure C.1: HYSYS process flow diagram of the Methane Reforming Process using CO_2 for the production of synthesis gas

Table C.1: HYSYS mass and energy balance for the production of synthesis gas using CO_2

	CH4	CO2	Cold_Feed	Hot_Feed	Final_Product	Final_Cooled_Product
Vapour fraction	1.00	1.00	1.00	1.00	1.00	1.00
Temperature (°C)	25.00	25.00	25.00	850.00	1 131.11	450.25
Pressure (kPa)	100.00	100.00	100.00	100.00	100.00	100.00
Molar Flow (kmol/h)	1 873.75	1 873.75	3 747.49	3 747.49	7 297.72	7 297.72
Mass Flow (kg/h)	30 060.30	82 462.96	112 523.26	112 523.26	112 525.39	112 525.39
Liquid Volume Flow (m3/h)	100.40	99.91	200.32	200.32	237.40	237.40
Heat Flow (MW)	-38.98	-204.96	-243.95	-198.51	-50.67	-96.11
Mass Flow Composition						
CH4	30 060.30		30 060.30	30 060.30	1 582.35	1 582.35
CO2		82 462.96	82 462.96	82 462.96	4 340.79	4 340.79
H2					7 157.25	7 157.25
CO					99 445.00	99 445.00

C.2 *Methane Reforming using a mixture of CO_2 and steam for the production of synthesis gas*

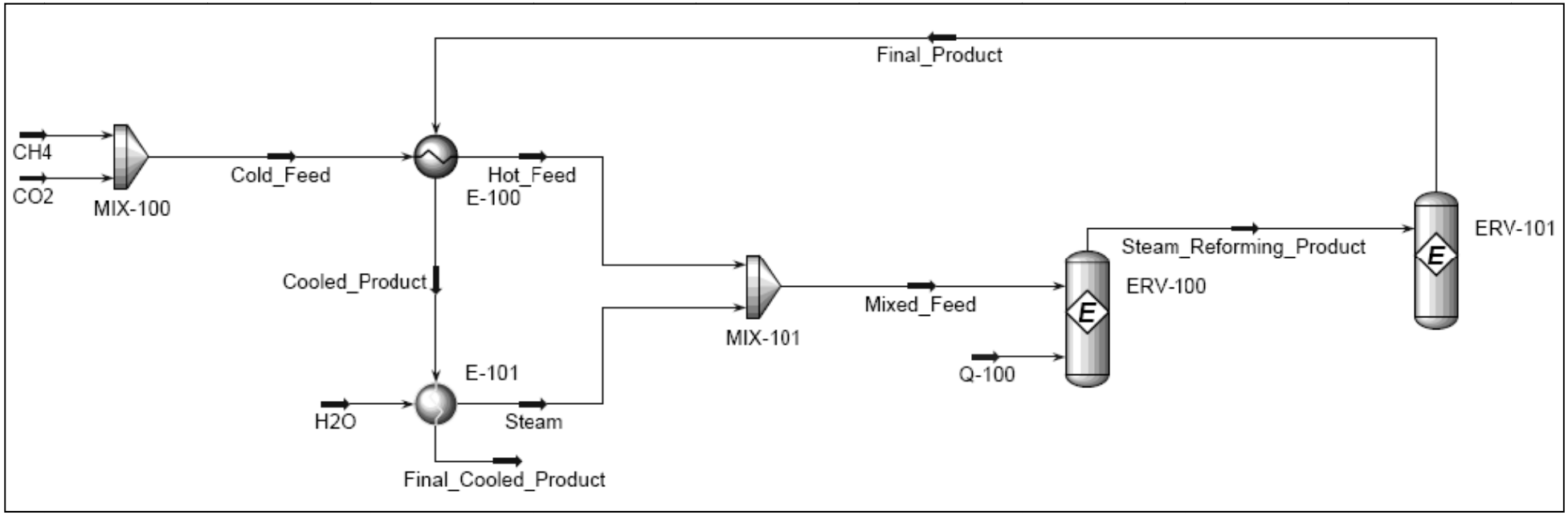

Figure C.2: HYSYS process flow diagram of the Methane Reforming Process using CO2 and steam for the production of synthesis gas

Table C.2: HYSYS mass and energy balance for a H_2-to-CO ratio of 1:1

	CH_4	CO_2	H_2O	Cold_Feed	Hot_Feed	Steam	Mixed_Feed	Steam Reforming Product	Final Product	Cooled Product	Final Cooled Product
Vapour Fraction	1.00	1.00		1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Temperature (C)	25.00	25.00	25.00	24.89	850.00	850.00	850.00	2 124.19	1 131.04	449.71	449.70
Pressure (kPa)	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Molar Flow (kmol/h)	1 873.76	1 873.71	0.06	3 747.47	3 747.47	0.06	3 747.53	3 747.63	7 297.78	7 297.78	7 297.78
Mass Flow (kg/h)	30 060.50	82 461.60	1.00	112 522.10	112 522.10	1.00	112 523.10	112 523.10	112 525.23	112 525.23	112 525.23
Liquid Volume Flow (m3/h)	100.40	99.91	0.00	200.32	200.32	0.00	200.32	200.32	237.40	237.40	237.40
Heat Flow (MW)	-38.99	-204.98	0.00	-243.97	-198.51	0.00	-198.51	-50.67	-50.67	-96.14	-96.14
Mass Flow Composition											
CH4	30 060.50			30 060.50	30 060.50		30 060.50	30 059.65	1 582.30	1 582.30	1 582.30
CO2		82 461.60		82 461.60	82 461.60		82 461.60	82 461.60	4 341.06	4 341.06	4 341.06
H2O			1.00			1.00	1.00	0.05	0.05	0.05	0.05
H2								0.32	7 157.42	7 157.42	7 157.42
CO								1.48	99 444.40	99 444.40	99 444.40

Table C.3: HYSYS mass and energy balance for a H_2-to-CO ratio of 1.5:1

	CH4	CO2	H2O	Cold_Feed	Hot_Feed	Steam	Mixed_Feed	Steam Reforming Product	Final Product	Cooled Product	Final Cooled Product
Vapour Fraction	1.00	1.00		1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Temperature (C)	25.00	25.00	25.00	24.90	850.00	850.00	849.98	1 993.60	1 229.20	679.03	433.57
Pressure (kPa)	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Molar Flow (kmol/h)	1 873.76	1 124.23	749.54	2 997.99	2 997.99	749.54	3 747.52	5 171.65	7 307.41	7 307.41	7 307.41
Mass Flow (kg/h)	30 060.50	49 477.00	13 503.00	79 537.50	79 537.50	13 503.00	93 040.50	93 041.14	93 042.43	93 042.43	93 042.43
Liquid Volume Flow (m3/h)	100.40	59.95	13.53	160.35	160.35	13.53	173.88	209.47	231.78	231.78	231.78
Heat Flow (MW)	-38.99	-122.99	-59.32	-161.98	-124.81	-43.66	-168.47	-20.63	-20.63	-57.80	-73.46
Mass Flow Composition											
CH4	30 060.50			30 060.50	30 060.50		30 060.50	18 636.98	1 505.08	1 505.08	1 505.08
CO2		49 477.00		49 477.00	49 477.00		49 477.00	49 477.00	2 479.90	2 479.90	2 479.90
H2O			13 503.00			13 503.00	13 503.00	675.15	675.15	675.15	675.15
H2								4 306.55	8 612.24	8 612.24	8 612.24
CO								19 945.47	79 770.06	79 770.06	79 770.06

Table C.4: HYSYS mass and energy balance for a H_2-to-CO ratio of 2:1

	CH4	CO2	H2O	Cold_Feed	Hot_Feed	Steam	Mixed_Feed	Steam Reforming Product	Final Product	Cooled Product	Final Cooled Product
Vapour Fraction	1.00	1.00		1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Temperature (C)	25.00	25.00	25.00	24.92	850.00	850.00	849.98	1 810.00	1 298.39	832.94	426.22
Pressure (kPa)	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Molar Flow (kmol/h)	1 873.76	624.57	1 249.22	2 498.32	2 498.32	1 249.22	3 747.55	6 121.07	7 307.70	7 307.70	7 307.70
Mass Flow (kg/h)	30 060.50	27 487.00	22 504.90	57 547.50	57 547.50	22 504.90	80 052.40	80 053.47	80 054.18	80 054.18	80 054.18
Liquid Volume Flow (m3/h)	100.40	33.30	22.55	133.71	133.71	22.55	156.26	215.57	227.97	227.97	227.97
Heat Flow (MW)	-38.99	-68.33	-98.86	-107.32	-75.68	-72.77	-148.45	-0.61	-0.61	-32.25	-58.34
Mass Flow Composition											
CH4	30 060.50			30 060.50	30 060.50		30 060.50	11 021.38	1 502.94	1 502.94	1 502.94
CO2		27 487.00		27 487.00	27 487.00		27 487.00	27 487.00	1 375.53	1 375.53	1 375.53
H2O			22 504.90			22 504.90	22 504.90	1 125.25	1 125.25	1 125.25	1 125.25
H2								7 177.54	9 569.78	9 569.78	9 569.78
CO								33 242.30	66 480.69	66 480.69	66 480.69

Table C.5: HYSYS mass and energy balance for a H_2-to-CO ratio of 2.5:1

	CH4	CO2	H2O	Cold_Feed	Hot_Feed	Steam	Mixed_Feed	Steam Reforming Product	Final Product	Cooled Product	Final Cooled Product
Vapour Fraction	1.00	1.00		1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Temperature (C)	25.00	25.00	25.00	24.96	850.00	850.00	849.97	1 592.66	1 348.13	942.30	421.02
Pressure (kPa)	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Molar Flow (kmol/h)	1 873.76	267.67	1 606.12	2 141.43	2 141.43	1 606.12	3 747.55	6 799.17	7 307.73	7307.73	7 307.73
Mass Flow (kg/h)	30 060.50	11 780.20	28 934.40	41 840.70	41 840.70	28 934.40	70 775.10	70 776.47	70 776.78	70776.78	70 776.78
Liquid Volume Flow (m3/h)	100.40	14.27	28.99	114.68	114.68	28.99	143.67	219.93	225.24	225.24	225.24
Heat Flow (MW)	-38.99	-29.28	-127.11	-68.28	-40.58	-93.56	-134.14	13.70	13.70	-14.00	-47.54
Mass Flow Composition											
CH4	30 060.50			30 060.50	30 060.50		30 060.50	5 582.05	1 502.66	1 502.66	1 502.66
CO2		11 780.20		11 780.20	11 780.20		11 780.20	11 780.20	589.41	589.41	589.41
H2O			28 934.40			28 934.40	28 934.40	1 446.75	1 446.75	1 446.75	1 446.75
H2								9 228.11	10 253.37	10 253.37	10 253.37
CO								42 739.37	56 984.59	56 984.59	56 984.59

Table C.6: HYSYS mass and energy balance for a H_2-to-CO ratio of 3:1

	CH4	CO2	H2O	Cold_Feed	Hot_Feed	Steam	Mixed_Feed	Steam Reforming Product	Final Product	Cooled Product	Final Cooled Product
Vapour Fraction	1.00	1.00		1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Temperature (C)	25.00	25.00	25.00	25.00	850.00	850.00	849.97	1 387.32	1 387.30	1 025.98	419.05
Pressure (kPa)	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Molar Flow (kmol/h)	1 873.76	0.02	1 873.84	1 873.78	1 873.78	1 873.84	3 747.62	7 303.80	7 303.83	7 303.83	7 303.83
Mass Flow (kg/h)	30 060.50	1.00	33 757.40	30 061.50	30 061.50	33 757.40	63 818.90	63 820.50	63 820.50	63 820.50	63 820.50
Liquid Volume Flow (m3/h)	100.40	0.00	33.83	100.41	100.41	33.83	134.23	223.10	223.10	223.10	223.10
Heat Flow (MW)	-38.99	0.00	-148.30	-38.99	-14.26	-109.16	-123.42	24.42	24.42	-0.31	-39.45
Mass Flow Composition											
CH4	30 060.50			30 060.50	30 060.50		30 060.50	1 534.80	1 534.51	1 534.51	1 534.51
CO2		1.00		1.00	1.00		1.00	1.00	0.22	0.22	0.22
H2O			33 757.40			33 757.40	33 757.40	1 724.95	1 724.95	1 724.95	1 724.95
H2								10 753.88	10 753.95	10 753.95	10 753.95
CO								49 805.87	49 806.86	49 806.86	49 806.86

C.3 *Methane reforming with CO_2 for the production of hydrogen utilising the electrical energy supplied by a Pebble Bed Modular Reactor*

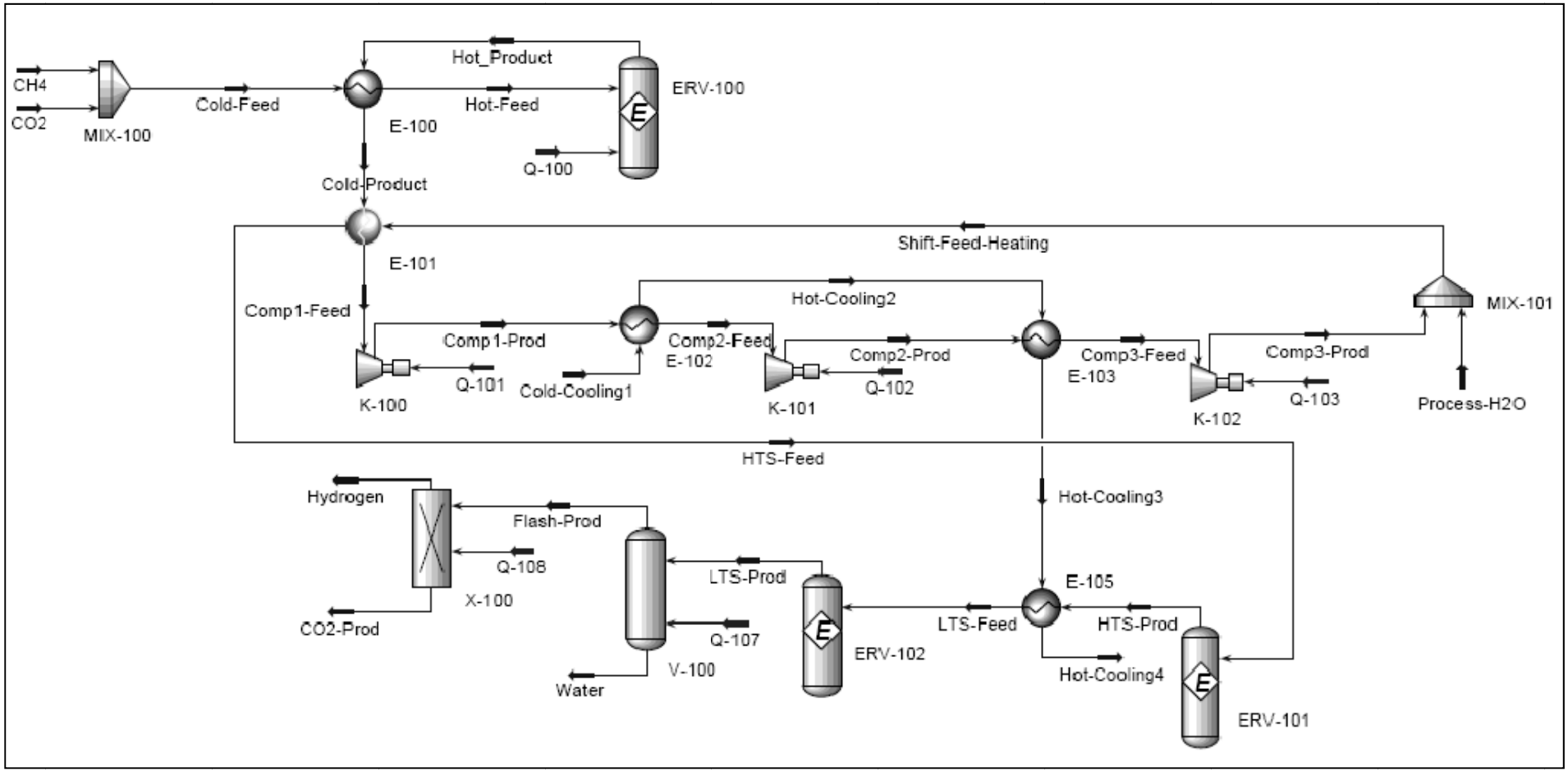

Figure C.3: HYSYS process flow diagram of the Methane Reforming Process using CO_2 and the electrical energy generated by a Pebble Bed Modular Reactor for the production of hydrogen gas

Table C.7: HYSYS mass and energy balance for the production of hydrogen gas using the electrical energy of the Pebble Bed Modular Reactor

	CH4	CO2	Cold-Feed	Hot-Feed	Hot_Product	Cold-Product	Comp1-Feed	Comp1-Prod	Comp2-Feed	Comp2-Prod
Vapour Fraction	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Temperature (°C)	25.00	25.00	24.89	850.00	1 131.05	449.72	99.00	200.00	100.00	200.00
Pressure (kPa)	100.00	100.00	100.00	100.00	100.00	100.00	100.00	216.81	216.81	465.90
Molar Flow (kmol/h)	1 873.75	1 873.75	3 747.49	3 747.49	7 297.71	7 297.71	7 297.71	7 297.71	7 297.71	7 297.71
Mass Flow (kg/h)	30 060.30	82 462.96	112 523.26	112 523.26	112 525.39	112 525.39	112 525.39	112 525.39	112 525.39	112 525.39
Liquid Volume Flow (m3/h)	100.40	99.91	200.32	200.32	237.40	237.40	237.40	237.40	237.40	237.40
Heat Flow (MW)	-38.99	-204.98	-243.98	-198.51	-50.67	-96.14	-117.54	-111.51	-117.48	-111.51
Mass Flow Composition										
CH4	30 060.30		30 060.30	30 060.30	1 582.39	1 582.39	1 582.39	1 582.39	1 582.39	1 582.39
CO2		82 462.96	82 462.96	82 462.96	4 340.90	4 340.90	4 340.90	4 340.90	4 340.90	4 340.90
H2O					7 157.24	7 157.24	7 157.24	7 157.24	7 157.24	7 157.24
H2					99 444.85	99 444.85	99 444.85	99 444.85	99 444.85	99 444.85
CO										

	Comp3-Feed	Comp3-Prod	Process-H2O	Shift-Feed-Heating	HTS-Feed	HTS-Prod	LTS-Feed	LTS-Prod	Flash-Prod	Water
Vapour Fraction	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	
Temperature (°C)	100.00	200.00	200.00	192.96	356.29	515.03	230.00	314.43	25.00	25.00
Pressure (kPa)	465.90	1 000.62	1 000.00	1 000.00	1 000.00	1 000.00	1 000.00	1 000.00	1 000.00	1 000.00
Molar Flow (kmol/h)	7 297.71	7 297.71	6 764.23	14 061.94	14 061.94	14 061.94	14 061.94	14 061.94	10 336.86	3 725.07
Mass Flow (kg/h)	112 525.39	112 525.39	121 858.21	234 383.60	234 383.60	234 383.00	234 383.00	234 382.69	167 082.22	67 300.47
Liquid Volume Flow (m3/h)	237.40	237.40	122.10	359.50	359.50	417.77	417.77	447.24	379.69	67.55
Heat Flow (MW)	-117.48	-111.50	-442.95	-554.45	-533.04	-533.04	-572.13	-572.12	-360.55	-294.93
Mass Flow Composition										
CH4	1 582.39	1 582.39		1 582.39	1 582.39	1 582.39	1 582.39	1 582.39	1581.65	0.74
CO2	4 340.90	4 340.90		4 340.90	4 340.90	92 489.33	92 489.33	137 084.49	136 720.00	364.49
H2O	7 157.24	7 157.24		7 157.24	7 157.24	11 195.15	11 195.15	13 237.97	13 235.04	2.93
H2	99 444.85	99 444.85		99 444.85	99 444.85	43 340.93	43 340.93	14 957.40	14 954.69	2.71
CO			121 858.21	121 858.21	121 858.21	85 775.20	85 775.20	67 520.44	590.84	66 929.60

Table C.8: HYSYS Mass And Energy Balance For The Production Of Hydrogen Gas Using The Electrical Energy of the Pebble Bed Modular Reactor (continued)

	Hydrogen	CO2-Prod	Cold-Cooling1	Hot-Cooling2	Hot-Cooling3	Hot-Cooling4
Vapour Fraction	1.00	0.99				0.02
Temperature (°C)	25.00	25.00	25.00	35.00	45.01	99.61
Pressure (kPa)	1 000.00	1 000.00	100.00	100.00	100.00	100.00
Molar Flow (kmol/h)	5 580.63	4 756.23	28 218.67	28 218.67	28 218.67	28 218.67
Mass Flow (kg/h)	11 265.17	155 817.05	508 362.14	508 362.14	508 362.14	508 362.14
Liquid Volume Flow (m3/h)	161.05	218.64	509.39	509.39	509.39	509.39
Heat Flow (MW)	-0.02	-360.92	-2 233.22	-2 227.24	-2 221.27	-2 182.18
Mass Flow Composition						
CH4	0.16	1 581.50				
CO2	13.67	136 706.33				
H2O	11 249.79	1 985.26				
H2	1.50	14 953.19				
CO	0.06	590.78	508 362.14	508 362.14	508 362.14	508 362.14

C.4 *Methane Reforming with CO_2 for the production of hydrogen utilising the electrical and thermal energy supplied by a Pebble Bed Modular Reactor*

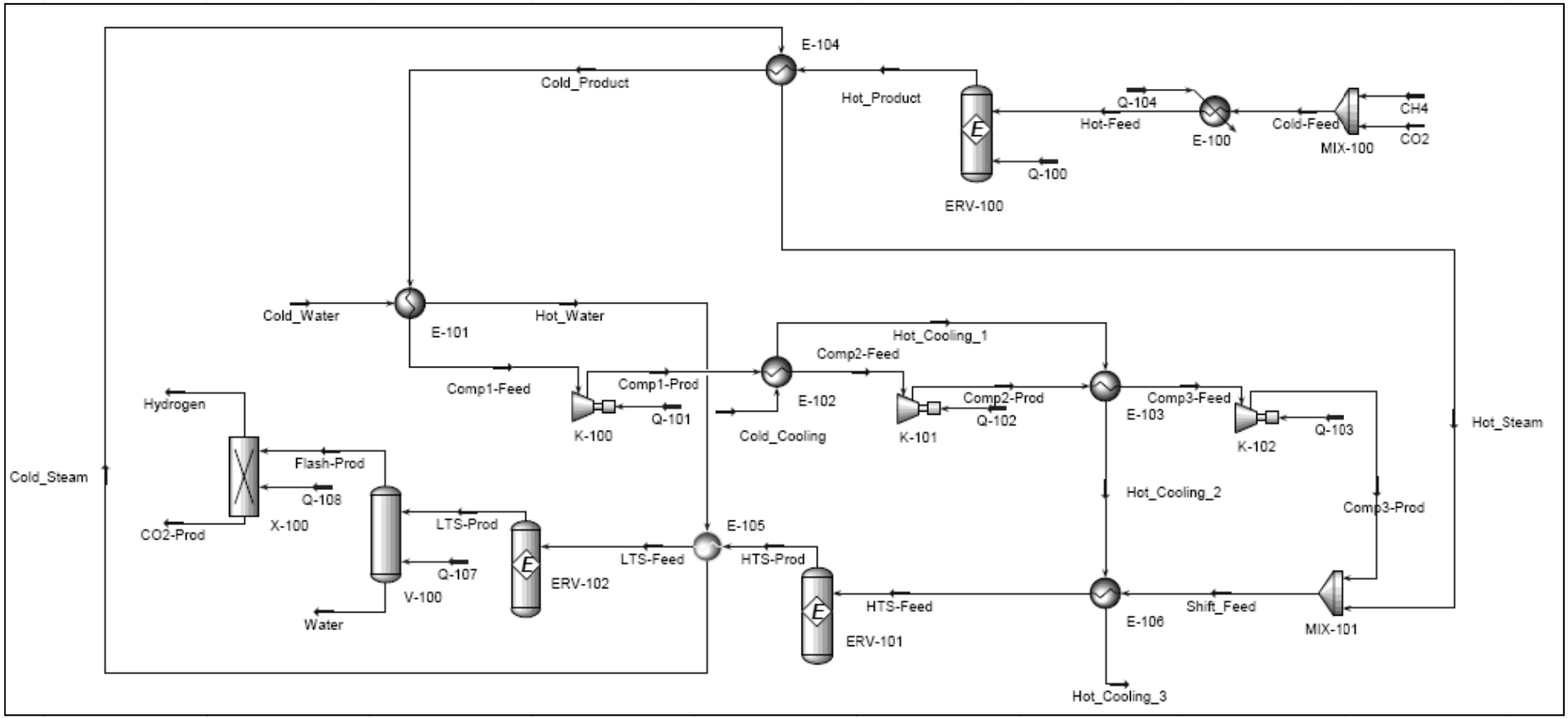

Figure C.4: HYSYS process flow diagram of the Methane Reforming Process using CO_2 and the electrical and thermal energy generated by a Pebble Bed Modular Reactor for the production of hydrogen gas

Table C.9: HYSYS mass and energy balance for the production of hydrogen gas using the electrical and thermal energy of the PBMR

	CH4	CO2	Cold-Feed	Hot-Feed	Hot_Product	Cold_Product	Comp1-Feed	Comp1-Prod	Comp2-Feed	Comp2-Prod
Vapour Fraction	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Temperature (°C)	25.00	25.00	24.89	850.00	1 131.05	200.00	99.00	200.00	100.00	200.00
Pressure (kPa)	100.00	100.00	100.00	100.00	100.00	100.00	100.00	216.81	216.81	465.90
Molar Flow (kmol/h)	1 695.30	1 695.27	33 90.57	3 390.57	6 602.66	6 602.66	6 602.66	6 602.66	6 602.66	6 602.66
Mass Flow (kg/h)	27 197.60	74 608.20	101 805.80	101 805.80	101 807.73	101 807.73	101 807.73	101 807.73	101 807.73	101 807.73
Liquid Volume Flow (m3/h)	90.84	90.40	181.24	181.24	214.79	214.79	214.79	214.79	214.79	214.79
Heat Flow (MW)	-35.28	-185.46	-220.74	-179.60	-45.84	-100.89	-106.34	-100.89	-106.29	-100.88
Mass Flow Composition										
CH4	27 197.60		27 197.60	27 197.60	1 431.98	1 431.98	1 431.98	1 431.98	1 431.98	1 431.98
CO2		74 608.20	74 608.20	74 608.20	3 926.64	3 926.64	3 926.64	3 926.64	3 926.64	3 926.64
H2O					6 475.57	6 475.57	6 475.57	6 475.57	6 475.57	6 475.57
H2					89 973.53	89 973.53	89 973.53	89 973.53	89 973.53	89 973.53
CO										

	Comp3-Feed	Comp3-Prod	Cold_Water	Hot_Water	Cold_Steam	Hot_Steam	Shift_Feed	HTS-Feed	HTS-Prod	LTS-Feed
Vapour Fraction	1.00	1.00			0.70	1.00	1.00	1.00	1.00	1.00
Temperature (°C)	100.00	200.00	25.00	67.22	179.87	716.00	481.95	350.00	534.06	230.00
Pressure (kPa)	465.90	1 000.62	1 000.00	1 000.00	1 000.00	1 000.00	1 000.00	1 000.00	1 000.00	1 000.00
Molar Flow (kmol/h)	6 602.66	6 602.66	6 120.32	6 120.32	6 120.32	6 120.32	12 722.98	12 722.98	12 722.98	12 722.98
Mass Flow (kg/h)	101 807.73	101 807.73	110 258.10	110 258.10	110 258.10	110 258.10	212 065.83	212 065.83	212 065.19	212 065.19
Liquid Volume Flow (m3/h)	214.79	214.79	110.48	110.48	110.48	110.48	325.27	325.27	386.80	386.80
Heat Flow (MW)	-106.29	-100.88	-484.33	-478.88	-421.27	-366.22	-467.10	-483.04	-483.05	-521.09
Mass Flow Composition										
CH4	1 431.98	1 431.98					1 431.98	1 431.98	1 431.98	1 431.98
CO2	3 926.64	3 926.64					3 926.64	3 926.64	97 021.20	97 021.20
H2O	6 475.57	6 475.57					6 475.57	6 475.57	10 740.06	10 740.06
H2	89 973.53	89 973.53					89 973.53	89 973.53	30 721.54	30 721.54
CO			110 258.10	110 258.10	110 258.10	110 258.10	110 258.10	110 258.10	72 150.41	72 150.41

Table C.10: HYSYS mass and energy balance for the production of hydrogen gas using the electrical and thermal energy of the Pebble Bed Modular Reactor (continued)

	LTS-Prod	Flash-Prod	Water	Hydrogen	CO2-Prod	Cold_Cooling	Hot_Cooling_1	Hot_Cooling_2	Hot_Cooling_3
Vapour Fraction	1.00	1.00		1.00	0.99				
Temperature (°C)	296.08	25.00	25.00	25.00	25.00	25.00	35.00	45.01	74.65
Pressure (kPa)	1 000.00	1 000.00	1 000.00	1 000.00	1 000.00	100.00	100.00	100.00	100.00
Molar Flow (kmol/h)	12 722.98	9 455.42	3 267.55	5 136.70	4 318.72	25 531.07	25 531.07	25 531.07	25 531.07
Mass Flow (kg/h)	212 064.98	153 017.42	59 047.55	10 368.99	142 648.43	459 944.72	459 944.72	459 944.72	459 944.72
Liquid Volume Flow (m3/h)	407.65	348.37	59.28	148.24	200.13	460.87	460.87	460.87	460.87
Heat Flow (MW)	*-521.08*	*-334.30*	*-258.72*	*-0.02*	*-334.65*	*-2 020.52*	*-2 015.12*	*-2 009.71*	*-1 993.77*
Mass Flow Composition	**LTS-Prod**	**Flash-Prod**	**Water**	**Hydrogen**	**CO2-Prod**	**Cold_Cooling**	**Hot_Cooling_1**	**Hot_Cooling_2**	**Hot_Cooling_3**
CH4	1 431.98	1 431.31	0.67	0.14	1431.16				
CO2	128 563.65	128 219.68	343.98	12.82	12 8206.86				
H2O	12 184.96	12 182.24	2.71	10 354.91	1827.34				
H2	10 645.68	10 643.74	1.94	1.06	1 0642.68				
CO	59 238.71	540.46	58 698.25	0.05	540.40	45 9944.72	45 9944.72	45 9944.72	45 9944.72