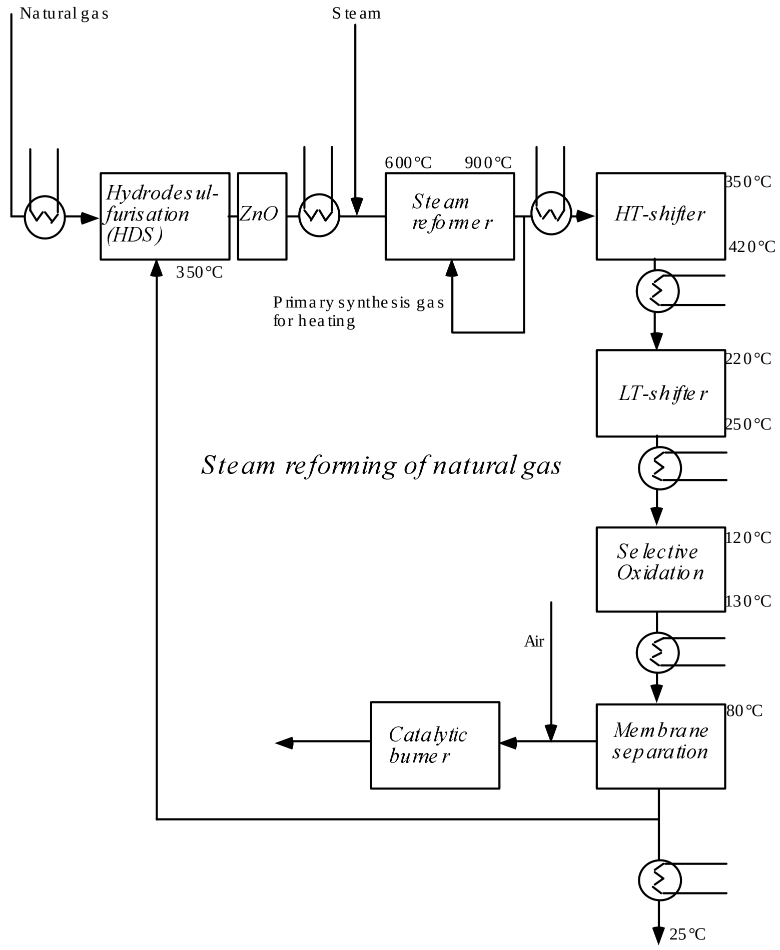
Rapport SGC 129

Catalytic Heat Exchangers for small-scale production of hydrogen – feasibility study



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Sydgas AB
Catator AB
SWEP International AB
Statens Energimyndighet

SVENSKT GASTEKNISKT CENTER AB

Johan Rietz

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Summary

A feasibility study concerning heat-exchanger reactors in small-scale production of hydrogen has been performed on the request of Svenskt Gastekniskt Center AB and SWEP International AB. The basic idea is to implement different catalysts into brazed plate-type heat exchangers. This can be achieved by installing catalytic cylinders in the inlet-and outlet ports of the heat exchangers or through treatment of the plates to render them catalytically active. It is also possible to sandwich catalytically active wire meshes between the plates.

Experiments concerning steam reforming of methanol and methane have been performed in a micro-reactor to gather kinetic data for modelling purposes. Performance calculations concerning heat exchanger reactors have then been conducted with Catator´s generic simulation code for catalytic reactors (CatalystExplorer). The simulations clearly demonstrate the technical performance of these reactors. Indeed, the production rate of hydrogen is expected to be about 10 nm^3/h per litre of heat exchanger. The corresponding value for a conventional steam-reforming unit is about 1 nm^3/h or less per litre of reactor volume. Also, the compactness and the high degree of integration together with the possibilities of mass production will give an attractive cost for such units.

Depending on the demands concerning the purity of the hydrogen it is possible to add secondary catalytic steps like water-gas shifters, methanation and selective oxidation, into a one-train unit, i.e. to design an all-inclusive design. Such reactors can be used for the supply of hydrogen to fuel cells.

The production cost for hydrogen can be cut by 60 – 70% through the utilisation of heat exchanger reactors instead of conventional electrolysis. This result is primarily a result of the high price for electricity compared to the feed stock prices in steam reforming.

It is important to verify the performance calculations and the simulation results through experimental investigations. The continued work should focus on three major areas according to:
- Verification and conceptual tests with methanol reforming
- Conceptual tests with reforming of natural gas and naphtha
- Development and design of a totally integrated reformer unit, i.e. the “all-inclusive reformer”

Sammanfattning

En studie avseende möjligheterna att utnyttja värmeväxlarereaktorer för småskalig produktion av vätgas har utförts på uppdrag av Svenskt Gasteknisk Center AB och SWEP International AB. Den grundläggande idén är att implementera katalysatorer i löda plattvärmeväxlare. Det är möjligt att installera cylindrar av nätkatalysator i inlopps- och utloppsportarna alternativt att placera nätkatalysator mellan plattorna. Som ett alternativ kan plattorna beläggas med ett katalysatorskikt.

Experiment har utförts avseende ångreformering av metanol och metan i avsikt att erhålla kinetiska data för reaktormodellering. Simuleringar avseende värmeväxlarereaktorer har utförts med Catator´s generiska simuleringsmodell för katalytiska reaktorer (CatalystExplorer). Simuleringarna visar tydligt den tekniska potentialen i konceptet och produktionskapaciteten med avseende på vätgas beräknas bli så stor som 10 nm^3/h per liter värmeväxlarereaktor. Motsvarande värde för en konventionell anläggning för ångreformering är normalt lägre än 1 nm^3/h. Kompaktheten, den höga graden av integration samt möjligheterna till massproduktion möjliggör vidare en gynnsam prisbild.

Beroende på kraven avseende renheten på vätgasen kan ytterligare katalytiska steg implementeras i värmeväxlarereaktorn, t.ex. steg för vattengasreaktion, metanisering och selektiv oxidation. Sådana ”allt-i-ett”-reaktorer kan exempelvis utnyttjas för produktion av vätgas till bränsleceller.

Produktionskostnaden för vätgas kan reduceras med 60-70% om värmeväxlarereaktorer används i stället för elektrolysörer vid vätgasframställning. Detta beror framförallt på den höga elkostnaden i förhållande till priset på råvarorna vid ångreformering.

Det är av stor vikt att verifiera prestandaberäkningarna och simuleringsresultaten genom experimentella studier. Det fortsatta arbetet bör fokuseras på tre huvudområden enligt:

- Verifiering och konceptstudier med metanolreformering
- Konceptstudier avseende reformering av naturgas och nafta
- Utveckling och design av en totalt integrerad reaktor, d.v.s. en ”allt-i-ett”-reaktor för framställning av ren vätgas

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1. Introduction

There is a growing interest in small-scale production of synthesis gas and pure hydrogen in the industry. These gases can be used either as make-up gases in certain oven processes but also as reactants in many processes (e.g. ammonia-and methanol synthesis and hydrogenation). Another future application might be small-scale hydrogen production for automotive fuel cells (the PEM-cell powered by pure hydrogen originating from alcohols, naphtha or natural gas).

Electrolysis is usually used in small-scale hydrogen production since conventional steam-reforming processes are associated with high initial costs. Consequently, the price per unit-volume of produced hydrogen will be too high. To cut the production price in steam reforming, it is necessary to develop a totally integrated reactor concept, which is easy to scale according to the desired delivery rate of reformer gases. The catalytic plate-type-heat-exchanger (CPHE) enables us to build totally integrated steam-reformer reactors as modules, which could be placed in parallel to increase the capacity.

The major technical problem in conventional steam reforming is associated with temperature gradients within the catalyst bed due to the endothermic nature of these processes. In the CPHE-concept there is a definite coupling between the endothermic processes and the heat supply, usually supplied through combustion on one side of the plate.

The CPHE-concept can be built upon a brazed plate-type-heat-exchanger, where one pass is coated with combustion catalyst to facilitate heat generation. The other pass will be coated with a reformer catalyst. The thin shell-like design of the catalyst coatings will offer superior mass-and heat transfer characteristics, which could be expressed in terms of reduced reactor volumes over conventional alternatives. The amount of catalyst necessary for a certain conversion degree is also greatly reduced due to less pore-diffusion-limitations. The temperature control of the catalyst is accurate and exact. As a simplified and cheaper solution it is also possible to integrate wire-mesh catalysts into the CPHE, preferably as wire-mesh cylinders. In this solution there is no need for coating the heat-exchanger surfaces with catalyst.

Introductory calculations indicate a possible hydrogen-production rate of more than 10 nm^3/h per litre of heat exchanger (gross volume). Also, the reactor will show a quick thermal response due to the low thermal inertia and the extremely high mass-and heat transfer capacities.

The reformer gas will, apart from water vapour, contain a mixture of hydrogen, carbon oxides and traces of hydrocarbons. In fuel-cell applications it is normally necessary to up-grade the gas to essentially pure hydrogen. The gas purification is performed down-stream the reformer reactor, either through conventional PSA (Pressure Swing Adsorption) or through membrane methods.

This project is a feasibility study concerning the CPHE-concept in fuel processing, i.e. steam-reforming and associated processes. The study will focus on technical performances as well as economical predictions (initial costs and running costs). The technical and economical characteristics will then be compared to existing alternatives, e.g. electrolysis.

The CPHE-design presented in this study is based on experimental data as well as results obtained through complex dynamic modelling of steam reforming in heat-exchanger reactors.

The CPHE-design must then be experimentally verified and evaluated in following-up projects.

2. Objective

The overarching objective with the study is to investigate the technical and economical potential of the Catalytic Plate-type-Heat-Exchanger (CPHE) in catalytic reforming for small-scale production of hydrogen.

The CPHE-concept presented in this report is based on experimental data concerning steam-reforming and dynamic simulations of the chemical processes. Steam reforming experiments where conducted to facilitate kinetic modelling of the processes. The kinetic models were then implemented into our simulation code for catalytic reactors (Catalyst Explorer), which enabled us to predict the technical performance of different CPHE-structures.

The objective of the study might be expressed as:

“To design an ultra-compact heat-exchanger reactor for small-scale production of hydrogen based on reforming processes and to evaluate the technical and economical performance of the concept in relation to other alternatives”

The study includes the following sub-items:

A) To derive rate data for steam reforming of methane/natural gas and methanol, either through experiments or via the literature

B) Dynamic modelling to estimate the amount of catalyst necessary for a certain conversion degree

C) Overarching design of the CPHE-reactor

D) System design (including make-up steps and gas purification)

E) Technical and economical evaluation of the process

F) Assessment of potential markets for the CPHE-concept

A prototype system will be erected and evaluated in a following-up project. The technical/economical predictions given in this report will then be calibrated with the experimental data acquired in the prototype rig.

3. Kinetic data for steam reforming and related reactions

3.1 Reaction pathways

Synthesis gas is a mixture of hydrogen and carbon monoxide, which can be used in number of reactions to prepare different compounds, e.g. methanol, ammonia, substitute natural gas and synthetic fuels. Synthesis gas can be produced in a number of ways and from different compounds (see Figure 1) but the normal route is from natural gas or naphtha through steam reforming or through partial oxidation of heavy oils or coal.

Most processes for synthesis gas production and synthesis gas utilisation are catalytic and different catalysts are used to promote the reactions. The ratio between hydrogen and carbon monoxide can be calibrated by means of the water-gas shift ($CO + H_2O = H_2 + CO_2$), which is catalysed by certain metal oxides at temperatures in the region of 200 – 500°C. The reaction is shifted to hydrogen and carbon dioxide by low reaction temperatures.

The first steam reformers where started by BASF in Germany during the 1920s and in the U.S. by Standard Oil Co. (Exxon) in the 1930s. The first processes where operated at atmospheric pressure. Beginning in the 1950s, the pressure has gradually increased and pressure levels of 30 bar(a) or more are not unusual today. In steam reforming, a mixture of naphtha or natural gas and steam is contacted with a suitable catalyst at elevated temperatures (500 – 900°C) and pressures. Precious metals are highly active in steam reforming but are relatively too expensive. Ni-catalysts can combine a reasonable catalytic activity with a low price and are consequently the preferred alternative nowadays.

Methanol is thermodynamically unstable at elevated temperatures and is readily decomposed into a mixture of hydrogen and carbon monoxide. By adding steam to the system, the yield of hydrogen can be increased through the combination of methanol decomposition and the water-gas reaction. Methanol decomposition can be performed over a number of catalysts (precious metals, Ni or Cu) at temperatures between 250 and 400°C. At still higher temperatures there is an increasing risk of methane formation through methanation reactions. Methanol reforming is normally performed at ambient pressure. High pressures will decrease the thermodynamically possible conversion of methanol.

Synthesis gas might also be derived from ammonia cracking, which is a high-temperature process. Ammonia cracking is performed at temperatures in the region of 800- 1000°C and at atmospheric pressure.

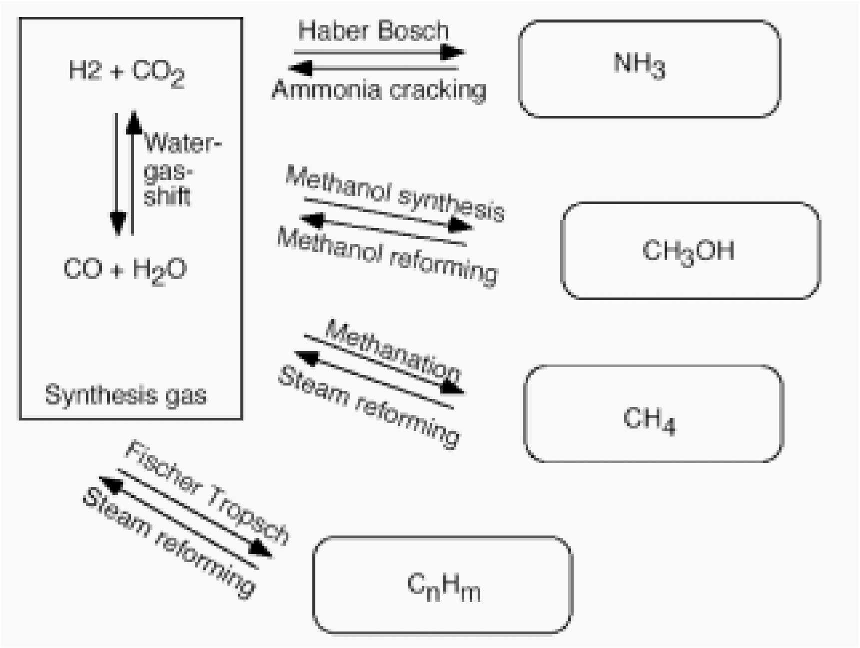


Figure 1 Important reaction pathways for synthesis gas

Steam reforming and ammonia cracking have opposite reactions, which normally utilise the same catalysts but other process conditions. Hence, ammonia synthesis is carried out at extreme pressures (150 – 300 bar(a)) and low temperatures (450°C). Methanol synthesis is carried out at 50 – 300 bar(a) and at temperatures ranging from 250°C (low-pressure process) to 400°C (high-pressure process). Methanation is often used as a method to purify syntesis gas from carbon oxides. The reaction is carried out at temperatures slightly above 300°C over a Ni-catalyst. The Fischer-Tropsch synthesis is defined as a reductive polymerisation of CO by H_2 to form organic products. Depending on the catalyst and the process conditions it is possible to produce light aliphatic hydrocarbons, naphtha hydrocarbons, alcohols and waxes. There is a growing interest for Fischer-Tropsch-related reactions in the process industry today.

3.2 Important reactions in steam reforming

There are a number of important reactions to take into consideration when developing a system for steam reforming (See Figure 2 below). The main reactions are, of course, the steam reforming reactions where the hydrocarbons are reacted with steam to form a mixture of carbon monoxide and hydrogen. Due to thermodynamic reasons, the reforming reactions are favoured by high temperatures. It is therefore conventional to install a secondary reformer with an exit temperature of about 1000°C downstream the ordinary reformer unit.

The gas mixture, which leaves the reactor has a composition close to the thermodynamic equilibrium (10 – 20°C approach to equilibrium is usual). Some of the carbon monoxide initially formed is converted into carbon dioxide via the water-gas reaction. Primary synthesis gas (the exit composition) normally holds about 12% by vol. of carbon monoxide and 50 – 70% by volume of hydrogen.

The water-gas shift is thermodynamically favoured by low temperatures. Hence, it is possible to decrease the content of carbon monoxide down to about 2000 ppm by installing a low-temperature shifter downstream the reformer unit.

Reforming reactions

$$CH_4 + H_2O \longleftrightarrow CO + 3\,H_2$$

$$C_nH_m + n\,H_2O \longleftrightarrow n\,CO + (n+m/2)\,H_2$$

Shift reaction

$$CO + H_2 \longleftrightarrow CO_2 + H_2$$

Oxidation reactions

$$C + O_2 \longrightarrow CO_2$$

$$2\,CO + O_2 \longrightarrow 2\,CO_2$$

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2H_2O$$

$$C_nH_m + (n + m/2)\,O_2 \longrightarrow n\,CO2 + m/2\,H_2O$$

Soot formation reactions

$$CH_4 \longrightarrow C + 2\,H_2$$

$$2\,CO \longrightarrow C + CO_2$$

Carbonyl formation

$$Ni + 4\,CO \longrightarrow Ni(CO)_4$$

$$Fe + 5\,CO \longrightarrow Fe(CO)_5$$

Figure 2 Main reaction and important side reactions during steam reforming

If even traces of oxygen are present, oxidation reactions will occur. These reactions are highly exothermic and might destroy the catalyst. However, it is possible to add small amounts of oxygen to the reaction mixture in order to balance for the endothermic reforming reactions, i.e. to arrive at temperature neutral conditions throughout the reactor. This combination of oxidation and reforming is called adiabatic reforming, and can be used in the CPHE-concept when reforming natural gas. From the figure it is clear that oxygen will react with carbon monoxide, hydrogen, hydrocarbons and soot, i.e. with all combustible components present in the system.

Carbon formation is a problem in steam reforming of unsaturated hydrocarbons and aromatics. Carbon deposition can cause blockage of catalyst pores and catalyst deterioration. The nature of the carbon deposit varies with operating conditions and causes catalyst deactivation in different ways. Three different forms have been reported [1].

- Encapsulating film through slow polymerisation (below 500°C)
- Carbon-filament growth (above 450°C)
- Formation of pyrolytic carbon through thermal cracking (above 600°C)

Carbon can also be produced via reaction between two carbon monoxide molecules, i.e. the Boudouard reaction [2]. It is possible to stimulate the carbon-steam reaction (carbon-removing reaction) by adding alkaline substances to the catalyst.

It is also important to choose correct materials qualities in the reactor system in order to avoid carbonyl formation. Carbonyl compounds are thermodynamically stable at low temperatures and they might consequently be formed in places subjected to cooling [3].

3.3 Typical process conditions

Typical process conditions in synthesis gas production and associated processes are given in Figure 3 [4]. Steam reforming of natural gas and naphtha is normally carried out at elevated pressures and at high temperatures. The ratio between the gas flow and the catalyst volume, i.e. the space velocity, is normally around 8 000 h^{-1} when pellet catalysts are used. On the other hand, methanol reforming is performed at atmospheric pressure and at moderate temperatures (250 – 400°C). The corresponding space velocity is around 5 000 h^{-1}.

The primary synthesis gas leaving the reformer contains considerable amounts of carbon monoxide. In order to decrease the content of carbon monoxide, a two-step process including a high-temperature shifter and a low-temperature shifter is used. The high-temperature shifter operates at 350 – 420°C whereas the low-temperature shifter operates at 220-250°C. The pressure level of the shifter units is the same as in the reformer unit upstream. Typical space velocities are in the neighbourhood of 5 000 h^{-1}. The carbon monoxide concentration will decrease to about 3% in the high-temperature shifter and to about 0.2% in the low-temperature shifter.

Steam reforming	*T (°C)*	*P (bar)*	*SV (h^{-1})*
$CH_4 + H_2O \longleftrightarrow CO + 3\,H_2$	500 - 900	1 -30	8 000
$C_nH_m + n\,H_2O \longleftrightarrow n\,CO + (n+m/2)\,H_2$	500 - 900	1 - 30	8 000
$CH_3OH \longleftrightarrow CO + 2\,H_2$	250 - 400	< 10	5 000
Water-gas shift			
$CO + H_2O \longleftrightarrow CO_2 + H_2$	220 - 250 350 - 420	1 - 30 1 - 30	5 000 5 000
Methanation			
$CO + 3\,H_2 \longrightarrow CH_4 + H_2O$	200 - 450	1 - 30	5 000
$CO_2 + 4\,H_2 \longrightarrow CH_4 + 2\,H_2O$			
Selective oxidation			
$2\,CO + O_2 \xrightarrow[H_2]{} 2\,CO_2$	80 - 150	1 - 30	80 000

Figure 3 Typical process conditions (conventional processes)

In order to purify the gas mixture from carbon oxides, it is possible to methanate traces of CO+ CO_2 via a reaction with hydrogen over a Ni-catalyst. This reaction is accomplished at a temperature of about 250 – 350°C after CO_2-scrubbing. The space velocity is typically around 5 000 $h^{-1}$and CO is reacted more readily than CO_2.

Small traces of carbon monoxide can also be removed through selective oxidation of carbon monoxide in the presence of hydrogen. It is a low-temperature process, although relatively quick since space velocities of 80 000 h^{-1} are used. The catalyst is a precious-metal catalyst, promoted with metal oxides [5].

In order to be able to calculate the performance of different CPHE-reactors in steam reforming, it is necessary to perform kinetic studies concerning a number of reactions over Catator´s wire-mesh catalyst. All kinetic studies were performed in a micro-reactor system at atmospheric pressure. Once appropriate expressions for the reaction rates have been determined, it is possible to include these expressions into our generic simulation code (CatalystExplorer) to evaluate different HE-reactors.

3.4 Reforming over wire-mesh catalysts

In order to facilitate performance calculations, a number of experiments were performed to gather kinetic data for steam reforming of methane and methanol. Experiments were also conducted to enable simulations of the water-gas shift and the methanation reaction.

The following types of experiments were performed:

- Activity screening, different catalyst compositions
- Tests of temperature dependence of the reaction rates
- Tests concerning the concentration dependence of the reaction rates
- Influence of the space velocity on the conversions

Figure 4 shows a typical result from a steam-reforming experiment. In this case, the reactants were diluted with nitrogen to bring down the reactant concentrations. From the figure it is obvious that high temperatures are required to arrive at high conversions of methane. The experimentally obtained data concerning methane conversion and carbon monoxide production are closely correlated to the data calculated with our simulation code. The simulation code underestimates the production of carbon dioxide somewhat in this example. In this experiment we used a Ni-coating as active phase. Similar experiments with precious metals indicated equal or even higher activities, especially for the WGS (water-gas shift). The specific activity of the wire-mesh catalyst is much higher than for a pellet catalyst. The space velocity during the experiments were normally between 50 000 and 100 000 h^{-1}, i.e. 10 times higher than in conventional steam reforming

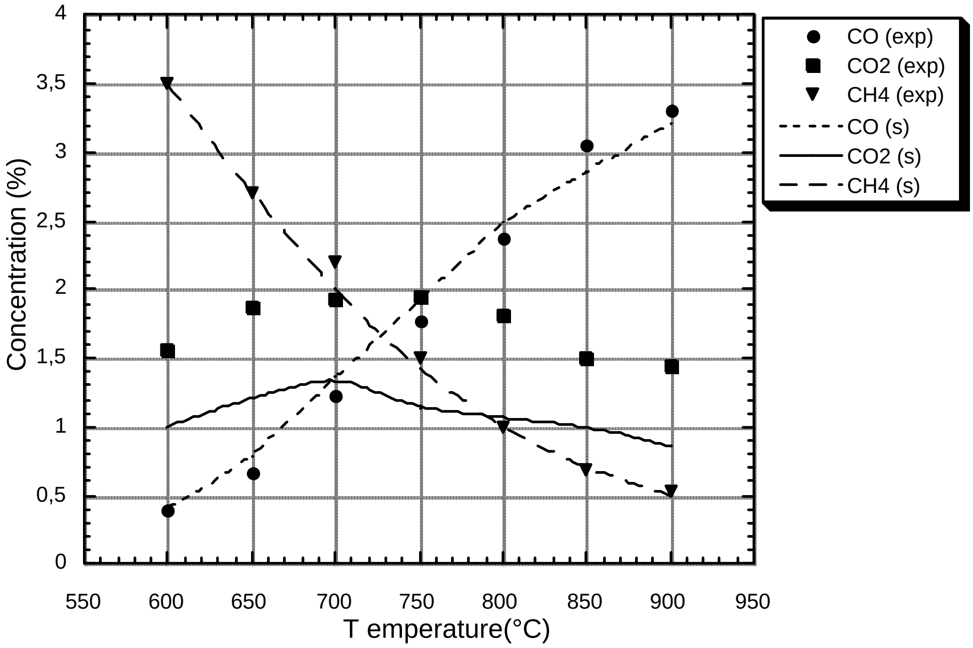


Figure 4 *Experimentally obtained conversion data in steam reforming. 5% CH_4, 10% H_2O, balance N_2. Flowrate - 0.8 nm^3/h. 10 pieces of wire-mesh catalysts (ø32) in series coated with Ni. Simulated data represented as graphs.*

The pressure dependence of the hydrogen productivity was studied with the simulation code. An increased pressure will lead to a higher catalytic activity. On the other hand, the steam reforming reaction is shifted towards the reactants when the pressure is increased. Figure 5 shows the hydrogen productivity expressed as the volume of hydrogen produced per unit-area of catalytically active wire mesh and time. From the figure it is obvious that as much as 300 nm^3/h of hydrogen can be produced over one square metre of wire-mesh catalyst. The pressure dependence is rather weak, especially above 5 bar(a).

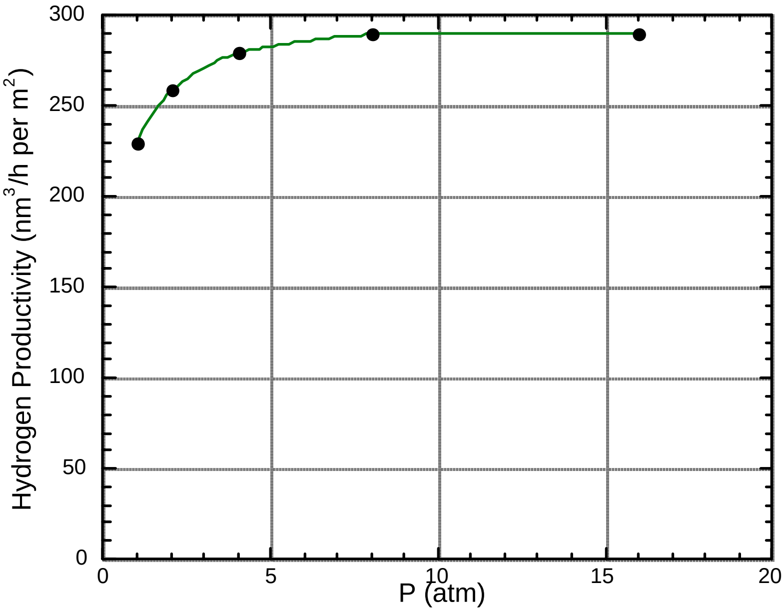
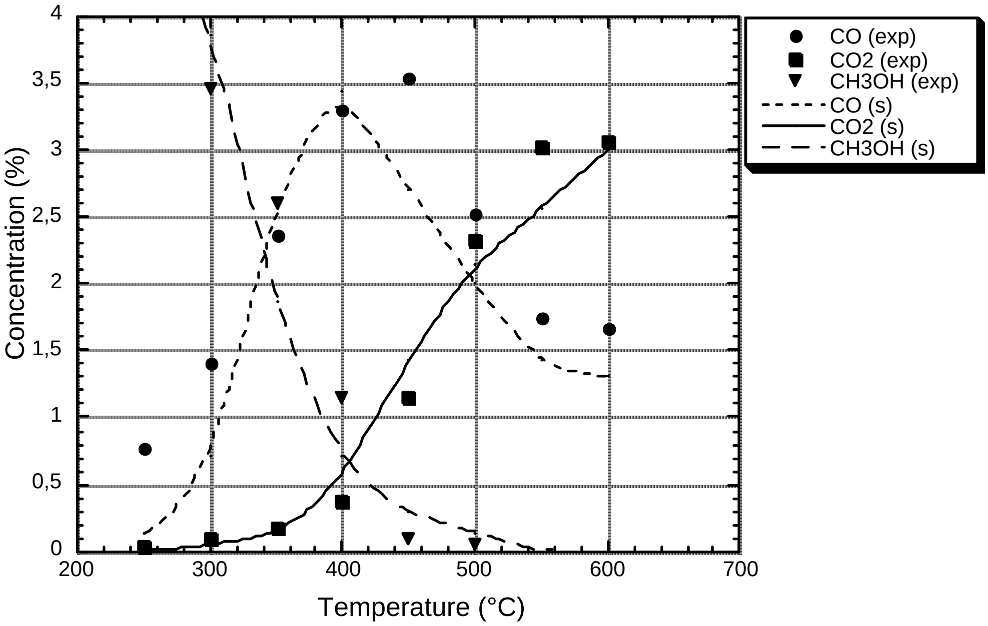


Figure 5 *Productivity of hydrogen (nm^3/h per m^2 of wire-mesh catalyst) vs. the gas pressure.*

Steam reforming of methanol is possible at much lower temperatures than steam reforming of methane, see Figure 6. All experimental data correlates to the ones forecasted by the simulation code. The reaction rate is high at temperatures above 350 – 400°C. At temperatures exceeding about 500°C, we observed small amounts of methane, formed through secondary methanation reactions. Different catalysts were investigated and precious metals (a mixture of Pt and Rh) showed the highest activity. The space velocities were the same as in methane reforming, i.e. at least ten times higher than in conventional methanol reforming (pellet catalysts).



Figur 6 *Experimentally obtained conversion data during steam reforming. 5% CH3OH, 10%* H_2O*, balance* N_2*. Flowrate - 0.8* nm^3/h*. 10 pieces of wire-mesh catalysts (ø32) in series coated with Pt/Rh. Simulated data represented as graphs.*

In order to describe the ratio between carbon dioxide and carbon monoxide, similar experiments were carried out for the water-gas reaction. Since methane formation might be a problem in high-temperature reforming of methanol, we also made some experiments with methanation.

4. Computer modelling

The results from the numerous experiments were boiled down into kinetic expressions, which were implemented into Catator´s generic simulation code for catalytic reactors, CatalystExplorer. Figure 7 indicates how the development work is conducted. The figure is splitted into one “real world” and one “virtual world”. The kinetic data were derived through experimental work in the real word. We summarised all data into kinetic expressions, which were implemented into the simulation code in the virtual word. The simulation code enables us to carry out performance calculations. The information from the experimental work together with the information from the performance calculations makes it possible to suggest possible design solutions (concepts). A prototype reactor can then be designed and constructed. Based on the experimental data from the prototype tests, it is possible to scale up the reactor.

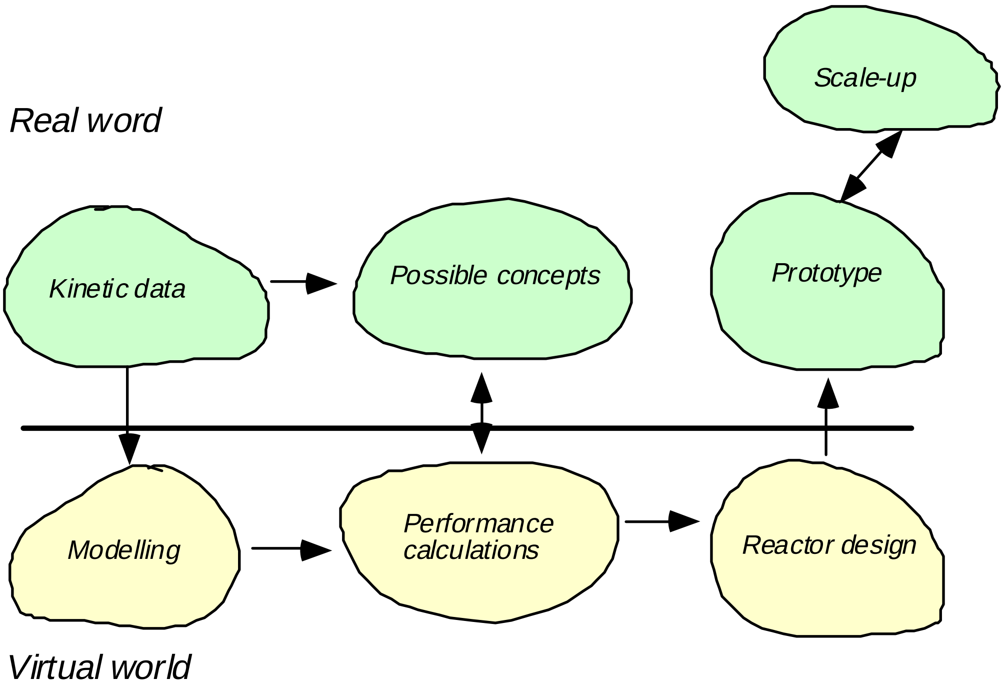


Figure 7 Schematic figure of the evaluation method.

CatalystExplorer is a simulation code for catalytic reactors, which has been developed over the years to enable predictions and performance calculations. The kinetic data are given as Langmuir-Hinshelwood expressions, and we are able to handle rather complex reaction schemes, e.g. steam reforming and complex synthetic chemistry.

The catalyst might consist of pellets, monoliths, wire-meshes or a combination of different catalysts. The characteristics of the catalysts (e.g. porosity, specific surfce area etc) might be varied along the bed.

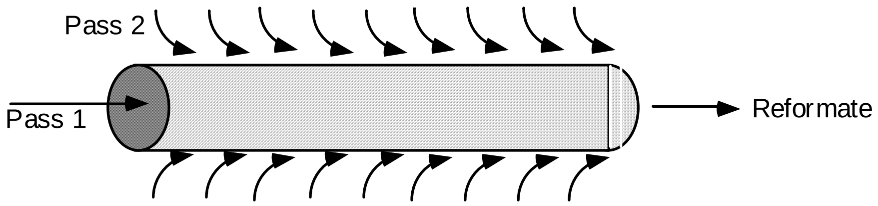
We are able to handle a number of different reactors, i.e.:
- batch and semi-batch reactors
- slurry reactors
- fluid bed reactors
- trickle bed reactors
- flow reactors (isothermal, adiabatic, non-isothermal/non-adiabatic, recuperative, regenerative)
- 2D-formulation of non-isothermal/non-adiabatic reactors
- heat-exchanger reactors

Starting with experiment in the micro reactor, we try to adjust the kinetic expressions to get an accurate prediction of the catalytic reactions. These experiments are conducted at isothermal conditions and at a specified pressure level. Parameters like concentrations, the temperature and the pressure can be varied to gather complementary information of the reaction schemes. When suitable kinetic expressions have been derived, it is possible to investigate the outcome of different reactors and catalyst characteristics for a specific reaction scheme.

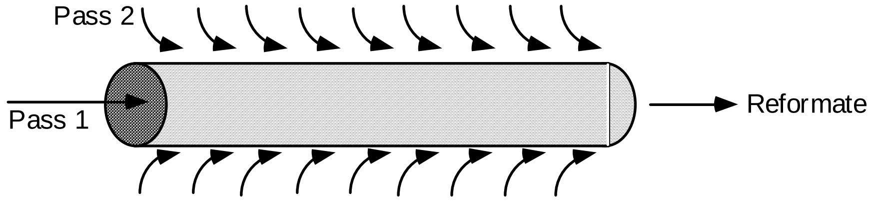
The code also makes it possible to model deactivation phenomena, e.g.:

- sintering of carrier and active phase
- evaporation of active phase
- poisoning (selective, non-selective)
- fouling
- clogging

More specific, for heat-exchanger reactors, we are able to simulate both tubular- and plate-type heat exchangers. It is possible to simulate wall reactors as well as HE-reactors, which are filled with catalysts. The flow direction might be current or co-current and we are able to use water, oil, gases or endothermal reactions as heat sinks. For instance, we are able to simulate a plate-type heat exchanger were oxidation of hydrocarbons/carbon monoxide/hydrogen is carried out in one pass and the endothermal steam reforming process in the other pass. Figure 8 shows the different possibilities concerning HE-reactors, included in CatalystExplorer.



Type 1 *Tubular Catalytic Wall/Wall*



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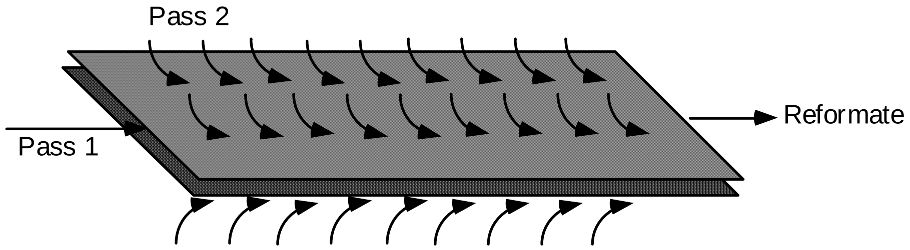
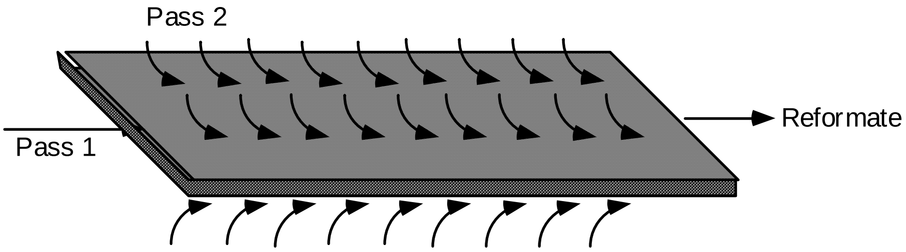


Type 3 *Plate Catalytic Wall/Wall*



Type 4 *Plate Catalytic Wall/Filled*

Figure 8 Different types of HE-reactors, which can be evaluated with CatalystExplorer.

The results from the simulations give us concentration- and temperature profiles through the reactor. The pressure drop is calculated and so are all relevant parameters associated to mass- and heat transfer. Since we are investigating the CPHE-concept, the simulations were focused on reactor concept no. 3 in Figure 8.

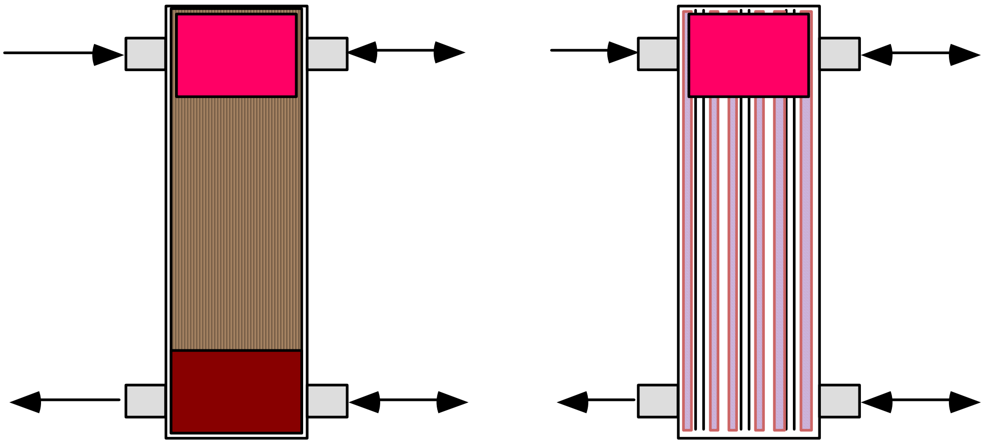
5. CPHE-reactor system for hydrogen production

5.1 Preferred design of a CPHE

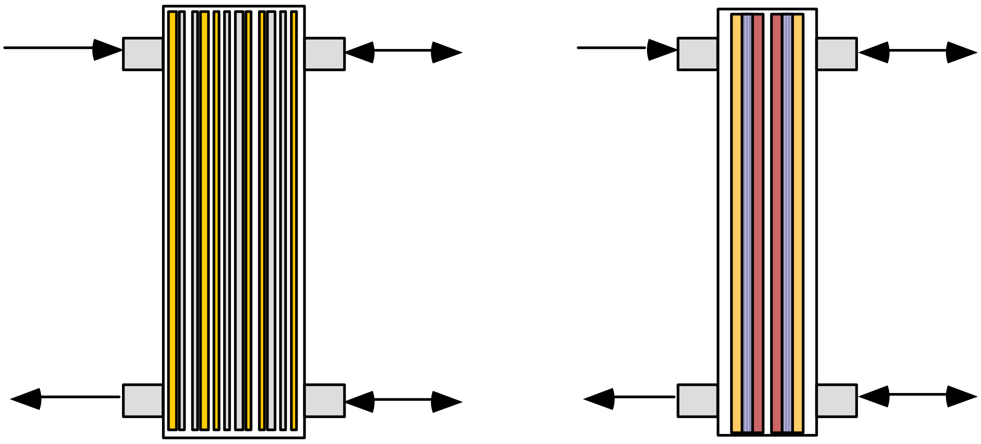
A catalytic plate-type heat exchanger can be designed in a number of ways. The simplest alternative is to keep the heat exchanger portion intact and to implement the catalyst in the inlet- and exit ports, preferably as catalytic cylinders. This concept is presently used in catalytic heat exchangers for domestic heat production (a SWEP/Catator- development project). However, this type of CPHE-reactor is probably only suitable for small production facilities since the amount of catalyst in this design is limited.

In larger appliances it is wiser to coat the surfaces of one pass of the heat exchanger with active catalyst. This design is, of course, more complicated and the cost will be higher. In the “Cylinder/wall”-concept, the reforming process is performed on the catalytic surfaces whereas the combustion process might be performed in the catalytic cylinder.

The double-wall concept includes catalytic coating of the surfaces of both passes. This reactor-concept is most effective of the alternatives but is also the most expensive.



"Double cylinder" "Cylinder/wall"



"Double wall" "Porous wall"

Figure 9 Different concepts for CPHE-reactors.

The porous-wall concept is an intriguing design for the future. By using catalytic membranes as plates, it would be possible to withdraw hydrogen continuously from the reforming pass. Consequently, it should be possible to reach conversions beyond the thermodynamic equilibrium.

The most realistic concepts in the short term are the double-cylinder- and the cylinder/wall-reactors.

5.2 Possible ways of manufacturing

The way to produce cylinder-reactors is already known from previously studies. The heat exchanger and the catalysts are separate entities, which is an advantage in maintenance. Hence, the catalyst might be replaced without replacing the catalyst and vice versa.

The wall-reactors need to be pre-coated prior to the brazing process. As an alternative it might be possible to place a catalytically active wire mesh between the plates prior to the brazing process. Brazing experiments show that the wire-mesh catalyst can survive the heat impact during the brazing process.

The pre-coated surfaces (porous structure) are then treated with wash-coats to arrive at catalytically active surfaces. The wash-coating process as well as the impregnation with active phase can be performed after the brazing process.

Again, the cylinder reactors are cheaper and easier to produce and to maintain. Consequently, the cylinder reactors should be considered as the first choice of design.

5.3 Pre-treatment systems for gases

The catalyst utilised in steam reforming (Ni) is highly sensitive to sulphur poisoning. Natural gas and naphtha contain small amounts of sulphur, which would poison the catalyst within a few days. Consequently it is necessary to de-sulphurise the feed by means of hydrodesulfurisation (HDS) and adsorption. In this reaction the sulphurous compounds are converted to hydrogen sulphide through hydrogen treatment over a catalyst. The hydrogen sulphide is then adsorbed in a bed of Zinc oxide.

HDS is normally not required in methanol reforming since methanol does not contain sulphur compounds.

5.4 Make-up systems for different qualities of hydrogen, solutions

The cost of the production unit is somewhat correlated to the demands concerning purity. The primary reforming gas will apart from hydrogen, carbon dioxide and steam contain about 12% by volume of carbon monoxide and traces of hydrocarbons. By implementing a high-temperature shifter it is possible to decrease the amount of carbon monoxide to about 3% by volume. Addition of a low-temperature shifter makes it possible to decrease the CO-content to about 0.2% by volume. Further refinement of the synthesis gas is possible through physical or chemical steps, see Figure 10.

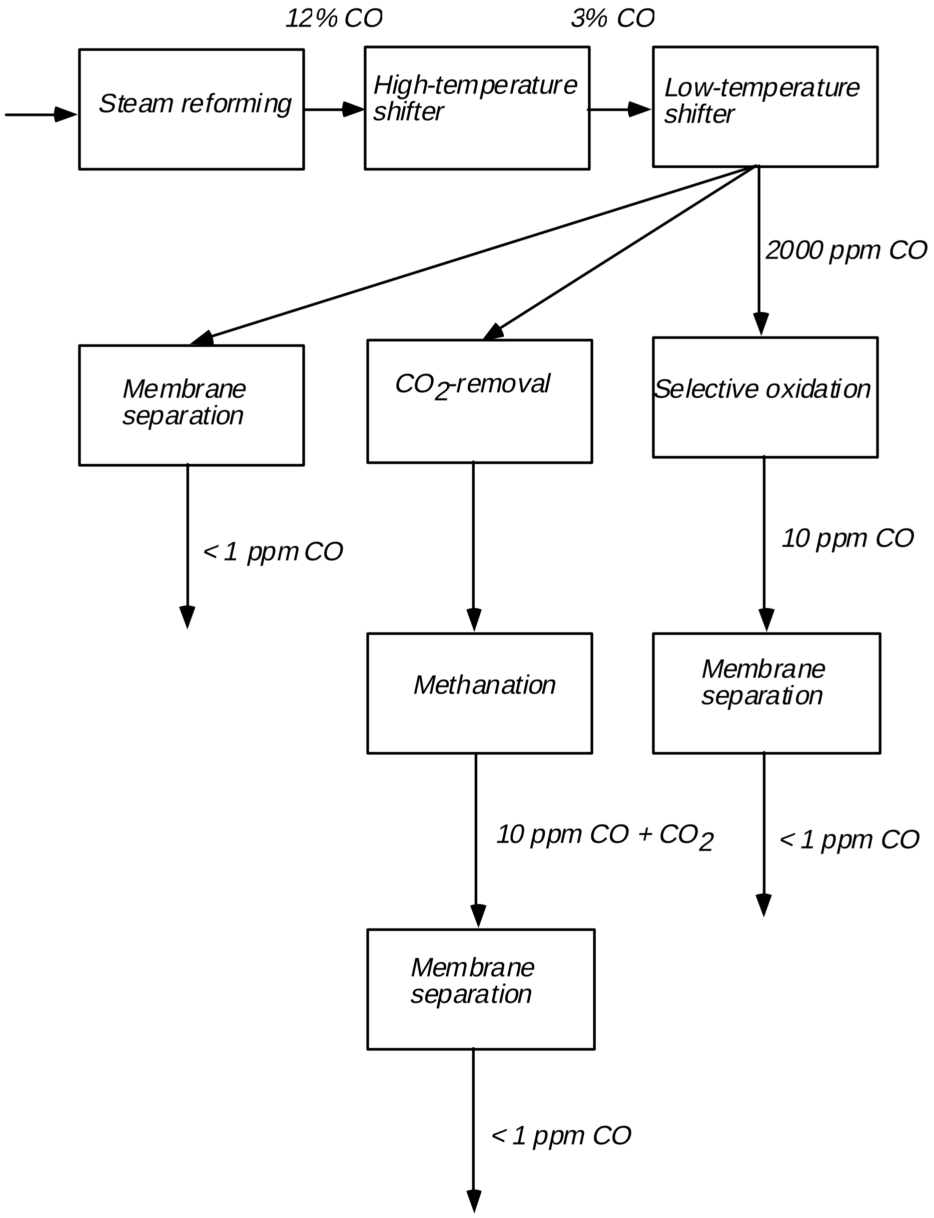


Figure 10 Different methods to purify the synthesis gas by means of CO.

Carbon dioxide can be effectively removed by means of a scrubbing process. After the scrubbing process, it is possible to remove traces of carbon oxides through methanation. The collective amount of carbon oxides is then below 10 – 20 ppm. Further refinement is possible through membrane separation. It is also possible to selectively remove carbon monoxide in the presence of hydrogen (utilisation of selective oxidation). In that case small amounts of air are added to the gas mixture and the oxygen preferably reacts with the carbon monoxide. It is possible to decrease the content of carbon monoxide to less than 10 ppm through selective oxidation. Consequently, it would be possible to use this gas in fuel-cell applications (i.e. the PEM-cell). If further refinement is required, it is possible to add membrane separation also in this case.

The need for pure hydrogen will vary due to the application:

- Reducing agent in oven processes, Primary reforming gas
- Hydrogenation, Gas composition leaving the low-temperature shifter
- Fuel-cell applications, Gas composition downstream the reactor for selective oxidation
- Electronic industry, Membrane filtration normally required

5.5 Hydrogen productivities of different CPHE-reactors

The performance of a number of CPHE-reactors where investigated with CatalystExplorer. In this section we use the notation by SWEP Int. AB for the different sizes of heat exchangers. The calculations are based on the wall-concept, since this concept will give the highest hydrogen productivity per unit volume of HE-reactor (gross volume). As an alternative, it is possible to use the cylinder concept. In that case it is necessary to implement 1 square metre of wire-mesh catalyst for a hydrogen productivity of 200 – 300 nm^3/h.

The smallest heat exchanger is abbreviated B5 and has the format l x b = 189 x 72 mm. The maximum number of plates is 60, which corresponds to a volume of 1.9 l and a weight of 3.2 kg. The estimated hydrogen productivity is 24 nm^3/h, equal to 12.6 nm^3/l of CPHE-reactor. In a cylinder alternative is would be necessary to install about 0.1 m^2 of wire-mesh catalyst for the same hydrogen productivity.

The maximum hydrogen productivity for the B12-format is expected to be about 108 nm^3/h. Hence, a B12 x 60 plates would be enough to supply a fuel-cell powered vehicle with hydrogen (necessary production rate about 50 nm^3/h of hydrogen). The largest hydrogen productivity for a single-train unit is 2 700 nm^3/h (B65 x 300 plates).

Calculated H_2-production for different types of SWEP-CPHE

Type	Format (lxb, mm)	Max. no. of plates	Volume (l)	Weight (kg)	Estimated H_2-prod (nm^3/h)
B5	189 x 72	60	1.9	3.2	24
B12	287 x 117	120	9.6	15.6	108
B35	393 x 243	250	58	93	775
B65	864 x 363	300	224	380	2700

Figure 11 Forecasted production rates of hydrogen for different types of CPHE-reactors (notation by SWEP Int. AB).

The performance calculations thus indicate a great potential for heat-exchanger reactors in steam reforming reactions. The reactors will be extremely compact and there is a good potential for integrating secondary steps (i.e. water-gas-shift and selective oxidation) into one single unit. Thus, it would be possible to design what might be called an “all-inclusive hydrogen generator”.

6. System lay-out

6.1 Steam reforming of natural gas

Figure 12 is a simplified diagram of a system for steam reforming of natural gas. Natural gas normally contains small amounts of sulphur compounds to enable detection of gas leakage. The reforming catalyst is highly sensitive to sulphur compounds and will be deactivated within a few days if these sulphur compounds are not removed.

The odorant species consist of a mixture of mercaptans and thiophenes. These compounds are not readily adsorbed on Zinc oxide and must consequently be converted into hydrogen sulphide prior to the adsorption on Zinc oxide. The process is called hydrodesulphurisation (HDS) and is carried out over a metal oxide catalyst at a temperature of 350°C. The sulphur compounds will react with hydrogen under formation of hydrogen sulphide.

Downstream the HDS-unit, steam is added in order to enable steam reforming of the hydrocarbons. The ratio between H_2O and C is normally above 3 to improve the yield during steam reforming and to avoid carbon formation. The inlet temperature to the reformer unit is around 600°C and the exit temperature is as high as 900°C. The reactions are highly endothermic and heat must be added to power the reforming process. Heat is generally supplied by means of separate burners, fired with hydrocarbons or primary synthesis gas.

The gas mixture will contain above 50% of hydrogen and about 10% of carbon monoxide at the exit. The concentration of hydrocarbons (mainly methane) is normally low, especially if secondary reforming is used. The balancing compounds are carbon dioxide and water vapour.

The gas mixture is cooled to about 350°C and contacted with a Fe/Cr-catalyst to convert carbon monoxide to carbon dioxide and hydrogen. This process is exothermic and the temperature of the gas mixture will increase through the reactor. The exit concentration of carbon monoxide is in the region of 3% by volume. The content of carbon monoxide is further reduced in the low-temperature shifter, which operates at 220 – 250°C. The catalyst contains CuO and ZnO and is highly sensitive to sulphur compounds. The exit concentration of carbon monoxide is as low as 0.2% by volume.

The next step in the consecutive gas purification might be selective oxidation of carbon monoxide with oxygen over a catalyst containing precious metals promoted with base metal oxides. The reaction is carried out at temperatures slightly above 100°C and the selectivity for carbon monoxide oxidation is indeed extremely high.

An optional concluding step might be membrane purification of hydrogen from other gases. The membrane can be either a porous polymer or a metal (Pd/Ag). The polymer membranes operate at temperatures below 100°C whereas metal membranes operate at temperatures between 300 and 400°C [6].

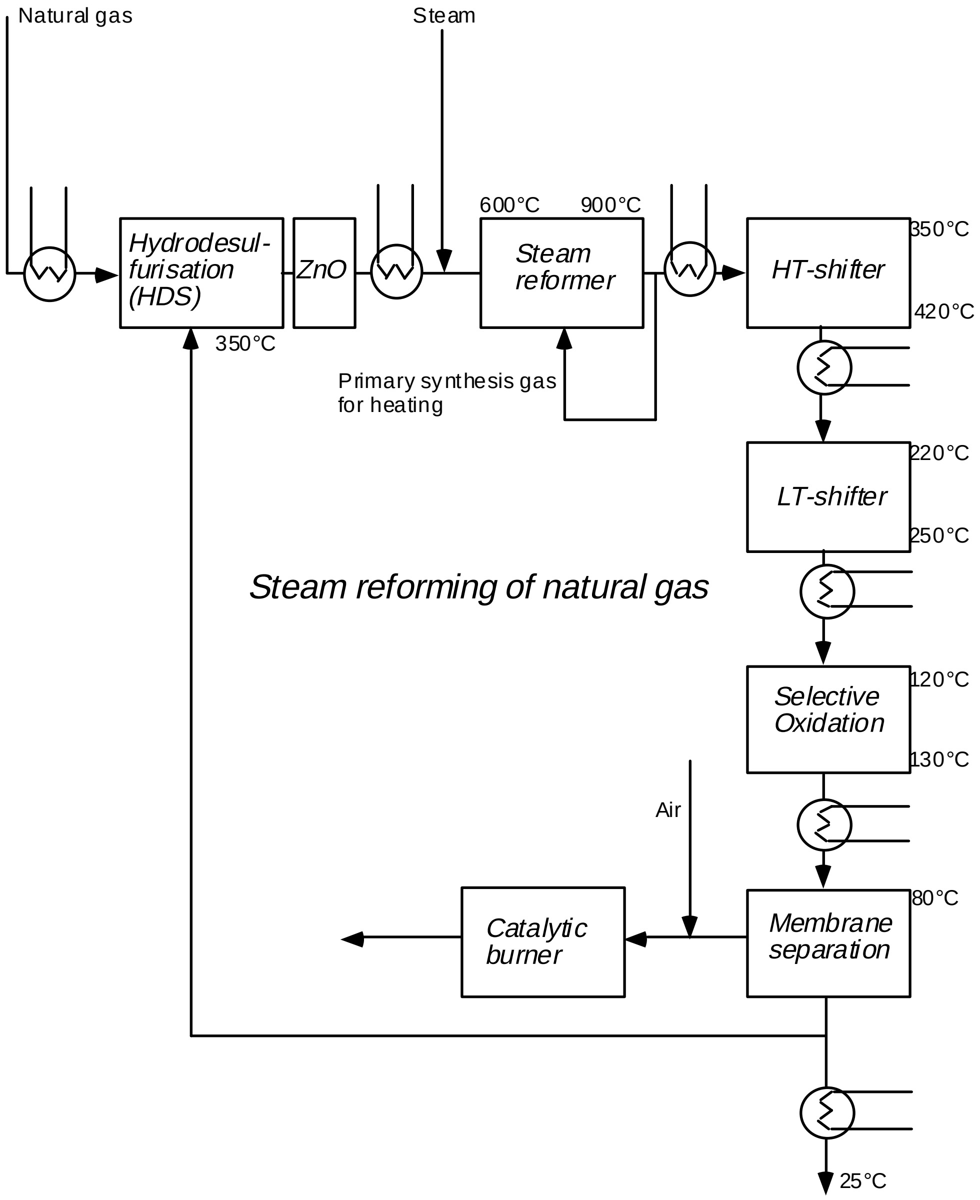


Figure 12 Lay-out of a system for steam reforming of natural gas.

The complete system for production of pure hydrogen from natural gas is rather complex. However, in situations where the quality of the hydrogen is less pronounced, the system might be considerably simplified.

6.2 Adiabatic reforming

Adiabatic reforming is when small amounts of air are added to the mixture of natural gas and steam. The heat necessary for carrying out the steam reforming reactions is produced through catalytic (or homogeneous) combustion. Adiabatic reforming will give less hydrogen yield but the process as such is convenient for the cylindrical CPHE-concept since the temperature of the plates can be decreased to improve the durability and life-time of the heat exchanger.

Adiabatic reforming is suggested to be the main alternative for steam reforming of natural gas.

6.3 Steam reforming of methanol

Steam reforming of methanol is much simpler than steam reforming of natural gas and naphtha. Since methanol is sulphur free it is possible to remove the HDS-step, see Figure 13. The temperature level is suitable for the wall coated CPHE-reactors (250 – 400°C). The gas purification train is similar to the system used in steam reforming of natural gas. Steam reforming of methanol is considered as the alternative to electrolysis in small-scale hydrogen production. Also, some major car manufacturers currently investigate the possibility of utilising methanol as a hydrogen carrier in vehicles powered by fuel cells. The necessary hydrogen supply (maximum load) would be around 50 nm^3/h of hydrogen. The gas mixture must be essentially free from carbon monoxide (only 10 – 20 ppm can be tolerated).

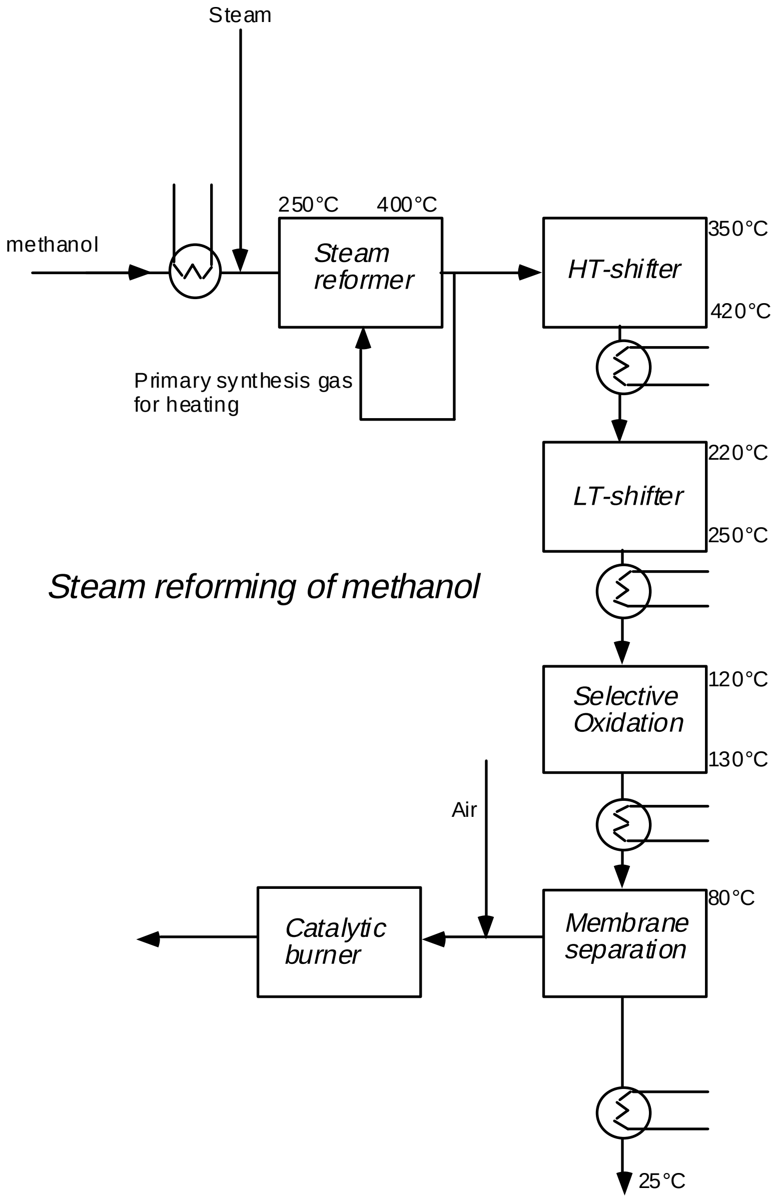


Figure 13 Lay-out of a system for steam reforming of methanol.

6.4 Ammonia cracking

Apart from steam reforming, it is also possible to produce hydrogen through ammonia cracking. In order to obtain high yields it is essential with high reaction temperatures and low pressures. Ammonia is sulphur free so it is possible to remove the HDS-unit. The gases leaving the reactor (if correctly dimensioned) will contain traces of ammonia, hydrogen and nitrogen. Figure 14 shows a simplified diagram of a cracking unit for ammonia. Figure 15 indicates the ammonia concentration if thermodynamic equilibrium is established.

Since no carbon monoxide is present, the gas purification train might be considerably simplified. The disadvantage with ammonia cracking is associated with ammonia storage and ammonia handling.

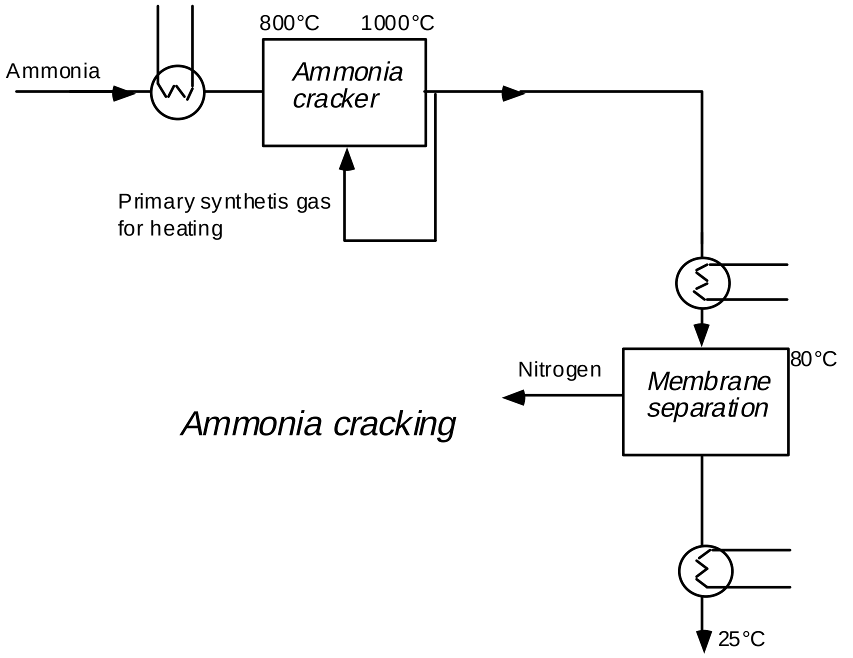


Figure 14 *Lay-out of a system for catalytic cracking of ammonia.*

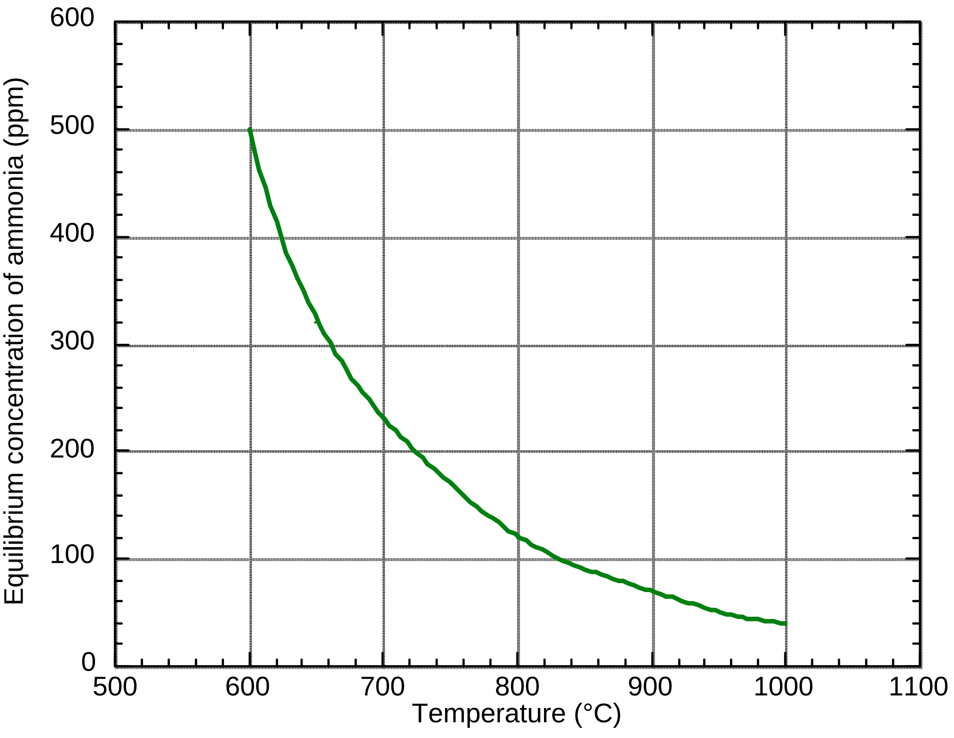


Figure 15 *Equilibrium concentration of ammonia vs. the temperature in ammonia cracking.*

7. Possible reactor lay-outs

7.1 Steam reforming

One possible lay-out of a system for adiabatic reforming of natural gas is shown in Figure 16. Sulphur free natural gas is mixed with small amounts of air and steam (water) at the inlet of the upper heat exchanger, which function as a pre-heater. The water is evaporated and the resulting gas mixture is heated to a temperature of above 300°C. The gas mixture is then fed into the second heat exchanger, which is of double cylinder type. The combustion-and reforming catalysts are installed as cylinders in the inlet port whereas a low-temperature shift catalyst is installed as a cylindrical catalyst in the outlet port. The air will cause combustion and heat production, which will power the endothermic steam reforming reactions. The gas mixture is cooled to about 250°C before it is brought in contact with the low-temperature shifter. Secondary air is injected and the gas mixture is cooled down to about 100°C in a third heat exchanger. A catalytic cylinder for selective oxidation of carbon monoxide is installed in the outlet port of the third heat exchanger. Temperature control is performed with a separate oil circuit, which guarantees that the maximum plate temperature is limited to about 350°C. Even if the adiabatic reforming is carried out at elevated temperatures, it is thus possible to decrease the thermal impact on the plates. The same principle is currently used in the domestic boilers, where natural gas is combusted in a heat exchanger cooled with water.

In order to obtain essentially pure hydrogen it is also possible to add membrane separation to the process.

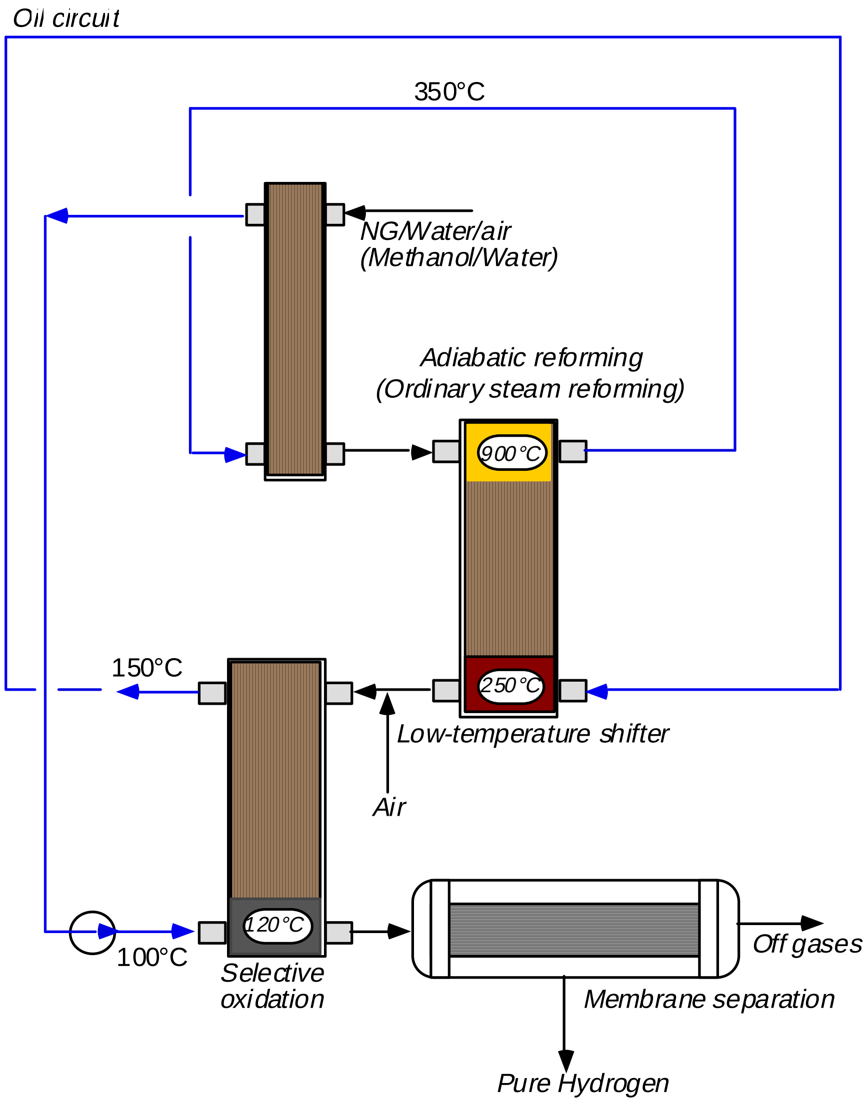


Figure 16 Possible lay-out of a system for adiabatic reforming of methane or ordinary reforming of methanol.

The lay-out for adiabatic reforming of natural gas may look complicated. Then again, if the demand concerning the hydrogen quality is less pronounced it is possible to simplify the system considerably.

If methanol is used as a feed stock it is not necessary to use adiabatic reforming, since the reaction temperature is between 250 and 400°C, i.e. close to the oil temperature. The oil must then be heated with a separate burner or by means of electricity.

In methanol reforming is also possible to integrate the reforming step and the high-temperature shifter into one structurised catalytic cylinder comprising of one portion of reforming catalyst and one portion of high-temperature shift catalyst. The plates are coated with low-temperature shift catalysts and selective oxidation is performed in the outlet port of the heat exchanger, see Figure 17. Some of the hydrogen is used to heat the gases entering the reforming reactor by means of catalytic combustion in a separate catalytic cylinder. As before, it is possible to add a membrane filtration step downstream the CPHE-reactors.

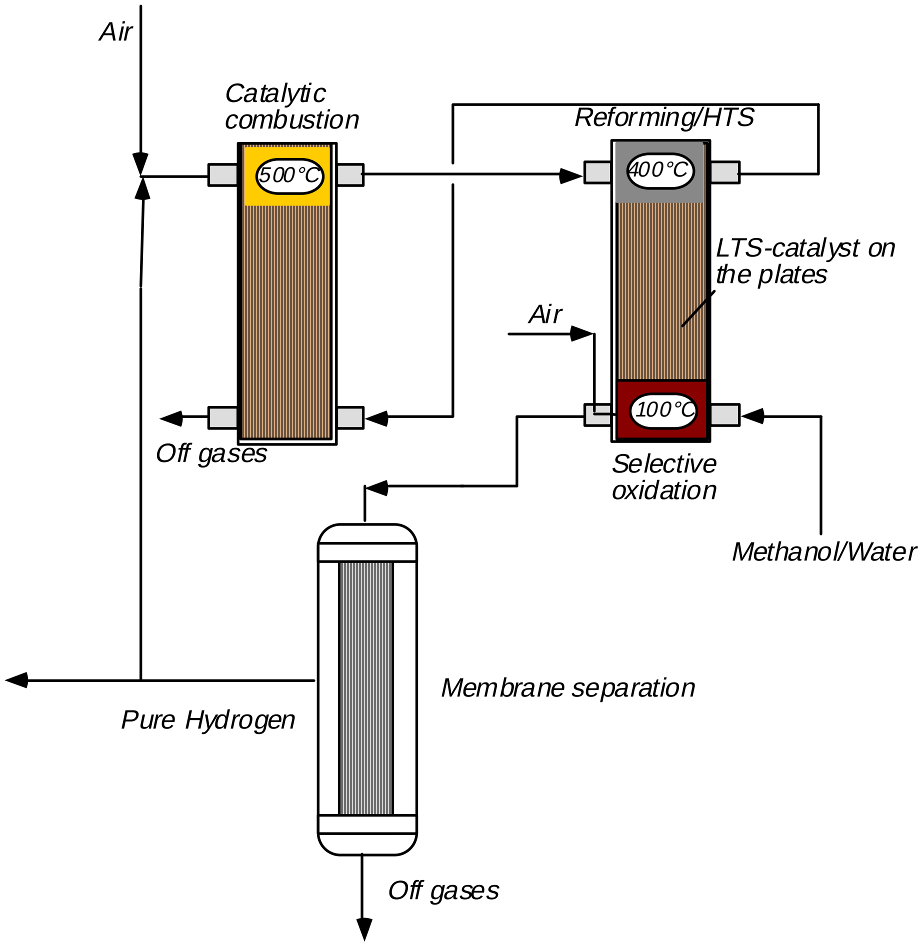


Figure 17 Integrated reformer unit for methanol.

The advantage with the integrated reformer unit is that the number of heat exchangers is reduced from three to two and that no oil circuit is required.

The ultimate solution would be to integrate combustion, reforming and high-temperature-shift into one structurised catalytic cylinder involving three different coatings (Figure 18). The plates are coated with catalyst for the low-temperature shift reaction and the selective oxidation is performed in the outlet port. Since the hydrogen leaving this reactor will be pure enough to be used in fuel-cell applications, we are talking about an all-inclusive methanol reformer. This unit will be extremely compact and highly integrated, which makes it suitable for automotive applications.

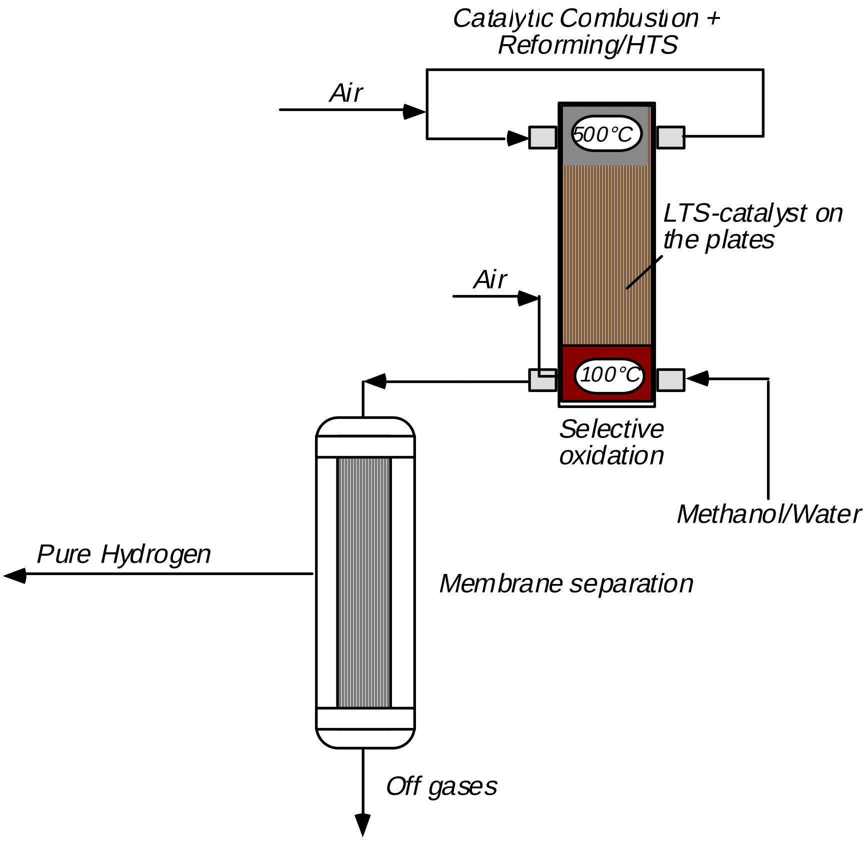


Figure 18 All-inclusive methanol reformer with structurised catalysis.

The all-inclusive methanol reformer is possible to design but will, of course, demand extensive development efforts. This kind of unit might be the solution to the current problems in small-scale automotive reforming of methanol. Similar systems might also be developed for reforming natural gas and naphtha. The problems here are associated to the high temperatures used in these processes. This fact will probably demand new materials in plates and brazing compounds.

7.2 Ammonia cracking

Ammonia cracking is a high-temperature process. The system could be designed as a recuperative heat exchanger with a catalytic cylinder and a catalytic wall coating. Ammonia cracking is performed within the catalytic cylinder at temperatures between 800 and 1000°C. Air is added to the hydrogen/nitrogen-mixture and a portion of the hydrogen is combusted catalytically (the plate is coated with combustion catalyst). The released heat will heat up the ammonia entering the reactor via conventional heat exchange.

The system is rather simple in process design. The problems are associated with the elevated temperatures, which will demand special materials in the heat exchanger and special brazing agents.

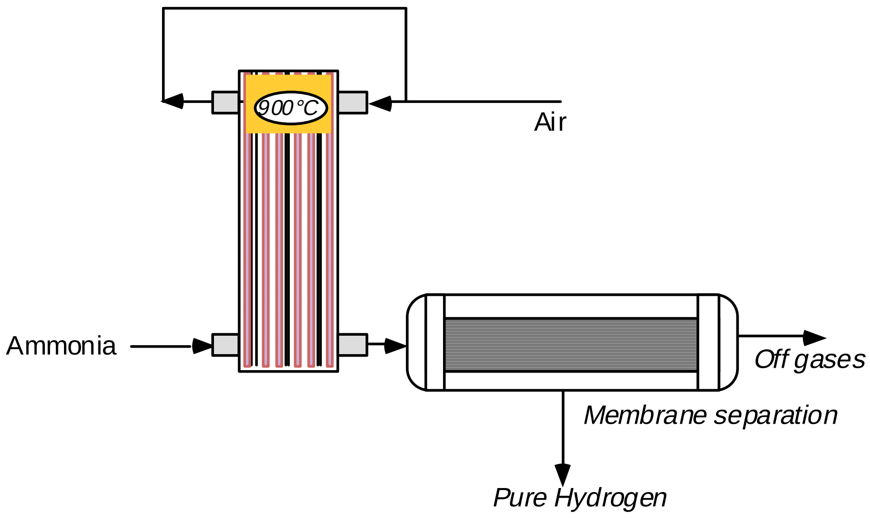


Figure 19 Possible lay-out of a system for ammonia cracking

It might be easier to design high-temperature units like this as tubular heat exchangers. The CPHE-design is probably suited for low-and medium temperature applications or for applications where the plate temperature can be controlled to acceptable levels.

8. Technical/economical evaluation of the CHE-process

8.1 Electrolysis for hydrogen production

Small-scale production facilities for hydrogen usually utilise electrolysis since such units are easy to operate and show low maintenance costs. The initial cost, however, is rather high. An electrolysis unit for production of about 50 nm^3/h will cost between 4 and 5 million SEK. The energy consumption for hydrogen production is between 4 and 5 kWh per nm^3 of hydrogen.

The hydrogen produced is rather clean but might need some purification from water vapour and traces of oxygen.

The expected lifetime of an electrolysis unit is above 10 years but it might be necessary to replace membranes and electrodes more often.

Apart from electrolysis there are number of other methods for small-scale production of hydrogen. However, these methods are only suitable for preparative production of hydrogen. Photo catalytic methods for water decomposition is a promising technology for the future.

In order to estimate the economical potential for CPHE-reactors in small-scale hydrogen production it is necessary to perform a detailed economic analysis where running costs as well as initial cost are considered.

8.2 Assumptions and production costs

In order to compare the CPHE-reactors with other commercial alternative it is important to define the input values for the economical analysis.

Figure 20 shows a comparison of the running cost for different techniques. The price for electricity is set to the window 0.8 – 1.0 SEK/kWh. The natural gas price is estimated to 40 – 60 SEK/GJ. The methanol price has varied greatly during the last few years [7]. Consequently the window for price variations concerning methanol is rather wide, 700 – 1500 SEK/t. The ammonia price has varied between 1600 and 2400 SEK/t during the same period of time [8].

The efficiency in steam reforming of natural gas is set to 0.7, i.e. about 30% of the energy in natural gas is lost in the process. The corresponding values for methanol reforming is 0.8. Ammonia cracking has an efficiency of about 0.7. In electrolysis, about 4.5 kWh of electricity consumed in the production of 1 nm^3 of hydrogen [9].

Four volumes of hydrogen can theoretically be produced for each volume of methane. The corresponding values for methanol and ammonia are 3 and 1.5.

It is possible to draw graphs showing the sensitivity to the electricity- and the feedstock prices. Such graphs have been plotted in Figure 20 for the various methods. The price windows with respect to electricity and feed stocks have also been indicated in the diagram. The estimated running costs can then be directly read from the y-axis in the diagram, i.e.:

- Electrolysis, about 4.50 SEK/nm^3
- Natural gas reforming, about 0.70 SEK/nm^3
- Methanol reforming, about 1.10 SEK/nm^3
- Ammonia cracking, about 1.30 SEK/nm^3

These figures clearly demonstrate why electrolysis cannot be used in large-scale production of hydrogen. Since the investment will add very little to the production cost in large facilities, it is extremely important to use a cheap feedstock, e.g. natural gas. When the size of the production unit is decreased it will be increasingly important to take the investment cost into consideration when making the economic analysis. Indeed for small units, methanol reforming and ammonia cracking are more economic alternatives than natural gas reforming. Electrolysis is probably always the most expensive method but is chosen due to simplicity and low maintenance cost.

At this moment, it is very difficult to estimate the investment costs for a CPHE-unit. If we assume a life time of 10 years of the units and anticipate that the investment cost shall be paid off according to the total volume of hydrogen produced during that time, it is possible to show the price sensitivity in relation to the size of the facility.

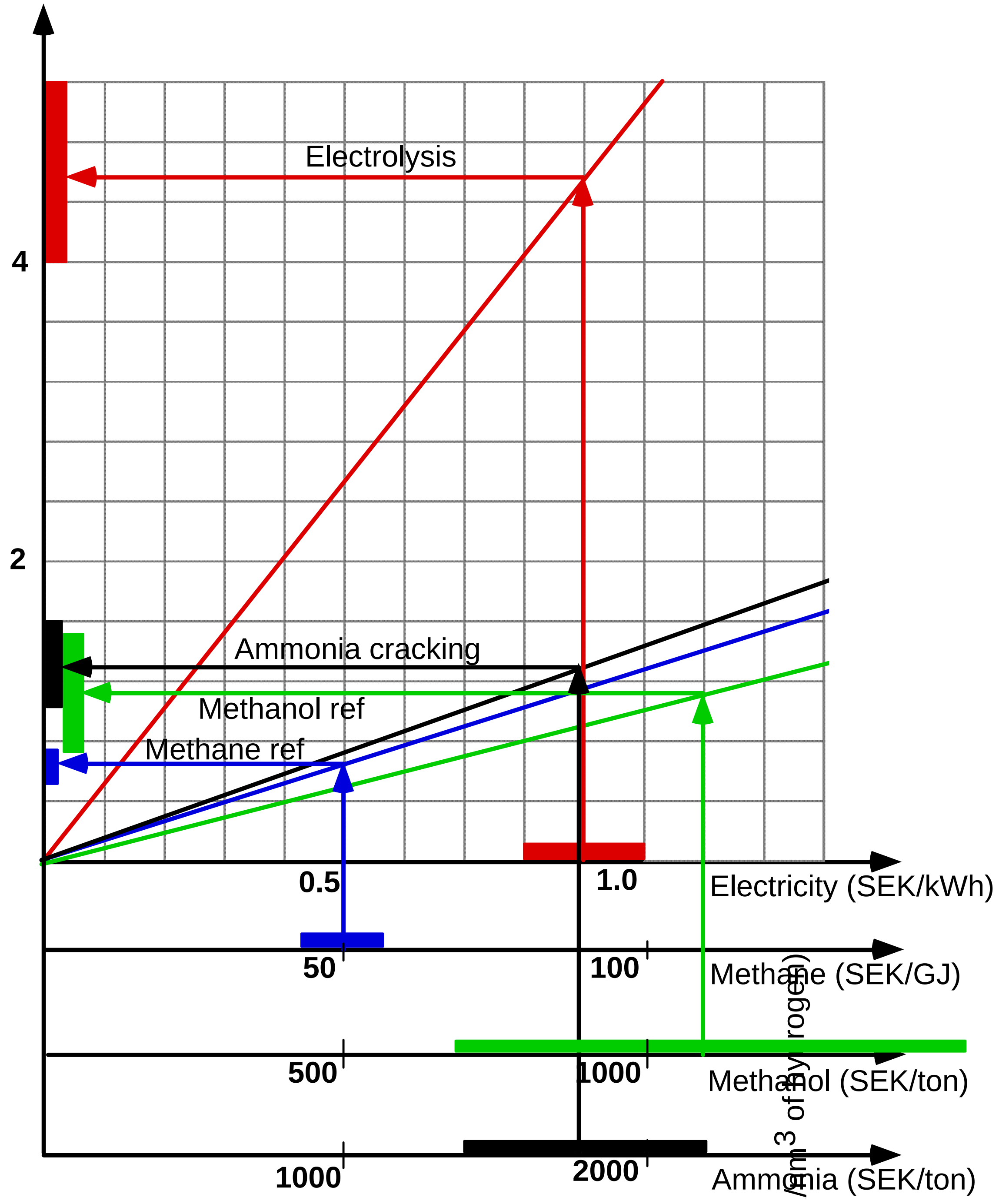


Figure 20 Comparison of the the hydrogen production cost for electrolysis, steam reforming (natural gas and methanol) and ammonia cracking. Only the sensitivities to the fuel-and electricity prices are shown.

The investment cost for an electrolysis unit for 50 nm^3/h is about 4.2 million SEK [10]. If we scale this investment cost according to an ordinary power-law function (exponent 0.67), we are able to derive corresponding investment costs for smaller and larger facilities. In the analysis, we assume that the investment cost for a CPHE-system for natural gas reforming is cost neutral in relation to electrolysis.

The methanol-reforming unit is expected to be 25% cheaper whereas the ammonia-cracking unit is expected to be 50% cheaper for the same size. These figures are of course rough estimates but are justified by the simpler process lay-out of these processes. Service and maintenance is set to 0.1 SEK/nm^3 of hydrogen produced, according to the literature [11].

When all parameters affecting the production costs are summarised, we end up with figures according to Table 1.

Table 1 Production cost in units with different sizes. Investment costs (I), running costs (R) and costs for maintenance (M) are taken into consideration. All figures are in the unit SEK/nm^3 of hydrogen produced.

Unit size (nm^3/h)	Electrolysis			Natural gas ref.			Methanol ref.			Ammonia cracking		
	I	R	M	I	R	M	I	R	M	I	R	M
10	2.00	4.50	0.10	2.00	0.63	0.10	1.50	1.06	0.10	1.00	1.30	0.10
100	1.10	4.50	0.10	1.10	0.63	0.10	0.83	1.06	0.10	0.55	1.30	0.10
1000	0.57	4.50	0.10	0.57	0.63	0.10	0.42	1.06	0.10	0.29	1.30	0.10

Figure 21 shows the total production cost (SEK/nm^3 of hydrogen) versus the production capacity of hydrogen (nm^3/h). The production price will decrease from about 7.50 SEK/nm3 to 6.50 SEK/nm^3 when the unit size is increased from 10 to 500 nm^3/h (largest single-train unit in electrolysis). The same cost window will be 3 SEK/nm^3 (at 10 nm3/h) to 1.30 SEK/nm^3 (at 3000 nm^3/h) when using CPHE-reactors for steam reforming (natural gas or methanol) or ammonia cracking. The production price is even lower in large-scale units (conventional units for steam reforming or partial oxidation). Such units can not be used in small scale production since the investment costs are to high.

We have also tried to estimate the specific cost for gas purification (arriving at pure hydrogen). The production cost for primary synthesis gas corresponds to the difference between the cost for reforming/cracking and the cost for gas purification.

The economical analysis clearly demonstrates the economical potential for small-scale hydrogen production in CPHE-reactors. These reactors might replace electrolysis in many applications where natural gas, methanol or ammonia is available. It is also important to notice that natural gas reforming, methanol reforming and ammonia cracking are equal from an economic point of view. In large-scale production of hydrogen, natural gas should be used as the feedstock, since the running costs then will be lower.

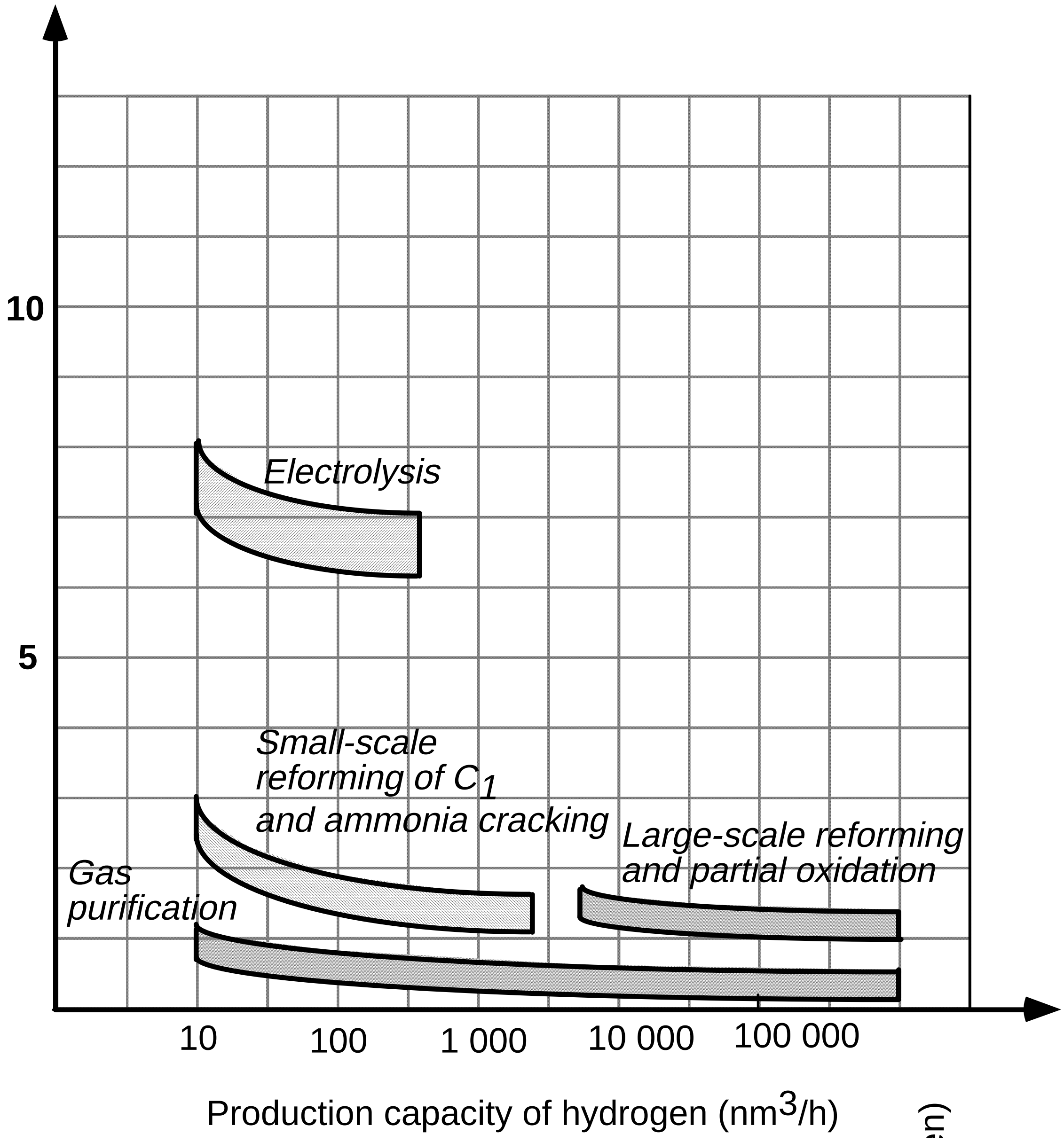


Figure 21 *Total production cost of hydrogen vs. the size of the units. Investments, fuel/electricity-prices and maintenace/operation are considered.*

8.3 Advantages of the CPHE-concept

The CPHE-concepts described in this report will make it possible to design and to produce compact and highly integrated reactors for small-scale reforming of natural gas and methanol and for ammonia cracking.

The volume of the production units could easily by decreased by a factor of 10 or more. A conventional unit for stem reforming of natural gas and naphtha will contain a number of long tubes placed in a combustion room, which is heated with gas burners. Thus, the unit-size for production of 3 000 nm^3/h of hydrogen can be as large as 10 m^3 or more. However, most of the volume is due to the burner installation, which is quite space demanding in traditional units. We expect to produce the same amount of hydrogen in a compact CPHE with a size of about 0.5 m^3 (B65 x 300 plates). Also, it might be possible to include carbon monoxide removal (the water-gas shifters) into the same unit through structurised catalysis to gain further compactness.

In the “all-inclusive”-design for methanol reforming it will be possible to produce essentially pure hydrogen for fuel cell applications in one single unit. The unit cost will of course be favoured by the high degree of integration. Even if the design calculations have been performed for ambient pressure, it is possible to pressurise the units to gain even more performance.

The production cost for hydrogen is expected to be much lower in the CPHE-units compared to conventional electrolysis. Thus, the CPHE-concept will give the customers new and cheaper alternatives for small-scale production of hydrogen. Apart from the low production cost, the CPHE-concept will bring additional advantages like compactness, a high degree of integration and simplicity to the customers. Depending on the format of the CPHE, the productivity for a single train unit might vary between about 2 nm^3/h (B5 x 6 plates) and 2700 nm^3/h (B65 x 300 plates).

It is possible to place a number of CPHE-units in parallel if a higher hydrogen production is requested. In real large-scale syngas production, e.g. upstream ammonia-and methanol production facilities, conventional one-train units utilising natural gas or naphtha as feed stocks will be economically favourable. The CPHE-concept should be utilised in small-and medium-scale hydrogen production.

9. Market assessments

Most of the hydrogen produced today is utilised in traditional processes. The overarching consumer of hydrogen is the process industry, see Figure 22, which show the breakdown of hydrogen utilisation in the U.S. [12]. From the Figure it is clear that most of the hydrogen goes to ammonia production and petroleum refining. Relatively small amounts are used by small consumers, e.g. in oven processes as reducing agents. However, the number of small users is much higher than the number of large-scale users of hydrogen. A large process chemical plant (e.g. ammonia production) may need as much as 100 000 nm^3/h of hydrogen whereas the corresponding need for small-scale users might be 10 – 1000 nm^3/h.

The large consumers of hydrogen are not using pure hydrogen, but synthesis gas. Since electrolysis provide essentially pure hydrogen, this alternative is not applicable to these processes from a technical point of view. On the other hand, CPHE-reactors for reforming might be used for the supply of synthesis gas for smaller production facilities. Figure 23 summarises the utilisation of synthesis gas in the process industry. CPHE-reactors could probably find applications in synthetic chemistry, i.e. in the production of special chemicals through hydrogenation or Fischer-Tropsch-releated chemistry.

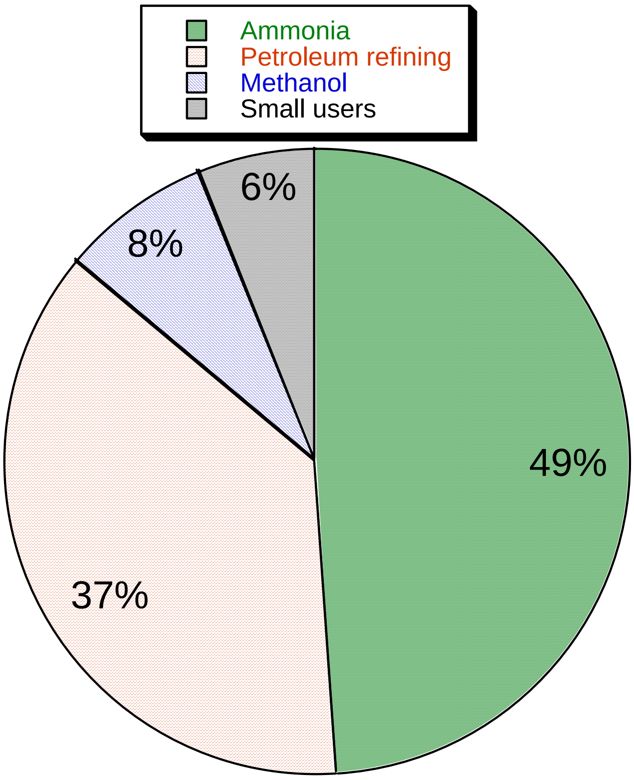


Figure 22 Relative importance of different hydrogen consumers.

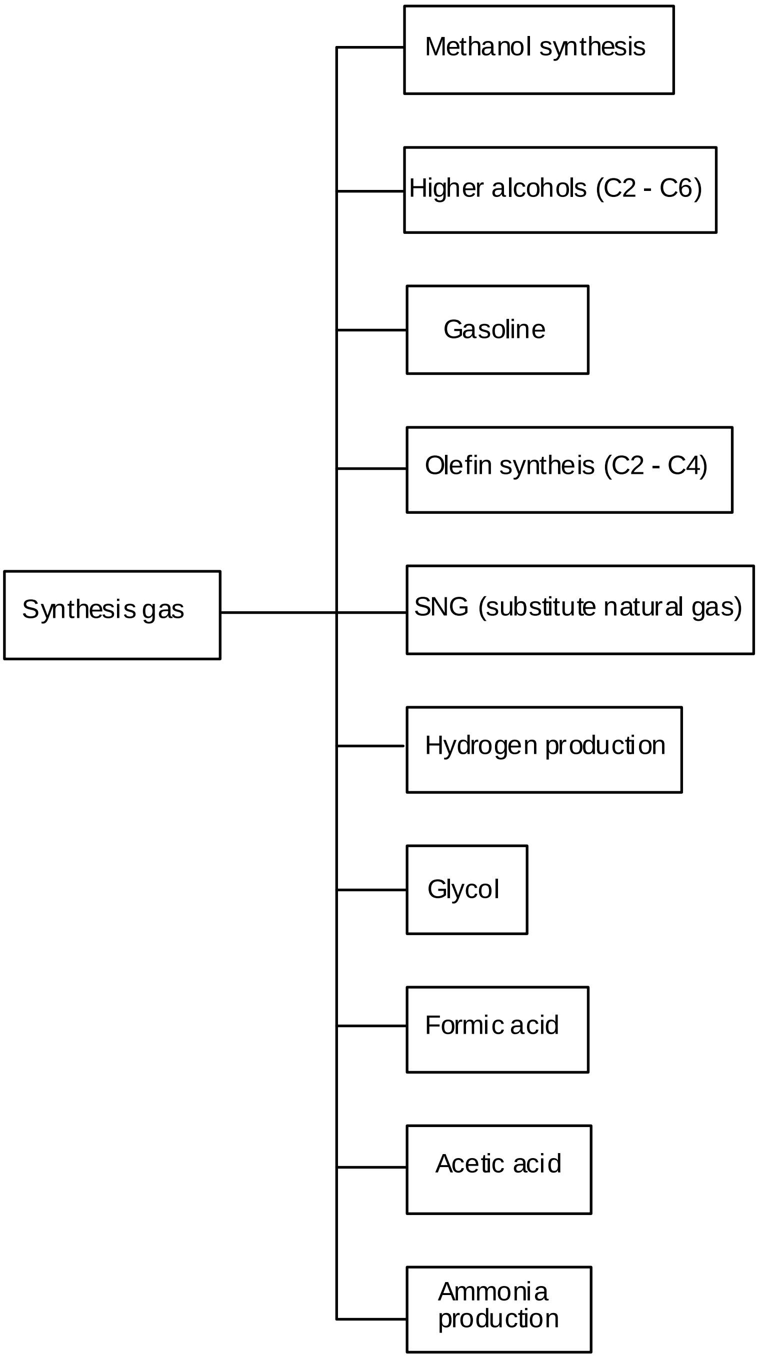


Figure 23 Utilisation of hydrogen and associated gases.

The worldwide consumption of hydrogen is expected to explode during the first decades of the 21st century, mainly as a result of the development of the fuel-cell technology and the evolution of a hydrogen economy. Figure 24 gives an indication of the annual hydrogen consumption from the 1980s and forward [13]. Today's worldwide consumption of hydrogen is in the neighbourhood of 1000 Gm^3/a.

However, the principal market for the CPHE-concept is as a complement or a substitute for electrolysis. Today about 5% of the hydrogen is produced by means of electrolysis, i.e. 50 Gm^3/a [14].

There are a number of applications for small-scale utilisation of hydrogen:

- Metallurgy (reducing agent)
- High-temperature flames (oxygen + hydrogen)
- Plasma technology (for heating purposes)
- Semiconductor technology (in chemical vapour deposition)
- Water treatment
- Fuel-cells (electricity production)

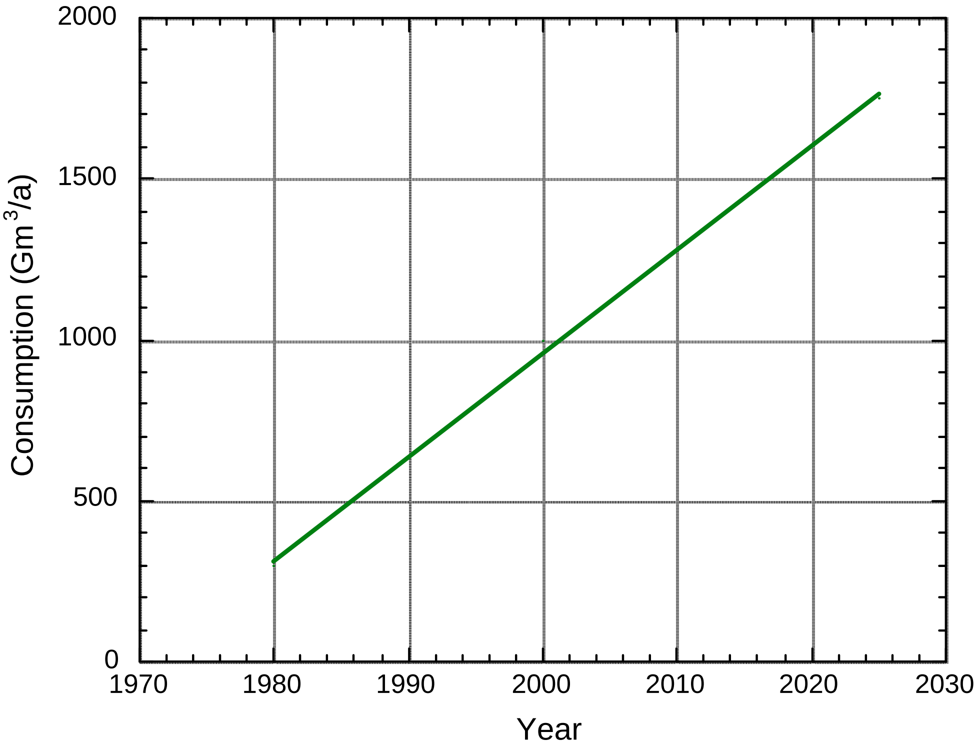


Figure 24 *Annual worldwide consumption of hydrogen. Actual consumtion and forecasted consumption during the fist decades of the 21th century.*

The need for small-scale production of hydrogen is expected to increase tremendously, if the car industry takes the step to introduce fuel-cell powered vehicles on the market. The major car manufacturers expect to launch such vehicles during the fist decade of the 21th century. The market is the expected to grow rapidly and the corresponding market potential might be as high as 20 – 30 million units/a in 2020. The current PEM-cell needs essentially pure hydrogen in order to work properly. The “all-inclusive” reformer presented in this report might be the solution for the hydrogen supply. However, there are different trends, which are followed by the car manufacturers:

- Methanol reforming on-board the vehicle
- Naphtha reforming on-board the vehicle
- Hydrogen storage on board the vehicle and reforming at the filling stations (natural gas)

Some car manufacturers also investigate the possibility to use hydrogen as the fuel in internal combustion engines in order to improve the efficiency and to decrease the emissions.

The CPHE-concept suits all these alternatives nicely. We are in all cases talking about small (individual vehicles) or medium (filling stations) hydrogen consumers. Indeed, the evolving market for alternative propulsion systems for vehicles might be the most important market for CPHE-reactors in fuel processing and steam reforming.

The long-term solution of the environmental impact on the global society, is of course the development of a hydrogen economy where hydrogen is produced by renewable sources, e.g. trough photo chemical methods.

10. Concluding remarks

This report clearly demonstrates the technical and economical potentials of CPHE-reactors in small-scale production of hydrogen. There are a number of possible design solutions, including heat exchangers with catalytic cylinders and/or heat exchangers with coated walls.
The superior mass-and heat transfer characteristics in wire-mesh catalysts and in CPHE-reactors enable us to improve the utilisation of the catalytically active material tremendously, as shown by the experiments. Indeed, it might be possible to decrease the reactor-size for a specific hydrogen production rate by a factor of 10 or more in comparison to traditional units.

Methanol reforming is easiest to realise since the reaction temperatures are moderate.
Reforming of natural gas and naphtha or ammonia cracking will demand much higher temperatures, which will increase the thermo-mechanical impact on the CPHE-units. In such high-temperature applications it will be necessary to use the cylinder concept and to certify that the plates are cooled by means of a cooling agent. In order to use the cylinder concept in reforming, we propose adiabatic reforming, where small amounts of oxygen (air) are introduced in the mixture of hydrocarbons and steam. The parallel combustion process will power the endothermic reforming processes.

Economic estimations indicate that the CPHE-concept might cut the hydrogen-production price by more than 60% compared to conventional electrolysis. Clearly, it is now important to follow up this pre-design study with prototype tests. It is necessary to verify the calculated hydrogen production rates but also to make conceptual studies concerning different CPHE-designs.

The first tests should focus on methanol reforming since this alternative is easiest to realise. Similar tests should be performed with other feed stocks, e.g. natural gas and naphtha in the continued studies. The development work must also focus on the possibilities of integration, i.e. the "all-inclusive-reformer" design. Thus, the continued work can be divided into the following phases:

- Verification and conceptual tests with methanol reforming
- Conceptual tests with reforming of natural gas and naphtha
- Development and design of a totally integrated reformer unit, i.e. the "all-inclusive reformer"

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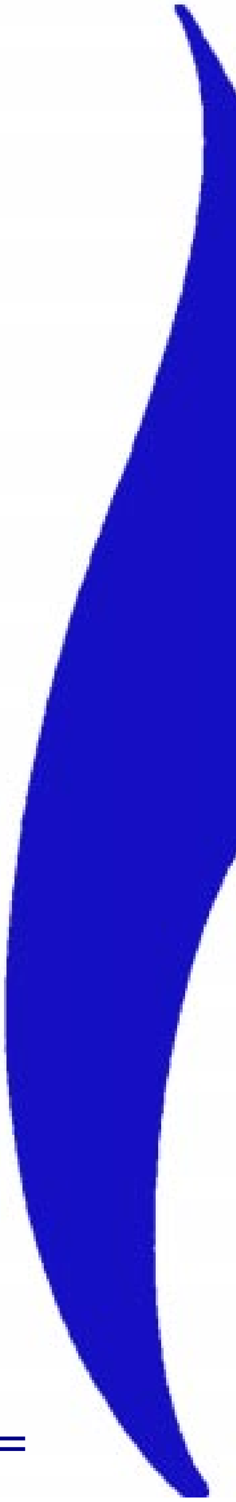

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