

# TOPSØE *Technologies*



## **Large-scale Hydrogen Production**

*by*

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## **Abstract**

There is a growing need for hydrogen and a future hydrogen economy is high on the political agenda. But where should the hydrogen come from? The “sustainable” routes are still too expensive. Steam reforming of hydrocarbons is the most feasible route today. If CO<sub>2</sub>-sequestration is accepted, fossil fuels may play an important role in a starting future “hydrogen economy”. This will happen by use of the reforming technologies.

## How Much?

### *Present use of hydrogen*

Hydrogen is an important raw material for the chemical and the refinery industry, and it may play a future role in the energy sector. The total hydrogen market was in 1998  $390 \cdot 10^9 \text{ Nm}^3/\text{y} + 110 \cdot 10^9 \text{ Nm}^3/\text{y}$  co-production. The present use of manufactured hydrogen is primarily for the production of ammonia and methanol (ca. 51% in mixtures with nitrogen or carbon oxides) followed by hydrotreating in refineries (44% incl. co-production, pure hydrogen). Pure hydrogen is also used for a number of hydrogenation reactions (4% of total consumption) such as hydrogenation of unsaturated hydrocarbons (including hardening of edible oil) and of aromatics, hydrogenation of aldehydes and ketones (for instance oxo-products), hydrogenation of nitrogen compounds (for instance for manufacture of aniline). Other present uses (1%) of hydrogen are related to the food industry, the semi-conductor industry, and the metallurgical industry (for instance direct reduction of iron ore).

Mixtures of hydrogen and nitrogen are used for the ammonia synthesis and mixtures of hydrogen and carbon oxides (synthesis gas) for synthesis of methanol, liquid hydrocarbons (for instance by Fischer-Tropsch synthesis), synthesis of higher alcohols (hydro-formulation) etc. This article deals only with technology for manufacture of pure hydrogen.

### *The refinery hydrogen balance problem*

The environmental objectives for providing better transportation fuels may lead to significant changes in the refinery industry [1]. Specifications for reformulated gasoline have meant less aromatics and olefins and constraints on light hydrocarbons and sulphur. New legislation for diesel requires deep desulphurization to 10-50 ppm S. This is done by reacting the sulphur compounds with hydrogen into hydrogen sulphide, which is removed from the hydrocarbon stream. The requirement of removing sulphur may be accompanied by a wish to remove aromatics.

In general, these trends result in an increasing atomic ratio H/C of the fuels approaching two [2], while available oil resources become heavier with higher contents of sulphur and metals. This has created a large requirement for more hydrotreating (HDS, HDN, HDM) and hydrocracking.

Traditionally, a major part of the hydrogen consumption in refineries was covered by hydrogen produced as a by-product from other refinery processes ( $110 \times 10^9 \text{ Nm}^3/\text{y}$ ), mainly catalytic reforming ("plat-forming"). A main reaction in catalytic reforming (not to be confused with catalytic steam reforming) is the conversion of paraffins into aromatics and hydrogen. As aromatics are not wanted in reformulated fuels, this means that less hydrogen will become available from catalytic reforming. Similarly, the gasoline and diesel fractions from catalytic crackers are highly unsaturated. The refinery hydrogen balance is illustrated in Fig. 1.

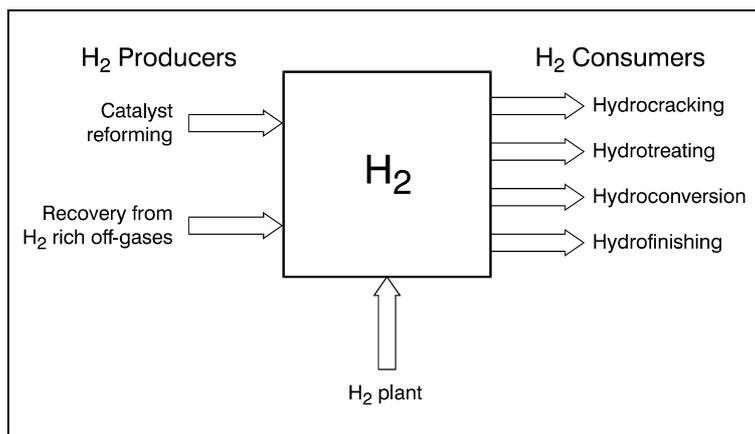


Fig. 1. Schematic of refinery hydrogen balance.

In conclusion, there is a fast growing need for increased hydrogen production capacity in refineries. This need is being met mainly by installation of steam reforming based hydrogen plants.

### ***Hydrogen as an “energy vector”***

Due to its environmentally benign properties, hydrogen has been discussed as a future “energy vector”. Key applications for hydrogen is as a carbon free fuel and as a fuel for hydrogen driven fuel cells for automotive applications.

Many technologies for production of hydrogen that do not co-produce CO<sub>2</sub> are being considered. Hydrogen production using non-fossil energy for electrolysis of water is one example. These schemes have not been introduced primarily due to reluctance concerning nuclear power and low efficiency of the electrolysis process. Hydrogen from bio-fuels, wind energy or solar energy is still expensive leaving fossil fuels as the most feasible feedstock for hydrogen generation in the near term.

Significant efforts are made to develop technologies for hydrogen production based on fossil fuels combined with CO<sub>2</sub> sequestration. A group of oil companies has joined forces in a CO<sub>2</sub> Capture Project (CCP) [3]. The aim of the CCP is to develop effective methods to capture significant amounts of CO<sub>2</sub> emitted from power generation and industrial sources and store the CO<sub>2</sub> in geologic formations below the earth's surface.

Hydrogen is being used in fuel cells typically in units of capacity 50 kW to 1 MW. The application of fuel cells has not grown as fast as predicted because of the high investment costs and competition from advanced gas turbines. Lately, hydrogen driven fuel cells (30-50 kW) have attracted great interest for mobile applications. The issue is then where to produce the hydrogen: in large centralized plants, at the gas stations or in the car. Difficulties in storing sufficient hydrogen mean that commercial vehicles will probably involve hydrogen generation on board the vehicle from hydrocarbons or methanol [4].

## How?

There are several production routes for hydrogen. The choice depends on size of production and cost of available feedstocks. The most important method is catalytic conversion (steam reforming) of hydrocarbons followed by gasification of coal, tar sands etc. For small scale production, investments are dominating and simple equipment may be preferred over high energy efficiency. Electrolysis of water accounts for less than 5%. For large scale production, steam reforming of natural gas (or refinery off-gases) becomes the preferred solution. Gasification of heavy oil fractions may play an increasing role as these fractions are becoming more available because of falling demands. Some refineries have installed gasification units for power production and co-generation of hydrogen [5].

<b>- Natural Gas</b> Refinery off-gases LPG Naphtha Kerosene, gas oil	Steam reforming
<b>- Methanol, DME, NH<sub>3</sub></b>	Cracking
<b>- Coal</b> Biomass	Gasification
<b>- Water</b>	Electrolysis

Table 1: Hydrogen Production Routes

In areas with high cost of hydrocarbon feedstocks, methanol may be considered as an alternative. One possible scheme involves production of methanol in an area with very inexpensive natural gas, with subsequent transportation of the methanol to the hydrogen plant location. A methanol based hydrogen plant is a simple unit [4] and less costly than a natural gas and naphtha based plant with a steam reformer. Fig. 2 indicates the conditions where a methanol based hydrogen plant is more economical than a naphtha based plant.

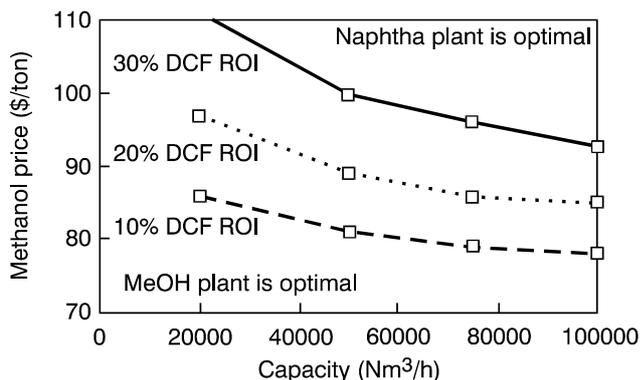


Fig. 2. Hydrogen Production from Naphtha or Methanol. Naphtha price: 140 USD/t. Steam credit: 8.3 USD/t. When competing against natural gas at 13 USD/Gcal, the methanol prices have to be about 10 USD/t less than indicated (ROI, Return on Investment). DCF ROI means rate of return based on discounted cash flow.

This paper will deal with large scale hydrogen production in stationary plants using steam reforming.

### Steam Reforming for Hydrogen Production

#### Reforming reactions

The principal process for converting hydrocarbons into hydrogen is steam reforming [6,7] which involves the following reactions:



Reaction (1) is the steam reforming of methane. It is reversible and strongly endothermic, and according to the principle of le Chatelier it must be carried out at high temperature, high steam to methane ratio, and low pressure to achieve maximum conversion. The design of the steam reforming process is in part dictated by these constraints. The equilibrium composition out of the steam reformer is shown in Fig. 3 as a function of steam reformer outlet temperature under typical industrial conditions (26 bar a with a feed steam to methane ratio of 2.5).

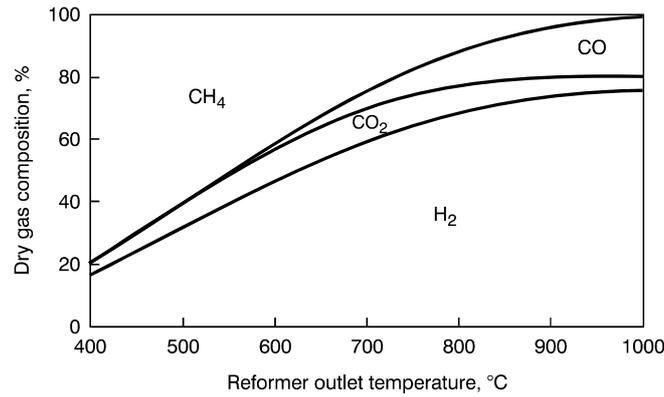


Fig. 3. Equilibrium composition out of a steam reformer at 26 bar with a feed steam to methane ratio of 2.5.

### Reformer types

Fig. 3 shows that in order to obtain a good utilisation of the feed for hydrogen production it is necessary to operate the steam reformer with an outlet temperature around 800 to 950°C. Heat has to be supplied to the process to achieve this outlet temperature. Several reforming technologies are available for getting the heat into the process. These technologies can be differentiated by the means of heat transfer, which ranked in increasing intensity are based on: convective heat transfer, radiant heat transfer and internal combustion. Most industrial hydrogen plants are based on radiant heat transfer in tubular steam reformers as described in the following.

### Tubular steam reforming

In industry, the reforming reactions are typically carried out in a heated furnace over a nickel catalyst. An example [8,9,10] of this *tubular reformer* is shown in Fig. 4. Such reformers are built today for capacities up to 300.000 Nm<sup>3</sup> H<sub>2</sub> (equivalent) /h. The furnace consists of a box-type radiant section including the burners and a convection section to recover the waste heat of the flue gases leaving the radiant section as illustrated in Fig. 4.

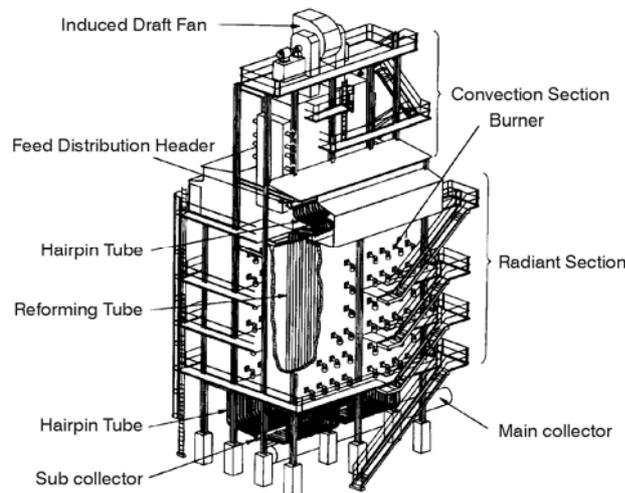


Fig. 4. Topsoe reformer with burners placed on side walls

In this lay-out, the convection section for recovery of waste heat is placed on top of the furnace. The convection section can also be placed at the side of the furnace. In the radiant section, a nickel catalyst is loaded in a number of high alloy reforming tubes placed in a row along the furnace. The outer diameter of the tubes ranges typically from 100 to 150 mm and the length is from 10 to 13 m. Typical inlet temperatures to the catalyst bed are 450-650°C, and product gas leaves the reformer at 800-950°C depending on the application. Tubular reformers are designed with a variety of tube and burner arrangements [10]. These include side-fired furnaces, top-fired furnaces and terrace wall furnaces.

Recent years have shown progress in steam reforming technology resulting in less costly plants not the least because of better materials for reformer tubes, better control of carbon limits, better catalysts, and process concepts with high feedstock flexibility [7]. This has been supplemented by better understanding of the reaction mechanism [11], the mechanisms for carbon formation and sulphur poisoning, and the reasons for tube failure [12].

### ***Adiabatic prereforming***

The heat required in the tubular reformer may be reduced by increased preheat temperature leading to reduced cost of the tubular reformer. However, the preheater may then work as a “steam cracker” producing olefins from higher hydrocarbons in the feed. The olefins easily form carbon in the reformer. Apart from the pressure, the conditions in the tubular steam reformer and in the preheater are not far from that of a steam cracker in an ethylene plant. This problem has been solved by introduction of an *adiabatic prereformer* as illustrated in Fig. 5 [13,14]. All higher hydrocarbons are converted in the prereformer in the temperature range of 350-550°C, and the reforming and shift reactions are brought into equilibrium. After a prereformer, it is possible to preheat to temperatures around 650°C, thus reducing the size of the tubular reformer. The prereformer may also operate on naphtha thus offering greater feedstock flexibility ranging from natural gas and refinery off-gas to heavy naphtha [13].

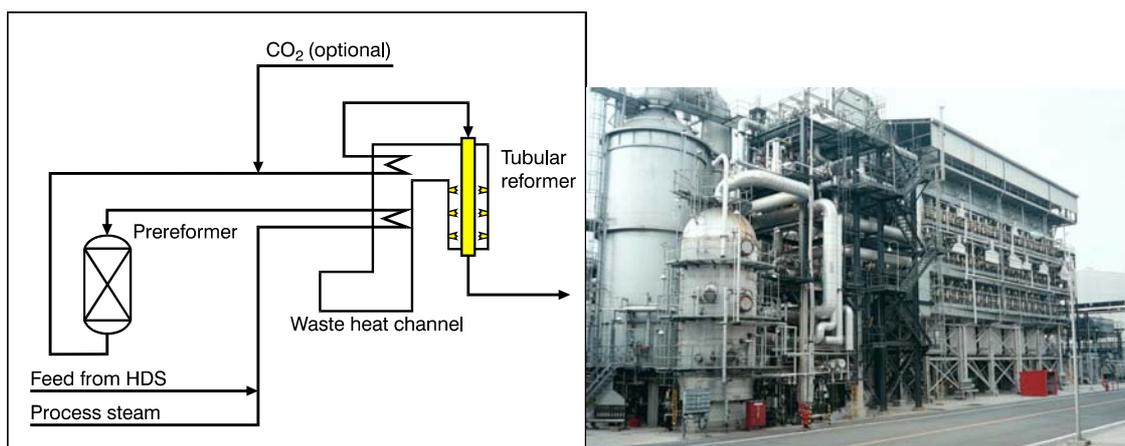


Fig. 5. A) Installation of a prereformer [12]. B) Prereformer shown in front of a tubular reformer in a 70.000 Nm<sup>3</sup>/h hydrogen plant at SK Corporation, Korea.

**Design of tubular steam reformers**

Tube materials available today allow design of tubular reformers for tube wall temperatures up to 1050°C, in particular when applying a side wall fired reformer furnace to ensure better control of the maximum tube wall temperature and optimum use of the high alloy material. The design of *reformer tubes* is normally done according to API-530 for an average lifetime before creep rupture of 100.000 h. Main parameters in the design are the design pressure, the design temperature and the creep rupture strength of the material used. However, the determination of these parameters is not unambiguous, and each reforming technology licensior applies his own procedures to determine the parameters and to introduce necessary design margins.

The calculation of the design temperature is demanding since it requires detailed understanding of the *heat transfer*. This includes several steps, i.e. the heat transfer [10] by radiation from the furnace internals, including furnace walls and neighbouring tubes, and from the gas by convection from gas to tube wall, by conduction through the tube wall, and by convection from the inner tube wall to the catalyst and the reacting gas. Secondly understanding of reaction kinetics, catalyst ageing, heat and mass transfer (radial and axial) in the catalyst bed etc. is required [6,10]. The interplay between catalyst, reacting gas, and reformer tube is also essential for the prediction of the limits for carbon formation. This understanding was obtained through extensive R&D using bench scale equipment, full size monotube pilot units, and analysis of data from industrial units [7,15]. As one result, a two dimensional homogeneous reactor model was established for the design of advanced reformers [1,10].

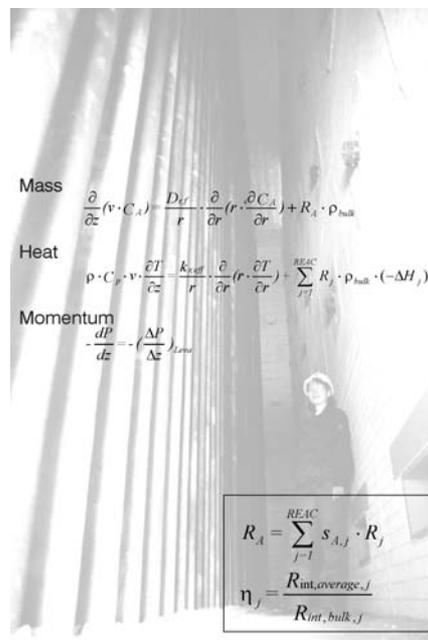


Fig. 6. Reactor Modelling – Tube side

### ***Developments in the design of tubular steam reformers***

Tube failures are very rare events in well designed and well operated reformers. They appear to be caused not so much by constant operation at design conditions as by transients [12] including start-up and shut-down or by operating errors leading to catalyst poisoning, carbon lay-down, or over-firing.

It has been normal practice to use the *average heat flux* as a measure for operating severity in reformers, but it appears that the most critical parameter is the maximum temperature difference over the tube wall. This parameter can be controlled in the side wall fired design in such a way that very high average heat flux can be obtained without exceeding critical values. Side fired tubular reformers are today designed for operation at average heat flux almost two times higher than what was industrial standard 20 years ago. High average heat flux leads to fewer tubes, smaller reformer furnaces, and thus significantly reduced cost.

### **Steam Reforming Catalysts**

The steam reforming catalyst is normally based on nickel. Cobalt and the noble metals are also active, but more expensive. Attempts to use non-metallic catalysts have not had commercial success because of low activity [6,17]. The catalyst properties are dictated by the severe operating conditions, i.e. temperatures of 450-950°C and steam partial pressures of up to 30 bar.



Fig. 7. The Reforming Catalyst

The *activity* depends on the nickel surface area. It can be shown by computer simulations that the catalyst is not the limiting factor for the operation of a tubular reformer. An increase of the heat flux and the load at given exit temperature by a factor of two results in an increase in methane leakage by only 10% [7]. For normal steam reforming catalysts, the utilisation of the activity (as expressed through the effectiveness factor) is smaller than 10% because of transport restrictions [6]. The low effectiveness factor means that for a given catalyst type, the activity is roughly proportional to the external surface area.

The *shape* of the catalyst pellet should be optimised to achieve maximum activity with minimum increase in pressure drop. The pressure drop depends strongly on the void fraction of the packed bed and decreases with increasing particle size. Hence, the optimum is a catalyst filling of pellets with large external diameter and with high void fraction as achieved with rings or cylinders with several holes (Fig. 7). Other solutions may be based on the use of catalysts based on ceramic foam, monoliths and even catalysed hardware [18].

### ***Catalysts for feedstock flexibility***

Many refineries benefit from flexibility in feedstock, taking advantage of the surplus of various hydrocarbon streams in the refinery. Steam reforming of liquid hydrocarbons is also used for hydrogen generation for fuel cells, with diesel and jet fuel considered as “logistic fuels”. With proper desulphurization, it has been possible to convert light gas oils and diesel into syngas with no trace of higher hydrocarbons in the product gas [19]. The higher hydrocarbons are also more reactive than methane with aromatics showing the lowest reactivity approaching that of methane.

The *formation of carbon* may lead to break-down of the catalyst and the build-up of carbon deposits and disintegrated catalyst pellets may cause partial or total blockage of the reforming tubes resulting in development of hot spots or hot tubes. The uneven flow distribution will cause a self-accelerating situation with further overheating of the hot tubes. Therefore, carbon formation cannot be tolerated in tubular reformers. The important problem is whether or not carbon is formed and not the rate at which it is formed [6].

Higher hydrocarbons show a higher tendency for carbon formation on nickel than does methane and, therefore, special catalysts either containing alkali or rare earths or based on an active magnesia support are required [6,18]. With low catalyst activity, the *thermal cracking* route (pyrolysis) may also take over in the reformer tube [13]. This is the situation in case of severe sulphur poisoning or in attempts to use non-metal catalysts with low activity. The risk for carbon formation depends on type of hydrocarbon with the contents of aromatics being critical. Ethylene formed by pyrolysis results in rapid carbon formation on nickel.

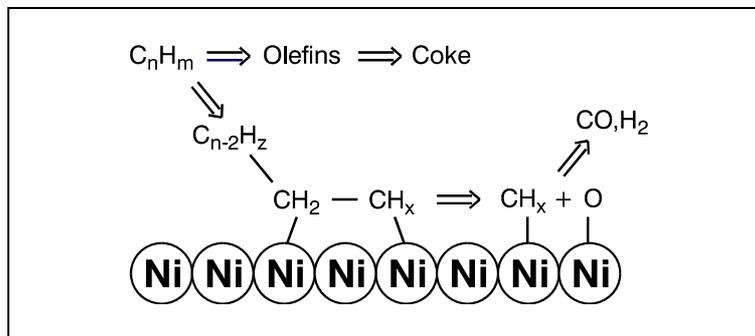


Fig. 8. Steam Reforming of Higher Hydrocarbons Mechanism

Naphtha can be processed directly in the tubular reformer when using special catalysts [6] as practiced in many industrial units, but the control of the preheat temperature and heat flux profile may be critical. These constraints are removed when using a *prereformer* as illustrated in Fig. 5. The prereforming catalyst is typically a highly active nickel catalyst. This catalyst also works as an effective sulphur guard for the tubular reformer and downstream catalysts, by removing any traces of sulphur still left after the desulphurization section.

### **Process Lay-outs**

Modern hydrogen plants will almost invariably be designed using a *low steam to carbon ratio*. A high steam to carbon ration (4-5 mol  $H_2O/C$ -atom) would result in higher conversion of the hydrocarbons, but a low steam to carbon ratio (typically 2.5 or lower) reduces the mass flow through the plant and thus the size of equipment. The lowest investment is therefore generally

obtained for plants designed for low steam to carbon ratio. Also, a low steam to carbon ratio results in a more energy efficient plant and thus in lower operating costs. In principle, a low steam to carbon ratio increases the methane leakage from the reformer, but this can be compensated for by increasing the reformer outlet temperature to typically 920°C.

Operation at a low steam to carbon ratio requires the use of non-iron containing carbon monoxide conversion catalyst, i.e. a copper-based *medium temperature shift* (MTS) catalyst. The conventional iron catalyst for high temperature shift (HTS) will be active for the Fischer-Tropsch synthesis below a certain steam carbon ratio, when there is potential for formation of iron carbide [20].

Pressure Swing Adsorption (PSA) for final hydrogen purification is normally used today. This layout gives a high purity hydrogen product (99.9% or higher) and a more efficient operation than traditional lay-outs with CO<sub>2</sub>-absorption [9].

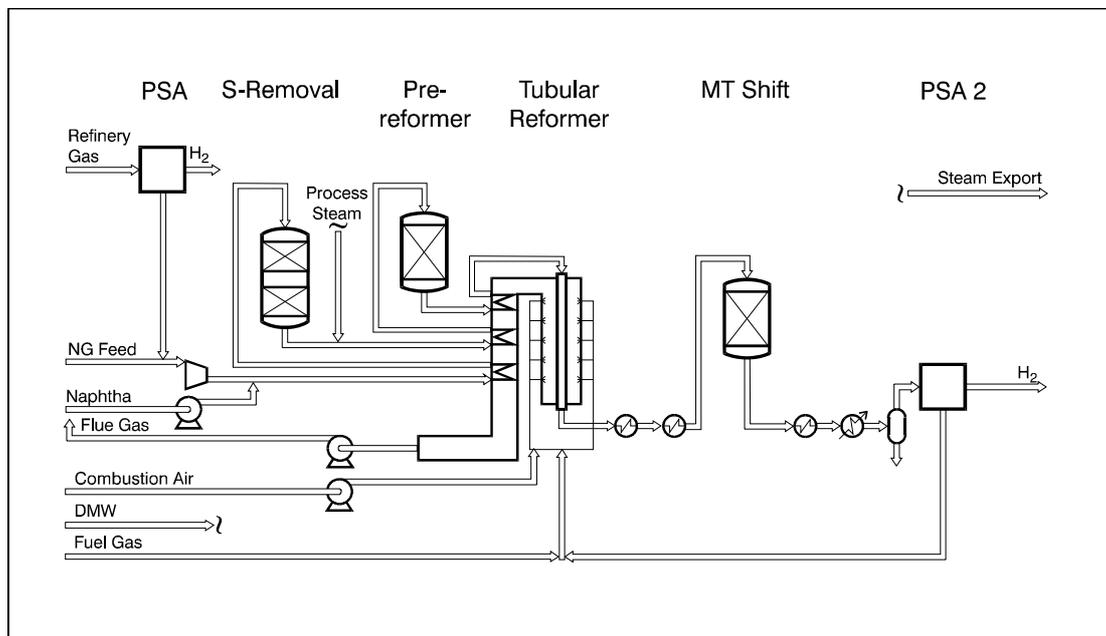


Fig. 9. Process Lay-out of a Typical Multi Feedstock H<sub>2</sub>-plant (Haldor Topsoe)

A typical *process lay-out* of a feedstock flexible hydrogen plant operating at 25 bar on refinery gas, natural gas and naphtha is given in Fig. 9. Refinery gas, containing large amounts of hydrogen, is sent to a PSA unit where pure hydrogen is extracted. The off-gas from the PSA, containing non-converted methane is compressed and used as feed in the hydrogen plant. In this way, low grade refinery gas is used as feed to a hydrogen plant and thereby substituting more expensive natural gas or naphtha. PSA off-gas is mixed with natural gas or vapourized naphtha, and the gas mixture is preheated, desulphurized (over CoMo-catalyst and ZnO), mixed with process steam and further heated before entering the adiabatic prereformer. Typical inlet temperatures are in the range 450-550°C, depending on feedstock and steam to carbon ratio. The prereformed gas is then heated to 650°C before entering the tubular reformer where final conversion to equilibrium of methane into hydrogen, carbon monoxide and carbon dioxide takes place at 850-950°C depending on lay-out. The reformed gas is cooled by producing steam before entering the shift converter, typically containing a medium temperature shift (MTS) (210-330°C). Over the copper-based shift catalyst,

more hydrogen is produced by converting carbon monoxide and steam to carbon dioxide and hydrogen (reaction (2)). The shifted gas is cooled to ambient temperature before entering the second PSA-unit. The off-gas from this PSA unit is used as fuel in the tubular reformer supplemented with fuel gas.

### ***Thermal efficient hydrogen plant design***

Today's Advanced Steam Reforming hydrogen plants are designed with a *high energy efficiency*. With no steam export, the theoretical net energy consumption is  $12 \text{ MJ/Nm}^3$  on LHV basis using liquid water as feed ( $11.8 \text{ MJ/Nm}^3 = 2.81 \text{ Gcal/1000Nm}^3$ ). The practical value for natural gas based plants is about  $13 \text{ MJ/Nm}^3/\text{H}_2$  ( $12.6 \text{ MJ/Nm}^3 = 2.98 \text{ Gcal/1000 Nm}^3$ ) corresponding to a LHV-based efficiency of 94%.

The thermal *efficiency* of the tubular reformer and waste heat recovery section approaches 95% [7,10], as most of the heat, which is not transferred to the process (ca. 50%) is recovered from the flue gas. This heat is used for steam production and for preheating of the reformer feed, combustion air, etc. The heat contained in the hot product gas exit the reformer ( $800\text{-}950^\circ\text{C}$ ) is most often used in a waste heat boiler for steam production of which some is used for the process and the rest is exported. For many situations, however, there is no use for the export steam.

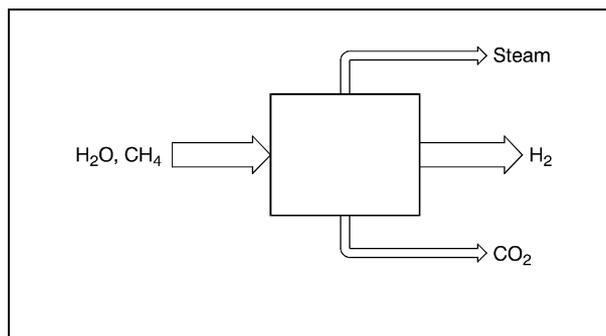


Fig. 10. Hydrogen from Natural Gas

It is possible to reduce the steam production from a hydrogen plant based on tubular steam reforming [16]. Introduction of a prereformer with reheat (re. Fig. 5) increases the thermal efficiency for reforming from 50% to about 60%. Another part of the flue gas heat content can be used for preheating of combustion air. However, it is not possible to completely eliminate the steam export. This can be done by using a convective *heat exchange reformer* [9,10], in which the flue gas as well as the hot product gas are heat exchange with the process gas, such that they leave the reformer at about  $600^\circ\text{C}$ . The amount of waste heat is reduced from 50% in the conventional design to about 20% of the fired duty in the heat exchange reformer. This means that the steam generated from the remaining waste heat just matches the steam needed for the process, such that export of steam can be eliminated. Convective reformers are industrially proven and are preferred for smaller units due to their compactness (Fig. 11).



Fig. 11. Topsoe Package Hydrogen Plants (2 x 5,000 Nm<sup>3</sup>/hr) at Air Liquide, Belgium

## Future Options

### *Membrane reforming*

The steam reforming process as practised today faces a number of *constraints* [18]. At first, thermodynamics require high exit temperatures to achieve high conversion of methane. This is in contrast to the potential of the catalyst showing activity even below 400°C [18]. This has led to efforts to circumvent constraints by the use of a selective *hydrogen membrane* installed in the catalyst bed [21,22]. Hydrogen is continuously extracted from the reaction thereby pushing the equilibrium to higher conversion at lower temperature. Reactor simulations and experiments [21] have shown that the reformer exit temperature can indeed be reduced to below 700°C while maintaining the same conversion. The economy of this scheme depends on membrane cost versus savings by elimination of the CO shift reaction and the PSA unit [22]. However, the produced hydrogen with this concept is at low pressure and must be compressed to the usual delivery pressure of 20 bars. This renders the process non-economical except, possibly, in specific scenarios with very low electricity prices [21], or in cases where hydrogen is used as a feedstock for a fuel cell or as low pressure fuel.

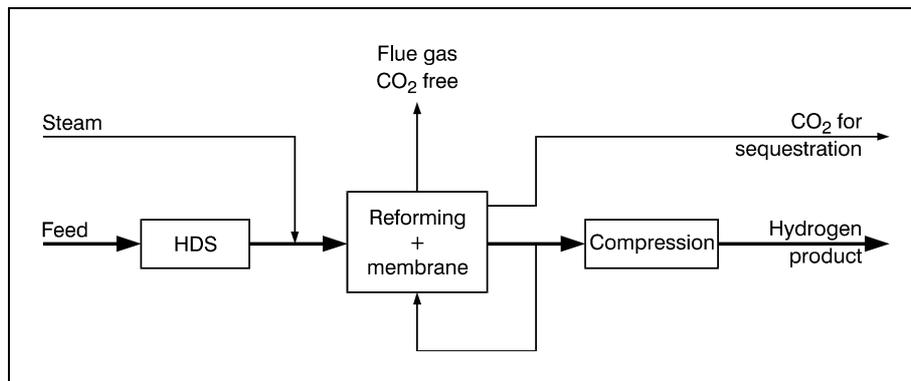


Fig. 12. Membrane Reforming. Hydrogen plant with CO<sub>2</sub> sequestration. The hydrogen is recovered from the reformer at low pressure. Part of the hydrogen is used as fuel to the reformer resulting in a CO<sub>2</sub> free flue gas. The product hydrogen may be compressed. Nearly all the carbon fed to the plant is recovered in a high pressure CO<sub>2</sub> stream for sequestration.

This scheme for hydrogen fuel production with CO<sub>2</sub> sequestration is much simpler than a scheme based on conventional reforming followed by shift, CO<sub>2</sub> separation and CO<sub>2</sub> compression. If CO<sub>2</sub> sequestration becomes accepted the membrane reforming scheme shown in Fig. 12 may become the preferred process for production of hydrogen fuel.

State-of-the-art commercial membranes (Pd-type) are still much too expensive to make the membrane reformer scheme attractive, although progress is made to prepare membranes with palladium films of a thickness approaching one micron. Furthermore, the current achievable flux with commercially available membranes is much too low. However, if significant amounts of hydrogen were to be produced by membrane reforming, the world supply of palladium would soon be exhausted. Hence, there is a need for new membrane types.

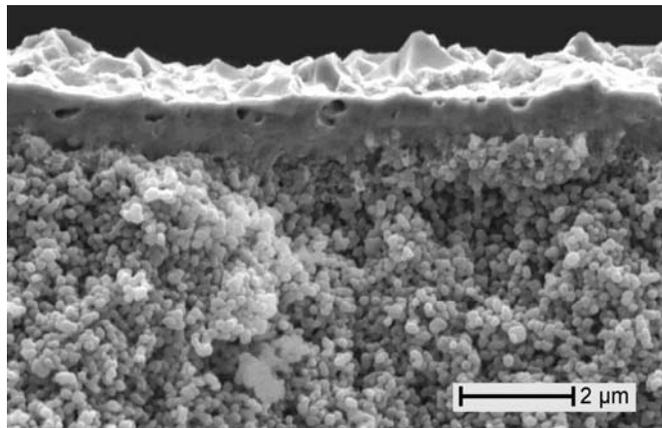


Fig. 13. Palladium Membrane. A micron thin palladium film is deposited on a functionally designed ceramic support tube.

### ***Non-tubular concepts***

In a reformer, the tube diameter is selected from the mechanical considerations and the heat flux from materials considerations or from restrictions in convective heat transfer leaving the space velocity (catalyst volume) fixed with the low utilisation of the catalyst [6,18].

Several suggestions have dealt with schemes circumventing the tubular concept. These include *reheat schemes* [14] in which the process gas is heated in a heater followed by reforming reaction in an adiabatic reactor. However, many steps are required to reheat the gas because of the strong endothermicity of the reaction.

A variation of the reheat process scheme is the use of a *circulating catalyst* bed using one bed for reaction and the other for heating up the catalyst [15]. This is also applied in other fluidized petrochemical processes. However, for steam reforming the recirculation rate would be very high. Moreover, catalyst dust in downstream heat exchangers would result in methane formation by the reverse reforming reaction (methanation) [23]. Other attempts [23] have aimed at utilizing the high heat transfer in fluidized beds or the use of heat pipes.

An alternative to the reforming process may be the use of a *cyclic process* [24] as illustrated in Fig. 14. Hydrogen is generated by reacting steam with a metal (Cu, Fe etc). The resulting metal oxide is

reduced by reaction with methane forming steam and CO<sub>2</sub> at pressure well suited for sequestration. The scheme involves a number of constraints relating to heats of reaction. The addition of air is necessary to ensure that the overall reaction becomes thermoneutral.

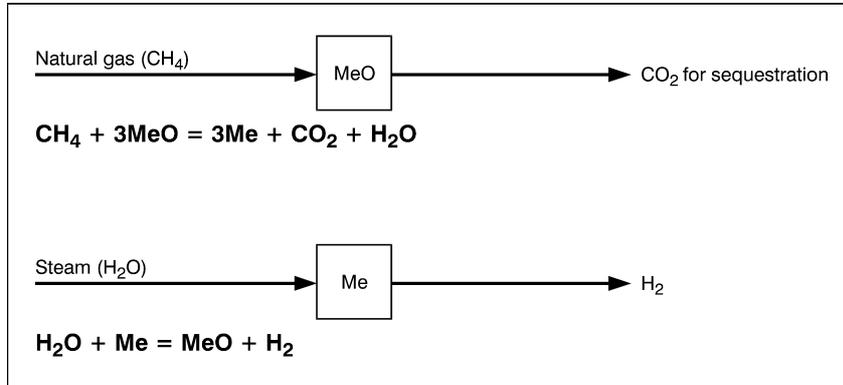
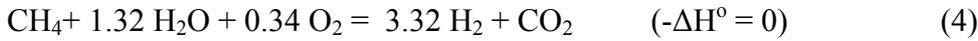


Fig. 14. Cyclic Process for CO<sub>2</sub>-free Hydrogen

### Partial oxidation

For very large grass root hydrogen plants (in excess of about 200.000 Nm<sup>3</sup> H<sub>2</sub>/h), the different economy of scale of tubular reformers and oxygen plants may favour the use of oxygen for partial oxidation of the hydrocarbon feed as practised in the *autothermal reforming process* [25]:

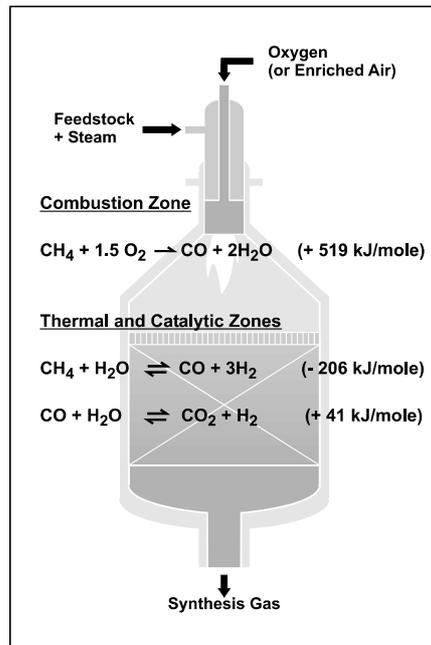


Fig. 15. Autothermal Reforming Process

In the autothermal reforming process, the feedstock is reacted with a mixture of oxygen and steam by the use of a burner and a fixed nickel catalyst bed for the equilibration (reactions (1) and (2) ) of the gas (Fig. 15). This results in a lower oxygen consumption,  $O_2/CH_4 = 0.5-0.6$  than used in non-catalytic routes. With addition of steam, it is possible to adjust the  $H_2/CO$  ratio. This cannot be achieved by non-catalytic routes, because the addition of steam results in a reduction of temperature and soot formation. On the other hand, the non-catalytic routes are the only technologies available for gasification of resid and at the non-distillate fuels [5].

Two-step reforming features a combination of tubular reforming (primary reformer) and oxygen-fired secondary reforming. In this concept the tubular reformer is operating at less severe operation, i.e. lower outlet temperatures.

A study was made to compare the three reforming technologies for the production of hydrogen ( $220.000 \text{ Nm}^3 \text{ H}_2/\text{h}$ ) based on natural gas feedstock [26]. Two parallel trains using the fired tubular reforming concept was compared to single-train concept for two-step reforming and ATR.

The comparison showed that the net energy consumption (feed + fuel - steam) was quite similar for the three technologies. The process scheme with the fired tubular reformer gives the highest export of steam. When comparing the oxygen-fired reforming technologies with the fired tubular reforming on investment cost, it shows that about 15-25% of the investment is reduced mainly by savings in the reformer section. However the cost of oxygen supply must be added to the oxygen-fired processes. Even for large scale plants ( $220,000 \text{ Nm}^3 \text{ H}_2/\text{h}$ ) the oxygen price necessary for making the ATR technology attractive is about 5-10 \$/ton, which is well below the current large scale production cost of oxygen.

The use of *air-blown* autothermal reforming (or catalytic partial oxidation) is considered for large scale manufacture hydrogen for power production combined with  $CO_2$ -sequestration as illustrated in Fig. 16. This scheme is based on known technology and its implementation will highly depend on imposed legislation – i.e. will only be feasible in case of significant taxation on  $CO_2$ -emission.

For small scale hydrogen plants, air-blown catalytic partial oxidation coupled with membrane separation may be a preferred route [4].

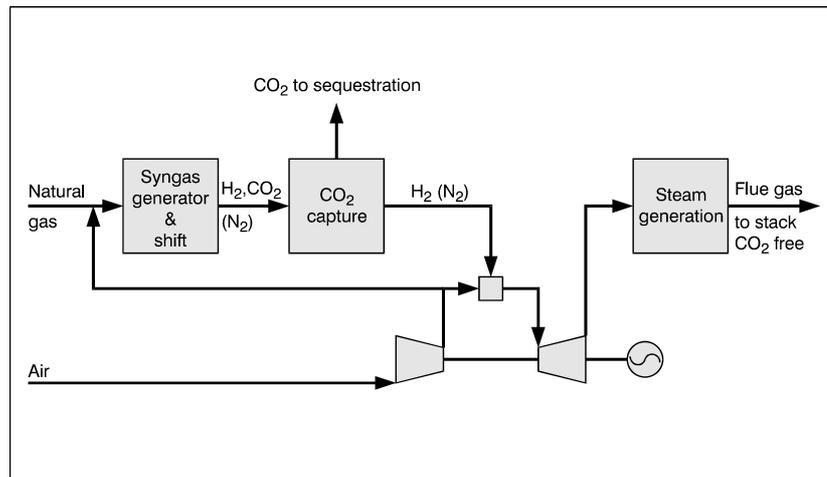


Fig.16. Hydrogen by Air-blown Reforming for  $CO_2$ -free Power Production

## CONCLUSIONS

There is a growing need for hydrogen. Hydrogen will play a key role in the manufacture of better transportation fuels. It may also play a role in the introduction of a “hydrogen economy” provided CO<sub>2</sub>-sequestration is accepted. Technologies are available offering a high degree of feedstock flexibility. The conversion of hydrocarbons is the most economic route to hydrogen. The steam reforming process appears as the most feasible technology. Oxygen-blown or air-blown reforming may only be feasible at very large scale conversions in connection with power production or co-production of chemicals [27].

### **Intermezzo: How Much CO<sub>2</sub>?**

When hydrogen is produced from carbon containing materials, CO<sub>2</sub> is formed as a co-product. The amount depends on the hydrogen content of the material and the efficiency of the process. Gasification of carbon results in 1 vol CO<sub>2</sub> per vol H<sub>2</sub>:



whereas steam reforming of methane results in 0.25 vol CO<sub>2</sub> per vol H<sub>2</sub> (reaction (1) and (2) plus the CO<sub>2</sub> formed by combustion of fuel to heat the reformer. The fuel consists of off-gas from the PSA-unit and additional fuel (natural gas) as shown in Fig. 9. For a high efficient natural gas based plant (LHV efficiency 94%), it means

0.37 vol CO<sub>2</sub> per vol H<sub>2</sub> , or

8.1 tons CO<sub>2</sub> per tons H<sub>2</sub>

### **What About Technology for Small-scale Hydrogen Plants?**

For each range of capacity, different technologies may represent the optimum choice. It is influenced by the cost of feedstock and the economy of scale of the technologies in question. This was illustrated in Fig. 2 with MeOH reforming being cheaper than naphtha reforming at small capacities.

For a given hydrocarbon feedstock, steam reforming remains the most economic and efficient technology in very small scale (50 Nm<sup>3</sup>/h). However, other parameters may play a role as well for small units such as simplicity, compactness and (for automotive units) short start-up time. Air blown catalytic partial oxidation fulfils these requirements in particular for fuel cell applications where it is normally acceptable that the hydrogen stream contains nitrogen. A CPO plant has a simpler steam and heat recovery system than a steam reforming plant, but an air compressor is needed, which makes the technology less suited for high pressure operation. If pure hydrogen is required, the costs of small oxygen plant or a hydrogen selective membrane should be added making CPO less favorable.

**Question: Does This Mature Industry Really Need a New Catalyst Composition?**

Yes.

Although there is a surplus of catalyst activity in the tubular reformer as reflected by an effectiveness factor less than 10% and a very close approach to equilibrium in the product gas, the catalyst activity is important for the local balance of heat transfer and catalytic reaction. For a given heat flux, a higher catalyst activity can be used to convert the corresponding amount of methane at a lower temperature. In practice, this means the higher the catalyst activity, the lower the tube wall temperatures in the reformer. This means longer tube life.

The challenge is to develop a catalyst having high activity and being better withstanding the risk for carbon formation and sulphur poisoning. It is a question to obtain better knowledge of sintering mechanisms, principles of promotion and still to find a non-metallic catalyst resistant to sulphur poisoning.

**What is CO<sub>2</sub> Sequestration?**

CO<sub>2</sub> is generally considered a greenhouse gas contributing to global warming. It is therefore of interest to identify fuels, which can be used without (or with limited) emission of CO<sub>2</sub> [28]. Hydrogen is such a fuel. However, many of the process for producing the hydrogen emit CO<sub>2</sub> as a by-product as is the case with steam reforming of hydrocarbon feedstocks. But, by combining steam reforming technologies with CO<sub>2</sub> separation technologies and permanent sequestration of the CO<sub>2</sub> (e.g. into depleted gas wells, deep aquifers or deep ocean), it is possible to produce hydrogen fuel with limited emission of CO<sub>2</sub>. This would allow continued large scale use of fossil fuels for hydrogen fuel production while substantially reducing CO<sub>2</sub> emissions. The envisioned schemes for CO<sub>2</sub> sequestration include pre-combustion decarbonization and post combustion CO<sub>2</sub> capture.

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