December 2000 ECN-C-00-122

FINAL REPORT
NOVEM contract no. 219.401–0012

SOFC AS A GAS SEPARATOR

M.A. Korobitsyn
F.P.F van Berkel
G.M. Christie

Revisions			
A	Progress report		
B	Final concept		
C	Final report		
Made by: F.P.F. van Berkel M.A. Korobitsyn	Approved: J.P.P. Huijsmans	ECN-Fuels, Conversion & Environment	
Checked by: G.M. Christie	Issued: C.A.M. van der Klein		

Justification

This work was performed on behalf of the Netherlands Agency for Energy and Environment Novem BV under contract 219.401–0012. Programme manager: A.H.M. Kipperman.

Abstract

The topic of this study is a technical and economic assessment of oxygen transport membrane (OTM) technology for syngas production in relation to existing and novel processes. Basic and advanced syngas technologies were reviewed, demonstrating that among the basic processes the steam methane reforming (SMR) is the most developed process and the catalytic partial oxidation (CPO) has proven to be the most promising process with respect to compactness and low syngas production costs. Among the advanced processes the combined technologies merit consideration on basis of their superior thermodynamics, although there is limited commercial experience.

Steam methane reforming (SMR) and catalytic partial oxidation (CPO) were selected for a comparison with OTM systems. There was predicted to be both performance and cost benefits for the use of OTM based technology as compared to conventional syngas producing technologies.

Keywords

Syngas, synthesis gas, steam methane reforming, partial oxidation, autothermal reforming, oxygen transport membrane, SEOS, MEOS, solid oxide fuel cell, methanol, Fisher-Tropsch, Gas-to-Liquids

Distribution list

Novem BV	1-5
F. Saris	6
W. Schatborn	7
C.A.M. van der Klein	8
H.J. Veringa	9
J.P.P. Huismans	10
D. Jansen	11
G.M. Christie	12
F.P.F. van Berkel	13
N.J.J. Dekker	14
A. Mutch	15
G.S. Schipper	16
J. Hugill	17
P.P.A.C. Pex	18
J.W. Dijkstra	19
F. Tillemans	20
Archive	21-40

CONTENTS

SUMMARY 5

1. INTRODUCTION 7

2. OBJECTIVES AND METHOD 7

3. RESULTS 9
3.1 Inventory of Competing Technologies 9
3.1.1 Introduction 9
3.1.2 Steam methane reforming (SMR) 10
Economic aspects 11
Development status 12
3.1.3 Partial oxidation (POX) 12
Process description 12
Economic aspects 13
Development status 14
3.1.4 CO_2 reforming 14
Process description 14
Economic aspects 15
Development status 15
3.1.5 Autothermal Reforming (ATR) 16
Process description 16
Economic aspects 16
Development status 17
3.1.6 Combined Reforming 17
Process description 17
Economic aspects 18
Development status 18
3.1.7 Kellogg's Reforming Exchanger System (KRES) 18
Process description 19
Economic aspects 19
Development status 19
3.1.8 Gas Heated Reforming (GHR) 20
Process description 20
Economic aspects 20
Development status 21
3.1.9 Combined Autothermal Reforming (CAR) 21
Background 21
Process description 21
Development status 22
3.1.10 Plasma Reforming 22
Economic aspects 23
Development status 23
3.1.11 Reforming with Cyclic Oxidation 23
3.1.12 Reforming by High Pressure Piston Reactor. 24
3.2 Membrane Conversion 25
3.2.1 Introduction 25
3.2.2 Process Description 25
3.2.3 Development Status 26
3.2.4 Economic Aspects 27
3.3 Summary of Inventory of Competing Technologies 27

3.4 System Study 29
3.4.1 Introduction 29
3.4.2 MEOS-1000 31
3.4.3 MEOS-CPO 32
3.4.4 SEOS 34
3.4.5 Summary of the System Study 35
3.5 Economic Analysis 36
3.5.1 Introduction 36
3.5.2 Capital Costs 37
3.5.3 Sensitivity Analysis on Capital Costs 39
3.5.4 Operational Costs 40
3.5.5 Sensitivity Analysis on Operational Costs 41
3.5.6 Conclusions 43

4. CONCLUSIONS AND RECOMMENDATIONS 44

5. REFERENCES 46

6. APPENDIX 1. OXYGEN GENERATION 50
6.1 Background 50
6.2 Process description 50
6.3 Manufacturers 51
6.4 Economic aspects 52

7. APPENDIX 2. ABBREVIATIONS 54

8. APPENDIX 3. ASPEN Plus PROCESS FLOW DIAGRAMS 55

SUMMARY

Syngas is being applied on a large scale in the chemical industry for the production of a variety of chemicals. These applications dictate the properties of syngas in terms of composition, temperature and pressure. The foremost applications of syngas are: 1/ Fischer-Tropsch synthesis and 2/ methanol synthesis. The topic of this study is a technical and economic assessment of oxygen transport membrane (OTM) technology for syngas production in relation to existing and novel processes. Therefore both basic and advanced syngas technologies were reviewed. In the case of the basic syngas technologies the steam methane reforming (SMR) is the most developed process. It is employed at the largest number of plants built and offers the highest H_2/CO ratio. The competitive partial oxidation process (POX) proceeds in a smaller reactor in a direct exothermic reaction, but requires oxygen which increases the production costs. The catalytic partial oxidation (CPO) technology has proven to be the most promising process offering compactness, low syngas production costs, and reliable operation. Among the combined technologies, the indirect-fired concepts such as gas heated reforming (GHR), Kellogg's Reforming Exchanger System (KRES) and Combined Autothermal Reforming (CAR) merit consideration. While these options are thermodynamically superior to the others, the limited commercial experience does not allow to judge about their competitiveness. Two emerging technologies are getting much interest in the late 1990s, namely, one based on a plasmatron and another that employs a membrane reactor. Plasma reforming allows a very precise control of the reforming reaction, features a compact size and could be attractive when an electric power source is available. The membrane reactor or oxygen transport membrane technology (OTM) combines the production of oxygen and syngas in one vessel thus saving on a separate oxygen generation step. This oxygen generation step is responsible for 35 to 60% of syngas production costs. Two oxygen transport membrane systems are possible, being the pressure driven membranes (MEOS) and the electric driven membranes (SEOS). The system analysis of the membrane systems indicated that syngas can be effectively produced in both configurations (MEOS and SEOS). In this report three syngas production technologies have been selected for a technical/economic evaluation, namely: 1/ Steam Methane Reforming as being the most developed technology, 2/ Catalytic Partial Oxidation CPO as currently being the most promising technology, and 3/ the membrane systems, being the pressure driven membranes (MEOS) and the electric driven membranes (SEOS) as the long term option. The conclusions from this technical economic evaluation are the following:

A/ The membrane technology has the potential to lead to lower investment as well as production costs compared to SMR and CPO syngas production technologies. It must be emphasised that this mainly depends on the cost price of the membrane reactor. On the basis of the cost price ratio between MEOS and SEOS, the MEOS technology is the most cost effective option and deserves the most attention in a possible continuation of the programme.

B/ The use of membrane technology will lead to a higher energy efficiency compared with the classical partial oxidation technology (POX) due to 1/ the fact that a cryogenic oxygen separator unit is not needed anymore and 2/ the possibility of co-generation of electricity in the case of a SEOS reactor.

C/ A membrane reactor has a modular character that has the advantage of scaling down being relatively simple compared to existing technologies. This means that the membrane technology can be coupled to conversion technologies for high efficiency and low emissions.

Since the oxygen transport membrane reactor is in the beginning of development its costs are uncertain. The sensitivity analysis showed that even at a specific cost of 2000 USD per square

metre membrane, syngas produced by the membrane systems remains competitive with SMR, but cannot be justified when compared with CPO. Therefore a detailed membrane reactor and optimisation study is recommended to determine the critical parameters and to obtain a better insight in the promising membrane technology.

1. INTRODUCTION

Synthesis gas or “syngas”, a mixture of hydrogen and carbon monoxide, is an intermediate product in the indirect conversion route from hydrocarbons to bulk chemicals such as ammonia, methanol, hydrogen, acetic acid, oxoalcohols, and synthetic fuels. Syngas manufacture is usually integrated with the synthesis of a certain chemical, thus providing an energy efficient operation.

The study limits itself to natural gas as a feedstock and includes nitrogen-free syngas production routes, thus excluding ammonia manufacture. A short overview of oxygen generation technologies is given in Appendix 1.

2. OBJECTIVES AND METHOD

2.1 Objectives

In order to asses the technical and economic potential of using oxygen transport membrane technology to produce syngas, the Netherlands Agency for Energy and the Environment NOVEM has awarded a project to ECN taking into account ECN’s expertise in the fields of fuel cells, advanced materials, membranes, and system studies..

The results of the study provide grounds for future decision-making concerning further development of oxygen transport membrane technology.

2.2 Method

Four tasks have been defined in this project:

Task 1: Inventory of Competing Technologies.

An inventory of the existing commercial and (pre)-commercial methods currently being developed for the production of syngas shall be drawn-up. Each technology identified shall be assessed in technical and economic terms and for so far as possible, both quantitative and qualitative information concerning that technology shall be provided.

Task 2: System Study

In this task potential future syngas producing systems based on oxygen transport membranes (OTM) shall be modelled. The results of the simulations shall provide process data that shall be used as input for task 3. The technical merits of the simulated OTM syngas systems shall be discussed and compared with those of existing commercial processes.

Task 4: Economic Analysis

Based on the process data generated within task 2, the economics of potential new synthesis gas producing systems shall be discussed and compared with the economics of existing commercial technologies.

Task 4: Reporting to Novem

3. RESULTS

3.1 Inventory of Competing Technologies

3.1.1 Introduction

There are a number of technologies available to produce syngas, these technologies are summarised in (Fig. 1). Of the technologies shown in Fig. 1, steam methane reforming (SMR) is the most common. In this process light hydrocarbon feedstock and steam are converted in an endothermic reaction over a nickel catalyst. Heat to the reaction is provided in a radiant furnace. Due to the sulphur content in heavier hydrocarbons their use in the SMR process can cause problems with the catalysts, also there is a risk of tar and coke deposition. The second most common technology is partial oxidation (POX) which proceeds exothermically. Non-catalytic oxidation reaction allows a wider range of feedstocks, however, an oxygen source is needed in most applications. Carbon dioxide reforming is a less common technology, which is primarily used for the production of syngas with a low H_2/CO ratio. The combined and advanced processes also detailed in Fig. 1 are either a combination or an enhancement of the three basic processes. In the following sections firstly the three basic processes are further described shorter descriptions of the combined and advanced processes follow later in the section.

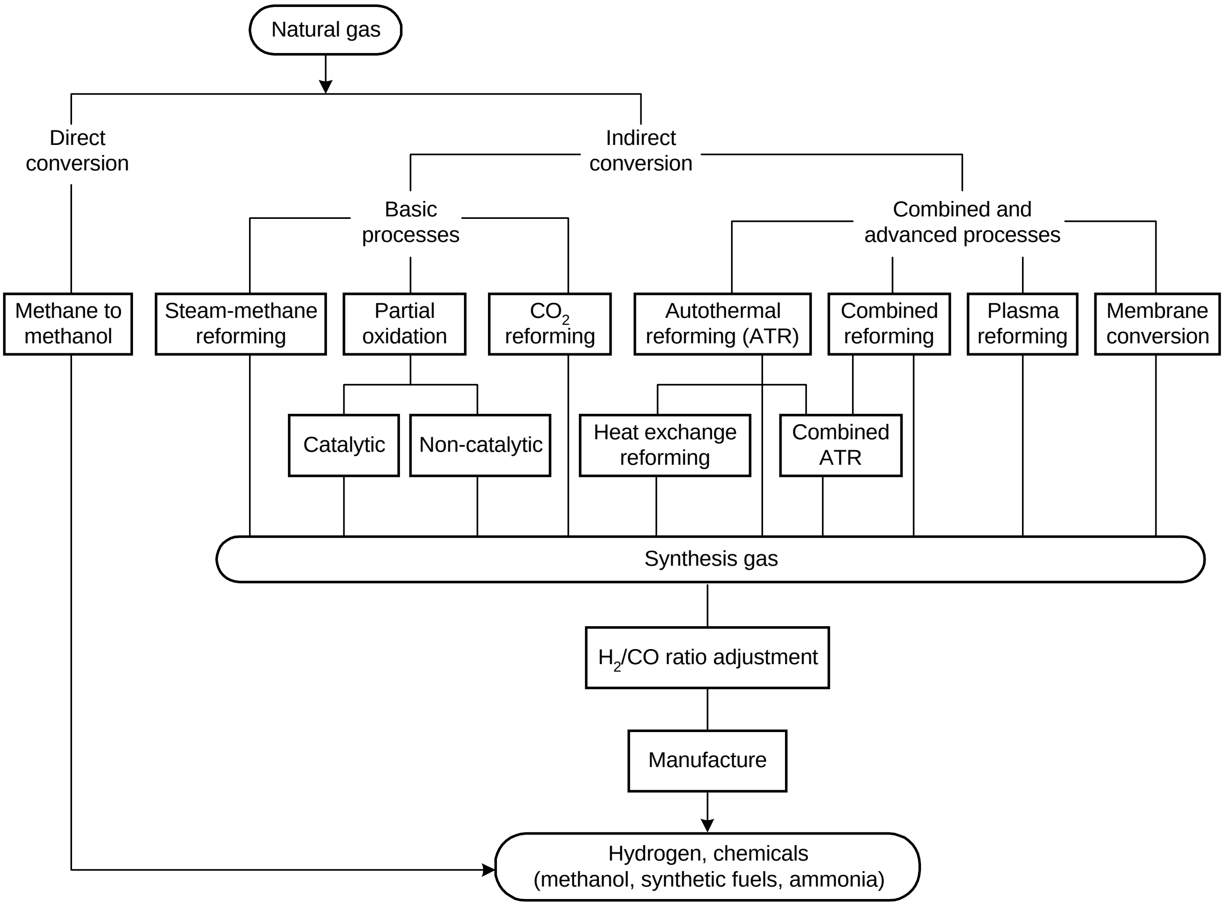

Fig. 1 *General overview of the routes from hydrocarbons to chemicals.*

3.1.2 Steam methane reforming (SMR)

Background

The steam methane reforming (SMR) process can be described by two main reactions:

$$CH_4 + H_2O = CO + 3H_2,\ \Delta H = 198 \text{ kJ/mol} \tag{1}$$
$$CO + H_2O = CO_2 + H_2,\ \Delta H = -41 \text{ kJ/mol} \tag{2}$$

The first reaction is reforming itself, while the second is the water-gas shift reaction. Since the overall reaction is endothermic, some heat input is required. This is accomplished by combustion of natural gas or other fuels in a direct-fired furnace. Reaction (1) favours high temperature and low pressure, and proceeds usually in the presence of a nickel-based catalyst.

The first patents on steam methane reforming were awarded to BASF in 1926 and the first reforming plants were built in the 1930s. Large-scale production has began only in the beginning of 1960s following the discovery of large gas fields in Europe and the subsequent change-over from use of coal to natural gas as a feedstock. In the early days, reforming proceeded at atmospheric pressure, later the process parameters were increased to pressures of up to 30 bar and temperatures of up to 1000°C. The increased pressure saves compression energy in the downstream synthesis stage, however, the high temperature necessitates an extensive heat recovery system.

Process description

In a direct-fired furnace a pre-heated mixture of natural gas and steam is passed through catalyst-filled tubes, where it is converted to hydrogen, carbon monoxide and carbon dioxide (Fig. 2). It is of a great importance to control the maximum tube temperature and heat flux in the reformer to maintain a reliable and prolonged performance. To obtain this, several burner arrangements are employed: top-fired, bottom-fired, side-fired, terrace-walled, and cylindrical type. Of these, the side-fired and terrace-wall types provide a better temperature control.

Due to the endothermic nature of SMR, 35-50% of total energy input is absorbed by the reforming process, of which half is required for temperature rise and the other half for the reaction itself. The produced syngas leaves the reformer at a temperature of 800–900°C. The heat of the flue gases is usually utilised in the convective part of the reformer by generating steam and preheating the feedstock, thus bringing the overall thermal efficiency to over 85%. Only a portion of the steam generated in the boiler is required for the reforming process, while most of the steam (about 60%) is consumed elsewhere. There are also arrangements to recover the heat of the syngas such as the regenerative burners developed by United Technology Corporation, KTI, and Haldor Topsøe (Pietrogrande and Bezzeccheri, 1993).

To avoid catalyst poisoning a de-sulphurisation stage is usually required. In addition to the usual nickel-based catalysts, cobalt and noble metals are often used in SMR processes. Non-metallic catalysts have not proved their feasibility due to their low activity (Rostrup-Nielsen et al, 1993). Another catalyst problem is carbon deposition, which is especially present when processing higher hydrocarbons. In this case, ruthenium, which can effectively resist carbon formation in steam reforming, can be used.

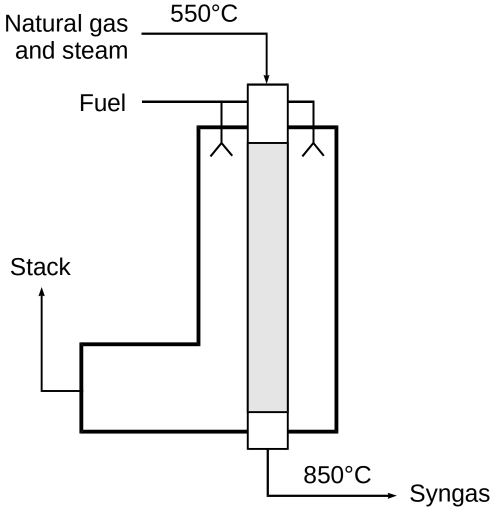

Fig. 2 *Steam methane reforming.*

Typical operating parameters of the SMR process are:

Pressure	20-26 bar
Temperature	850–950°C
H_2/CO ratio	2.9–6.5
Plant capacity	0.4 to 21 mln Nm^3/day

Complete conversion cannot be obtained in the SMR process: typically 65% of methane is converted, at best it is about 98% (Appl, 1992), so secondary reforming must be used if a higher conversion rate is desired (see Section on combined reforming, page ?).

In view of the high H_2/CO ratio, steam reforming is the most effective means for hydrogen production. The carbon monoxide then is oxidised to CO_2 in the shift reaction (2), thus producing even more hydrogen, which is subsequently purified in a pressure-swing adsorption (PSA) unit.

Summarising the advantages of the SMR process, it should noted that this is the most proven technology with a great deal of industrial experience, it requires no oxygen and produces syngas with a high H_2/CO ratio. It also has relatively low operating temperatures and pressures in comparison to other technologies. Nevertheless, expensive catalyst tubing and a large heat recovery section make an SMR plant a costly investment that can only be justified for very large-scale production. The large size of the reformer and the potential risk of local overheating leads to a complicated heat management system with a slow response, furthermore, external heating results in relatively high atmospheric emissions from the combustion process. The presence of catalyst imposes other problems: care should be taken to avoid sulfurization and carbon deposition, also the catalyst should be regularly refilled due to its deterioration. These prevent the use of heavy hydrocarbons as a feedstock in the SMR process.

Economic aspects

The large size of an SMR plant results in a higher capital cost than other technologies due to its high-alloy tubes, catalyst, and bulky heat recovery section. Chauvel and Lefebvre (1989) indicated that an SMR plant of 2 mln Nm^3/day syngas capacity would cost 80 mln USD (data for France, situation in 1986). For each 1000 m^3 of syngas (H_2/CO ratio of 2) about 14 GJ of natural gas will be required. In addition, 7 GJ of fuel, 45 kWh of electricity, and 85 m^3 of cooling water will be consumed as utilities. A study by SINTEF (Sogge et al, 1994) gave a figure of 145 mln USD (battery limits) for an 8 mln Nm^3/day syngas plant. Thus, these sources indicate a range of specific investment costs for an SMR-based syngas plant between 20 and 40 USD per Nm^3/day (40–80 USD per kg per day).

Unlike other syngas processes, the SMR process does not need oxygen, it is therfore usually the preferable choice when oxygen is expensive. Tindall and Crews (1995) indicated that an oxygen price of 30 USD or more per ton makes the SMR a more attractive investment.

Development status

Of the syngas production technologies, steam methane reforming is the most developed and commercialized. Lurgi, for example, has built more than 100 plants to date (Lurgi, 1999). Many engineering companies design and build SMR plants, among them M.W. Kellogg, Haldor Topsøe, ICI, Howe-Baker, KTI, Foster Wheeler, Kværner.

3.1.3 Partial oxidation (POX)

Background

In the partial oxidation reaction, which proceeds exothermically according to

$$CH_4 + \tfrac{1}{2} O_2 = CO + 2H_2 , \ \Delta H = - 44 \text{ kJ/mol}, \qquad (3)$$

complete conversion of methane is obtained above 750°C, resulting in a H_2/CO ratio of 2. Since the reaction is exothermic, no fuel is required. When applied to heavy hydrocarbons, coal, or vacuum residue this process is commonly referred to as gasification.

First papers on this conversion route appeared in the 1930s. In the early experiments by Padovani in 1933 (Eastman, 1956) and by Prettre et al in 1946 (Arutyunov and Krylov, 1998) a nickel catalyst was used. Temperatures of the reaction varied between 750 and 900°C and the pressure was slightly above atmospheric. From 1946 to 1954 Texaco Laboratory in Montebello performed a series of experiments on their pilot plant to provide syngas by partial oxidation for the Fisher-Tropsch process (Eastman, 1956). In the late 1970's interest in the partial oxidation of methane was resumed. Nowadays, pressures up to 75 bar and temperatures up to 1400°C are employed. In addition to the non-catalytic oxidation, a lower-temperature catalytic process has been developed. The catalytic partial oxidation (CPO) has a higher flexibility and is less susceptible to soot formation.

Process description

A refractory-lined pressure vessel is fed with natural gas and oxygen at a typical pressure of 40 bar (Fig. 3). Both natural gas and oxygen are preheated before entering the vessel and mixed in a burner. Partial oxidation reaction occurs immediately in a combustion zone below the burner. To avoid carbon deposition the reactants should be thoroughly mixed and the reaction temperature should not be lower than 1200°C. Sometimes steam is added to the mixture to suppress carbon formation. In the case of catalytic partial oxidation steam is not required and the temperature can be below 1000°C.

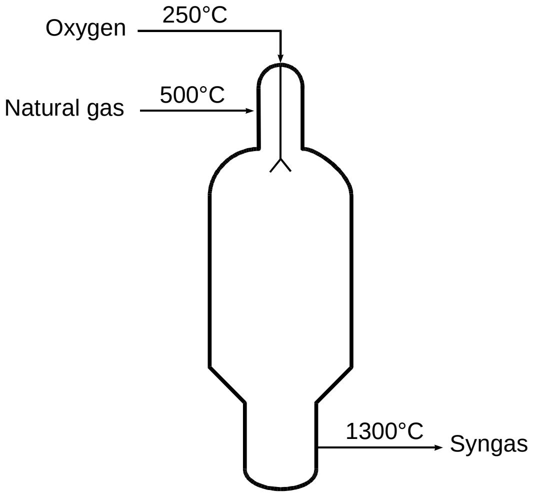

Fig. 3 *Partial oxidation reactor.*

The syngas produced leaves the reactor at temperatures of 1300–1500°C. Since the natural gas is usually supplied from a network at high pressure and oxygen is delivered in the liquid form, the costs of upstream compression are almost negligible. In this manner, compression work is saved in the downstream synthesis process. In practice, syngas from the POX process has a H_2/CO ratio between 1.6 and 1.8, so a shift converter or steam injection should be employed to increase this ratio, for instance, for methanol synthesis.

The non-catalytic process allows the use of a broad range of hydrocarbon fuels from natural gas to coal and oil residue and remains the only viable technology for heavy hydrocarbons. Almost 100% conversion is obtained in the POX reaction, and this is the reason why a POX reactor is used in combined reforming to complete conversion of methane coming from a steam methane reformer (Section 3.1.6). At high temperatures carbon particles are burned completely, so that no steam is required, this simplifies the process operation. However, the need for oxygen results in high operating costs, and also provisions should be made to minimise the risk of explosion.

The catalytic process has a reduced size and consumes less oxygen, but runs the risk of catalyst destruction by local thermal stress.

Economic aspects

According to the SINTEF study (Sogge et al, 1994), the investment costs for a POX-based syngas plant constitute 80% of the reference SMR plant, while a CPO plant would require an investment of just 55% of the reference. Another source indicated that the syngas production costs from a POX plant are 60 to 70% of those of SMR (Norman, 1998).

The SINTEF report (Sogge et al, 1993) cites an investment of 116 mln USD for a POX-based syngas plant with an output of 5.5 Nm^3/day, resulting in specific costs of 21 USD per Nm^3/day. Institut Français du Petrole (IFP) gives a figure of 80 mln USD for a smaller plant of 2 mln Nm^3/day, i.e. 40 USD per Nm^3/day.

The oxygen costs can constitute 50% of operational costs of the syngas production at the POX plant (Sogge et al, 1994).

Development status

Syngas production via the POX route is an established technology. Texaco and Shell technologies have been employed for many years for partial oxidation of petroleum cuts and other heavy hydrocarbons. In the field of coal gasification, along with Texaco and Shell, other companies are active in this field such as Lurgi, Koppers, Foster Wheeler, British Gas, Starchem. In 1992, Texaco had more than 100 licensed commercial POX plants on their reference list, of which 28 were using gaseous and 62 were using liquid feedstock. (Falsetti, 1993).

The POX technology is used at the Shell Middle Distillate plant in Bintulu, Malaysia, where a natural-gas feedstock is processed via Fischer-Tropsch synthesis to produce synthetic fuels and waxes at a scale of 12 000 barrels per day.

Exxon has developed a fluid bed in which partial oxidation and steam reforming reactions are carried out simultaneously in a single large reactor containing a bed of catalyst particles. Between 1990 and 1992 test runs were performed at the demonstration unit in Baton Rouge, Louisiana (Woodfin, 1997).

3.1.4 CO_2 reforming

Background

In the CO_2 reforming process, syngas with a H_2/CO ratio of 1:1 is produced according to the reaction:

$$CH_4 + CO_2 = 2CO + 2H_2, \ \Delta H = 247 \text{ kJ/mol} \qquad (3)$$

As indicated in Wang et al (1996), this reaction was first proposed by Fischer and Tropsch in 1928 as an alternative to steam methane reforming. The absence of steam is the reason why this-reforming process is also called “dry reforming”. The overall reaction kinetics are comparable to that of SMR, however, the potential for carbon formation is much higher. Two reactions are responsible for the carbon formation: methane dissociation and carbon monoxide dis-proportionation. Nickel and Ni/SiO_2 catalysts are often used for CO_2 reforming (Schmitz and Yoshida, 1998). Rostrup-Nielsen et al. (1993) suggest the use of noble metal catalysts such as rhodium or iridium, which are less susceptible to carbon formation. Other sources name iron, cobalt, and non-metallic catalysts (Arutyunov and Krylov, 1998).

Process description

After sulphur removal the feed is mixed with carbon dioxide and passed into the catalyst tubes of a direct-fired reformer in the same manner as in the SMR process (Fig. 4). The produced syngas contains H_2, CO, CO_2, and some unconverted CH_4. At a temperature of 1000°C and pressures of between 1 and 20 bar, selectivity and conversion rates approach 100% (Arutyunov and Krylov, 1998). Sometimes CO_2 in the flue gas and that from the syngas post-treatment is recycled (Teuner, 1985).

Due to the relatively high CO content in the produced syngas, this technology is mainly employed to produce carbon monoxide, which, in turn, is used in acetic acid and phosgene manufacture.

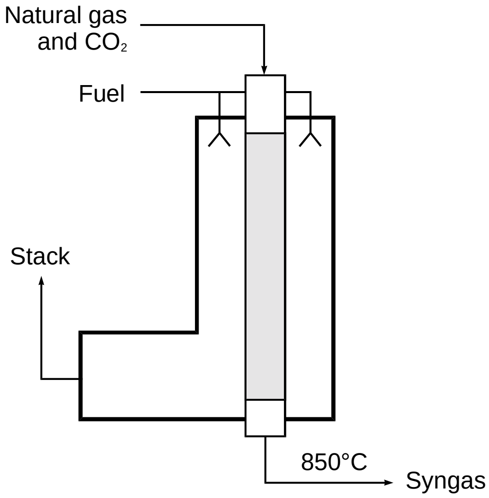

Fig. 4 *CO_2 reforming*

To produce 1 ton of CO the following utilities are required: 500 Nm^3 of imported CO_2, 550 Nm^3 of methane, 200 m^3 of cooling water, and 300 kWh of electricity, as given by Teuner in 1985. In a later publication, the input was changed to 816 Nm^3 of methane, also 240 Nm^3 hydrogen was cited as a by-product (Caloric, 1997).

Economic aspects

Little was found in literature concerning the investment costs for CO_2 reforming, but because this process in many ways resembles the steam methane reforming their costs can be regarded as comparable. Arutyunov and Krylov (1998) reported that the operational costs for a CO_2 reforming plant would be lower than those of SMR and ATR, but higher than those of combined and gas-heated reforming.

Development status

Caloric Anlagenbau GmbH holds patent rights on the Calcor process. The company has built plants for CO production since the late 1980s. The plants are available in two schemes: “standard scheme” for outputs up to 10 000 Nm3/h; and “economy scheme” for 40 to 400 Nm3/h (Caloric, 1997). In the economy scheme, there is no CO_2 recovery and membranes instead of absorbers are used to separate hydrogen and carbon monoxide.

A combination of partial oxidation of methane combined with the endothermic CO_2-reforming reaction has been proposed by University of Oxford (Ashcroft et al, 1991). Their experiments showed that in such a thermally neutral reaction syngas yields up to 90% are possible. It will also allow an effective upgrading of natural gas contaminated with CO_2.

Carbon dioxide reforming is gaining more interest lately due to the concerns about CO_2 emissions as it is a technology that effectively utilizes this greenhouse gas to produce a valuable product such as syngas. Especially the application of carbon dioxide reforming using plasmatron is being investigated by various research groups (see Section 3.1.10).

3.1.5 Autothermal Reforming (ATR)

Background

This process combines partial oxidation and steam reforming in one vessel, where the hydrocarbon conversion is driven by heat released in the POX reaction. Developed in the late 1950's by Haldor Topsøe and Société Belge de l'Azote (Chauvel ane Lefebvre, 1989; Christensen and Primdahl, 1994), the process is used for methanol and ammonia production. Both light and heavy hydrocarbon feedstocks can be converted. In the latter case, an adiabatic pre-reformer is required.

Process description

A preheated mixture of natural gas, steam and oxygen is fed through the top of the reactor. In the upper zone, partial oxidation proceeds at a temperature of around 1200°C. After that, the mixture is passed through a catalyst bed, where final reforming reaction takes place (Fig. 5). The catalyst destroys any carbon formed at the top of the reactor. The outlet temperature of the catalyst bed is between 850 and 1050°C.

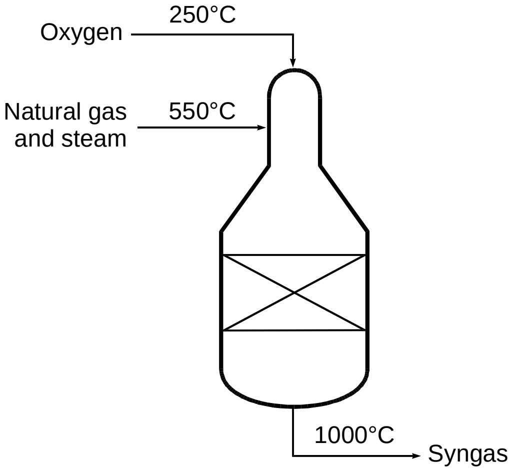

Fig. 5 *Autothermal reforming*

The main advantages of ATR are a favourable H_2/CO ratio (1.6 to 2.6), reduction of emissions due to internal heat supply, a high methane conversion, and the possibility to adjust the syngas composition by changing the temperature of the reaction. However, it requires an oxygen source.

Economic aspects

The capital costs for autothermal reforming are lower than those of the SMR plant by 25%, as reported by Haldor Topsøe (Dybkjær and Madsen, 1997). Operational costs, however, are the same or even higher due to the need to produce oxygen. The SINTEF study (Sogge et al, 1994) reported a capital-cost reduction of 35%, but an 8%-increase in operational costs for the ATR technology in comparison to the SMR process.

Development status

ATR technology is commercially available, but still has limited commercial experience. The main licensors are Haldor Topsøe, Lurgi, ICI, Foster Wheeler.

3.1.6 Combined Reforming

Background

Since less than 100% of methane is converted in the SMR reaction, a secondary reformer behind the SMR unit can be installed to provide complete methane conversion and the possibility to adjust H_2/CO ratio. In addition, the size of the costly SMR plant can be reduced by shifting part of its load to the secondary, oxygen-fired reactor. This is why this process is also called two-step reforming, or oxygen-enhanced reforming.

Process description

As the schematic of the process shows (Fig. 6), it consists of a primary SMR unit and a secondary ATR or POX reformer with oxygen supply.

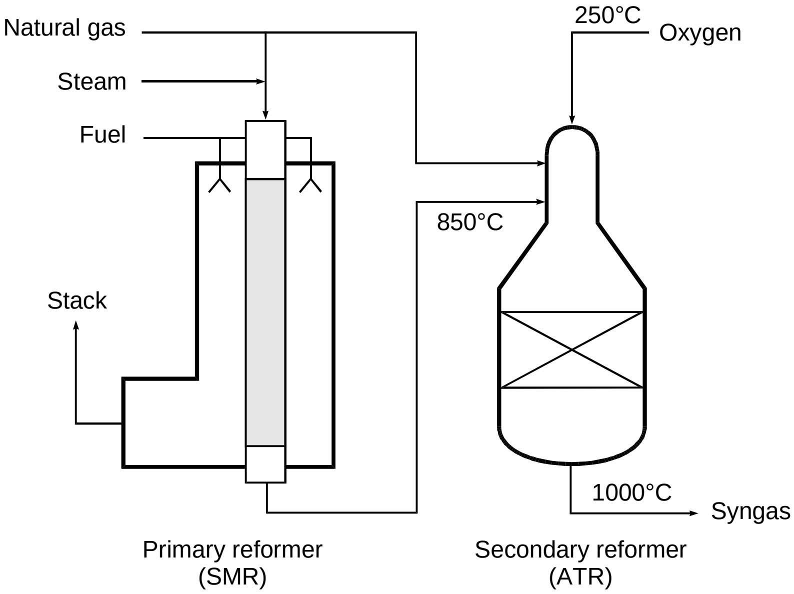

Fig. 6 *Combined reforming*

A pre-reformer is often installed before the main reformer (Fig. 7). Pre-reforming, which proceeds at low temperatures, is usually adiabatic. The pre-reformer widens the range of hydrocarbons suitable for reforming. It also takes over some duty from the primary reformer, in order that it can operate under less severe conditions. This, in turn, allows for less costly materials and a smaller heat transfer surface, which results in reduced costs of the equipment. However, the need for an oxygen plant might overweigh this advantage.

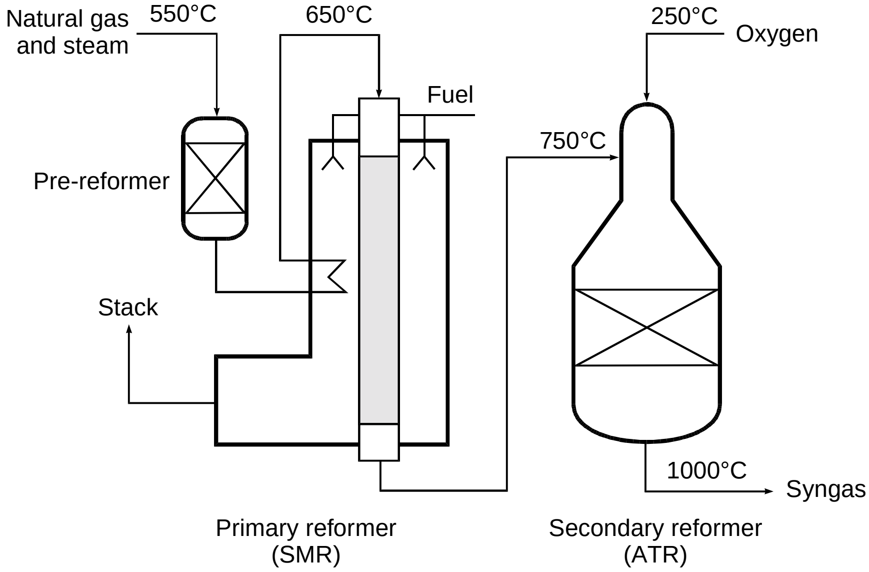

Fig. 7 *Combined reforming with prereforming*

Outlet temperatures of up to 1050°C are common. Methane conversion of above 99.6% can be obtained, as reported by Pietrogrande and Bezzeccheri (1993).

Economic aspects

Schneider and LeBlanc (1992) reported that a combined reforming plant would consume about 3% less energy than an SMR plant. Sogge et al (1994) confirm this figure giving a 1-6% decrease in operational costs. The capital costs, however, are lower: these constitute 72–76% of those by SMR. A study undertaken by Haldor Topsøe (Dybkjær and Madsen, 1997) indicated that the required investment for the combined reforming scheme would be 15% lower, mainly due to the savings in the reformer section.

Development status

This is a technology based on two established processes. Its advancement is directly related to the developments of these processes. Combined reforming technology is being offered by the main contractors in the process industry (Haldor Topsøe, M.W. Kellogg, etc).

3.1.7 Kellogg’s Reforming Exchanger System (KRES)

Background

Only half the heat generated by burning fuel in an SMR furnace is used for the reforming reaction, while the rest has to be recovered in a complicated heat recovery steam generator. The amount of the transferred duty to the catalyst bed can be increased up to 80% if a heat exchange reformer is used. The following three types of reformers (KRES, GHR, and CAR) employ this principle to improve performance and reduce emissions.

Process description

In 1991 M.W. Kellogg was granted a US patent for the Reforming Exchanger System (Schneider and Thomas, 1992). In this scheme, the feed flow is split between the catalyst tube reformer and a secondary reformer. The split is of 75/25 to the secondary and reforming exchanger respectively. A methane and steam mixture enters the reformer at the top, passes the catalyst-filled tubes and exits at the bottom, where it mixes with the ATR outlet flow (Fig. 8). After mixing, this stream serves as a heating medium for the main reformer as it passes the reformer's shell to the top.

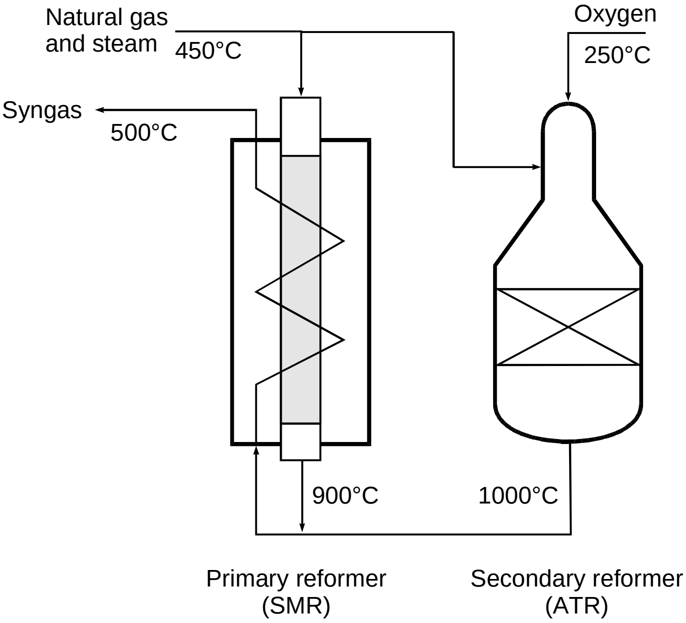

Fig. 8 *Kellogg Reforming Exchanger System*

The main advantages of the KRES compared to the steam reforming are: lower capital cost, improved energy efficiency, reduced NO_X and CO_2 emissions, reduced operator demands (easier maintenance), and less plot space. Some mechanical design difficulties should, however, be mentioned such as thermal expansion and tube sheet problems. This option, due to its parallel configuration has a higher methane slip than the series-arranged GHR option, namely 2.3% vs 0.7% (Farnell, 1996).

Economic aspects

Sogge et al (1994) reported figures for the KRES-type syngas plant: the investment costs would be 64% of the SMR plant, while the operational costs would be comparable. Evaluations made by M.W.Kellogg itself suggested a less optimistic outcome: an article by Schneider and LeBlanc (1992) indicated that a KRES-based methanol plant would cost 10–15% more than a simple steam reforming-based facility, but would consume about 5% less feedstock and fuel.

Development status

M.W. Kellogg holds the patent rights on this technology and promotes this concept for both methanol and ammonia synthesis, also integration of the KRES system with a gas turbine is being considered. Until now, no information has been found on any demonstration or commercial units.

3.1.8 Gas Heated Reforming (GHR)

Background

In a similar manner to KRES, the gas heated reforming concept is an unfired process where the heat for the endothermic reaction is supplied by cooling down the reformed gas from the secondary reformer. This technology, originally developed in the 1960s by ICI, was first demonstrated during 1988 at two ammonia plants in Severnside, UK.

Process description

In contrast to the KRES approach, the feed in the gas-heated reformer is not split between the reformers, but is passed first to the primary reformer where about 25% of reforming takes place. The partially reformed gas is then passed to a secondary oxygen-fired reformer (Fig. 9). The effluent of the latter is used to heat up the feed in the primary reformer. For start-up, an auxiliary burner is employed.

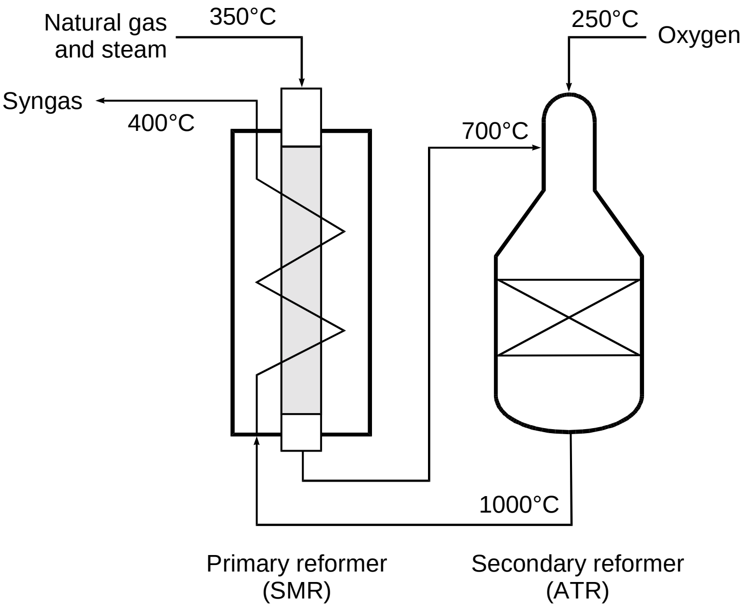

Fig. 9 *Gas heated reforming*

The volume of a GHR is typically 15 times smaller than the volume of a fired reformer (SMR or CO_2) for the same output (Kitchen and Mansfield, 1992).

Overheating of hot metal parts and a poor temperature control can lead to problems concerning the reliable operation of heat exchange reformers. To overcome these problems, reformers usually use counter-current flows in the low-temperature part with effective heat transfer and co-current flows in the hot section for a better temperature control.

Economic aspects

Sogge et al (1994) estimated that the GHR plant would cost about 40% less to build than a comparable SMR plant, while operational costs would be about the same. As indicated by Abbott (1998), the GHR scheme requires 33% less oxygen than the ATR plant.

Development status

The main developer of GHR technology is ICI and its subsidiary Synetix. To date three ammonia plants (two in the UK, one in the USA) and one methanol plant (Australia) have been built using this syngas technology (Abbott, 1999). The compact size of the reactor makes it feasible for implementation of the GHR technology on board of a ship. The GHR concept is also being promoted by Chiyoda (Appl, 1992).

3.1.9 Combined Autothermal Reforming (CAR)

Background

The CAR system combines steam reforming and partial oxidation processes in one single pressure vessel. In a way, this is a logical development of the Gas Heated Reforming concept. Uhde GmbH began developing its process in 1982. And while ICI saw difficulties in putting both reactors within one shell (Kitchen and Mansfield, 1992), Uhde succeeded in engineering and building a demonstration unit based on the single-vessel principle.

Process description

As depicted in Fig. 10, a mixture of steam and primary feed is reformed first in the primary, SMR-type section, utilizing heat produced in the following partial oxidation reaction. The POX reaction proceeds in the lower part of the vessel between the unconverted feedstock and oxygen at a temperature of 1200–1300°C. The temperature and the degree of conversion can be adjusted by controlling the amount of oxygen. And just like in the GHR case (Section 3.1.8), no emissions are produced since there is no external firing.

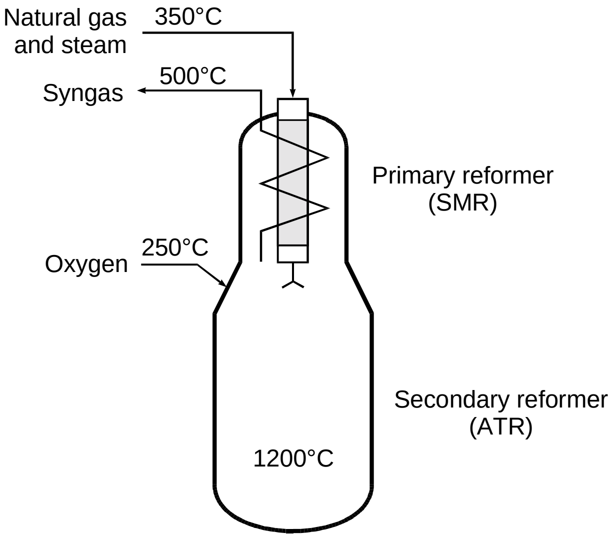

Fig. 10 *Combined Autothermal Reforming*

The following are the process data of a demonstration CAR reactor (Babik and Kurt, 1994):

H_2/CO	2.8	POX zone temperature	1290°C
CO_2	7.2%	CAR outlet temperature	500°C
CH_4	0.5%	Pressure	17 bar

Economic aspects

The CAR unit reduces consumption of oxygen by 35% and consumption of natural gas by 15% in comparison to an existing POX unit (Babik and Kurt, 1994). However, an economic evaluation by SINTEF (Sogge et al, 1994) showed that operational costs of the CAR -based plant are 10% higher than those of POX, while the difference in investment costs are in favour of the CAR concept (about 20% less).

Development status

Uhde built and operated a pilot plant at UK-Wesseling, Germany in 1987-88 (Appl, 1992). A larger demonstration unit has been in operation since 1991 at Strazke Refinery in Slovakia (Babik and Kurt, 1994). Up until March 1994, the demonstration reactor logged about 17 000 hours of operation. It showed a high operating flexibility without problems at loads from 30% to 100%.

3.1.10 Plasma Reforming

A plasmatron can generate very high temperatures (above 2000°C) which are suitable for reforming reactions to produce clean chemical feedstock from liquid, slurry or gaseous feed. The plasma reactor can be operated in a SMR mode with the addition of steam, the reactor can also be put in partial or full oxidation mode with the addition of oxygen or air in the plasma gas mixture. Temperatures in the reactor can be regulated over a wide range.

Thermal Conversion Corp. uses induction-coupled plasma in their pilot plant (Blutke et al, 1999). The plasma conversion process proceeds at conditions closer to reaction equilibrum, resulting in a high-quality syngas without soot, CO_2, or N_2. The formation of water is not higher than 1% (mol) of the methane feed.

Another group of developers at the Université d'Orléans carried out lab scale experiments to generate syngas for Fischer-Tropsch syntheis from methane and carbon monoxide feed (Czernichowski, 1998). They measured a power consumption of 3 kWh/Nm^3 operating at temperatures under 700°C with a gliding arc plasmatron. A carbon conversion of 17 to 23% was noted, no soot or coking were observed. The experiments showed that to produce 1 Nm^3 of syngas, 3 kWh and 0.6 m^3 of hydrocarbon and CO_2 mixture are required.

A similar study by ABB (Kogelschatz et al, 1998) reported on plasma reforming of CH_4 and CO_2. In their work, a H_2/CO ratio of 2 was obtained with 20% of CO_2 in the feed. From 100 moles of feed the reaction produced 20 moles of syngas. At high CO_2 concentrations (up to 80%) a syngas mixture with a H2/CO ratio of 3 was produced at cost of 87kWh/Nm^3.

To produce a H_2/CO ratio of 2, some steam should be added, according to:

$$3\ CH_4 + 2\ H_2O + CO_2 = 4\ CO + 8\ H_2 \qquad (4)$$

In general, the plasma reforming technology is marked by its compact size and low weight, good control of the conversion, a wide range of feed rates and compositions, conversion up to 100%, and a very fast response. Nevertheless, the process proceeds with difficulty at high pressures and is dependent on electric energy.

Economic aspects

This technology is still in development at a lab scale, so it is not possible to give a cost estimate for a large-scale production facility. However, it can be compared with a cost estimate given for a commercial plasma-arc plant for the production of hydrogen from methane consisting of 20 modules each 6 mln H_2 m^3 per year. According to this evaluation the plant will cost 300 mln DM (Hyweb, 1997).

Development status

Although plasma reforming is being developed by a number of companies and research groups, such as MIT (USA), Kvaerner (Norway), Fulcheri (France), Thermal Conversion Corp. (USA), ABB, it has only been demonstrated at lab and pilot scale.

Thermal Conversion Corporation runs a 1-MW test facility in a joint project with Rentech, a developer of Gas-to-Liquids technology (Blutke et al, 1999). The unit operates at a frequency of 370–440 kHz, and temperatures up to 1200°C. Operating pressure is atmospheric, however, pressures up to 5 bar can be reached. An electrical-to-thermal efficiency of 45% has been reported. This value is expected to reach 60% next year, and a level of 70% seems feasible. At this moment CO_2 - plasma is used, the resulting syngas has a H_2/CO ratio of 1:1. In the future SMR and POX options will be tested.

Kvaerner have operated a pilot plant, which produces 500 kg/h carbon black and 2000 Nm^3/h hydrogen from 1000 Nm^3/h natural gas and 2100 kWe since 1992 (Hyweb, 1997).

3.1.11 Reforming with Cyclic Oxidation

To avoid the costly oxygen plant, a cyclic oxidation reactor has been proposed by Van Looij (1994). Here, oxygen from air is consumed periodically by an oxygen storage compound (OSC) located in two vessels (Fig. 11). While one vessel extracts oxygen, the other releases it for POX or SMR reaction. Both vessels also exchange heat to complete methane oxidation (Stobbe, 1999). Manganese oxides can serve as an oxygen storage compound.

The proposed system is being investigated at a lab scale at Utrecht University. The research is aimed on finding a suitable OSC. According to Stobbe (1999), the drawbacks of this process are technically complicated switching and purging steps, and an expensive valve system.

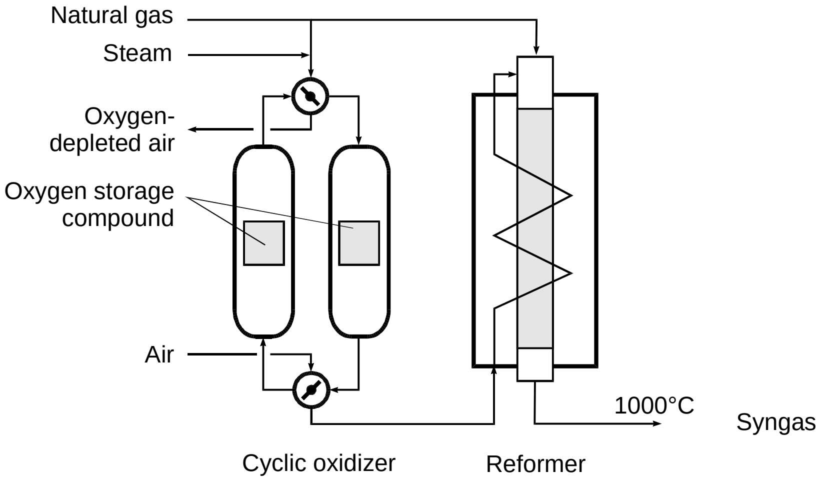

Fig. 11 *Reforming with cyclic oxidation*

3.1.12 Reforming by High Pressure Piston Reactor.

Hickman and Schmidt (1992) have performed experiments that noted the possibility for methane conversion with very short contact times. Methane at high space velocity (up to 4 x 10^6 h^{-1}) was passed along rhodium-coated monolith. In the partial oxidation reaction conversions above 90% were measured.

Another proposed system also operates at short contact times and in the POX mode (Glushenkov and Parashyuk, 1997). In the High-Pressure Piston reactor, the feedstock gas (natural gas) enters the vessel through the inlet valve (Fig. 12). During start-up, the spring gas brings the piston in the upper position, where partial oxidation of the feedstock gas takes place. The released energy drives the piston downwards and the product gases leave the reactor through the outlet valve. A portion of natural gas is then submitted in the upper chamber and the pressure of the spring gas brings the piston back to the upper point. As soon as the piston has obtained its operating amplitude and frequency, the supply of spring gas can be shut off, and the cycle will be maintained in operation only by natural gas input.
Cooling of the piston is the major problem in the development of such a reactor. According to the authors, a number of lab-scale units have been tested to date.

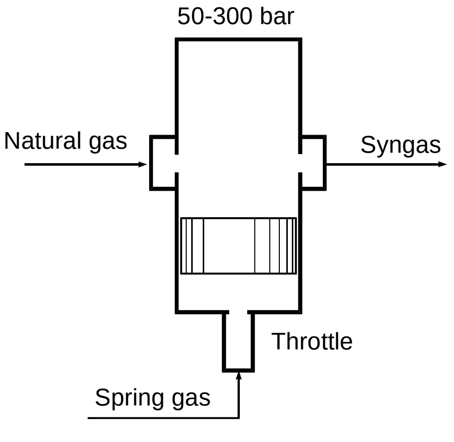

Fig. 12 *High-pressure piston for syngas production.*

3.2 Membrane Conversion

3.2.1 Introduction

The idea of air separation using membranes is not new, but the concept of combining two processes, oxygen production and partial oxidation of methane, in one unit has drawn attention only in the last decade. Currently, research work on the membrane separators is being carried out by a large number of research institutions, oil and chemical concerns, and utilities. This technology is also known as Oxygen Transport Membrane (OTM), Ionic Transport Membrane (ITM) or Solid State Membrane (SSM) technology.

3.2.2 Process Description

Two types of membrane systems are known: the mixed electrolyte oxygen separator (MEOS) and the solid electrolyte oxygen separator (SEOS), both types of process are described below.

Mixed Electrolyte Oxygen Separator (MEOS) Membranes

The operating principle of the MEOS technology is shown in Fig. 13, dense, complex metal oxide ceramics that conduct both oxygen ions and electrons are used to separate oxygen from air. They operate by adsorbing and dissociating oxygen molecules onto the compressed air side of a MEOS membrane, where the dissociated oxygen is ionised and transferred through the membrane at temperatures of > 700°C.

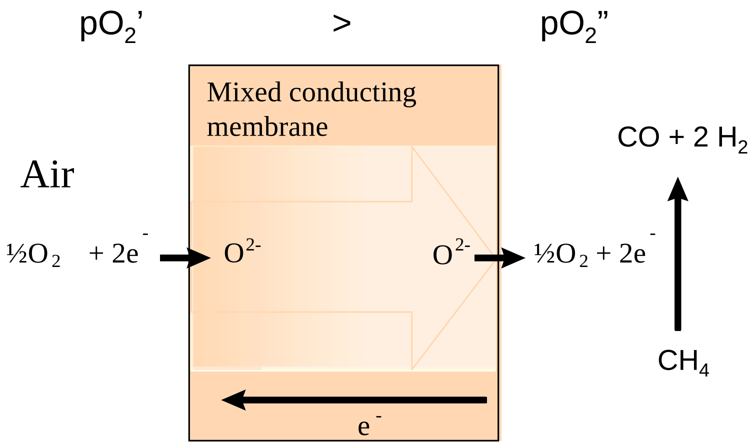

Fig. 13 *The operating principle of MEOS membrane technology.*

In simplest terms, natural gas (CH_4) is allowed to flow along the other side of the membrane. Driven by the difference in oxygen partial pressure, oxygen ions flow through the membrane at high flux rates, reacting with the CH_4 according to the partial oxidation reaction at the permeate side. The electrons released by the recombination of the oxygen ions are transported back to the air side through the electronically conducting membrane. In this way air separation and reforming processes have been combined into a single process operation.

Solid Electrolyte Oxygen Separator (SEOS) Membranes

The operating principle of the SEOS technology is shown in figure 14. The SEOS membrane technology is no different from Solid Oxide Fuel Cell (SOFC) technology. In the previous case (MEOS membrane technology) the dense, metal oxide ceramic membrane conducts both oxygen ions and electrons. In SEOS membrane technology the metal oxide membrane conducts only oxygen ions (as is the case for an SOFC electrolyte material). The principle is exactly the same as for the MEOS case, however in SEOS, the electrons released by the recombination of the oxygen ions are transported back to the air side via an external circuit. In this manner air separation, reforming processes and the generation of heat and power are all combined in one electrochemical process.

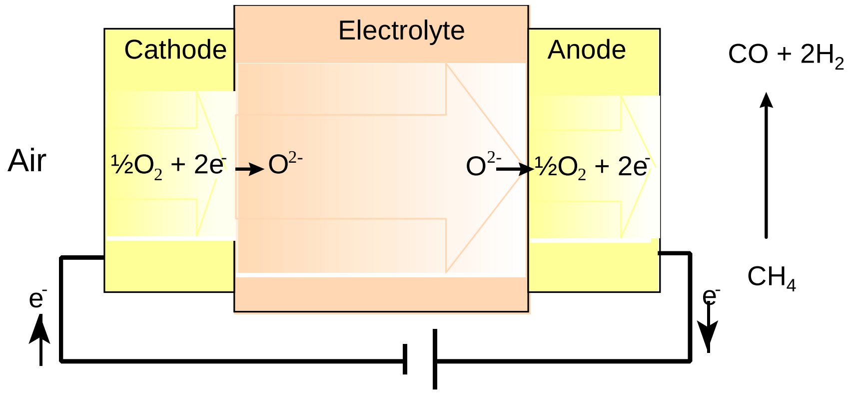

Fig. 14 *The operating principle of SEOS membrane technology.*

3.2.3 Development Status

At the present time the development of SEOS membrane technology has been limited to a few paper studies in which conceptual systems have been proposed.

The use MEOS membrane technology for the partial oxidation of natural gas is however being very actively developed, primarily in the U.S.A. Two large, competing consortia based around Air Products and Praxair have been formed. The principal companies / laboratories involved in the consortia are as follows:

Consortium 1*:
Air Products, Chevron, Norsk Hydro, Argonne National Lab., Ceramatec, Eltron.

Consortium 2:
Praxair, BP-Amoco, Statoil, Sasoil, Phillips.

* Consortium 1 has been awarded an $ 80 m contract for an 8-year project with the DOE's Offices of Fossil Energy and of Energy Efficiency and Renewable Energy to develop the technology. In this joint programme, a number of test units will be built, starting from a process development unit (340 Nm^3/day), a sub-scale engineering prototype (14 000 Nm^3/day), and finally, a pre-commercial technology demo unit with a capacity of 500 000 Nm^3/day.

Little or nothing is published concerning the technical status of the technology being developed by the two competing consortia, however it is clear that it shall take another 8-10 years before the first commercial products shall enter the marketplace (Bobinsky, 1998).

3.2.4 Economic Aspects

It has been stated that by eliminating the oxygen plant, costs can be reduced by 25% or more thus bringing the costs of syngas-derived liquid fuel from USD35 to USD 20 per barrel, as indicated in a paper by DOE (1997). In an evaluation study by Bredesen and Sogge (1996) a 5% to 10% reduction in the investment costs was reported. This technology is especially attractive for utilization of the large resources of remote natural gas via the Fischer-Tropsch route. Here, OTM technology should compete with ATR, POX/CPO, combined and non-fired reforming (KRES, GHR, CAR). All these processes require an oxygen production unit and have a rather large plot size, while an OTM plant incorporates the high-flux oxygen plant in the reactor itself, what results in very compact design and light weight.

3.3 Summary of Inventory of Competing Technologies

In the following tables (Table 1 through Table 3), an overiview of syngas technologies is given. Considering the criteria listed in the tables, it can be concluded that the most attractive technologies for syngas production are CPO and a number of the combined processes (ATR, KRES, GHR, CAR). Their advantages can be listed as follows. These technologies produce a syngas of the required H_2/CO ratio that can be directly used for methanol or Fischer-Tropsch synthesis; these require the smallest investments and have commercial or pre-commercial status of development. Against this background, the membrane systems should prove their competitiveness in terms of technical and economic feasibility. The following chapters address these issues in detail.

Table 1 *Overview of the basic processes.*

	SMR	**POX**	**CPO**	**CO2**
Temperature, °C	800–900	1000–1450	800–1000	900–1000
Pressure, bar	20–30	30–85	15–40	10
H_2/CO ratio	3–6	1.6–2	1.6–2	1
CH_4 conversion, %	65–95	95–100	95–100	?
Oxygen	none	high	high	none
Steam consumption	high	optional	optional	optional
Capital costs, %	100 (refer.)	80–110	55–80	?
Emissions	high	low	low	low
Scale	large	small to large	small to large	medium
Development status	commercial	commercial	pre-commercial	commercial

Table 2 *Overview of the combined processes.*

	ATR	**Combined**	**KRES**	**GHR**	**CAR**
Temperature, °C	850–1300	primary: 800, secondary: 1000–1200	primary: 800, secondary: 1000	primary: 450, secondary: 1000	1200–1300
Pressure, bar	20–70	20–30	20–30	20–30	20–30
H_2/CO ratio	1.6–2.5	2.5–4	2.5–4	3.4	2.4
CH_4 conversion	95–100	95–100	95–100	95–100	95–100
Oxygen	high	low	medium	medium	medium
Steam consumption	low	medium	medium	medium	medium
Capital costs, %	65–80	75–115	65–90	60–80	65–85
Emissions	low	medium	low	low	low
Scale	large	large	large	medium–large	medium–large
Development status	commercial	commercial	pre-commercial	3 commercial units	1 demo, 1 commerc. unit

Table 3 *Overview of the advanced processes.*

	Membrane	**Plasma**	**High-pressure**	**Direct**
Temperature, °C	850–1100	1100–1800	up to 3000	100
Pressure, bar	20–30	1–3	up to 400	1–2
CH_4 conversion, %	95	25–50	95–100	<5
H_2/CO ratio	1.6–2.5	1–2	1.6–2	?
Oxygen consumption	none	none	none	none
Steam consumption	optional	optional	optional	none
Capital costs, %	60–85	?	?	?
Emissions	low	low	low	low
Scale	small	small	small	small
Development status	lab	lab	lab	lab

Note: Capital costs are given as a percentage of the reference SMR plant (100%).

3.4 System Study

3.4.1 Introduction

The process simulation package ASPEN Plus (Version 9.3) was used to simulate MEOS and SEOS systems. Along with the membrane reactor, the system models include all required balance-of-plant equipment such as compressors, expanders, heat exchangers and burners. Heat of the produced syngas is utilised in a steam bottoming cycle to generate electricity. The general assumptions are listed in Table 4. Specific assumptions are detailed later in the text.

Table 4 *Main assumptions.*

System:	
Syngas production	about 2500 t/day
Syngas pressure	80 bar
Syngas temperature	160-190°C
Pressure drop in pipelines	nil
Heat loss in pipelines and equipment	nil
Feedstock:	
Composition	100% CH_4
Pressure	100 bar
Temperature	5°C
Membrane reactor:	
Oxygen utilization (stage cut)	50%
MEOS oxygen flux	10 ml/cm^3
MEOS operating pressure	27 bar
SEOS oxygen flux	3.4 ml/cm^3
MEOS operating pressure	2.5 bar
Methane conversion	95% (min.)
CO selectivity	97% (min.)
Heat exchangers:	
Pressure drop	0.1 bar
Heat transfer coefficient	100 W/m^2K
Turbomachinery:	
Isentropic efficiency	0.85

Four models were set up: three MEOS and one SEOS system. The first system model considered, (MEOS-1121) is based on a POX reactor that obtains an equilibrum at specified conversion and selectivity rates, the corresponding temperature is 1121°C. The second system model, (MEOS-1000) also reaches equilibrum, but the operating temperature here is limited to 1000°C due to material constraints. In the last MEOS model, (MEOS-CPO), thermodynamic equilibrum is not reached, nevertheless, the requirements for CO-selectivity and methane conversion are satisfied. The SEOS model has an operating temperature of 850°C. Due to the lower pressure in the SEOS scheme, desired conversion and selectivity figures can be reached at such a temperature.

The general process flow diagrams (PFD) of the membrane system are shown in Fig. 13 through Fig. 16. Complete ASPEN Plus models and process data sheets are presented in Appendix 4.

Methane enters the system from a pipeline at a pressure of 100 bar and a temperature of 5°C. To come to the operating pressure (2.5 bar for SEOS, and 27 bar for MEOS), the gas is passed through an expander. To prevent ice forming in the expander, preheating of methane before expansion is provided by the outgoing air flow. Following the expander, methane gains in temperature again by exchanging heat with the same air flow and, finally, enters the membrane reactor at a temperature of 340–480°C. In the reactor methane reacts with oxygen coming from the other side of the membrane. In this partial oxidation reaction syngas is formed. Its heat is utilised in the steam bottoming cycle indicated on PFDs as Cooler. Here syngas is cooled down to 50°C (or higher, if water condensation takes place) and steam is produced for power generation. The power output of the bottoming cycle is calculated assuming heat-to-power efficiency of 17%, as a value comparable to that in the SINTEF study (Sogge et al, 1994).

On the air side of the system, air is first compressed to the operating pressure of 2.5–2.7 bar, then it is preheated in a heat exchanger, and finally obtains the membrane inlet temperature in a burner located in the air flow. Depending on the system, the inlet temperature varies from 670 to 1090°C. Oxygen-depleted air follows then three heat exchangers, where it heats up the incoming syngas, and finally expands to the atmospheric pressure through an expander, thus delivering additional power.

3.4.2 MEOS-1121

All MEOS models operate at elevated pressure and temperature in order to reach the required CO-selectivity en CH_4-conversion.

It is assumed that in the MEOS-1121 model complete chemical equilibrium is reached and the oxygen flux across the membrane is $10 Nml/cm^2 \cdot min$. The flow diagram with process data is given below.

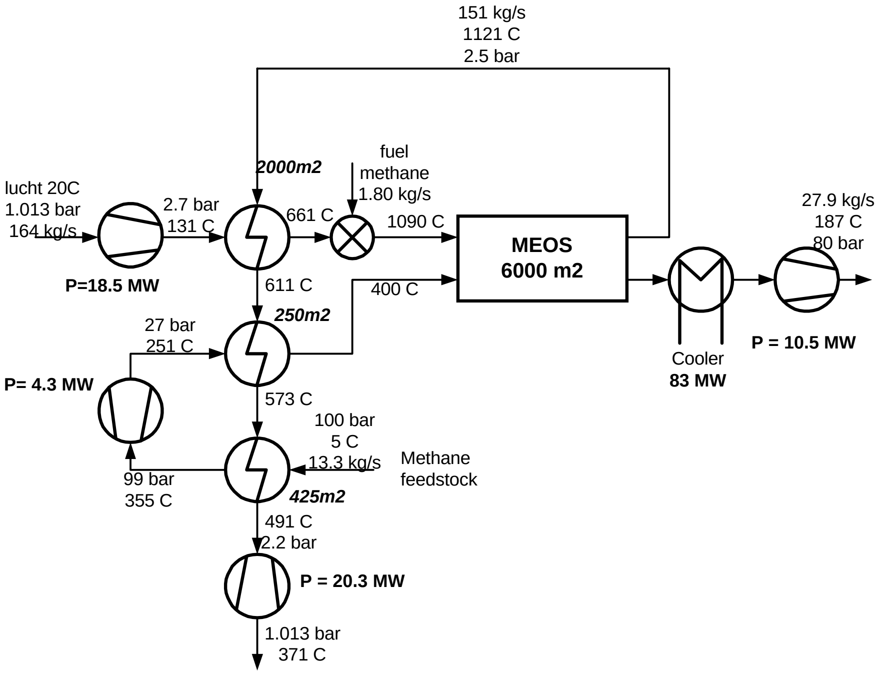

Fig. 13 *MEOS-1121 simplified process flow diagram.*

The temperature of 1121°C is the lowest possible temperature where the system still can satisfy the requirements for CO-selectivity en CH_4-conversion. During the simulations, these figures were controlled by changing the amount of fuel in the burner. The main results of the modelling work are listed in Table 5. The system consumes about 15 kg/s of methane and produces 28 kg/s of syngas and 9.7 MW of electricity. The membrane reactor has an area of about 6000 m^2.

Table 5 *Main results for MEOS-1121 model.*

Feedstock	kg/s	13.3
Burner fuel	kg/s	1.8
Total:	kg/s	15.1
Air flow	kg/s	163.9
Air compressor	MW	-18.5
Syngas compressor	MW	-10.5
Offgas expander	MW	20.3
Methane expander	MW	4.3
Bottoming cycle	MW	14.1
Total:	MW	9.7
Heat exchanger 1	m^2	2000
Heat exchanger 2	m^2	250
Heat exchanger 3	m^2	425
Total:	m^2	2675
CH_4-conversion		0.956
CO-selectivity		0.970
Membrane temperature	ºC	1121
Membrane area	m^2	6141

3.4.3 MEOS-1000

The assumptions for MEOS-1000 system (chemical equilibrum, oxygen flux) were comparable with those of the MEOS-1121 system model with the exception of the maximum temperature of the reactor.

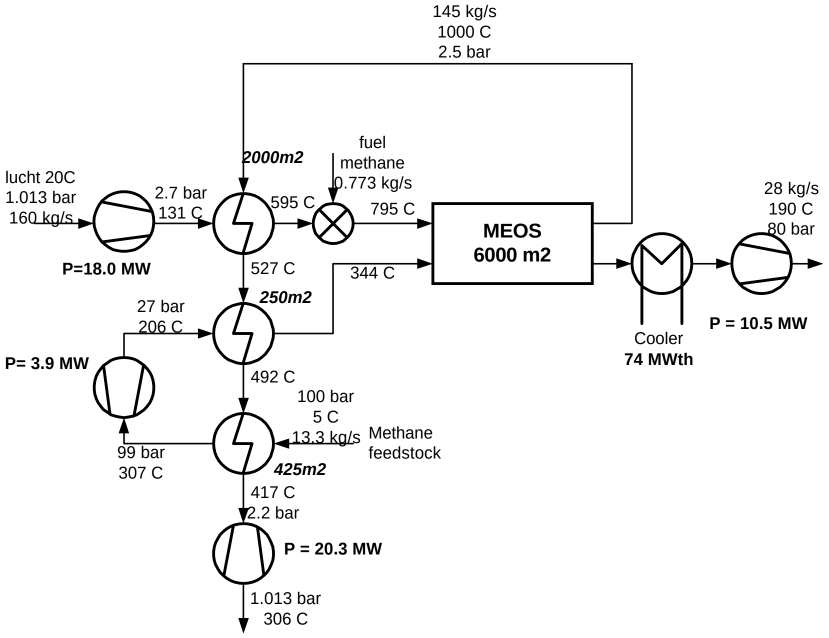

Fig. 14 *MEOS-1000 simplified process flow diagram.*

In this case, the maximum temperature of the reactor was limited to 1000°C owing to material constraints. Owing to this temperature restriction, the required CO-selectivity and CH_4-conversion were not reached (0.949 and 0.938 respectively). To obtain the highest possible values at 1000°C, both air and fuel flow were controlled. Process data is given on the flow diagram (Fig. 14), and the results of simulation are summarised in the following table(Table 6).

Table 6 *MEOS-1000 main results.*

Feedstock	kg/s	13.3
Burner fuel	kg/s	0.8
Total:	kg/s	14.1
Air flow	kg/s	160.1
Air compressor	MW	-18.0
Syngas compressor	MW	-10.5
Offgas expander	MW	20.3
Methane expander	MW	3.9
Bottoming cycle	MW	12.6
Total:	MW	8.3
Heat exchanger 1	m^2	2000
Heat exchanger 2	m^2	250
Heat exchanger 3	m^2	425
Total:	m^2	2675
CH_4-conversion		0.949
CO-selectivity		0.938
Membrane temperature	ºC	1000
Membrane area	m^2	6141

This system also generates about 28 kg/s of syngas and 8.3 MW of electricity, consuming 14 kg/s of feedstock and fuel.

3.4.4 MEOS-CPO

In the final MEOS model, the POX reaction was substituted by the catalytic partial oxidation (CPO) using the following assumptions. The required values for conversion and selectivity are reached (i.e) there is no thermodynamic equilibrum in the reactor. 97% of the methane is partially oxidised, 3% of the methane feedstock is combusted completely the oxygen flux is 10 $Nml/cm^2 \cdot min$ and the membrane temperature is 1000ºC. The basic flow diagram is given below (Fig. 15).

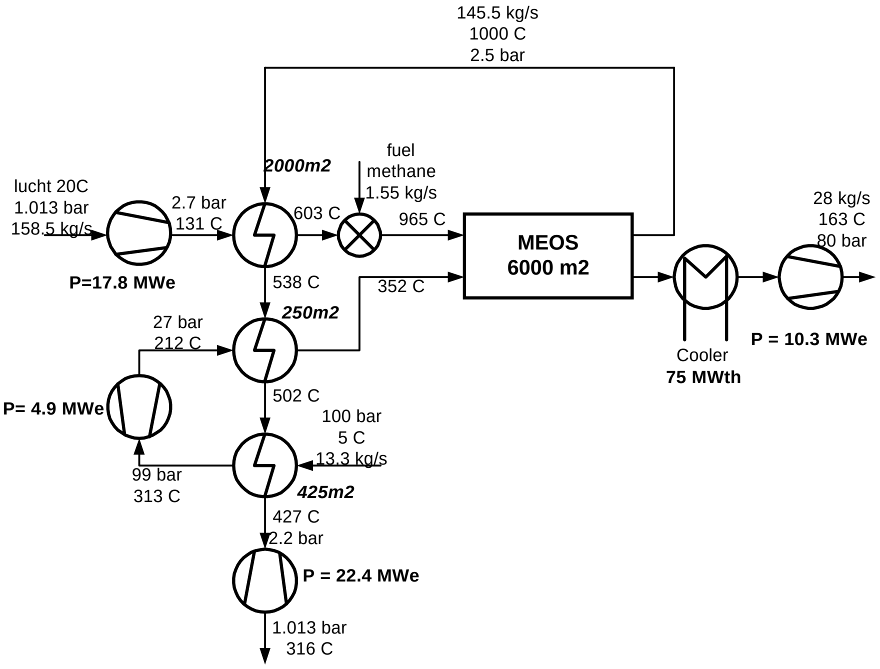

Fig. 15 *MEOS-CPO simplified process flow diagram.*

As the main results show (Table 7), the MEOS-CPO system has in general similar performance as to the other MEOS options. There are some deviations, that are due to different syngas compositions and a non-optimised system.

Table 7 *MEOS-CPO main results.*

Feedstock	kg/s	13.33
Burner fuel	kg/s	1.55
Total:	kg/s	14.88
Air flow	kg/s	158.5
Air compressor	MW	-17.8
Syngas compressor	MW	-10.3
Offgas expander	MW	22.4
Methane expander	MW	4.9
Bottoming cycle	MW	12.8
Total:	MW	11.7
Heat exchanger 1	m^2	2000
Heat exchanger 2	m^2	250
Heat exchanger 3	m^2	425
Total:	m^2	2675
CH_4-conversion		1.000
CO-selectivity		0.970
Membrane temperature	ºC	1000
Membrane area	m^2	6089

3.4.5 SEOS

Owing to the specific construction of the SEOS reactor, a lower operating pressure was chosen for the SEOS model. This allowed the required conversion and selectivity rate to be satisfied at 850°C. Co-production of electric power makes the SEOS system especially attractive. However, due to a lower oxygen flux in the SEOS membrane, a 2–3 times larger membrane area would be needed for the production of the same amount of syngas as in the MEOS plant. Also, an account for a DC/AC converter and other additional balance-of-plant equipment should be given.

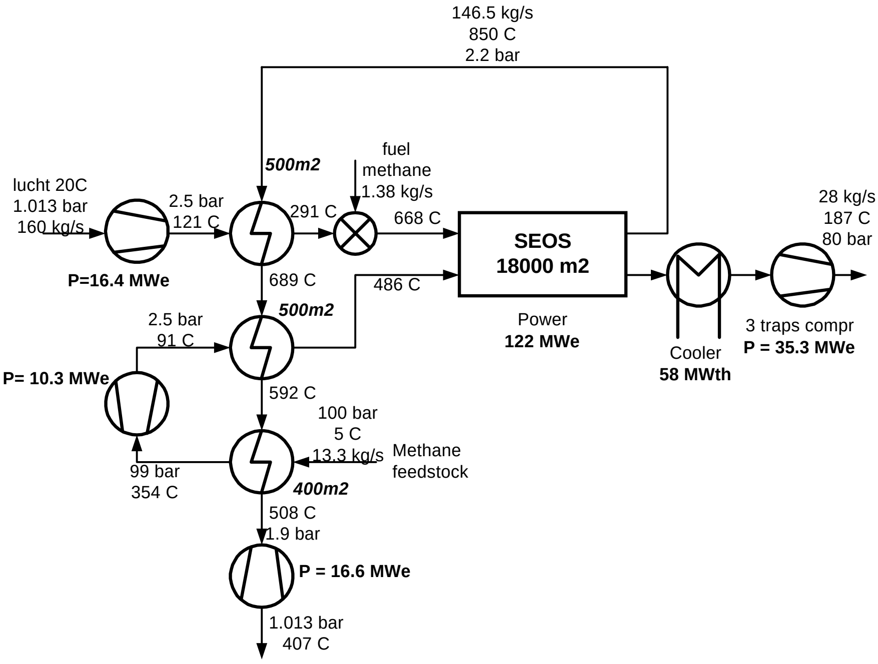

Fig. 16 *SEOS simplified process flow diagram.*

It was assumed in the simulations that thermodynamic equilibrium is reached and the oxygen flux in the SEOS membrane is 3.4 Nml/cm^2·min. Such a low flux resulted in a three times larger membrane area than for the MEOS plants. Due to the lower operating pressure, the syngas compressor duty is also about 3 times higher. Nevertheless, SEOS produced about 120 MW of electric power, which gave a net output of 107 MWe, as shown in Table 8.

Table 8 *SEOS main results.*

Feedstock	kg/s	13.33
Burner fuel	kg/s	1.38
Total:	kg/s	14.71
Air flow	kg/s	160.0
Air compressor	MW	-16.4
Syngas compressor	MW	-35.3
Offgas expander	MW	16.6
Methane expander	MW	10.3
SEOS DA converter	MW	122.0
Bottoming cycle	MW	9.6
Total:	MW	106.8
Heat exchanger 1	m^2	500
Heat exchanger 2	m^2	500
Heat exchanger 3	m^2	400
Total:	m^2	1400
CH_4-conversion		0.958
CO-selectivity		0.942
Membrane temperature	ºC	1000
Membrane area	m^2	18000

3.4.6 Summary of the System Study

The summary table (Table 9) lists main parameters of the modelled systems. As can be seen, the MEOS cases do not differ considerably, while the SEOS model with its large power output represents a different type of syngas plant. All models, except for MEOS-1000 could reach the required conditions for conversion and selectivity.

The simulation models were not optimised for minimum fuel consumption or heat exchanger area. Nevertheless, the process data calculated in all cases are representative enough to evaluate the performance of membrane reactor systems and to carry out a basic economic analysis.

Table 9 *Summary of results*

	MEOS-1121	**MEOS-1000**	**MEOS-CPO**	**SEOS**
Reactor temperature, °C	1121	1000	1000	850
Reactor pressure, bar	27	27	27	2.5
Syngas flow:				
kmol/hr	8674	8652	8974	8695
kg/s	27.95	29.56	27.8	28.35
Syngas composition:				
CH_4	0.017	0.019	0.000	0.016
CO	0.318	0.307	0.323	0.309
CO_2	0.010	0.020	0.010	0.019
H_2	0.613	0.579	0.647	0.614
H_2O	0.042	0.075	0.020	0.042
H_2/CO ratio	1.93	1.89	2.00	1.99
Methane consumption, kg/s				
- feedstock	13.33	13.33	13.33	13.33
- burner fuel	1.8	0.77	1.55	1.38
CH_4-conversion	0.956	0.949	1.000	0.958
CO-selectivity	0.970	0.938	0.970	0.942
Net power production, MWe	8	9.4	11.7	106.8

3.5 Economic Analysis

3.5.1 Introduction

In this chapter the economics of the MEOS-CPO, MEOS-POX and SEOS installations are discussed. The systems were compared with the most developed syngas technology, Steam Methane Reforming (SMR). Also, a comparison was made with Catalytic Partial Oxidation (CPO), as a promising advanced syngas technology.

It should be noted that the economic results determined in this study for MEOS and SEOS processes are approximations. The complete syngas production unit consists of the main reactor and associated heat recovery equipment (recuperators and waste heat boilers). Part of the steam is used to generate electricity by a steam bottoming-cycle, similar to that of a combined-cycle power plant. The cost parameters chosen in this study are derived from a report written by SINTEF Applied Chemistry (Sogge et al., 1994). These parameters are shown in the table below. The economic results of the processes SMR and CPO are also taken over from this report. The CPO process used in this study is a constructed, theoretical case. For this process, it has been assumed that the syngas is generated catalytically and that the natural gas and oxygen is completely converted to CO and H_2 by pure partial oxidation.

Table 10 *Assumptions for economic analysis.*

Cost parameter	**Chosen values**
Location	US Gulf Coast
Stream Days	330 /year
Production	about 2500 ton syngas/ day
Depreciation	10 % of GRCC [1]
Return on Investment	20 % of GRCC
BLCC [2]	250 % of Major Equipment Costs
OSBLCC [3]	19 % of BLCC
Maintenance	5 % of GRCC
Power price buying	0.031 USD/kWh
Power price, selling	0.025 USD/kWh
Natural gas	0.050 USD/Nm^3
LP steam price	0.010 USD/kWh
Water price	0.282 USD/m^3
Labour	25000 USD/year
Membrane price with catalyst	1100 USD/m^2
Membrane price without catalyst	1000 USD/m_2

Notes:
BLCC: In the SINTEF report SMR had the highest percentage for BLCC, namely 280 % of the main equipment costs. ATR had the lowest value, 230 %.
OSBLCC: This value is taken the same as for the CPO process.
Labour: For the calculation of the operational cost it is assumed that the total amount of workers is equal to the amount of major equipment plus 17.
Prices: For the comparison purposes, the feedstock and utilities cost assumptions in Table 10 were kept the same as in the SINTEF study.

---

[1] GRCC = Grass Roots Capital Costs

[2] BLCC = Battery Limit Capital Costs

[3] OSBLCC = Outside Battery Limit Capital Costs

3.5.2 Capital Costs

Both capital and operating costs have been calculated for all the processes in the system models. The major equipment costs of MEOS and SEOS plants are given in Table 11 through Table 14.

Table 11 *MEOS-1121 major equipment cost.*

Major Equipment	Size	Unit	Material	Bare Cost (USD) (ME)	% of Total
Membrane reactor	6141	m2		6 191 333	22.51
Air compressor	18.5	MW	Carbon Steel	4 287 710	15.59
Combustion chamber				1 500 000	5.45
			Tube / Shell side		
Air heat exchanger	2000	m2	SS 316 / CS	956 000	3.48
Natural Gas heat exchanger 1	250	m2	SS 316 / CS	119 524	0.43
Natural Gas heat exchanger 2	425	m2	SS 316 / CS	180 476	0.66
Syngas compressor	10.5	MW	Carbon Steel	2 933 710	10.67
Natural Gas expander	4.3	MW	Carbon Steel	1 610 792	5.86
Offgas expander	20.3	MW	Carbon Steel	4 556 570	16.57
Electric generator	4.3	MW		14 336	0.05
Electric generator	20.3	MW		67 680	0.25
Steam bottoming cycle				1 651 000	6.00
Steam turbine	14.1	MW		3 356 400	12.31
ST electric generator	14.1	MW		107 688	0.17
Total ME cost				**27 502 575**	100.00

Table 12 *MEOS-1000 major equipment cost.*

Major Equipment	Size	Unit	Material	Bare Cost (USD) (ME)	% of Total
Membrane reactor	6141	m2		6 191 333	21.49
Air compressor	18	MW	Carbon Steel	4 209 717	14.61
Combustion chamber				1 500 000	5.21
			Tube / Shell side		
Air heat exchanger	2000	m2	SS 316 / CS	956 000	3.32
Natural Gas heat exchanger 1	250	m2	SS 316 / CS	119 524	0.41
Natural Gas heat exchanger 2	425	M2	SS 316 / CS	180 476	0.63
Syngas compressor	10.5	MW	Carbon Steel	2 933 710	10.18
Natural Gas expander	3.9	MW	Carbon Steel	1 508 791	5.24
Offgas expander	20.3	MW	Carbon Steel	4 556 570	15.82
Electric generator	3.9	MW		13 003	0.05
Electric generator	20.3	MW		67 680	0.25
Steam bottoming cycle				1 472 000	5.50
Steam turbine	12.6	MW		3 019 200	11.28
ST electric generator	12.6	MW		41 942	0.16
Total ME cost				**26 769 946**	100.00

Table 13 *MEOS_CPO major equipment cost.*

Major Equipment	Size	Unit	Material	Bare Cost ($) (ME)	% of Total
1. Membrane reactor	6089	m2		6 747 973	24.20
2. Air compressor	17,8	MW	Carbon Steel	4 178 320	14.98
3. Combustion chamber				1 500 000	5.38
			Tube / Shell side		
4. Air heat exchanger	2000	m2	SS 316 / CS	956 000	3.43
5. Natural Gas heat exchanger 1	250	m2	SS 316 / CS	119 524	0.43
6. Natural Gas heat exchanger 2	425	m2	SS 316 / CS	180 476	0.65
7. Syngas compressor	10.3	MW	Carbon Steel	2 896 152	10.38
8. Natural Gas expander	4.9	MW	Carbon Steel	1 758 114	6.30
9. Offgas expander	22.4	MW	Carbon Steel	4 867 230	17.45
10. Electric generator	4.9	MW		16 337	0.06
11. Electric generator	22.4	MW		74 682	0.27
12. Steam bottoming Cycle				1 492 000	5.35
13. Steam turbine	12.75	MW		3 060 000	10.97
14. ST electric generator	12.75	MW		42 509	0.15
Total ME cost				**27 889 316**	100.00

Table 14 *SEOS major equipment cost.*

Major Equipment	Size	Unit	Material	Bare Cost ($) (ME)	% of Total
1. Membrane reactor	18000	m2		18 050 000	42.95
2. Air compressor	16.4	MW	Carbon Steel	3 955 175	9.41
3. Combustion chamber				1 500 000	3.57
			Tube / Shell side		
4. Air heat exchanger	500	m2	SS 316 / CS	206 667	0.49
5. Natural Gas heat exchanger 1	500	m2	SS 316 / CS	206 667	0.49
6. Natural Gas heat exchanger 2	400	m2	SS 316 / CS	171 905	0.41
7. Syngas compressor	35.3	MW	Carbon Steel	7 010 425	16.68
8. Natural Gas expander	10.3	MW	Carbon Steel	2 892 122	6.88
9. Offgas expander	16.6	MW	Carbon steel	3 981 880	9.48
10. Electric generator	9.9	MW		32 873	0.08
11. Electric generator	10.3	MW		34 340	0.08
12. Electric generator	16.6	MW		55 344	0.13
13. DAC Converter	122.0	MW		406 748	0.97
14. Steam turbine	9.9	MW		2 366 400	5.63
15. Bottoming Cycle				1 154 000	2.75
Total ME cost				**42 024 546**	100.00

Table 15 *Investment costs for different synthesis gas processes.*

	SMR	CPO	MEOS-1121	MEOS-1000	MEOS-CPO	SEOS
Major Eq. Cost (mln USD)	51.16	35.13	27.50	26.77	27.89	42.02
BLCC (mln USD)	145.46	77.43	68.76	66.92	69.72	105.06
OSBLCC (mln USD)	22.53	14.52	13.06	12.92	13.25	19.96
GRCC (mln USD)	167.99	91.95	81.82	79.64	82.97	125.02
Relative GRCC	1.0	0.547	0.487	0.474	0.494	0.744

The total investment costs of the syngas processes are given in Table 15. Both BLCC and OSBLCC in this table include the oxygen plant except for steam reforming, MEOS, and SEOS. The GRCC of steam reforming is set to 1.0 and relative GRCC have been calculated for other processes. It should be mentioned that the SMR plant produces syngas with a higher H_2/CO ratio, so the total amount of syngas produced is at SMR higher than in the other options (see also Table 16).

GRCC of the ‘idealised’ CPO process is 45 % lower than steam reforming and 10% higher than those of MEOS cases. MEOS-1000 has the lowest investment: 52 % and 13 % lower than SMR and CPO respectively. The significant difference is due to the lack of an oxygen plant required for CPO. The investments of SMR are higher than MEOS because of the large furnace and steam cycle. As shown in Table 15, the investments of SEOS due to the expensive membrane are the highest among all membrane options.

3.5.3 Sensitivity Analysis on Capital Costs

The steam reforming process is a commercial process and therefore it is relative easy to find reliable costs for the process equipment. However. this is not the case for CPO, MEOS and SEOS processes. In these processes the reactor costs has been estimated. Therefore, it is worthwhile to perform a sensitivity analysis in which the reactor prices are varied to see the effect on the total investment or GRCC. The results of this sensitivity analysis are presented in Fig. 17.

From this figure it can be seen that if the basic reactor price is tripled the total investments of MEOS processes as well as those of CPO still stay below the steam reforming process. The investments for MEOS and CPO processes differ not significantly much from each other even at high deviations.

At low deviation, the GRCC of SEOS are lower than SMR, but at 80 %-deviation the GRCC of SEOS becomes equal. This figure shows clearly the sensitivity of the reactor price on the investment costs. The most sensitive process is SEOS as the slope of this line is very steep. For MEOS and CPO the sensitivity of the reactor cost is less profound.

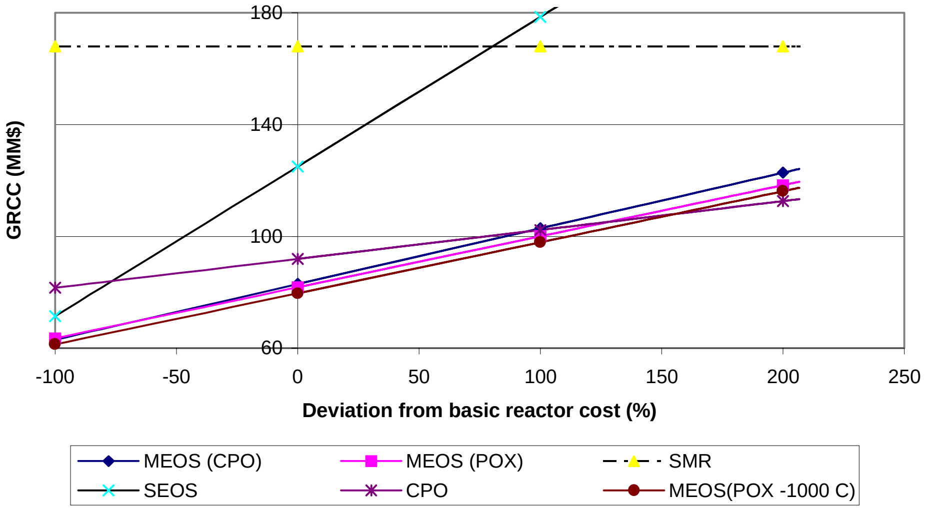

Fig. 17 *Sensitivity of reactor costs on GRCC*

3.5.4 Operational Costs

Table 16 shows the operational costs of the processes considered. As indicated in the table, the amount of natural gas dominates the operational cost. The raw material costs for all processes do not differ significantly from each other, except for CPO. This is because MEOS and SEOS processes use fuel for combustion to raise the temperature of the air, which enter the reactor. SMR, in turn, use fuel not only for the endothermic reaction, but also to produce steam for reforming.

The heat of the syngas produced is utilised to generate steam and electricity. As can be seen from the table: the amount of electricity generated (given in square brackets) in MEOS processes is two to three times as much as CPO and about equal to that of SMR. The reason for this is that MEOS processes consume no steam, so all the steam generated in the heat recovery systems is used for power generation. Another reason is because of the offgas, which is expanded to atmospheric pressure after heating up methane and air. The electricity generated with the steam cycle in SMR is about three times higher than in MEOS processes, but it is about equal to the sum of the electricity generated in bottoming cycle and the offgas expansion. The electricity demand is also in favour of MEOS: it is about 11 % lower than CPO and 6 % lower than SMR. The main reason is the absence of an oxygen plant.

SEOS has relatively high electricity demand, 30 % higher than in MEOS and other processes. This is due to the relatively high power requirements of the syngas compressor (about 3 times more than in MEOS cases). The amount of electricity generated is the obvious advantage of SEOS, which 4 to 10 times higher than in other processes. The total operational costs of MEOS are 15 % lower than those of SMR and 8% lower than of CPO. The operational costs of SEOS are the most expensive.

In Table 16 the production costs per ton syngas are also given. These costs are obtained by dividing the annual costs by the amount of produced syngas. The production costs for MEOS and CPO processes are about equal. The cost per ton syngas of SMR is the highest, about 8% more expensive than the rest. SEOS and MEOS- 1000 have the lowest production costs of all the processes in evaluation.

Table 16 *Operational costs (in million USD unless otherwise stated).*

	SMR	CPO	MEOS-1121	MEOS-1000	MEOS-CPO	SEOS
Natural gas costs	30.67	26.01	31.47	29.33	30.95	30.60
Water costs	1.11	0.33	0.40	0.40	0.40	0.40
Total Raw material costs	31.78	26.34	31.87	29.73	31.35	31.00
Net electricity costs (Power, MW [generated] [demand])	-1.39 [38.3] [31.3]	4.68 [14.3] [33.4]	-1.86 [38.7] [29.3]	-1.58 [36.8] [28.8]	-2.31 [40.1] [28.4]	-21.15 [158.8] [52.0]
Labour costs	1.38	1.68	0.88	0.88	0.88	0.94
Maintenance	8.40	4.60	4.09	3.98	4.15	6.25
Total operational costs/year	40.16	37.29	34.98	33.01	34.07	17.04
20% ROI + 10% Depreciation	50.40	27.60	24.55	23.89	24.89	37.51
Total annual costs	90.56	64.89	59.52	56.90	58.96	54.55
Production costs ($/ton) [Syngas, (ton/day)]	80.14 [3424]	75.37 [2609]	74.69 [2415]	67.51 [2554]	74.38 [2402]	67.49 [2449]

3.5.5 Sensitivity Analysis on Operational Costs

The sensitivity of the reactor cost on the production costs of pure synthesis gas is shown in Fig. 18. The sensitivity of the reactor cost on the production costs for MEOS, SEOS as well as CPO processes is clearly depicted on this chart. The reactor cost is a very important cost parameter. The most sensitive process is SEOS as the line of this process is very steep.

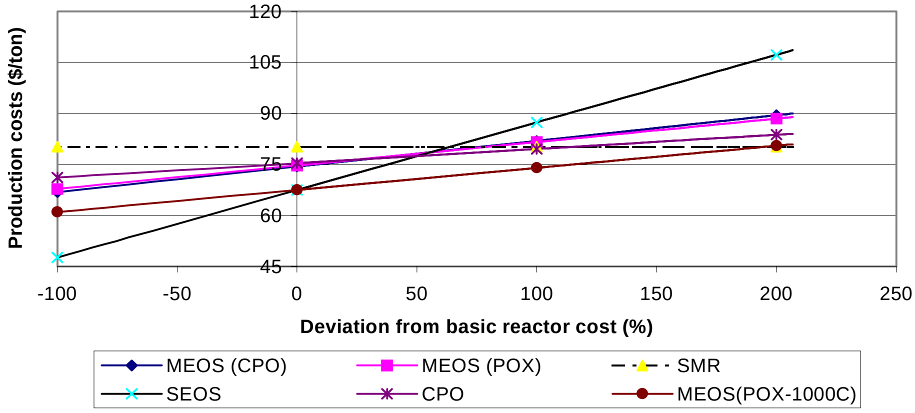

Fig. 18 *Sensitivity of reactor costs on production costs.*

As discussed earlier, the electricity generated with the MEOS processes are relatively high in comparison to other processes in evaluation. From this point of view it is relevant to perform a sensitivity analysis of the electricity price on the total operational cost. The sensitivity analyses are given in Fig. 19 and Fig. 20.

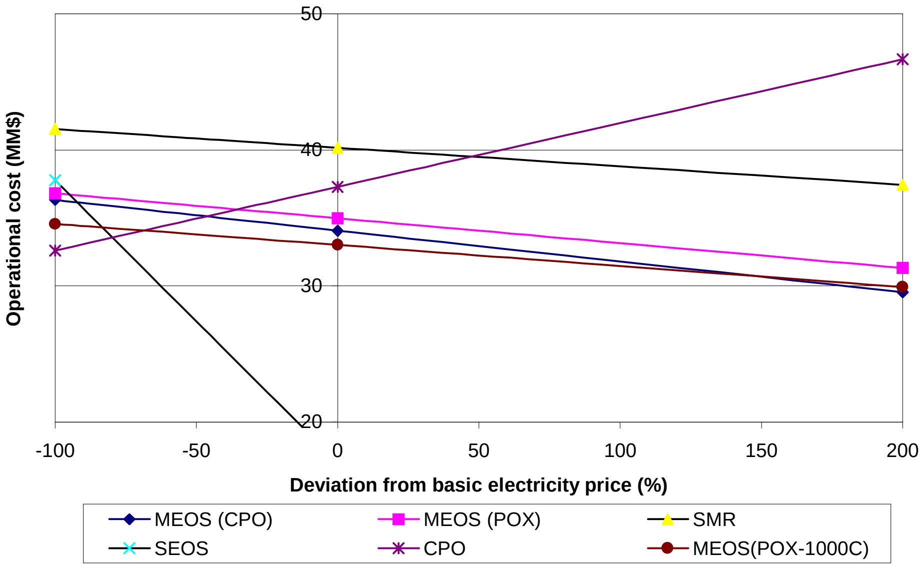

Fig. 19 *Sensitivity of electricity price on operational costs*

As seen from Fig. 19, if the electricity price is increased the operational costs of SEOS and MEOS processes are far more favourable than other processes. The higher the price the more advantageous become these processes. The sensitivity of the electricity price on the operational cost of SEOS is very pronounced. The CPO process is the most vulnerable to an increase in electricity prices as this is the only process which have to buy electricity.

Because SMR, just as MEOS, produces surplus electricity it is also a very beneficial process. The total operational costs of both MEOS processes and MEOS-CPO process hardly differ from each other.

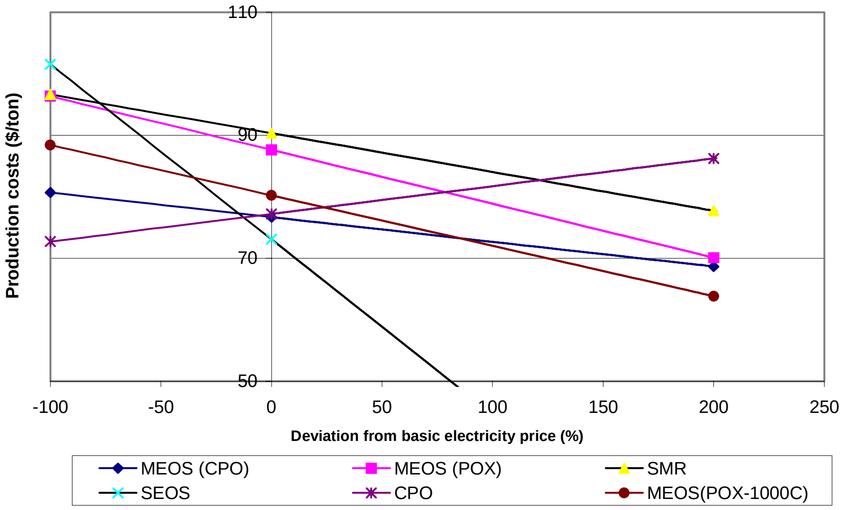

Fig. 20 *Sensitivity of electricity price on production costs.*

The conclusions drawn above concerning MEOS and SEOS for the operational costs are also valid for the production costs. Generally, synthesis gas produced by SMR is the most expensive of all the processes in this study. At 120% deviation, the production costs of CPO become higher than those of SMR.

3.5.6 Conclusions

In preceding chapters the economic results of different syngas processes are discussed. The following conclusions can be drawn:

- It is obvious that SEOS is the most economical process of all the process in evaluation if operational costs are compared. This is mostly due to the very high amount of the electricity generated in the reactor. On the other hand it is also a very sensitive process if the reactor cost get higher which makes SEOS not a favourable process. Because of the fact that at this moment the reactor costs are very uncertain it is not possible to draw an absolute answer.

- The investments for MEOS processes are the lowest. The sensitivity on the reactor and electricity costs is much weaker than that of SEOS. Comparing to CPO the sensitivity on the reactor costs is about the same. This is also the case for the production costs. As mentioned earlier, MEOS processes are more favourable if the electricity price becomes higher, which also applies for SMR. The sensitivity of the electricity price on the production costs for SMR is by far not sensitive as in MEOS processes (Fig. 20).

- The effect of the reactor costs on the investment as well as the production costs is for MEOS and CPO processes about the same. MEOS-1000 is the most profitable of all MEOS processes.

4. CONCLUSIONS AND RECOMMENDATIONS

1. Of the syngas technologies reviewed the steam methane reforming is the most developed process. It is employed at the largest number of plants built and offers the highest H_2/CO ratio. The competitive partial oxidation process proceeds in a smaller reactor in a direct exothermic reaction, but requires oxygen which increases the production costs. The catalytic partial oxidation (CPO) technology has proved to be the most promising process offering compactness, low syngas production costs, and reliable operation.

2. Among the combined technologies, the indirect-fired concepts such as gas heated reforming (GHR), Kellogg's Reforming Exchanger System (KRES) and Combined Autothermal Reforming (CAR) merit consideration. While these options are thermodynamically superior to the others, the limited commercial experience does not allow to judge about their competitiveness.

3. Two emerging technologies are getting much interest in the late 1990s, namely, one based on a plasmatron and another that employs a membrane reactor. Plasma reforming allows a very precise control of the reforming reaction, features a compact size and could be attractive when an electric power source is available. The membrane reactor combines the production of oxygen and syngas in one vessel thus saving on a separate oxygen generation step. The latter is responsible for 35 to 60% of syngas production costs.

4. The system analysis of the membrane systems indicated that syngas can be effectively produced in different configurations (MEOS and SEOS). Using SMR and CPO as reference systems, MEOS models showed comparable or better performance.

5. Assuming a specific cost for a membrane of 1000 USD/m^2. the economic analysis gave estimates for investments and production costs. The MEOS schemes were found to be at the level of the CPO technology both requiring about 50% lower investments than SMR. The investment costs for an oxygen plant in the CPO case (22 mln USD) were found comparable with those of the MEOS reactor and its associated equipment (air compressor, heat exchangers, burner). The latter were estimated as high as 20 mln USD, of which 6.7 mln USD for the membrane reactor (33.5%). The investmens for the SEOS system were about 74% of those for SMR. This is due to the more costly membrane reactor.

6. Using comparable assumptions, the syngas production costs (in USD/ton) were calculated as follows: SMR – 80, CPO – 75, MEOS - between 67 and 74, and SEOS - 67. Therefore, MEOS systems allow a 7–16% reduction in production costs. SEOS system, which in addition to syngas also generates electric power, has lower production costs due to the electric credit. This figure, however, should be taken cautiously since the liberalisation of the power market would probably lead to a drop in electricity prices.

7. Since the membrane reactor is in the beginning of its development the membrane costs are uncertain. The present sensitivity analysis, based on a concept system model, showed that even at a specific cost of 2000 USD per square metre membrane, syngas produced by the membrane systems remains competitive with SMR, but cannot be justified when compared with CPO.

8. A detailed membrane reactor modelling and optimisation study is required to determine the critical design parameters that determine costs and performance in order to obtain a better insight in the technical and economic feasibility of the promising membrane technology.

9. Modular construction of the membrane reactor allows its application at both small and large scale at the same level of the specific investments, what is not the case for other syngas production technologies.

5. REFERENCES

1. Abbott, J., Personal communication, ICI/Synetix, Cleveland, UK, July 6, 1999.
2. Abbott, J., “GTL Syngas Generation Using Synetix Gas Heated Reforming Technology”, Synetix, 1998.
3. Air Liquide, “Gas Solutions, Technologies and Services for the Glass Industry”, company brochure, 1998.
4. Air Products, “PRISM Oxygen VSA Systems”, company brochure, 1998a.
5. Air Products, “Hydrogen Separations”, 12th Annual Conference on Fossil Energy Materials, 1998b.
6. Appl, M., “Modern Ammonia Technology: Where Have We Got To. Where We Are We Going?”, *Nitrogen*, No. 199, p. 46–74, September-October, 1992.
7. Arutyunov, V.S. and Krylov, O.V., *Oxidative Conversion of Methane,* Nauka Publishers, Moscow, 1998.
8. Ashcroft, A.T., Cheetham, A.K., Green, M.L.H., and Vernon, P.D.F., “Partial Oxidation of Methane to Synthesis Gas Using Carbon Dioxide”, *Nature*, Vol. 352, pp. 225–226, 1991.
9. Babik, A. and Kurt. J., “Slovakian Refiner Operating New Hybrid Hydrogen-Production Process”, *Oil & Gas Journal,* March 21, 1994.
10. Bennett, D., “Ionic Transport Membrane Technology for Gas-to-Liquids Processing”, Gas-to-Liquids Processing Conference, San Antonio, Texas, March 18–20, 1998.
11. Blutke, A.S., Bohn, E.M., and Vavruska, J.S., “Plasma Technology for Syngas Production for Offshore GTL Plants”, Managing Associated Offshore Natural Gas meeting, Houston, Texas, April 28–30, 1999.
12. BOC, “Air Separation”, http://www.boc.com/gases/air.html, 12 May 1999.
13. Bolland, O., *Analysis of Combined and Integrated Gas Turbine Cycles*, PhD Thesis, Norwegian Institute of Technology, Trondheim, 1990.
14. Bobinsky, E., “Membrane Magic”, BP Amoco Review, No. 30, October-December 1998.
15. Bredesen, R. and Sogge, J., “A Technical and Economic Assessment of Membrane Reactors for Hydrogen and Syngas Production”, Seminar on the Ecological Applications of Innovative Membrane Technology in the Chemical Industry, Cetraro, Italy, May 1–4, 1996.
16. Bredesen, R., “Keypoints in the Development of Catalytic Membrane Reactors”, 13th International Congress of Chemical and Process Engineering, Prague, Czech Rebublic, August 23–28, 1998.
17. Bromberg, L., Cohn, D.R., and Rabinovich, A., “Plasma Reformer–Fuel Cell System for Decentralized Power Applications”, *International Journal of Hydrogen Energy,* Vol. 22, pp. 83–94, 1997.
18. Bromberg, L., Cohn, D.R., and Rabinovich. A., “Plasma Reforming of Methane”, *Energy & Fuels,* Vol. 12, pp. 11–18, 1998.
19. Brown, A.S., “Air Products. Air Liquide Will Acquire BOC and Split the Business Between Them”, *Hydrocarbon Online,* July, 1999.
20. Caloric Anlagenbau GmbH, “CO = Calcor”, Company Information, 1997.
21. Chauvel, A. and Lefebvre, G., *Petrochemical Processes, Part 1: Synthesis-Gas Derivatives and Major Hydrocarbons,* Editions Technip, Paris, France, 1989.
22. Czernichowski, A., “Electrically Assisted Conversion of Carbon Dioxide into Synthesis Gas”, 4th International Conference on Greenhouse Gas Control Technologies, Interlaken, Switzerland, 30 August - 2 September, 1998.
23. DOE, “DOE Selects Research Partner for Project to Make Liquids from Natural Gas”, DOE Fossil Energy Techline, May 20, 1997.
24. Dybkjær I. and Madsen S.W., “Advanced Reforming Technologies for Hydrogen Production”, *The International Journal of Hydrocarbon Engineering,* December–January, 1997–1998.
25. Eastman, D., “Synthesis Gas by Partial Oxidation”, *Industrial and Engineering Chemistry,* Vol. 48, No. 7, pp. 1118–1122, 1956.

26. Falsetti, J.S., “Gasification Process for Maximalising Refinery Profitability”, *Hydrocarbon Technology International*, pp. 57-61, 1993.
27. Farnell, P.W., “ICI Katalco’s Advanced Gas Heated Reformer”, ICI Katalco brochure, 1996.
28. Genna, A., “Stable Prices Ahead Despite Rising Demand”, *Purchasing Online,* March 6, 1997.
29. Glushenkov, M.Yu. and Parashyuk D.A., “Apparatus for Pulse Compression of Gases”, Russian patent RU2097121, 1997.
30. Hickman, D.A. and Schmidt, L.D., *Journal of Catalysis*, Vol. 136, No 2, pp. 300–308, 1992.
31. Kitchen, D. and Mansfield, K., “ICI’s New Synthesis Gas Technology”, European Applied Research Conference on Natural Gas Eurogas ‘92, Trondheim, Norway, June 1–3, 1992.
32. Klosek, J., Personal communication, Air Products and Chemicals, Inc., August 9, 1999.
33. Linde AG, “Air Separation Plants”, company brochure, 1999.
34. Lurgi, “Hydrocarbons, Gas and Chemicals”, http://www.lurgi.com, 1999.
35. Mark, M.F., Mark. F., and Maier, W.F., “Reaction Kinetics of the CO_2 Reforming of Mehtane”, *Chemical Engineering & Technology,* Vol. 20, pp. 361-370, 1997.
36. Mleczko, L., Malcus, S., and Wurzel, T., “Catalytic Reformer - Combustor: A Novel Reactor Concept for Synthesis Gas Production”, *Ind. Eng. Chem. Res.,* Vol. 36, pp. 4459–4465, 1997.
37. Nataraj, S. and Russek, S.L., “Utilization of Synthesis Gas Produced by Mixed Conducting Membranes”, European Patent Application EP 0 926 097 A1, 1998.
38. Pietrogrande, P. and Bezzeccheri, M., “Fuel Processing”, in: *Fuel Cell Systems* (L. Blomen and M. Mugerwa. eds.), Plenum Press, New York, 1993.
39. Queneau, P.E. and Marcuson, S.W., “Oxygen Pyrometallurgy at Copper Cliff – A Half Century of Progress”, *Journal of Metallurgy,* Vol. 48, pp. 14–21, 1996.
40. Recupero, V., et al., “Fuel Cell Electric Vehicle: Evaluating the Realistic Fuel and Fuel Processor”, The 4th International Conference on New Energy Systems and Conversions, Osaka, Japan, June 27–30, 1999.
41. Reilly, C., “Prices Stay Stable Despite Margin Pressure”, *Purchasing Online,* July 15, 1999.
42. Rogers, G.F.C. and Mayhew, Y.R., *Engineering Thermodynamics. Work and Heat Transfer.* Longman, 1992.
43. Rostrup-Nielsen, J., Dybkjær, I., and Christiansen. L.J., “Steam Reforming: Opportunities and Limits of the Technology”, in: *Chemical Reactor Technology for Environmentally Safe Reactors and Products,* (H.I. de Lasa et al, eds.), Kluwer, 1993.
44. Rostrup-Nielsen, J., Christiansen, L.J., and Aasberg-Petersen, K., “Fuel Processing for High Efficiency Fuel Cell Systems”, Grove III Fuel Cell Symposium, London, September 2830, 1993.
45. Schneider, R.V. and LeBanc, J.R., “Choose Optimal Syngas Route”, *Hydrocarbon Processing,* March, 1992.
46. Scientific American, “Brininging Life to Mars”, Special Issue, March 1999.
47. Smitz, A.D. and Yoshida, T., “Minimizing Carbon Deposition on Ni/SiO_2 Catalysit in CH_4 - CO_2 Reforming”, 4th International Conference on Greenhouse Gases Control Technologies, Interlaken, Switzerland, 30 August - 2 September, 1998.
48. Sogge, J., Strøm, T., and Sundset, T., “Technical and Economic Evaluation of Natural Gas Based Synthesis Gas Production Technologies”, SINTEF Report STF21 A93106, Trondheim, Norway, 1994.
49. Solbakken, A., “Synthesis Gas Production”, in: *Natural Gas Conversion* (A. Homen et al. eds), Elsevier, Amsterdam, 1991.
50. Stobbe, E.R., *Catalytic Routes for the Conversion of Methane to Synthesis Gas,* PhD Thesis, Utrecht University, 1999.
51. Teuner, S., “Make CO from CO_2”, *Hydrogen Processing,* May, 1985.
52. Tindall, B. and Crews, M.A., “Alternative Technologies to Steam-Methane Reforming”. *Hydrocarbon Processing,* November, 1995.
53. Tindall, B.M. and King, D.L., “Desinging Steam Reformers for Hydrogen Production”, *Hydrocarbon Processing*, July 1994.

54. Van Berkel, F.P.F., Schipper, G.S., and Christie. G.M., "Production of Synthesis Gas Using SOFC Technology", 6th Symposium on Solid Oxide Fuel Cells, Honolulu, Hawaii, October 17–22, 1999.
55. Van der Laan, G.P., *Kinetics, Selectivity, and Scale-Up of the Fischer-Tropsch Synthesis,* PhD Thesis, Rijksuniversiteit Groningen, 1999.
56. Van Looij. F., *The Catalytic Partial Oxidation of Methane to Synthesis Gas,* PhD Thesis, Utrecht University, 1994.
57. Wang, S., Lu, G.Q., and Millar, G.J., "Carbon Dioxide Reforming of Methane to Produce Synthesis Gas over Metal-Supported Catalysts", *Energy & Fuels,* No. 10, pp. 869–904, 1996.
58. Woodfin, T.W., "Recent Advances in Syngas Production from Natural Gas", 20th World Gas Conference, Copenhagen, Denmark, June 10–13, 1997.
59. Zittel ,W. and Wurster, R., "Hydrogen in the Energy Sector", http://www.hyweb.de, 1996.

6. APPENDIX 1. OXYGEN GENERATION

6.1 Background

Oxygen is required for most syngas conversion processes. The only exception is SMR. where oxygen is provided by steam. and ammonia synthesis. which consumes nitrogen. There are three basic technologies for oxygen generation: (1) cryogenic; (2) adsorption. including Pressure Swing Adsorption (PSA). Vacuum Pressure Swing Adsorption (VPSA). and Vacuum Swing Adsorption (VSA); and (3) membrane separation.

While many consumers buy oxygen from a large gas manufacturer that operates a cryogenic plant with an output of 100–1000 t/d. on-site oxygen generation technologies as adsorption and membrane separation are becoming more popular due to their advantages such as low capital costs; the absence of the liquid phase (no cylinders. no storage); and production of nitrogen as a by-product. To produce one gas molecule on-site is about 20 to 40% less the costs to produce the liquid molecule (Reilly. 1999). also there are no logistics. distribution and inventory costs.

As the following graph (Fig. 21) indicates. with a demand of lower than 100 t/d and a purity of less than 95%. the adsorption technologies is the most common option. The specific power consumption is. of course. higher at lower production rates. so it is a matter of an optimization study to find out whether the local electricity tariff is low enough to justify the investment in on-site oxygen generation. At present. non-cryogenic generation of oxygen and nitrogen accounts for 25% of the total production figure. and this figure is expected to increase within the next few years to 40% (Genna. 1997).

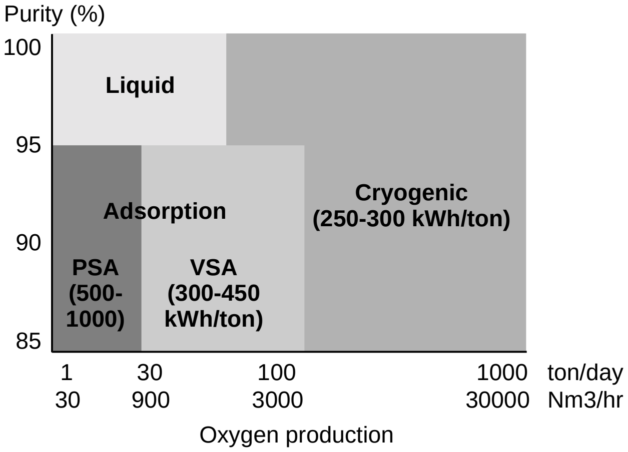

Fig. 21 *Oxygen production technologies and power consumption. Derived from Van Ree (1992). Air Products (1998). and Cirmac (1998).*

6.2 Process description

Large capacity cryogenic plants utilize the Linde process to generate oxygen. The ambient air after compression is cooled down to a temperature of -148°C (Fig. 22). Subsequently. oxygen is separated in a distilling process. Typical power consumption (mostly required for compression of the air) is about 300 kWh per ton of oxygen.

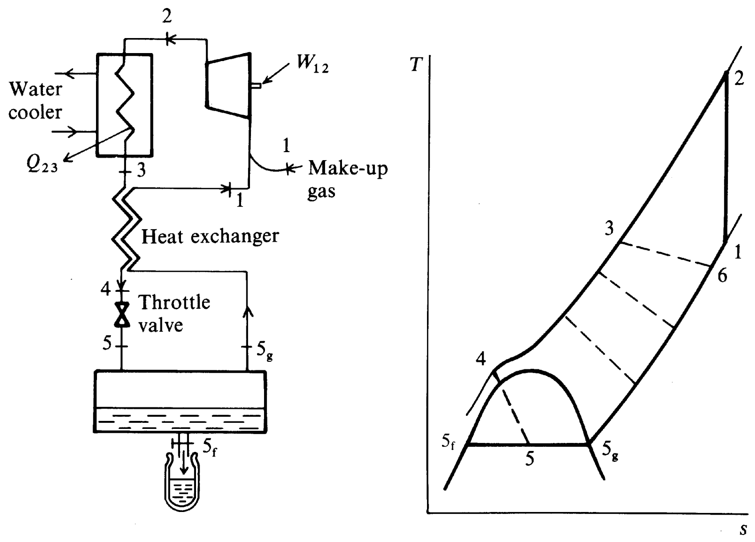

Fig. 22 *Cryogenic liquefaction plant (Rogers & Mayhew. 1992).*

For smaller outputs (less than 150 t/d) adsorption units are more common. In these systems air is passed periodically through a pair of vessels with adsorbent. And while one vessel adsorps nitrogen from air at higher pressure. the other resides in the recovery mode. In this swing process. the pressure difference is maintained either by an air compressor (PSA), or by a vacuum pump (VSA). The latter is outlined below (Fig. 23). Oxygen utilization factor at the 100 Nm^3/hr plant is around 14 Nm^3 air per Nm^3 of oxygen (Cirmac. 1998).

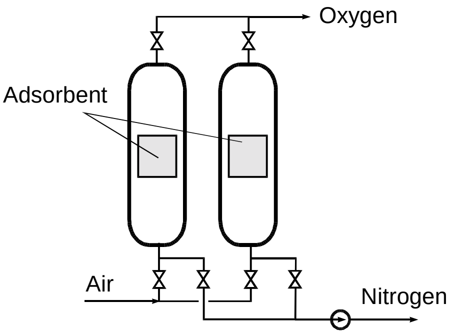

Fig. 23 *Vacuum Swing Adsorption for air separation.*

6.3 Manufacturers

The oldest oxygen manufacturer is Linde AG established in 1879 by Dr Carl von Linde. After the invention of process for the liquefaction of atmospheric air in 1895 over 2700 air separation plants have been built by Linde AG. The cryogenic plants range from 25 tons per day of air input to tens of thousands tons. The company also did pioneering work in developing adsorption technology for air separation. The world's first adsorption plant was put into operation in 1954. PSA inits are sold now with capacities up to 140 t/d of oxygen (Linde. 1999).

Air Products' cryogenic plants supply gaseous oxygen in capacities up to 80000 Nm^3/h. while liquid oxygen is produced in volumes between 1500 and 40000 Nm^3/h. .Smaller VSA systems for on-site production have capacities from 0.5 to 150 t/d (10 to 4000 Nm^3/hr) and purity up to 95%. Comparing to the PSA plants. 30% savings in production costs can be possible.

Together with the conventional cryogenic plants. Air Liquide provides non-cryogenic compact VSA units from 5 to 150 t/d of oxygen at a purity of 90 to 94% at pressures of 1.7 bar for glass furnaces. at 12 bar for paper and pulp industry. and at 30 bar for electric arc furnaces (Air Liquide. 1998).

Another large player in the market of industrial gases is BOC that manufactures cryogenic generators able to produce oxygen at high purities (up to 98%) and at a delivery pressure up to 18 bar without the use of a blower or compressor (BOC. 1999). BOC provides non-cryogenic air separation units in two designs. PSA and VSA. The low capital cost. simple-design PSA generator supplies oxygen at a pressure of 1 to 3.5 barg. As air compressor consumes electric energy. the PSA system is attractive in regions with cheap electricity. If the cost of electricity is rather high. the VSA scheme is more attractive. since instead of operating at elevated pressure. the unit makes use of a vacuum pump. which results in a 40 to 45% lower energy consumption than the PSA unit. The VSA system is proposed for outputs from 20 to 80 t/d. However. an oxygen compressor would be required if the gas should be supplied at an elevated pressure.

Messer Griesheim. partially owned by Hoecht. offers a range of non-cryogenic technologies for on-site oxygen production including PSA systems (0.5 - 150 Nm^3/hr up to 99% purity) and membrane systems (MG Generon. 1999). Since in a single stage the membrane unit can produce oxygen of 35–55% purity. membrane separation is employed for the production of oxygen-enriched air. for example. at steel works. To achieve higher purity (up to 90%) a second stage is required. The membrane systems are sensitive to air humidity and contaminants. also a compressor is needed to create a pressure drop across the membrane.

BOC holds a 15% share of the global industrial gases market. Air Liquide has a 17% share. Praxair 15%. and Air Products and Chemicals around 8%. A recent acquisition of BOC by Air Products and Air Liquide will increase their total share to 40% (Brown. 1999). A merger between other industrial gases manufacturers. Linde and Messer Griesheim. is being discussed.

6.4 Economic aspects

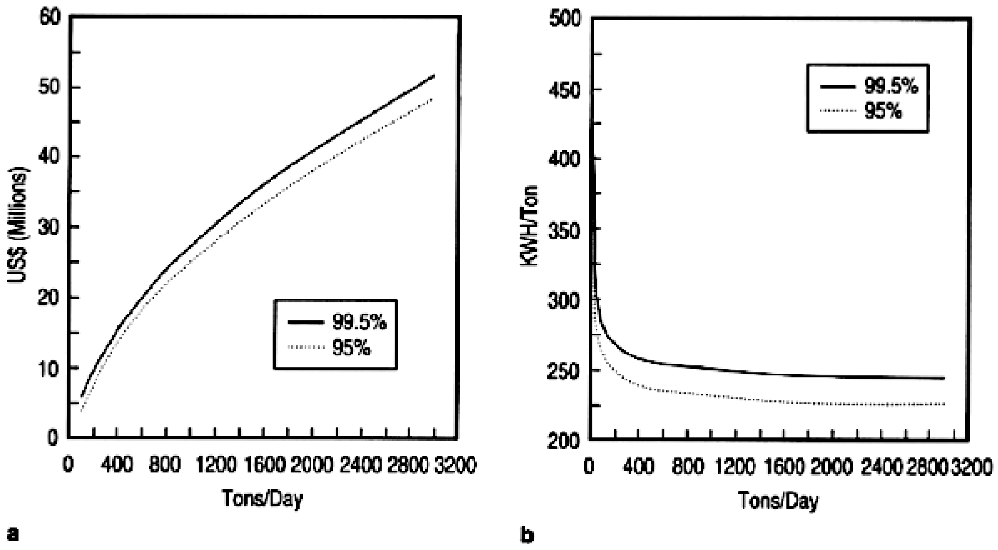

Fig. 24 *Oxygen production requirements at cryogenic plants: (a) plant investment for oxygen at 1.4 barg; (b) power requirements for oxygen at 1.4 barg. (Queneau and Marcuson. 1996).*

An investment of 18 mln USD was cited for a 600 t/d plant producing 95%-purity oxygen at 30 bar. which results in specific costs of 30 000 USD/t/d (Klosek. 1999). This figure agrees with the chart where plant cost are plotted against the output (Fig. 24a).

Queneau and Marcuson (1996) indicated that electric power is the main component of the oxygen production costs. which amounts up to 80%. Taking this into account. an investment for an oxygen plant can also be calculated on the basis of the power consumption rate (Fig. 24b).

7. APPENDIX 2. ABBREVIATIONS

ATR = Autothermal Reforming
BLCC = Battery Limit Capital Costs
CAR = Combined Autothermal Reforming
CPO = Catalytic Partial Oxidation
GHR = Gas Heated Reforming
GRCC = Grass Roots Capital Costs
GTL = Gas-to-liquids
KRES = Kellogg’s Reforming Exchanger System
OSBLCC = Outside Battery Limit Capital Costs
PFD = Process Flow Diagram
POX = Partial Oxidation
PSA = Pressure Swing Adsorption
SMR = Steam Methane Reforming
VPSA = Vacuum Pressure Swing Adsorption
VSA = Vacuum Swing Adsorption

8. APPENDIX 3. ASPEN Plus PROCESS FLOW DIAGRAMS