

# **Review of Synthesis Gas Processes**

**This review is extracted from the following report:**

**SOFC AS A GAS SEPARATOR**

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# Synthesis gas production

## 1. Introduction

Synthesis gas (syngas) is a general term used in describing a mixture hydrogen and carbon monoxide (CO) in different ratios and can be generated from any hydrocarbon feedstock. Synthesis gas can be produced from a large variety of materials which includes natural gas, petroleum cuts, biomass and coal. There are a number of technologies available to produce syngas, these technologies are summarized 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 sulfur 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 feedstock, 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<sub>2</sub>/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.

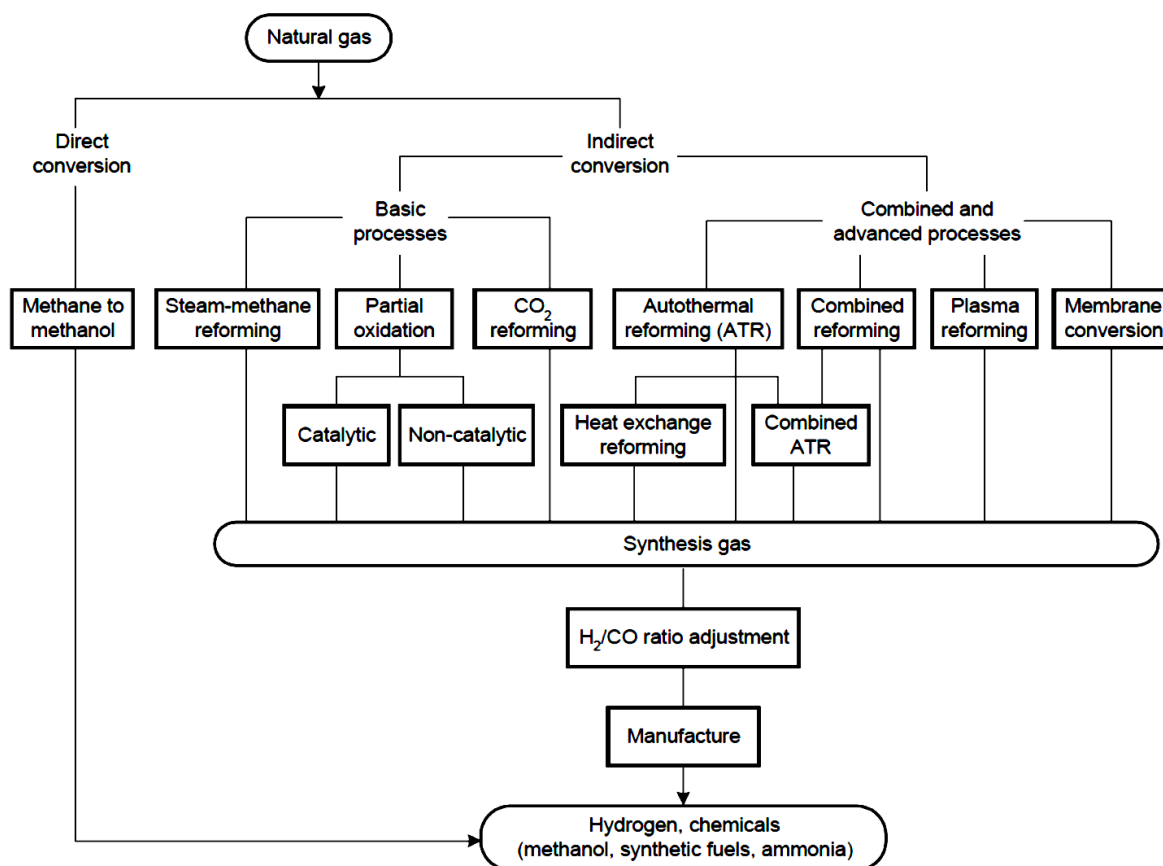
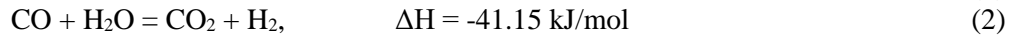
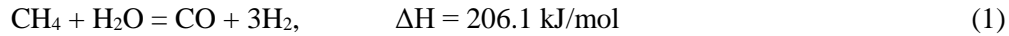


Fig. 1 General overview of the routes from natural gas to chemicals.

## 2. Steam methane reforming (SMR)

### Background

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



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) favors 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 begun 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 conditions 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.

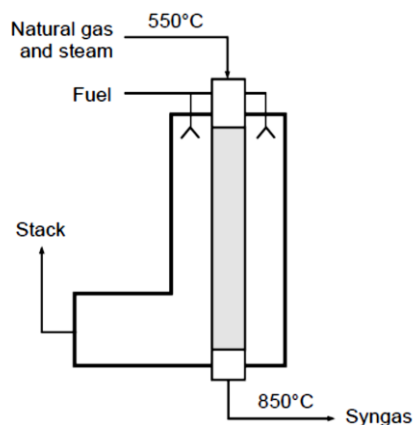
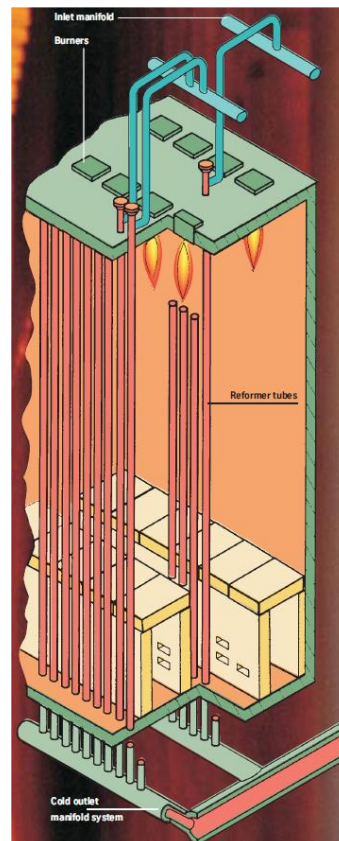


Fig. 2 Steam methane reforming.



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 utilized 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-sulfurization 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.

Typical operating parameters of the SMR process are:

Pressure: 20-30 bar

Temperature: 800–900°C

H<sub>2</sub>/CO ratio: 3–6

Plant capacity 0.4 to 21 MMNm<sup>3</sup>/day

Complete conversion cannot be obtained in the SMR process: typically 65% of methane is converted, so secondary reforming must be used if a higher conversion rate is desired (see Section on combined reforming).

In view of the high H<sub>2</sub>/CO ratio, steam reforming is the most effective means for hydrogen production. The carbon monoxide then is oxidized to CO<sub>2</sub> in the shift reaction (2), thus producing even more hydrogen, which is subsequently purified in a pressure-swing adsorption (PSA) unit. Summarizing the advantages of the SMR process, it should be 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<sub>2</sub>/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 MMNm<sup>3</sup>/day syngas capacity would cost 80 MM USD (data for France, situation in 1986). For each 1000 m<sup>3</sup> of syngas (H<sub>2</sub>/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<sup>3</sup> of cooling water will be consumed as utilities. A study by SINTEF (Sogge et al, 1994) gave a figure of 145 MM USD (battery limits) for an 8 MMNm<sup>3</sup>/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<sup>3</sup>/day (40–80 USD per kg/day).

Unlike other syngas processes, the SMR process does not need oxygen, it is therefore 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.

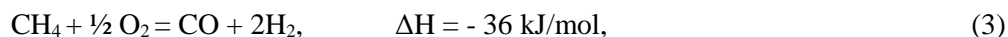
### *Development status*

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. Partial oxidation (POX)**

### *Background*

In the partial oxidation reaction, which proceeds exothermically according to



Complete conversion of methane is obtained above 750°C, resulting in a H<sub>2</sub>/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.

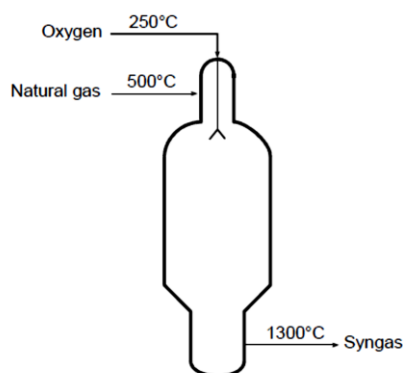


Fig. 3 *Partial oxidation reactor.*

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<sub>2</sub>/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 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 minimize 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 MM USD for a POX-based syngas plant with an output of 5.5 MMNm<sup>3</sup>/day, resulting in specific costs of 21 USD per Nm<sup>3</sup>/day.

Institut Français du Pétrole (IFP) gives a figure of 80 MM USD for a smaller plant of 2 MMNm<sup>3</sup>/day, i.e. 40 USD per Nm<sup>3</sup>/day.

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

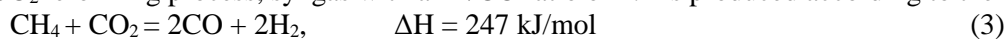
#### *Development status*

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).

## 4. CO<sub>2</sub> reforming

### *Background*

In the CO<sub>2</sub> reforming process, syngas with a H<sub>2</sub>/CO ratio of 1:1 is produced according to the reaction:



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 disproportionation. Nickel and Ni/SiO<sub>2</sub> catalysts are often used for CO<sub>2</sub> 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 sulfur 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<sub>2</sub>, CO, CO<sub>2</sub>, and some unconverted CH<sub>4</sub>. 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<sub>2</sub> 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.

To produce 1 ton of CO the following utilities are required: 500 Nm<sup>3</sup> of imported CO<sub>2</sub>, 550 Nm<sup>3</sup> of methane, 200 m<sup>3</sup> of cooling water, and 300 kWh of electricity, as given by Teuner in 1985.

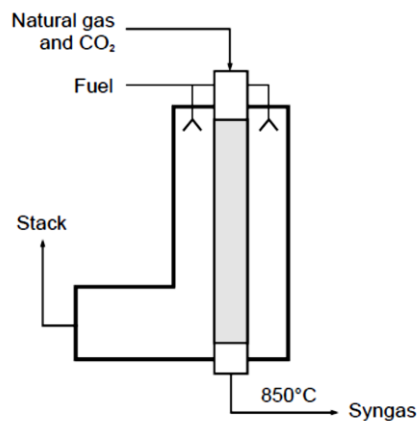


Fig. 4 CO<sub>2</sub> reforming.

#### *Economic aspects*

Little was found in literature concerning the investment costs for CO<sub>2</sub> 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<sub>2</sub> 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 10000 Nm<sup>3</sup>/h; and “economy scheme” for 40 to 400 Nm<sup>3</sup>/h (Caloric, 1997). In the economy scheme, there is no CO<sub>2</sub> recovery and membranes, instead of absorbers, are used to separate hydrogen and carbon monoxide.

Carbon dioxide reforming is gaining more interest lately due to the concerns about CO<sub>2</sub> emissions as it is a technology that effectively utilizes this greenhouse gas to produce a valuable product such as syngas.

## **5. Autothermal Reforming (ATR)**

#### *Background*

This process combines partial oxidation and steam methane 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 and 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.

The main advantages of ATR are a favorable H<sub>2</sub>/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.

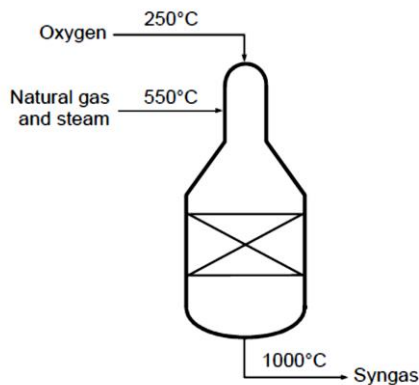
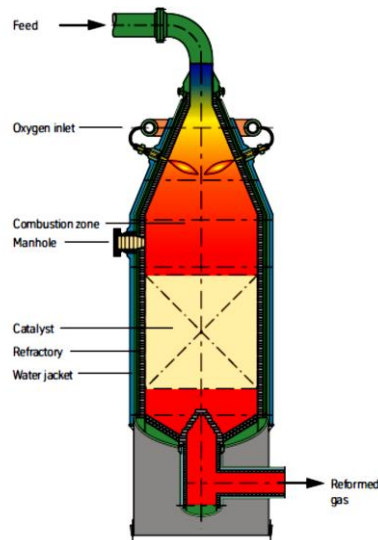


Fig. 5 Autothermal reforming.



#### *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 process 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.

## 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.

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 outweigh this advantage.



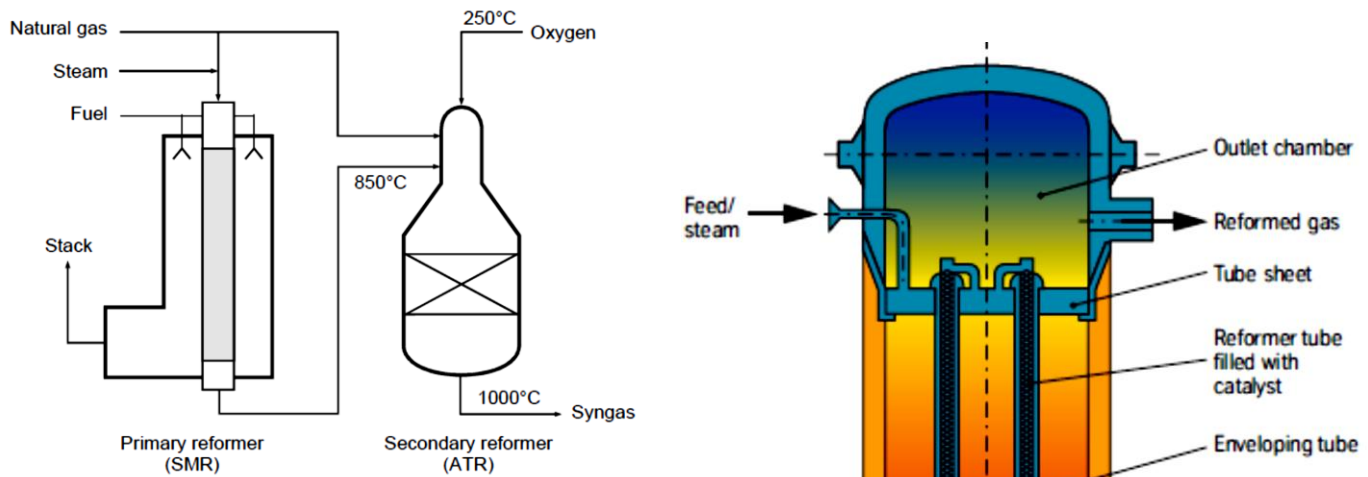


Fig. 6 Combined reforming.

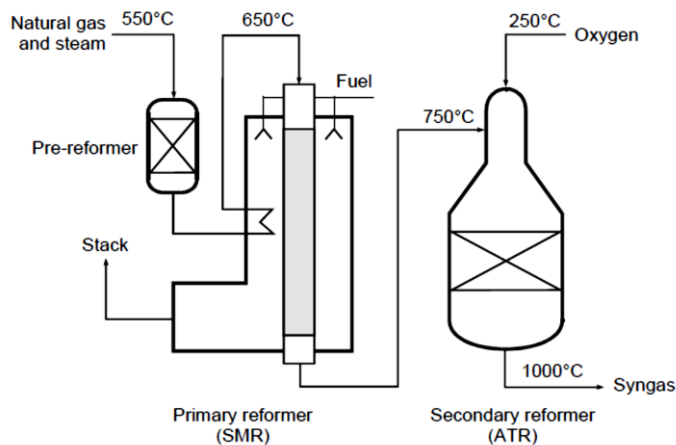
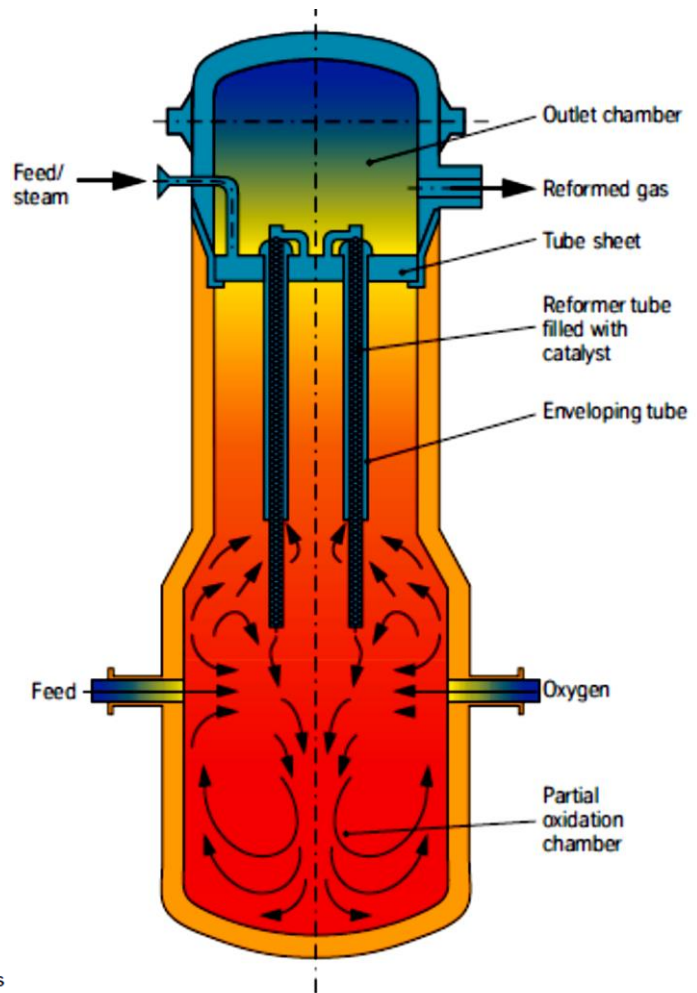


Fig. 7 Combined reforming with pre-reforming.



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 Le Blanc (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).

## 7. Summary

In Table 1, an overview of syngas technologies is given. Considering the criteria listed in the table, it can be concluded that the most attractive technologies for syngas production are CPO and combined reforming. Their advantages can be listed as follows. These technologies produce a syngas of the required H<sub>2</sub>/CO ratio that can be directly used for methanol or Fischer-Tropsch synthesis; these require the smallest investments and have commercial status of development.

Table 1 *Overview of the reforming processes.*

	SMR	POX	CPO	CO <sub>2</sub>	ATR	Combined
Temperature, °C	800 – 900	1000 - 1450	800 - 1000	900 - 1000	850 - 1300	P: 800 S: 1000-1200
Pressure, bar	20 - 30	30 - 85	15 - 40	1-20	20 - 70	20 - 30
H <sub>2</sub> /CO ratio	3 - 6	1.6 - 2	1.6 - 2	1	1.6 – 2.5	2.5 - 4
CH <sub>4</sub> conversion, %	65 - 95	95 - 100	95 - 100	high	95 - 100	95 - 100
Oxygen	none	high	high	none	high	low
Steam consumption	high	optional	optional	optional	low	medium
Capital costs, %	100 (refer.)	80 - 110	55 - 80	?	65 - 80	75 - 115
Emissions	high	low	low	low	low	medium
Scale	large	Small to large	Small to large	medium	large	large

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