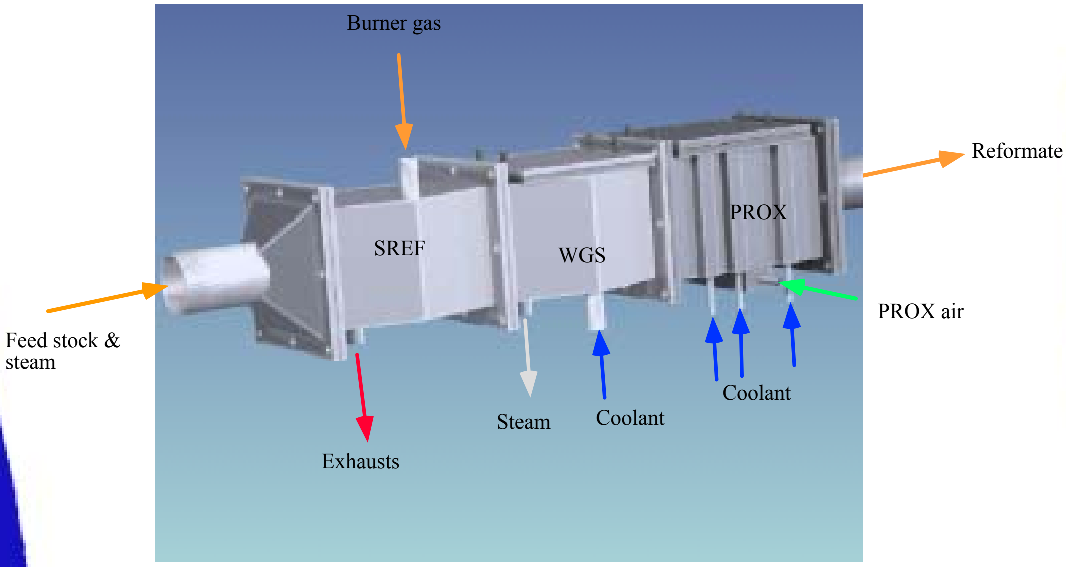
Rapport SGC 139

Fuel processor for small-scale production of hydrogen – Experimental study



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Catator AB
Försvarets Materielverk
Sydkraft Gas AB
OptiCat International AB
ABB Group Services AB, Corporate Research
Statens Energimyndighet

SVENSKT GASTEKNISKT CENTER AB

Johan Rietz

SUMMARY

A compact fuel processor (Ultraformer) has been designed, constructed and experimentally evaluated on the request of Swedish Gas Centre (SGC). The design suggestion was based on Catator's background knowledge concerning catalysis, active phases and reactor design, previously reported (appendix A).

The overarching goal was to present a compact and scalable reactor concept including fuel processing and gas purification with respect to CO in order to reach fuel-cell quality (for PEMFC applications). The unit should be able to run on a variety of feedstocks, i.e. biogas, natural gas, LPG, alcohols and heavier hydrocarbons. It should have a wide turn-down ratio (preferably 1:10) and a high thermal efficiency (about 80%). The unit should also enable a quick start-up.

The design work indicated that it is possible to build a single-train reactor with the above characteristics. The single-train reactor comprises all the necessary catalytic steps including steam reforming, water-gas shift and preferential oxidation. The reactors were constructed and evaluated individually prior to system assembly. It was found that all reactors could meet the specifications concerning outlet gas qualities. The next step was to assemble the integral system including not only the single-train reactor but also all auxiliary components necessary for operation, i.e. heat exchangers, fans, pumps, valves and automation.

The design of the integral system was performed in accordance with the P/I-diagram previously suggested. The system enables an effective recuperation of the process with limited heat losses and a simple control algorithm including cheap components.

The commissioning work was performed in steps. The unit was first run in manual mode in order to check all mechanic components and the overall performance. The automation was then included in a second step.

Experimental evaluations were performed with a number of feedstocks including biogas, natural gas, LPG, Naphtha, methanol and ethanol. The hydrogen yield varied between 90 (hydrocarbons apart from alcohols) and 99% (alcohols) and the outlet CO-concentration varied between a few ppm and about 150 ppm. In order to increase the hydrogen yield further it is necessary to decrease the exit concentration of hydrocarbons (especially methane). The most effective way of doing this is to increase the steam reforming temperature. Experiments with extremely high reformer temperatures (850°C+) indicated a potential to bring up the hydrogen yield to 98/99% in natural gas processing. The outlet concentration of CO was rather stable in the region 10 – 40 ppm, independent on the steam:air ratio (2.5 –5), the steam reforming temperature (700 –850°C), the load (10 –100%) and the O_2:CO-ratio in the PROX-step (if the ratio is above 1.3).

Experiments with some air injection into the steam reformer indicated a simple way to improve the system performance further; improved thermal response and higher temperatures in the steam reformer (higher hydrogen yields). Start up without air injection into the reformer was within 30 minutes (calculated from start-up to fuel-cell quality of reformate at full load). This lag time could be decreased to about 15 minutes if air-injection was used (rapid heat). Optimisation of the start-up sequence with distributed air-supply would enable us to reach start-up times of less than 10 minutes.

The automatic control is simple and reliable. It is based on a start-up sequence, which is trigged by an ignition button. A number of temperature alarms are used as trig points for starting the water supply and the supply of feed stock. Load modulation is via solenoid valves powered by pause/pulse relays. Load control is by choosing an appropriate ratio between pause- and pulse times. This control system was found to work well and is indeed simple and cheap. Further improvements and refinements are possible but the basic concept give good enough performance.

There are a number of potential problems, which remains to be solved The most relevant issues for further studies are:

- Catalyst deactivation and system degradation
- System stability and robustness
- Mechanical design including material choice to avoid damages (thermal fatigue etc).

Catalyst deactivation will in time affect the performance of the system. It is necessary to gather complementary information on the stability of the active phases chosen and possibly to find better candidates. This is probably of special interest if fuels with a high sulphur content and a low H:C-ratio are used. The system can probably be built to give an improved stability against process deviations caused either by catalyst deactivation, fouling or by changes in the performance of mechanical components like fans and pumps. The strength of the construction should be reviewed in the light of thermal fatigue and chemical corrosion (e.g. metal dusting) since such phenomena might give rise to catastrophic system injuries.

A number of following-up projects are proposed, starting from the knowledge gathered in this project. The following-up studies are directed to deactivation & reliability issues concerning the Ultraformer system and to the integration of fuel cells (PEMFC and SOFC) into the Ultraformer system.

SAMMANFATTNING

En kompakt vätgasgenerator (Ultraformer) har designats konstruerats och utvärderats experimentellt på uppdrag av Svenskt Gastekniskt Center AB. Designförslagen baserades på Catators bakgrundskunskap inom områdena katalysatorteknik, aktiva faser och reaktordesign, vilket tidigare redovisats (appendix A).

Det övergripande målet var att presentera en kompakt och skalbar reaktor innefattande vätgasgenerering och gasrening med avseende på kolmonoxid (CO). Avsikten var att erhålla en gasblandning med bränslecellkvalitet. Enheten ska kunna utnyttja olika bränslen, d.v.s. biogas, naturgas, gasol, alkoholer, och tyngre kolväten. Vidare ska verkningsgraden vara hög (≈80%) och reglerintervallet brett (1:10). Enheten ska kunna startas snabbt och vara följsam vid lastväxlingar.

Designarbetet visade att det skulle vara möjligt att konstruera en integrerad reaktor med ovan nämnda egenskaper. Reaktorsystemet innehåller reformer, vattengasreaktor och en reaktor för selektiv oxidation av CO. Samtliga reaktorer utvärderades individuellt före montaget i en speciell försöksrigg. Undersökningarna visade att samtliga reaktorer uppfyllde målspecifikationerna. I följande steg skedde montage av hela bränsleberedningssystemet, innefattande reaktorer och olika hjälpkomponenter (värmeväxlare, pumpar, fläktar, ventiler etc).

Systemdesignen följde tidigare redovisat processchema. Bränsleberedningssystemet möjliggör en effektiv värmeåtervinning med små värmeförluster samt kontrolleras av ett enkelt och robust styrsystem.

Driftsättningsarbetet skedde i steg. Enheten utvärderades först i manuellt läge (utan automation) i avsikt att kontrollera all hårdvara och olika samspelseffekter. Automationen kopplades in/undersöktes i ett senare skede.

Experimentella utvärderingar skedde med ett flertal gasformiga/flytande bränslen (biogas, naturgas, gasol, metanol, etanol samt bensin). Vätgasutbytet varierade mellan 90% (kolväten utom alkoholer) och 99% (alkoholer) och CO-halten varierade mellan ett fåtal ppm och ca 150 ppm. För att ytterligare öka vätgasutbytet måste halten av kolväten (speciellt metan) sänkas, vilket kan ske genom en ökning av reaktionstemperaturen. Experiment med extremt höga reformertemperaturer (850°C+) visar att det är möjligt att nå vätgasutbyten så höga som 98-99% då naturgas utnyttjades som bränsle. CO-halten låg samtidigt i intervallet 10 – 40 ppm, relativt oberoende av ånga:kolväteförhållande (2.5 – 5), ångreformeringstemperatur (700 – 850°C), last (10-100%) och O_2:CO-förhållande i PROX-steget (om förhållandet översteg 1.3).

Försök med luftinjektion i reformern visade på ett enkelt sätt att förbättra systemets egenskaper; förbättrad termisk respons och ökade vätgasutbyten (högre reaktionstemperatur). Om kallstart sker utan luftinjektion tar det ca 30 minuter innan gasblandningen har bränslecellskvalitet. Denna tid kan reduceras till ca 15 minuter om luft tillförs vid starten. Det är troligt att starttiden kan reduceras till under 10 minuter om driftparametrarna optimeras. ytterligare.

Kontrollsystemet är enkelt och tillförlitligt. Det baseras på en uppstartssekvens som triggas av en startknapp. Ett antal temperaturalarm används därefter som triggsignaler för start av olika delsystem. Lastmodulering sker via paus/puls-reläer, som styr olika magnetventiler i systemet. Lasten ställs härigenom via paus/puls-förhållandet. Styrsystemet fungerar väl, är enkelt och dessutom förhållandevis billigt. Ytterligare förbättringar är möjliga men grundkonceptet ger tillräckligt goda egenskaper för aktuell tillämpning.

Det finns ett antal potentiella tekniska problem/risker som måste kartläggas, varvid de viktigaste är:

- Katalysatordeaktivering
- Systemstabilitet och robusthet
- Mekanisk design och materialval (termisk utmattning etc)

Katalysatordegraderingen kommer så småningom att påverka systemets prestanda negativt. Det är härvid nödvändigt att samla ytterligare information om stabiliteten hos de valda aktiva faserna och möjligtvis att finna bättre alternativ. Detta är av speciell vikt då bränslen med högt svavelinnehåll och lågt H:C-förhållande används. Systemet kan sannolikt modifieras för att ge en förbättrad stabilitet vid processavvikelser orsakade av katalysatordegradering, försämrad värmeöverföring eller felfunktion i mekaniska komponenter. Den mekaniska konstruktionen bör utvärderas i ljuset av termisk deaktivering och kemisk korrosion (grafitbildning) eftersom sådana fenomen kan leda till katastrofala skador på systemet.

Ett antal uppföljningsprojekt presenteras med utgångspunkt från de vunna erfarenheterna i detta projekt. Uppföljningsprojekten inriktas mot deaktiveringsfenomen och tillförlitlighetsaspekter samt kring studier avseende integration av bränsleceller (PEMFC och SOFC) med Ultraformersystemet.

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Appendices:

1. Background

Catator AB (CAT) has evaluated a fuel processor system for small-scale production of hydrogen from various hydrocarbons on the request of Swedish Gas Centre (Svenskt Gastekniskt Center AB). The project as a whole was divided into two consecutive phases, a) Feasibility and design phase and b) Construction and evaluation phase. The results obtained during the first phase of the project are reported elsewhere (see appendix A).

There is an increasing interest worldwide to develop novel reactor systems for small-scale hydrogen production. The main driving force is associated with the development of a fuel cell market for different automotive and stationary applications. Fuel cells are powered by hydrogen and the only reasonable source for hydrogen today is hydrocarbons, fossil or renewable. It is also believed that fuel cells will replace a majority of the internal combustion engines in the future. Hence, the development of a hydrogen economy goes hand in hand with the worldwide efforts in the areas of small-scale fuel processing and fuel cell technology. Apart from the fuel cell area there are a number of applications for small-scale hydrogen production in various areas, e.g. metallurgic industry, electronic industry, food industry and pharmaceutical industry.

CAT has during the last years been heavily engaged in the development of novel catalyst- and reactor systems. The main focuses have been directed to process intensification, i.e. to increase the output of a chemical reactor system per unit volume. CATs design solutions are especially favourable in cases where the reaction is performed under simultaneous heat transfer, like in combustion and fuel processing.

During the first phase of the project a tentative reactor design was proposed and evaluated from a theoretical point of view. It was found that a single-train reactor comprising a steam reformer a water-gas-shift reactor and a PROX-reactor should be able to deliver a hydrogen rich gas mixture with fuel cell quality. The design was based on CATs patented wire-mesh catalysts and heat-exchanger structures. The catalysts carried novel formulations in order to increase the performance and decrease the problems with deactivation. All catalyst formulations were carefully evaluated with the gas compositions present in the reformer system. Catalyst- and reactor dimensioning were performed with CATs dynamic simulation code for catalytic reactors, CatalystExplorer. A control algorithm for the reactor system was also proposed. The control system is based on a number of temperature regulators and pause/pulse relays, which control solenoid valves for different medias, e.g. fuel, water and air. The fuel processor was designed to yield about 10 nm^3/h of hydrogen at full conversion of the feedstock. This hydrogen production corresponds to about 30 kW of hydrogen and is enough to power a fuel cell designed for 15 – 20 kW of electricity.

The second phase of the project is directed to the construction, assembly, commissioning and experimental evaluation of the fuel-processor system designed during phase one. The reactors are evaluated individually prior to the system assembly. These evaluations are performed in order to verify the dimensioning work. The entire reactor system is then assembled and commissioned. A number of relevant parameters are investigated and different feedstocks are evaluated.

This final report describes the design work as well as the experimental verifications/evaluations. The report relates important findings and highlights possible problems and technical risks. In order to evaluate the long-time operability of the system, a long-time test should be performed. This evaluation is not included in the current project but should be carried out later on.

The design work was based on a specification of demands, which gave a number of design goals concerning technical performance and volume/weight. The specification, if met, was set to yield a unit in the frontline of research & development worldwide. Thus the design expectations on the single-train reactor were as follows:

- Scalable design for small-scale fuel processing (1 – 1000 nm^3/h of hydrogen)
- All-inclusive unit including feed stock purification and gas purification
- Reformate with fuel cell quality (<20 ppm CO)
- Wide turn-down ratio, preferably 1:10
- Compact unit, < 2 litre per kWH_2 (gross volume)
- High thermal efficiency, > 80% calculated on the LHV of the feed stock
- The unit shall be able to process different feed stocks (NG, LPG, alcohols and heavier HCs)
- The thermal response of the unit shall be high

The data obtained during the construction and experimental evaluations are compared with the design expectations and a number of possible improvements are suggested.

The next step will be to implement the improvements and to carry out extensive long-time evaluations to confirm the reliability and operability of the fuel processor system. Different projects aiming at incorporating fuel cells into the fuel-processor system are also planned for. The goal will here be to build APU-units for different applications, automotive as well as stationary. Different fuel cell concepts should be evaluated (PEMFC and SOFC) for reliability and operability. In some applications it is also necessary to be able to use logistic feedstocks like kerosene or diesel. These blends of hydrocarbons normally also contain large amounts of sulphur compounds. Specific studies should also be directed to the utilisation of such fuels in a complete APU-system. The APU-system (designed for hydrocarbons with low sulphur contents) must then be complemented with a more powerful desulphurisation unit to protect the fuel cell from poisoning.

2. Overarching objectives

The overarching aim of the project was to design, construct and evaluate a novel reactor system for small-scale fuel processing. The project was divided into two consecutive steps with different ambitions.

Phase 1 focused on design considerations and catalyst evaluations concerning the different unit steps of the process. A complete reactor system was proposed and detailed reactor designs were discussed. A control strategy was developed and discussed. It was found that the specification of demands, previously described, could be met with a single-train reactor complemented with the necessary auxiliary components.

The reactors were constructed and evaluated during phase 2 of the project. Some modifications were implemented into the P/I-diagram and the complete system was assembled, commissioned and evaluated experimentally. The objective of phase 2 was to verify the design work performed in the previous project phase and to suggest improvements concerning the catalysts, the reactors and the system including the control strategy.

3. Previous development work and results

The first phase of the project focused on activity tests, reactor design and reactor dimensioning. A complete process scheme for the fuel processor system was suggested based on calculations of material- and energy balances. A control system for the unit was also proposed. The control system consists of a number of solenoid valves, which are controlled by temperature regulators and pause/pulse relays.

Under sulphur-free conditions, the reforming reactions are extremely quick and it is possible to use space velocity as high as 100 000 – 200 000 h^{-1} with our wire mesh catalysts. Figure 1 relates the hydrogen yield when reforming a variety of hydrocarbons (methane, propane, hexane, dodecane, methanol and ethanol) at a steam:carbon- ratio of 3. From the Figure it is evident that the steam-reforming reactions are extremely quick at temperatures above 700°C. In order to reduce the problems with coke formation, it is advisable to include some pre-reforming at lower temperatures to increase the ratio between hydrogen and hydrocarbons. If no pre-reforming is utilised, it is possible to re-circulate some of the reformer gas to yield a high enough hydrogen:hydrocarbon-ratio. The exit temperature of the reactor should preferably be above 900°C to minimise the residuals of methane. Especially in the case of methanol reforming, which normally is performed at rather low temperatures, there are problems with methane formation. In Figure 1 it is possible to identify a minimum in the hydrogen yield at about 600°C, which is caused by said methane formation

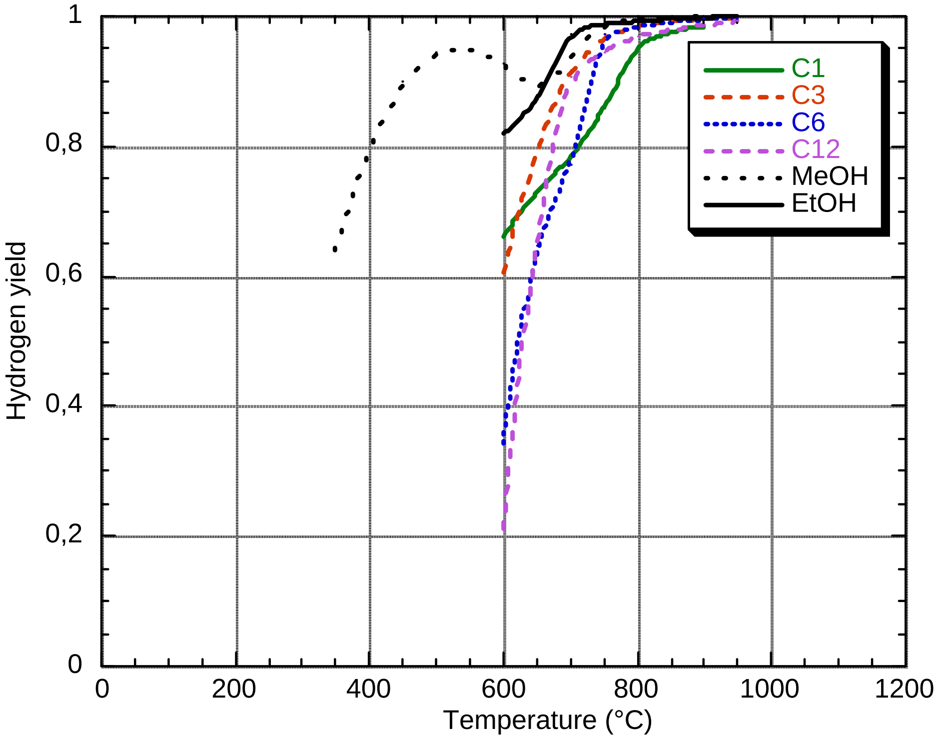


Figure 1 Steam reforming of pure feed stocks at SV ≈200 000 h^{-1}. Steam:carbon=3:1. Catalyst: Pt/alumina on wire meshes (16 mesh/0,5 mm).

CAT has also developed a number of catalyst formulations for downstream reactions, i.e. the water-gas-shift reaction and preferential oxidation of CO. The WGS-catalysts have an increased sulphur tolerance and contains small amounts of precious metals (preferably Pt) on a high-surface material comprising rare earth metal oxides. Depending on the stabilisation of the high-surface material, these catalysts split into two major groups: high-temperature WGS (HWGS) and low-temperature-WGS (LWGS). The high-temperature version tolerates temperatures as high as 500 – 600°C and is not susceptible to sintering on activation (reduction). The low-temperature version can be used at temperatures between 200 and 400°C.

CAB has also studied conventional active phases like mixtures of oxides of iron and chromium and formulations based on copper and zinc. The Fe/Cr-type of catalysts shows a far too low intrinsic activity for this application. The Cu/Zn-containing catalysts, although much more active, suffer from a high sensitivity to sintering phenomena (thermal deactivation).

For extremely high sulphur concentrations in the feed stream (% by volume), we have also developed a sour-shift catalyst, which needs to be in the form of a sulphide to be active. During sulphur free conditions the sulphides will decompose and the corresponding oxides will be formed. During that process the catalysts also looses its activity. Figure 2 shows an example of CATs HWGS catalyst when processing a gas mixture downstream a steam reformer (steam:carbon ratio of 4:1) at high space velocities. Thermodynamic (theoretical values) are given as a reference. From the Figure it is obvious that the thermodynamic equilibrium limits the reaction at temperatures above 400 – 450°C.

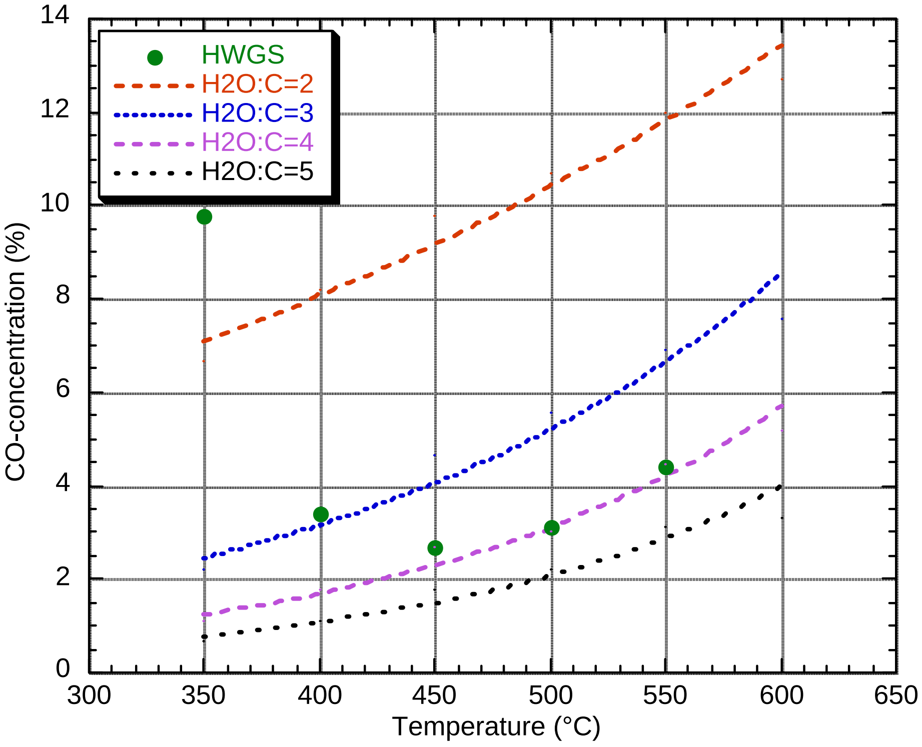


Figure 2 Performance of CATs WGS-catalyst in the WGS-reaction at SV 200 000 h^{-1}. Gas composition corresponding to downstream conditions when reforming methane at steam:carbon = 4:1. Catalyst: Pt/$ReMeO_x$ on wire meshes (16 mesh/0.5 mm). Thermodynamic data are given for different steam:carbon ratios (as lines).

In order to reach fuel-cell quality [10 – 20 ppm CO (v/v)], it is necessary to add a catalytic step including preferential oxidation of CO. PROX is a competitive reaction between oxygen and carbon monoxide and oxygen and hydrogen. The CO-removal shows a maximum at a specific temperature. At higher temperatures, oxygen is consumed by hydrogen, thus leaving CO. CAB has a number of formulations suitable for PROX. They show a high selectivity for CO-removal if runaway conditions can be avoided with respect to the temperature. Hence, temperature control is crucial for the PROX-step since the oxidation reactions are extremely quick and highly exothermic. In order to control the process, it is essential to add effective cooling to the catalyst and preferably to supply the necessary oxygen in steps. The best result is obtained with dispersed oxygen supply on a cooled catalytic membrane. Under such circumstances it is possible to arrive at selectivities above 70 – 80%. Figure 3 below show the performance of different PROX-compositions during isothermal conditions at high space velocities.

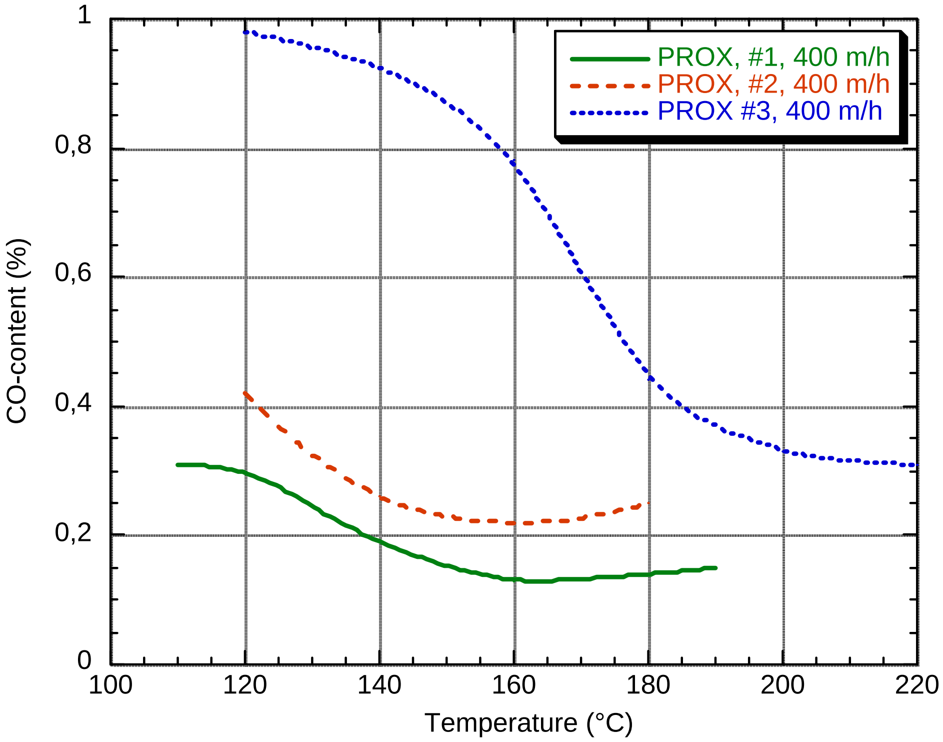


Figure 3 Performance of different PROX-catalysts at SV≈200 000h^{-1}. O_2:CO-ratio=1:1. Inlet concentration of CO, 1 % (v/v).

The scope of the first project phase was to design a reactor system for steam reforming of different fuels. The design work was focused on a single-train concept with a compact architecture. It was found (via computer simulations and experiments) that a system comprising all catalytic steps previously described, could be designed, See Figure 4 below. The reactors were fitted with wire-mesh catalysts carrying active phases previously developed by CAT (see Figure 1 – 3).

The reactors contain a number of catalytic zones each with intermediate heating or cooling. Computer simulations concerning conversions and temperature profiles throughout the reactors are shown in the Design study (appendix A).

The feed stock/steam mixture enters the steam reforming reactor at a temperature of about 600°C. Additional heat is supplied via the heat exchanger burner and the exit temperature will normally lie in the interval 700 – 800°C. There is a merit in bringing up the steam reforming temperature since the hydrogen yield then will be higher (less methane in the reformate). In cases where the feedstock carries sulphur compounds, the negative impact of these components will be less pronounced if a high stem reforming temperature is used. The reformate is then cooled by an additional heat exchanger block and by means of water addition (to power the WGS-reaction).

The inlet temperature to the WGS-reactor is typically 500°C. The WGS-reaction is mildly exothermic and intermediate cooling is essential to bring down the CO-concentration to the desired values. The CO-concentration will typically decrease from about 10% down to 1 – 1.5% when the gas mixture passes through the WGS-reactor. The outlet temperature of the WGS-reactor is about 200°C.

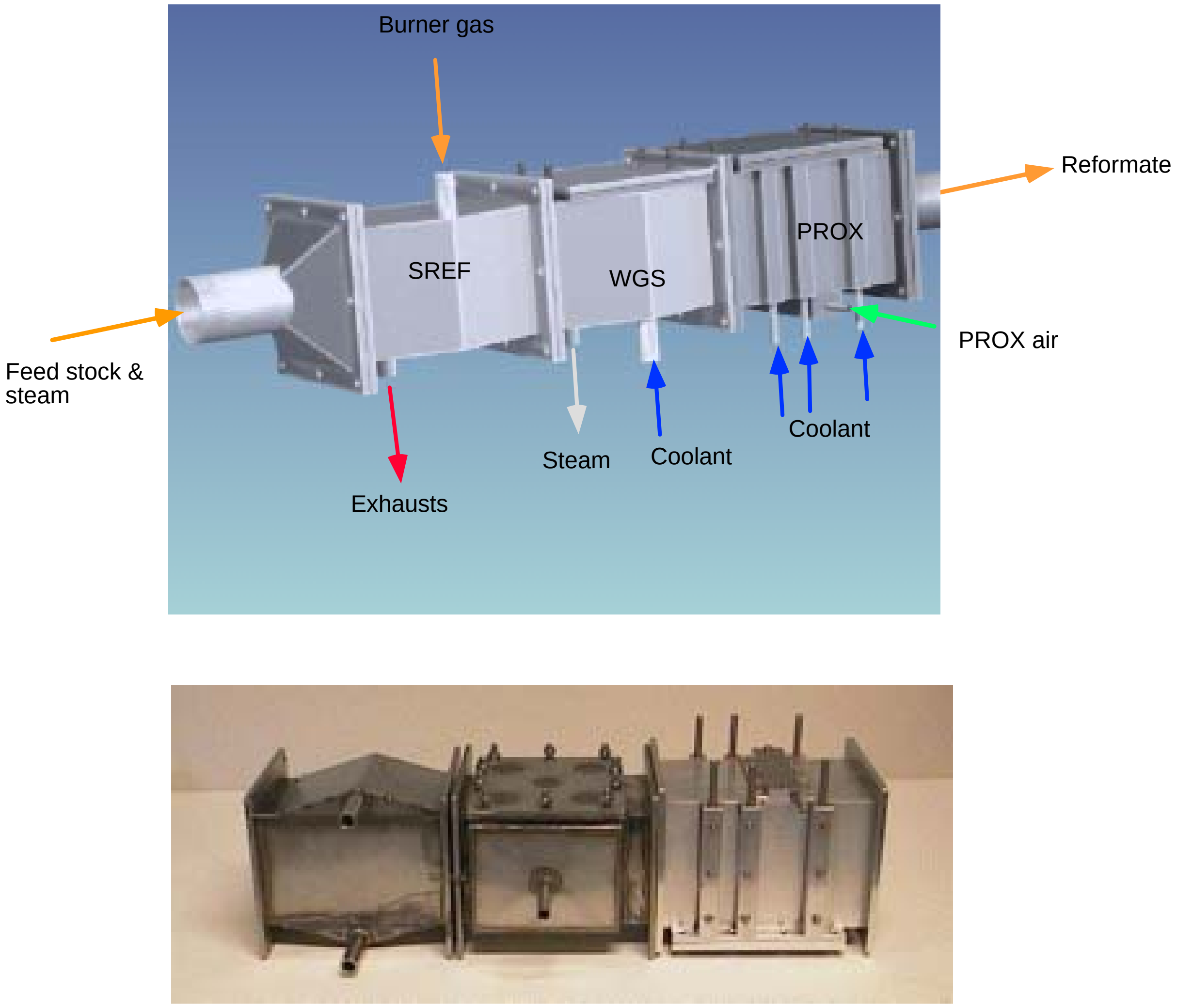


Figure 4 Single-train reactor concept comprising steam reformer, water-gas shift reactor and PROX reactor, i.e. the Ultraformer unit.

The PROX-reactor operates isothermally at about 150°C and will enable us to reach CO-concentrations as low as 10 ppm – 20 ppm. All figures given above are calculated values under steady-state conditions. The outlet concentration of CO might be higher during transients and start-up. The single-train reactor must be fitted into a supply system comprising a number of auxiliary components like heat exchangers, pumps, valves, fans, control electronics etc. The entire system is described in the next section together with the start-up sequence.

4. Detailed design & P/I-scheme

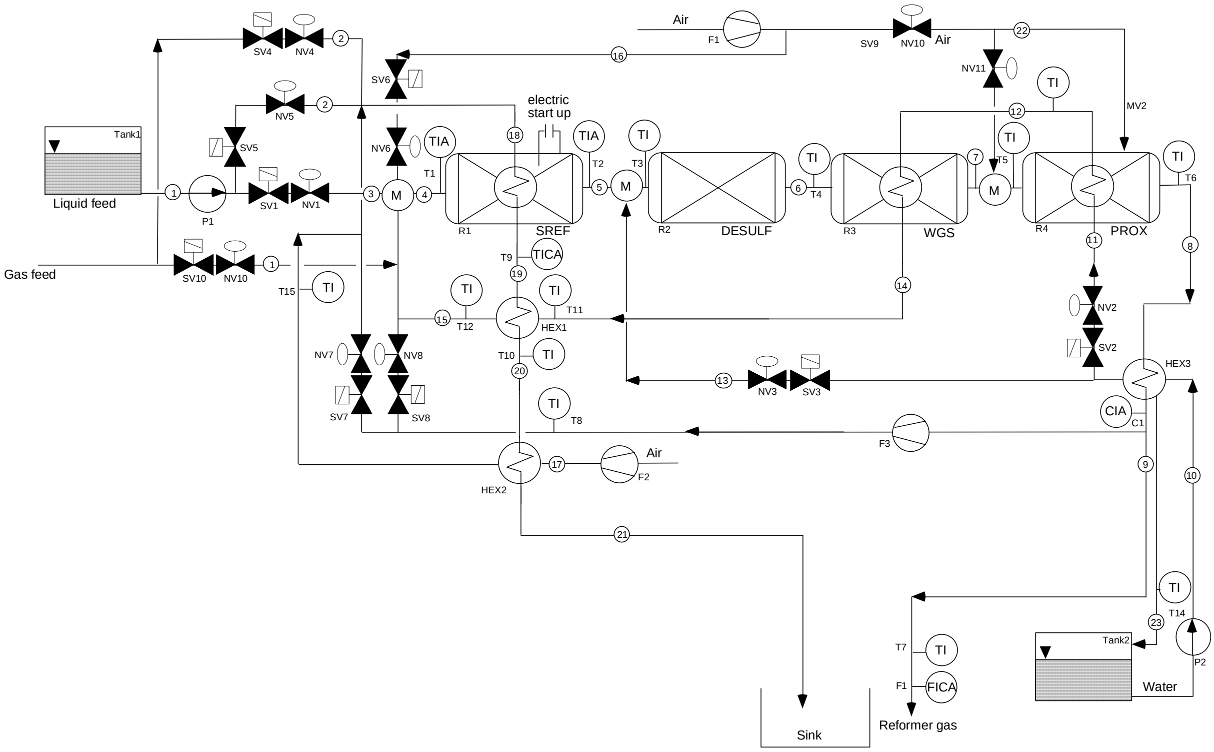
The Ultraformer unit is designed to enable reforming of liquid as well as gaseous fuels. A complete P/I-diagram is presented in Figure 5 below. Gas is fed via solenoid valve SV 10 to the reformer and via SV4 to the burner system. Liquid fuel is fed from a tank by means of the liquid pump (P1). The liquid flow is divided into two lines; one for the burner system and one for the reformer system. Control of the fuel flow is by means of the solenoid valves SV1 and SV5.

Water is supplied from a water tank via the water pump (P2). Water is supplied to the cooling/steam generation line (via SV2) and to the additional water line (via SV3).

A number of air membrane pumps/fans are included in the system according to:
F1, Air for rapid heat (partial oxidation air) and PROX-air
F2, Air supplied to the burner system
F3, Recirculation pump

The core of the FPS-system is associated with reactors and heat exchangers. The steam reformer (SREF) is supplied with pre-heated fuel/steam in the reformer section and fuel/air in the burner section. The fuel is catalytically converted into a mixture of carbon oxides, hydrogen and methane. This mixture is cooled by means of water addition upstream the WGS-reactor. The WGS-reactor will typically bring down the CO-concentration to less than 1 % (v/v). The reformate is then led into the reactor for preferential oxidation (PROX), which is operated close to isothermal conditions. Air is supplied at different sections of the reactor and the outlet concentration of CO typically ranges from a few ppm to about 50 ppm.

A number of temperature sensors (TI) are installed in the system. The control of the burner utilises a temperature sensor in the reformer unit (TICA). A number of alarm functions (TIA) are included to enable the sequential start-up of the unit.



No	T	p	m	V	ρ	H_2	CO	CO_2	H_2O	CH_4	C_{12}	O_2	N_2
unit	°C	kPa	kg/h	nm^3/h	kg/m^3	%	=>	=>	=>	=>	=>	=>	=>
1	25	107	3.0	n/a	0.75	n/a	n/a	n/a	n/a	n/a	100	n/a	n/a
2	25	107	1.0	n/a	0.75	n/a	n/a	n/a	n/a	n/a	100	n/a	n/a
3	25	107	2.0	n/a	0.75	n/a	n/a	n/a	n/a	n/a	100	n/a	n/a
4	600	107	9.6	9.7	0.99	n/a	n/a	n/a	97.3	n/a	2.7	n/a	n/a
5	800	105	9.6	15.9	0.60	47.8	11.4	7.9	32.4	0.50	0.00	n/a	n/a
6	500	105	11.9	18.9	0.63	40.3	9.6	6.7	43.0	0.42	0.00	n/a	n/a
7	300	103	11.9	18.9	0.63	48.9	0.96	15.4	34.3	0.42	0.00	n/a	n/a
8	100	102	13.0	19.6	0.66	46.3	0.002	15.7	34.1	0.41	0.00	0.00	3.5
9	68	101	11.8	18.0	0.66	50.3	0.002	17.1	28.3	0.45	0.00	0.00	3.8
10	25	110	10.0	n/a	1000	n/a	n/a	n/a	100	n/a	n/a	n/a	n/a
11	100	109	7.6	n/a	1000	n/a	n/a	n/a	100	n/a	n/a	n/a	n/a
12	100	108	7.6	5.25	1.45	n/a	n/a	n/a	100	n/a	n/a	n/a	n/a
13	100	108	2.4	n/a	1000	n/a	n/a	n/a	100	n/a	n/a	n/a	n/a
14	132	108	7.6	9.5	0.80	n/a	n/a	n/a	100	n/a	n/a	n/a	n/a
15	752	107	7.6	9.5	0.8	n/a	n/a	n/a	100	n/a	n/a	n/a	n/a
16	25	107	0.00	0.00	1.28	n/a	n/a	n/a	n/a	n/a	n/a	21	79
17	25	107	3.8	30.0	1.28	n/a	n/a	n/a	n/a	n/a	n/a	21	79
18	500	105	39	30.0	1.30	n/a	n/a	n/a	n/a	n/a	0.3	20.9	78.8
19	900	104	39	30.9	1.26	n/a	n/a	5.2	5.5	n/a	n/a	12.5	76.8
20	690	103	39	30.9	1.26	n/a	n/a	5.2	5.5	n/a	n/a	12.5	76.8
21	190	102	39	30.9	1.26	n/a	n/a	5.2	5.5	n/a	n/a	12.5	76.8
22	25	102	0.84	0.68	1.28	n/a	n/a	n/a	100	n/a	n/a	n/a	n/a
23	68	101	1.26	n/a	1.00	n/a	n/a	n/a	n/	n/a	n/a	n/a	n/a

Figure 5 P/I-diagram for the Ultraformer unit. The table shows relevant process data when processing a liquid hydrocarbon, like kerosene.

The start-up sequence is shown in Figure 6 below. Burner air and fuel are supplied together with air for rapid start-up (oxidation in the reformer) and PROX-air. The electric igniter system is operated for a few seconds to initiate the combustion process in the burner. When the exhaust gas temperature has reached the set point (900 – 1000°C), SV4 starts to modulate to keep the temperature at the set point. It typically takes 5 minutes to reach this set point. A few minutes later, the temperature at the outlet of the reformer has reached the alarm level (500°C) and water is supplied to the reformer. When the inlet temperature to the reformer has reached a certain level (250°C) fuel is supplied to the reformer and the steam reforming starts. Modulation is then possible by means of the solenoid valves.

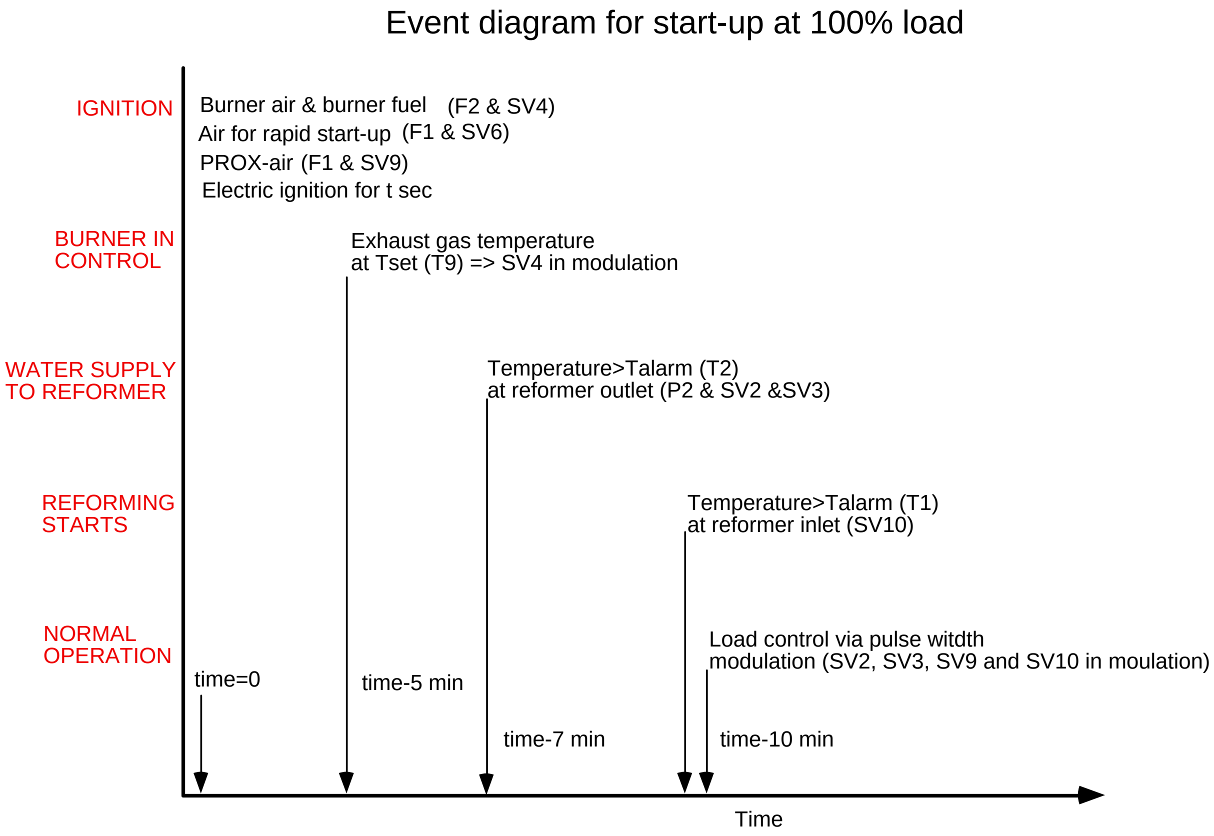


Figure 6 Event diagram for start-up of reformer system.

The entire start-up process will take about 10 minutes if air is injected into the steam reformer (rapid heat). If no air is supplied to the steam reformer, the start-up will be slower.

5. Assembly and commissioning work

The reactors were constructed in accordance with the design work, previously reported (appendix A). The commissioning work will be divided into four consecutive phases, i.e. Individual reactor evaluation, System assembly, Automation and Modifications & improvements. The commissioning scheme is shown if Figure 7.

The individual reactor evaluation will be performed in CATs test rig for larger reactors. The idea behind the individual reactor evaluation is to verify that the reactors meet the design data.

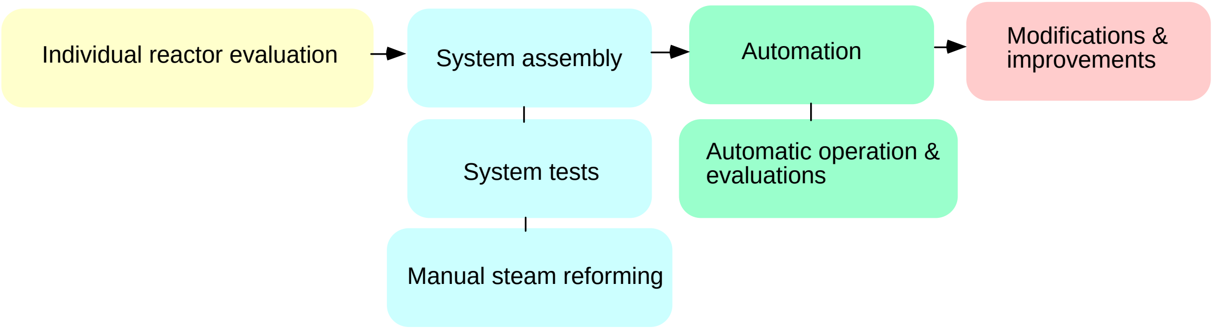


Figure 7 Scheme for the commissioning work.

The reactors will then be assembled into the single-train system and complemented with all necessary auxiliary components like heat exchangers, fans, pumps, valves etc. System tests will then be performed in the manual mode to see if the integral system meets the design data. The control system will then be implemented and tests with automatic operation will be performed.

Some modifications might be necessary to reach the specifications. Improvements that are reasonable to implement on the system are included in this project. Activities aiming at optimisation and improved reliability should be performed in a following-up project.

6. Experimental work

6.1 Evaluation of individual reactors

The individual reactors were evaluated in CATs rig for large reactors. A synthetic gas mixture was produced by means of mixing pure gases with mass flow controllers and a special steam generation system. The gas mixture could be pre heated to simulate the recuperation process of the Ultraformer unit.

The steam reformer was evaluated with natural gas at a steam:carbon ratio of 4 and an inlet temperature (steam + natural gas) of 500 – 600°C. Figure 8 relates results obtained in the verification test. The flow rate of natural gas has been varied from 0.76 nm^3/h to 2.66 nm^3/h (30 – 106% load). The gas composition was analysed at the outlet by means of IR and GC and the dry gas compositions are shown in the Figure. The hydrogen concentration was rather stable and ranged between 75 and 78%. The concentration of un-reacted hydrocarbons increased with the load and reached about 5% at the highest load situation. The ratio between CO and CO_2 decreased with the load, thus indicating decreased reforming temperatures with increased load. Indeed, the outlet temperature was about 750°C at the lowest load and somewhat above 700°C at the highest load.

In order to increase the conversion of hydrocarbons further the reactor temperature should be increased. This can be performed by either increasing the recuperation (pre heating) or by increasing the load of the burner.

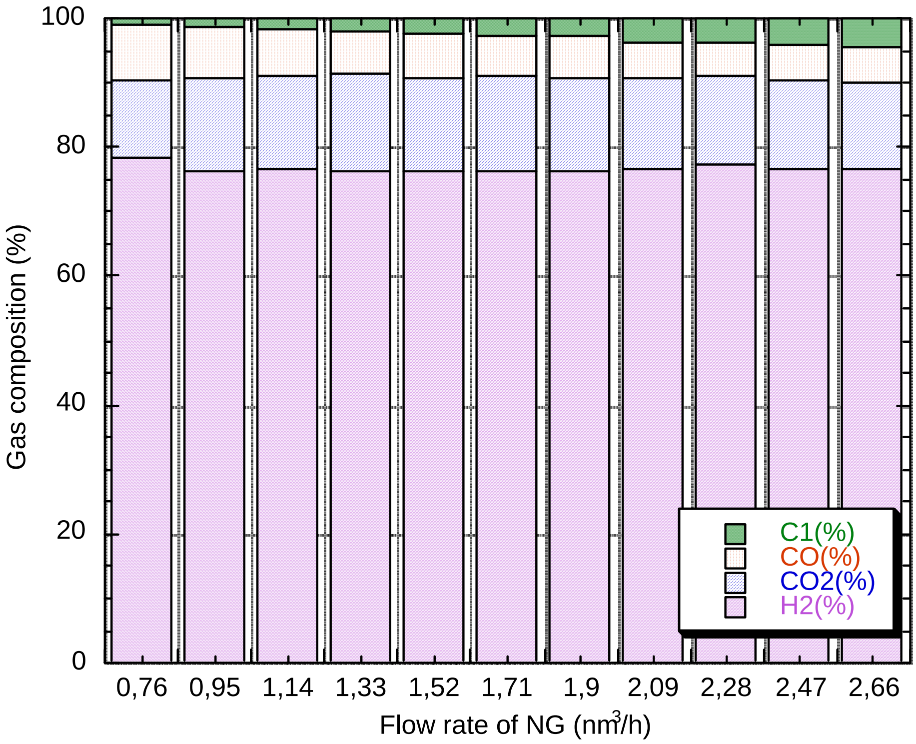


Figure 8 Results obtained during steam reforming of natural gas at steam:carbon=4:1 and 700 – 750°C. The flow rate of natural gas has been varied during the tests. Gas compositions given at the outlet of the reformer.

From a theoretic point of view it should be possible to produce 4 nm^3 hydrogen per nm^3 of methane. However this theoretical value implies total conversion of the hydrocarbons and no losses in the PROX-reactor. The experimental data concerning hydrogen production are shown together with the theoretical hydrogen yield in Figure 9. It is obvious that there exists a deviation between theory and reality, mainly caused by incomplete conversion of hydrocarbons. Some additional hydrogen will be produced in the WGS-reactor when the residual CO is converted into H_2 and CO_2 by water.

It is possible to converge towards the theoretical line if the reaction temperature is increased. However, too high temperatures in the reactor might violate the durability of the reactor (thermal fatigue and thermal corrosion).

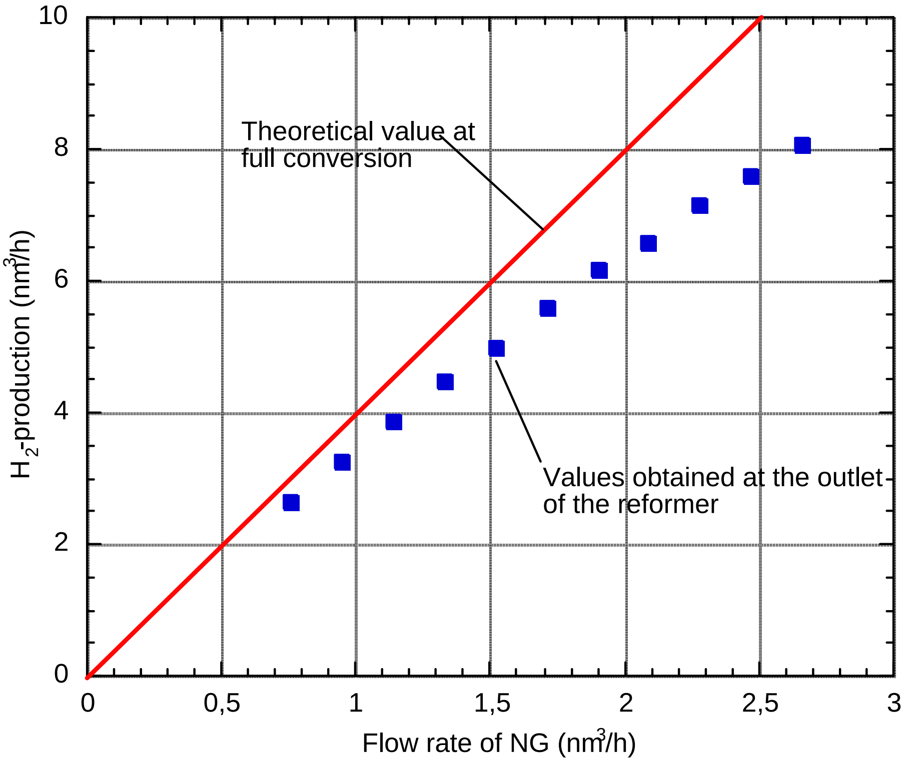


Figure 9 Results obtained during steam reforming of natural gas at steam:carbon=4:1 and 700 – 750°C. Theoretical values for full conversion are given in the same diagram (as line).

It can be concluded that the expectations on the steam reformer reactor can be met. It can produce the desired quantity of hydrogen provided the conversion of hydrocarbons can reach high values (close to unity). The main issue is to arrive at high enough temperatures in the steam reformer through effective recuperation, a high burner load and possibly by air injection into the reactor (some oxidation in the steam reformer).

A representative gas composition for downstream conditions of a steam reformer was produced with the mass flow controllers and the steam generation system. The gas mixture entered the WGS-reactor at about 500°C and was cooled along the reaction pathway. The effective catalyst temperature was about 350°C. Figure 10 shows the experimental results together with thermodynamic data. It is clear that the reaction converge towards thermodynamic equilibrium as indicated by the Figure. The CO:CO$_2$-ratio range between 0.087 and 0.148 in the temperature region of interest. The experimentally obtained data are located within this interval.

Indeed, the WGS-reactor is heavily over dimensioned from a catalytic point of view (SV≈ 20000 h^{-1}). Consequently, it is not surprising that thermodynamic equilibrium is reached at all loads.

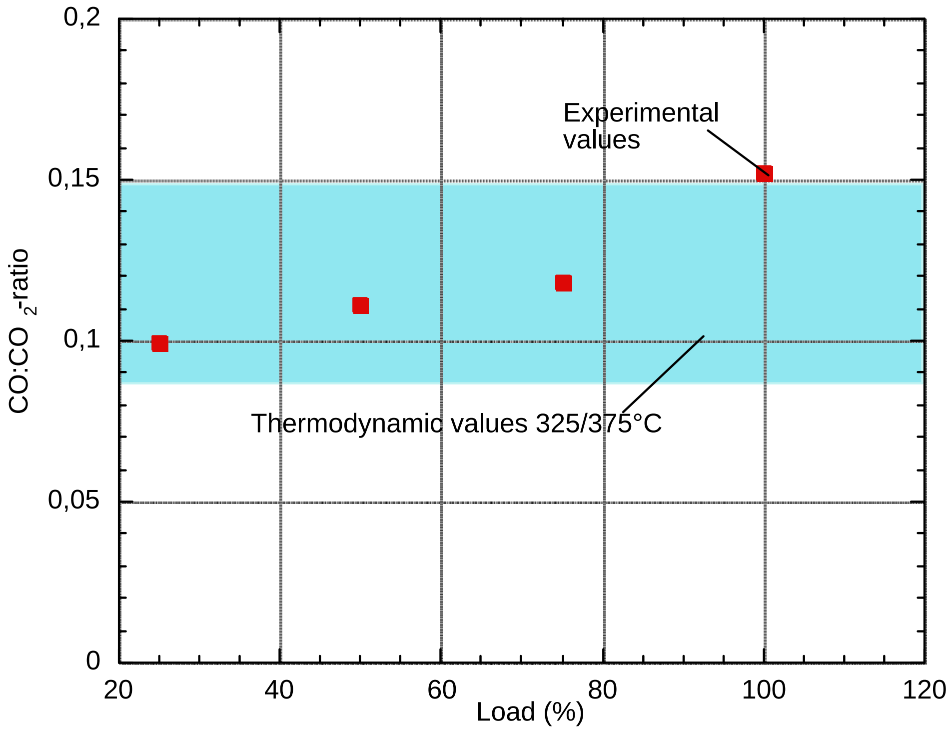


Figure 10 Results from tests of the WGS-reactor. Data obtained for a mixture containing 10% of CO/CO_2, 31% H_2O and balance H_2.
The catalyst temperature was about 350°C.

The water concentration of the gas mixture was varied in a series of experiment. Again, the thermodynamic equilibrium dictated the outcome of the chemical reaction (see Figure 11). Figure 11 shows the experimentally obtained CO:CO_2-ratios together with theoretical values at a reaction temperature of 350°C.

The minor deviations between practice and theory is associated with some problems to exactly determine the reaction temperature in this gradient reactor. It can be concluded that the WGS-reactor behaves as expected and that the performance of the reactor is entirely governed by the thermodynamic equilibrium of the gas mixture.

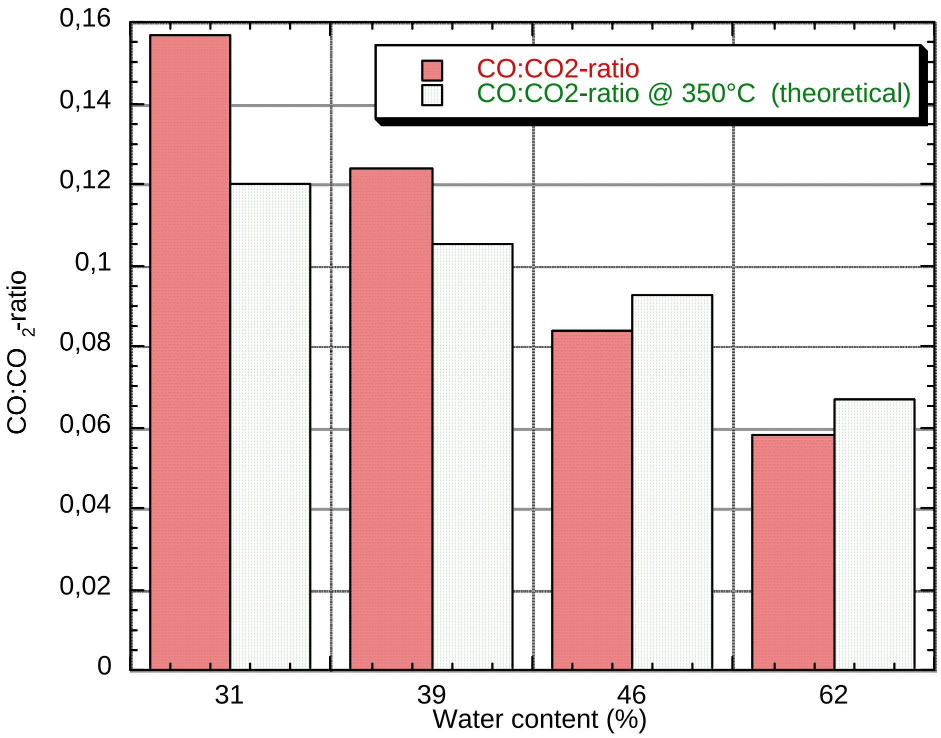


Figure 11 Results from tests of the WGS-reactor at full load. Data obtained for a mixture containing 10% of CO/CO_2 (dry). The water concentration was varied between 31 and 62% and the catalyst temperature was about 350°C.

In order to reach fuel-cell quality of the reformate gas, it is necessary to include a step with preferential oxidation of residual CO. CO is strongly adsorbed onto the catalyst and a high selectivity for CO-removal is achieved in a certain temperature window. Some hydrogen is consumed in parallel with the CO-removal.

If the CO-concentration of the reformate stream shall be as low as 20 ppm downstream the PROX-reactor, it is necessary to reach conversion degrees as high as 99.8% (at an inlet concentration of CO=1.0%). It is normally difficult to reach so high conversions since effects like poor mixing and by pass will affect the outcome of the reaction.

In order to evaluate the PROX-reactor a synthetic gas mixture representative of the gas mixture downstream the WGS-reactor was produced. The reactor was held at 120°C, which is an optimum temperature for the PROX-reaction with the catalyst chosen. The O_2:CO-ratio was 1.5:1, which means that two hydrogen molecules will be consumed per CO-molecule. Figure 12 shows some of the introductory experiments where the conversion was too poor to yield low enough CO-concentrations at the outlet. The desired conversion degree was set to 99.5% or more (corresponds to less than 50 ppm CO) but the conversion degree never reached higher values than 99.2%. Moreover, the conversion degree decreased with the load and was only about 98% at full load.

A number of measures were taken to improve the performance of the reactor. Increasing the O_2:CO-ratio further enabled us to reach a conversion of 99.6% at full load (see Figure 13).

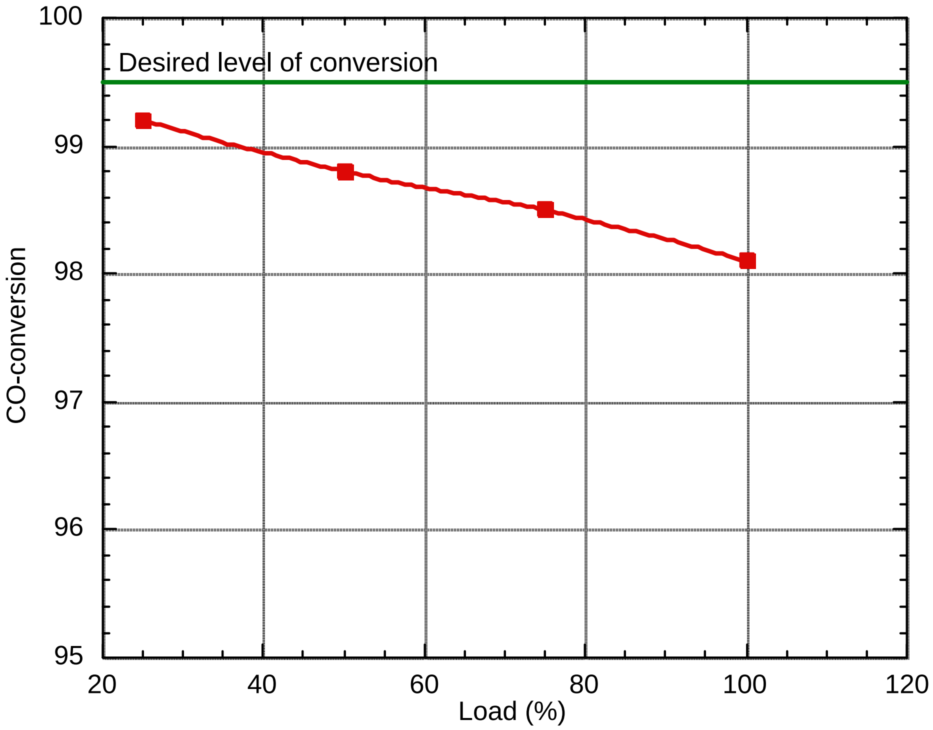


Figure 12 Results from tests with the PROX-reactor. Inlet concentration of CO was 1% at a O_2:CO-ratio of 1.5:1. The catalyst temperature was about 120°C.

We examined the reactor to detect possible gas slip and imperfections in the oxygen/reformate-mixing. Complementary CFD-simulations indicated a possibility of poor mixing over the cross section and a separate air/reformate mixer was constructed and installed. Following that measure it was possible to comply with the conversion demand; the CO-concentration could be held at levels lower than 15 ppm at all loads and at a O_2:CO-ratio of 1:5:1.

Further improvements are possible but are without the scope of this project. It can be concluded that all the individual reactors meet the expectations and the next step was to assemble the individual reactors into a single-train reactor system. The results from the evaluations of this system are discussed in the next sections.

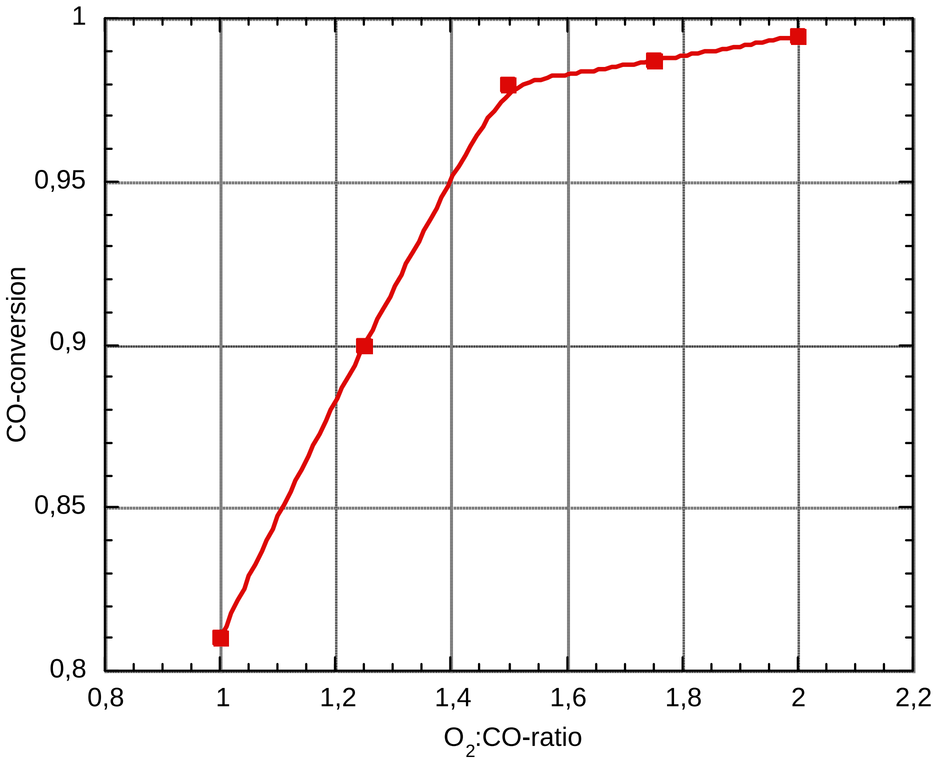


Figure 13 Results from tests with the PROX-reactor at full load. Inlet concentration of CO was 1% and the catalyst temperature about 120°C.

6.2 Tests performed with manual operation of the reformer

A number of experiments were performed with the Ultraformer unit in manual operation. Previous experiments with the individual reactors indicate that they will meet the specification. Hence, it is of great interest to see if the total system can comply with the specification of demands concerning, load, reformate quality, start-up times etc.

The experimental evaluations included the following tests:

a) Steam reforming of different feed stocks
b) Variation of the steam reforming temperature
c) Variation of steam:carbon ratio
d) Study of the O_2:CO-ratio in the PROX reactor
e) Air injection into the steam reforming reactor

Tests were performed with different feed stocks, gaseous as well as liquid. The first experiments were performed with pure methane (biogas). It was found that the hydrogen yield was about 92 % in comparison to the theoretical value (full conversion of hydrocarbons), see Figure 14a. Since the mixture will carry un-reacted hydrocarbons, the hydrogen yield will be less than this theoretical value. The steam reforming temperature was about 750°C in the experiments with different feed stocks. The outlet concentration of CO was as low as 8 ppm at full load. The hydrogen yield increased with decreased load and reached 98-99% at the lowest load condition (10%) whereas the CO-concentration was on the same level (about 10 ppm).

Since the Ultraformer system reached the specification in biogas processing it was of interest to study commercial gas fuels carrying low concentrations of sulphur. Hence natural gas and LPG were evaluated in the Ultraformer unit. It was found that the hydrogen yield was somewhat lower (88-91%) and the outlet concentration of CO somewhat higher in comparison to pure methane processing. Again, the hydrogen yield reached almost unity at the lowest load condition (10%). The CO-concentration typically varied between 10 and 30 ppm, rather unaffected by the load situation (see Figure 14a and 14b).

Even if these fuels carry low concentrations of sulphur, the overall performance of the Ultraformer unit was still in control and the data were in agreement with the expectations.

Additional experiments were performed with steam reforming of liquid feed stocks like naphtha and alcohols. The hydrogen yield was extremely high when methanol and ethanol, were used as feed stocks, see Figure 14a. The CO-concentration was in control with ethanol whereas it turned out to be somewhat higher with methanol as the feed stock. Methanol yielded relatively high CO-values all over the load widow (80 – 250 ppm), which makes this feed stock unique in the tests. This deviation was possible to reproduce and might be connected to contaminants in the methanol although this only is a hypothesis. Further studies are necessary to find a firm answer to this phenomenon.

Naphtha gave, as expected, a hydrogen yield similar to the gaseous fuels previously studied. The CO-concentration was somewhat higher at full load (about 60 ppm). The hydrogen yield increased to values close to unity at the lowest load and the CO-concentrations scattered between 40 and 70 ppm.

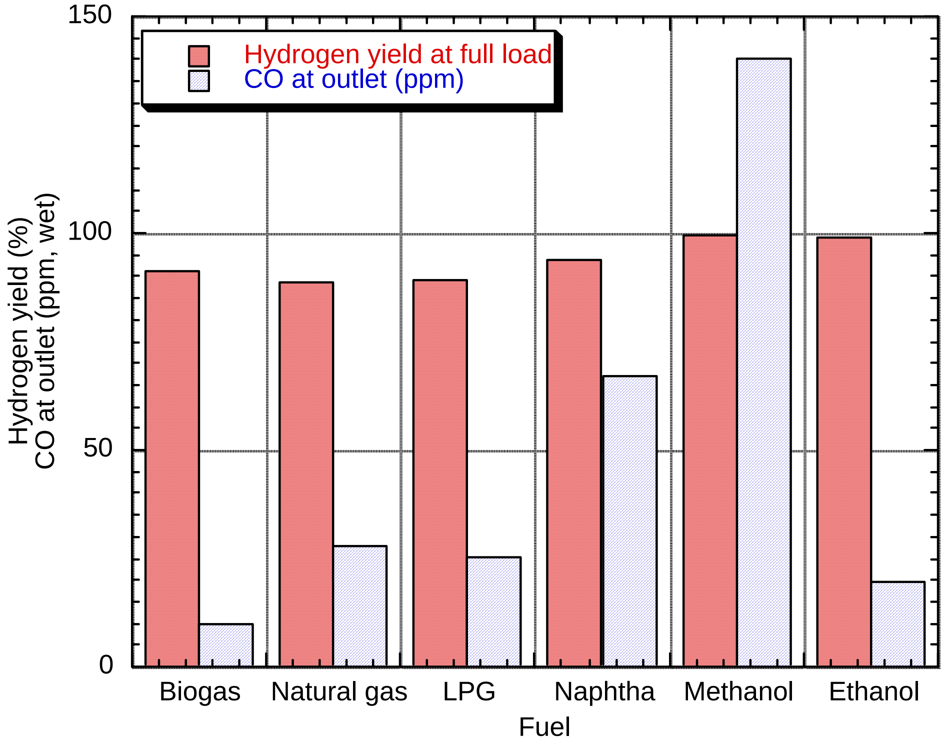


Figure 14a Evaluation of different fuels. Steam reforming at full load at a steam:carbon ratio of 4:1. Hydrogen yield (% of theoretical) and outlet CO-concentration (ppm, wet) given for a number of fuels.

The study concerning different fuels clearly indicated that the specification concerning load and turn-down could be met. The quality of the reformate gas could be met for most fuels and in most load situations. Methanol and to some extent naphtha gave some difficulties concerning the reformate quality with respect to CO. It is difficult to state the reason for this observation and to give a firm answer it would be necessary to make careful evaluations for these fuels. It is most probably possible to eliminate the problem through minor optimisations concerning the operation parameters in these cases.

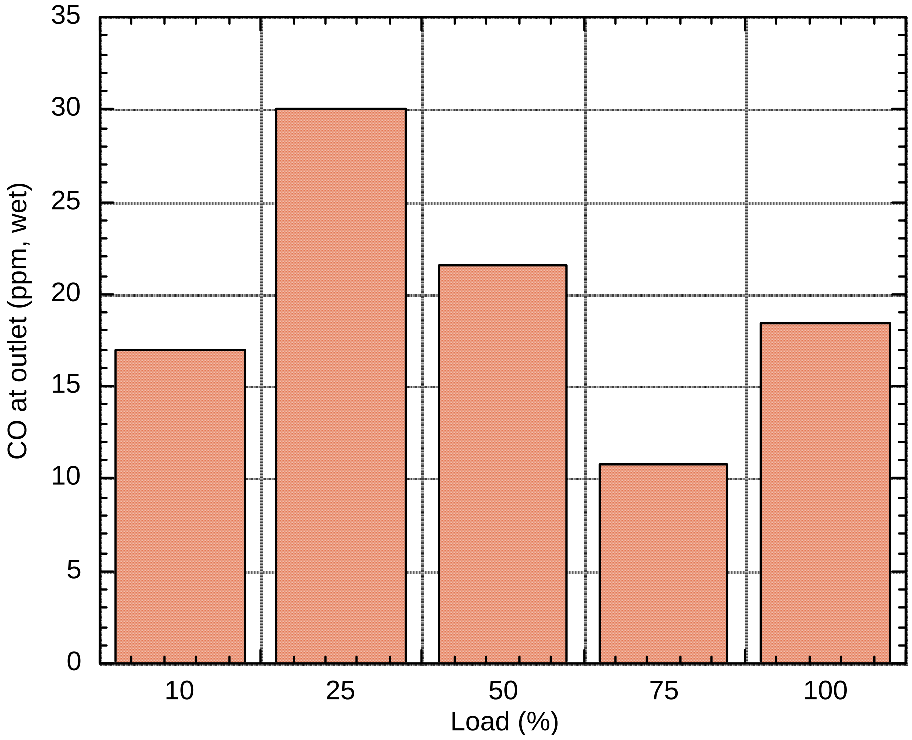


Figure 14b Steam reforming of natural gas at different loads (10-100%). CO-concentration (ppm, wet) versus load.

The steam reforming temperature was held about 750°C during the experiments described above. Some additional experiments were performed too indicate the temperature sensitivity of the process. The output of the burner was increased to enable us to increase the outlet temperature of the reformer. Figure 15 shows data concerning the hydrogen yield as a function of the outlet temperature of the reformer. Increasing the temperature to levels above 800°C will enable us to reach hydrogen yields in the neighbourhood of 96 – 98%. One problem is that the reactor construction is under a high thermal stress at extremely high reforming temperatures. In one high-temperature experiment, the rector was damaged and it was necessary to repair it.

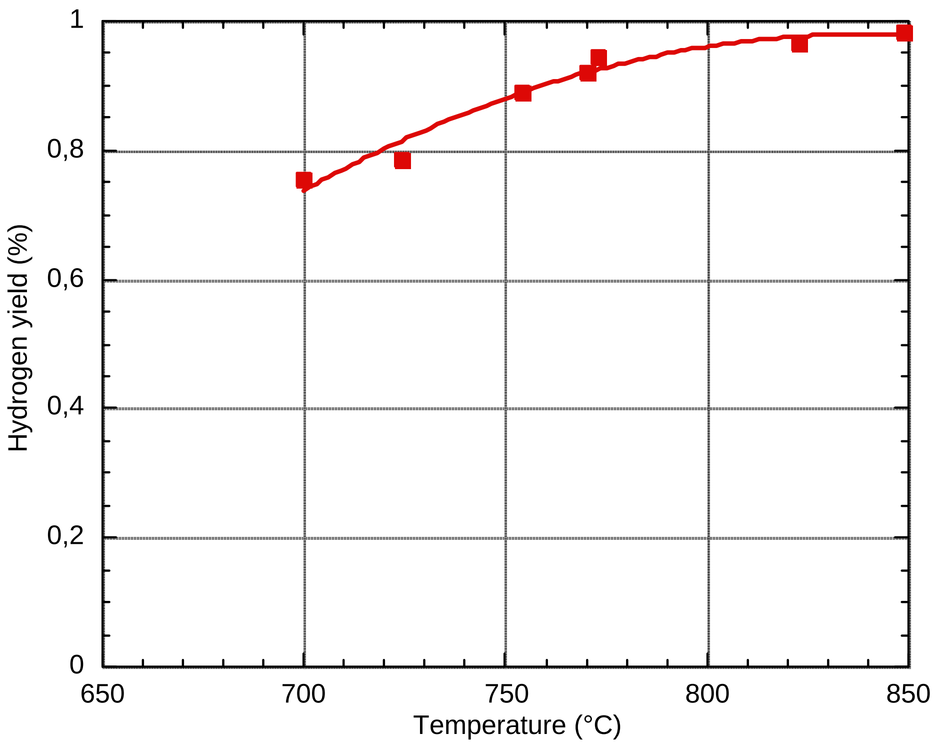


Figure 15 Hydrogen yield versus the reaction temperature in steam reforming of natural gas at full load and a steam:carbon ratio of 4:1.

It is possible to decrease the steam:carbon ratio to rather low values in natural gas steam reforming since the hydrocarbons involved have a low susceptibility to coke formation and the sulphur concentration is low. Figure 16 below shows data from experiments with different steam:carbon ratios in natural gas processing. The CO-concentration of the reformate gas will increase when the steam:carbon ratio is decreased, which can be seen in the Figure.

The concentration of CO downstream the WGS-reactor was in all cases around 1% whereas the outlet concentration of the PROX-reactor was around 25 ppm. Indeed, very small effects were seen by varying the steam:carbon ratio in this case. In cases with heavier hydrocarbons, there are risks with decreasing the steam:carbon ratio too much since coke formation then will occur.

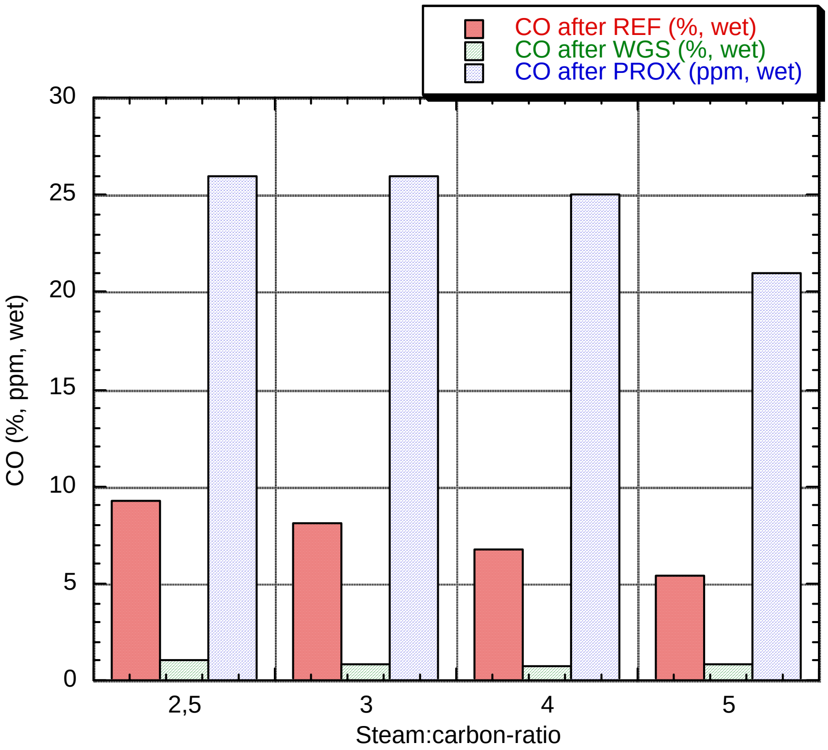


Figure 16 Effects of steam:carbon-ratio in natural gas steam reforming at full load. Reaction temperature ≈ 750°C.

The selectivity of the PROX-reactor was studied in a separate experiment. The Ultraformer unit was run at full load with natural gas as feed stock. The O_2:CO-ratio was varied and the outlet concentration of CO was determined as a function of this ratio. The inlet concentration of CO to the reformer unit was rather stable in the range 8000 – 11000 ppm.

From Figure 17, it is obvious that increasing the O_2:CO-ratio higher than about 1.5 has negligible effects on the outlet concentration. Hence, the O_2:CO-ratio should be kept at 1.5 to enable an effective CO-purification without too much hydrogen losses and risks of runaway reactions.

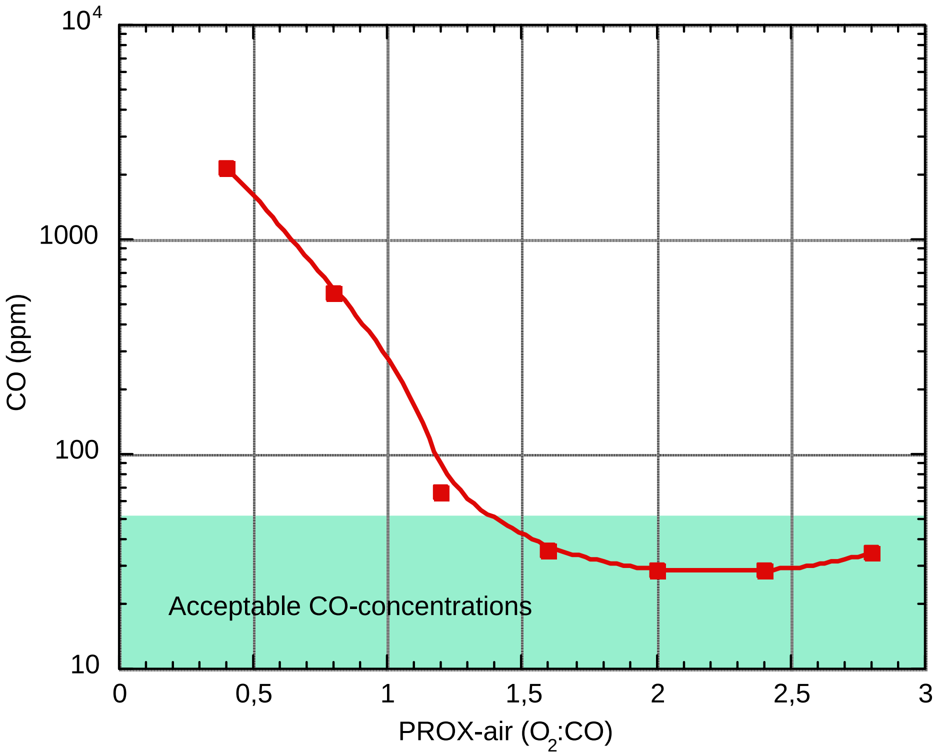


Figure 17 Effects of air injection into the PROX-reactor during steam reforming of natural gas at full load and at steam:carbon=4:1.

As previously discussed. it is possible to inject some air into the steam reformer in order to decrease the burden for the burner system and to speed up the start-up process. The effects of injecting small amounts of air into the reformer at stable steam reforming of natural gas are shown in Figure 18a. Without air injection, the outlet concentration of hydrocarbons (as C_1-equivalents) is as high as 5%, which clearly affects the overall hydrogen yield of the process. The steam reforming temperature is then increased in steps by adding additional air into the steam reformer unit. The concentrations of un-reacted hydrocarbons decrease when the reformer temperature is increased. This effect is very similar to the phenomenon observed when increasing the burner load but air injection is a more convenient way of getting high temperatures in the reformer.

The maximum air:C-ratio used in this study corresponds to 1.25, which means that about 10% of the feed stock is consumed inside the steam reformer in order to produce additional heat. The outlet concentration of un-reacted hydrocarbons is decreased to less than 1% by this measure. The negative effects are that the hydrogen concentration will decrease due to combustion and inertation (with nitrogen) in comparison to pure steam reforming.

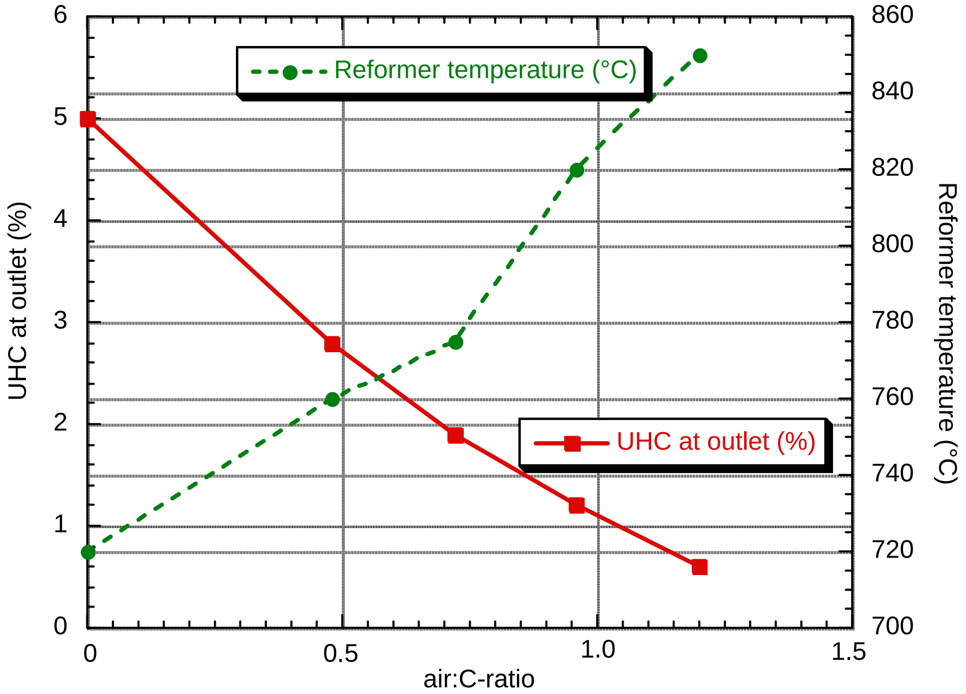


Figure 18a Effects of partial oxidation in the steam reformer when adding minute amounts of air to the feed stock. Steam reforming of natural gas at steam:carbon=4:1. λ=0.1 corresponds to an air:C ratio of 1.

However, when using minute air additions, the process gain is more pronounced than the losses. Figure 18b shows that there exists a maximum in the hydrogen yield when going from pure steam reforming with incomplete hydrocarbon conversion to steam reforming with air injection. Air injection will bring up the reaction temperature and the conversion. Adding to much air will result in a decreased hydrogen yield since some of the feed stock is consumed. If we are talking about small air:C-ratios, the effects are generally positive (see Figure 18b) since small amounts of feed stock is consumed in relation to the positive effects on the conversion degree. Moreover, the total flow and the hydrogen concentration of the reformate gas are only affected to a small extent. Figure 18c shows that the total flow is increased by 10% and the hydrogen concentration is decreased by 25% through the addition of air corresponding to an air:C-ratio of 1. These effects are acceptable also in cases where pure steam reforming is desired.

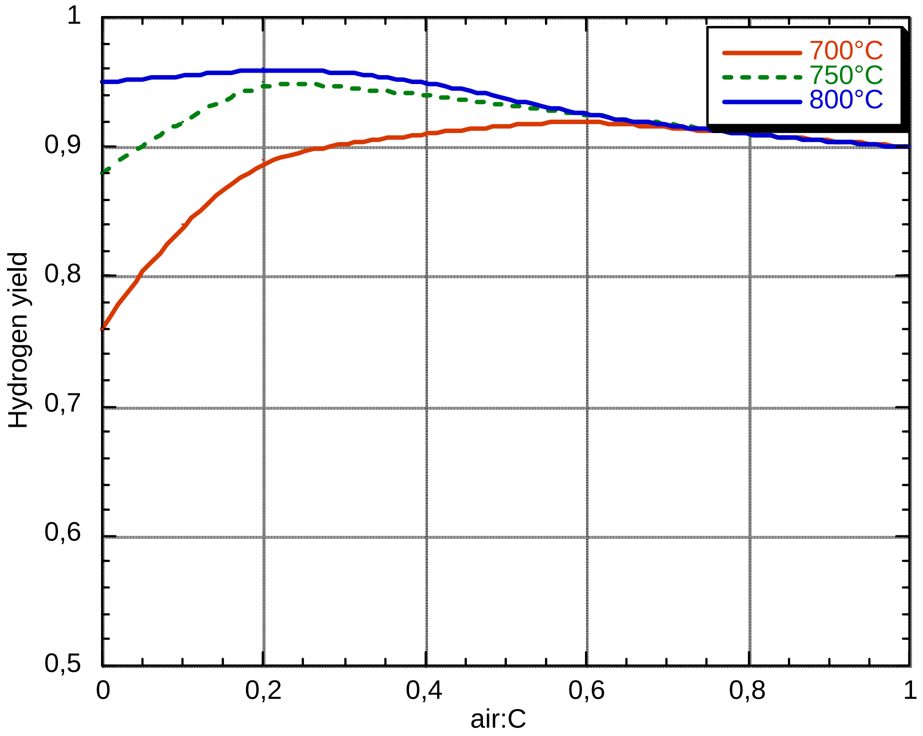


Figure 18b Effects of adding air to the reformer when starting from different steam reforming temperatures (at air:C=0). air:C=1 corresponds to a lambda value of about 0.1.

If the process with minute air injection is compared with autothermal reforming (ATR) or catalytic partial oxidation (CPO) it is possible to see the differences in hydrogen yield and reformate concentration of hydrogen. From Figure 18d, it is obvious that minute air injection into the steam reformer only affects these two parameters very slightly in comparison to the other two processes, which often are considered in fuel cell systems. Consequently, minute air injection should be acceptable from a process technological point of view.

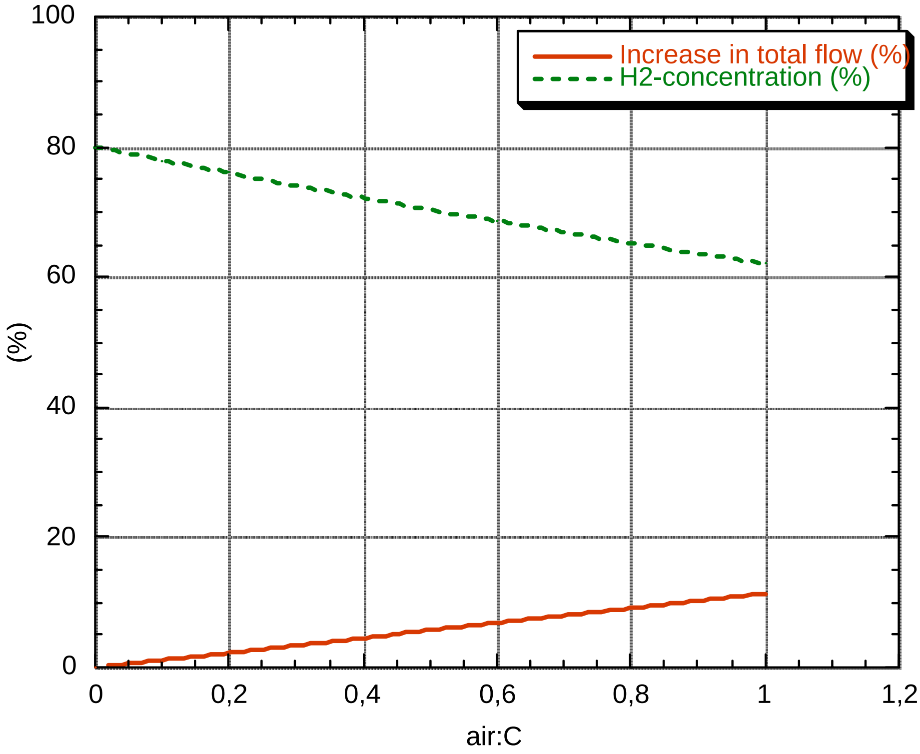


Figure 18c Effects in the total flow (wet gases) and in hydrogen concentration (dry analysis) when adding air to the reformer.

Air injection also has a merit during start-up of the Ultraformer system. Since it is possible to burn some of the fuel inside the steam reformer in order to increase the thermal input, start-up is expected to be much quicker. Indeed, it is possible to use much higher air injections during start-up in order to compete with the start-up performance normally found in fuel processors based on partial oxidation.

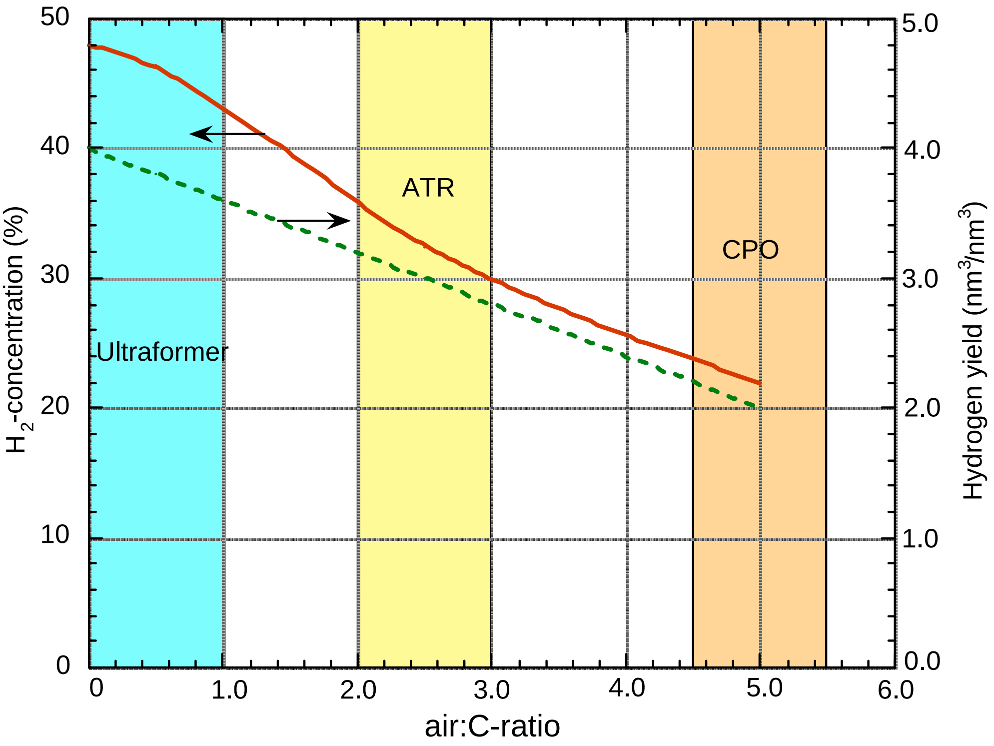


Figure 18d Comparison between SREF/SREFOX, ATR, CPO with respect to hydrogen concentration in reformate (dry analysis) and possible hydrogen yield (at full conversion of CO). λ=0.1 corresponds to an air:C ratio of 1.

6.3 Experiments with automation

The control system previously described, was implemented on the Ultraformer rig. The electric scheme is shown in Figure 19. The control system is built on temperature regulators and pause/pulse relays.

An ignition button is used to initiate the electric ignition on the burner and to start the sequential start-up. Start-up of water supply and feed stock supply are trigged by separate temperature alarms whereas the control of the burner is by a separate temperature regulator.

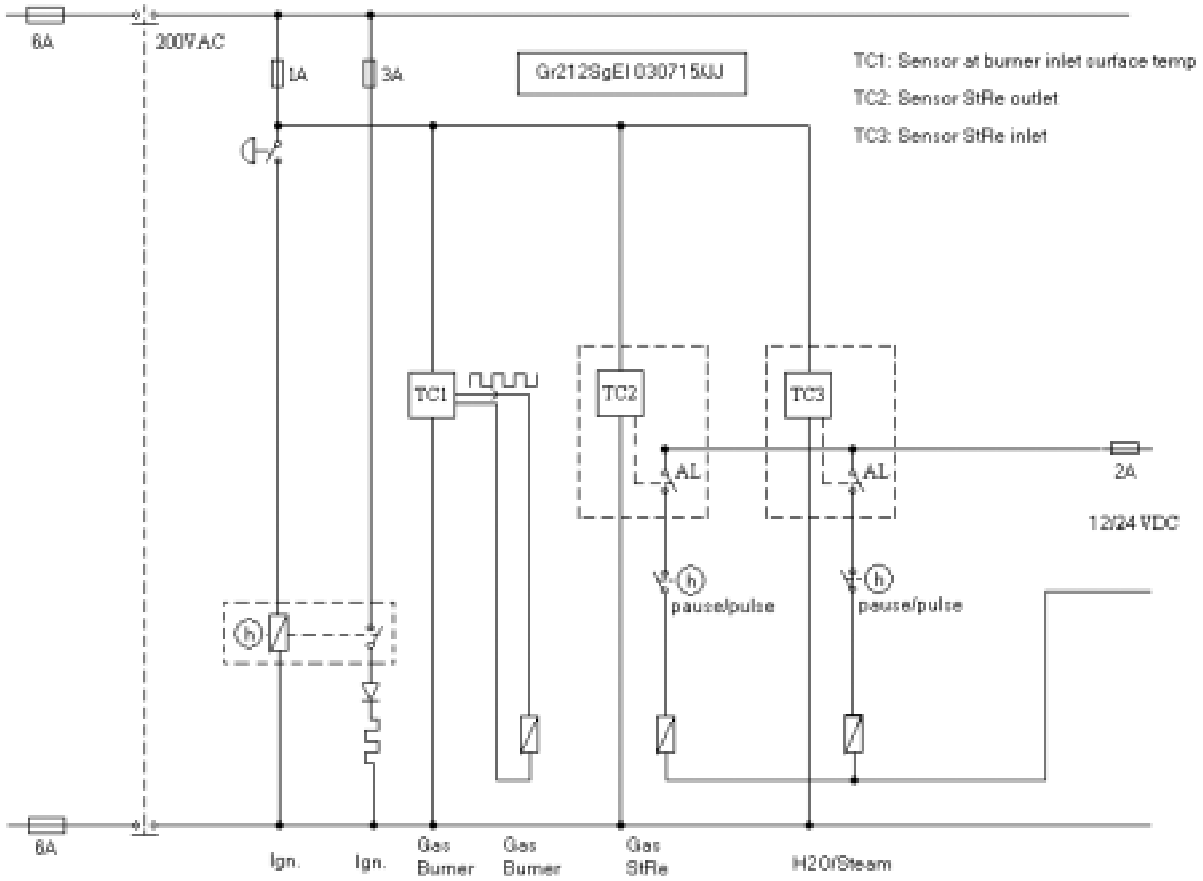


Figure 19 Electric scheme.

The automatic control was used in the start-up experiments (see next chapter). The control system works according to the expectations. Start-up is quick and the load control is via pulse width modulation (via pause/pulse relays).

6.4 Start-up experiments

A number of start-up experiments were performed with and without the addition of air into the steam reformer reactor. Air can be supplied to the system since the unit utilises oxygen resistant catalyst formulations. In traditional steam reformer system, the presence of oxygen would violate the stability of the active phases and initiate sintering and degradation.

The start-up experiments were performed in the automatic mode and some temperatures and the CO-concentration were logged as a function of the time. Start-up by means of ignition was performed at time=0.0 minutes.

Figure 20 shows the results obtained when no air was supplied to the steam reformer reactor. The trig-point for starting water supply is when the outlet temperature of the reformer is 550°C. The supply of feedstock is trigged by the inlet temperature to the reformer (250°C). It might be possible to find better trig points and also to calibrate the alarm levels to enable a quicker start-up. However, these measures are not within the scope of this project.

From Figure 20 it is obvious that the temperature response of the system is quick. The rather slow warm-up of the WGS/PROX-reactors is caused by condensation of water during the initial phase of the water supply. Ideally, these reactors should be by-passed during the first few minutes. Another way to avoid condensing phenomena is to decrease the cooling during the initial phase of start-up (i.e. to by-pass the cooling water). These condensing phenomena are especially severe if high steam:carbon ratios are chosen and if no air is supplied to the steam reformer (nitrogen will dilute the reformate and decrease the water concentration). If condensation could be avoided and if the feedstock could be supplied earlier, the start-up time could be considerably decreased. The reformate reaches fuel-cell quality 30 minutes after start-up when no air is supplied to the steam reformer.

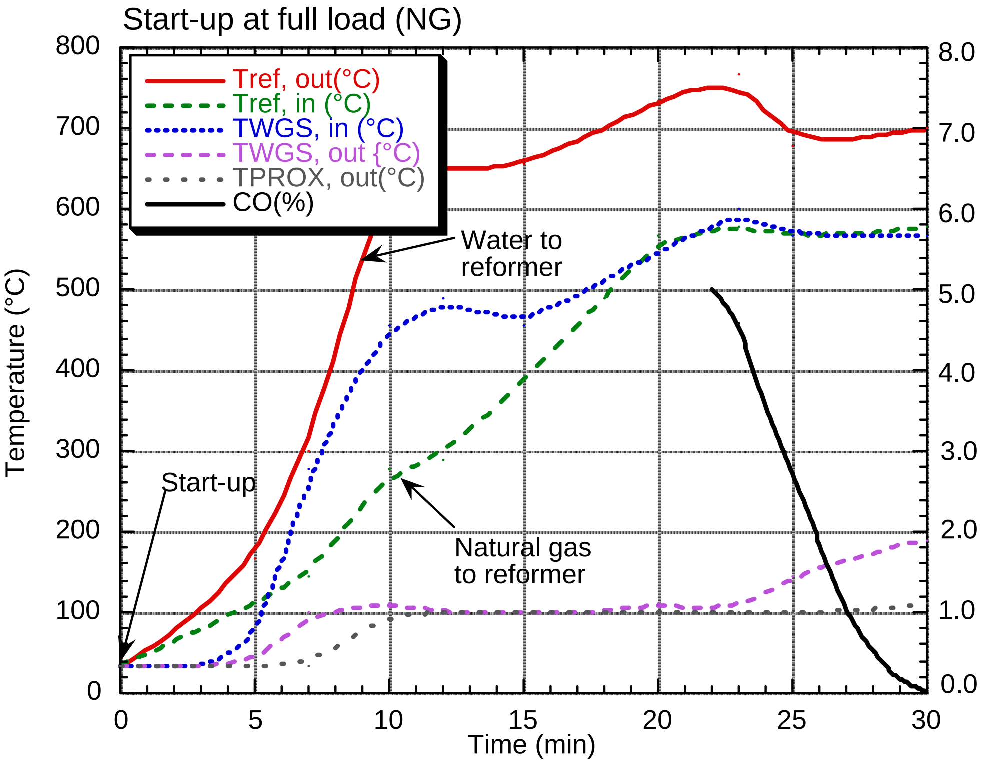


Figure 20 Start-up experiment without rapid heat (oxidation in the reformer). Temperature profiles given as a function of the time together with the CO-signal.

Addition of air into the steam reformer has two significant advantages: a) the steam reforming temperature will be increased quicker and b) nitrogen will dilute the moist reformate and the problems with condensation in the WGS/PROX-reactor can be reduced. Figure 21 shows a start-up experiment with relatively small amounts of air added to the steam reformer reactor (air:C ≈ 1). However, it is clear that these rather minute amounts of air effectively speed up the start-up process. We see a quicker temperature rise throughout the system and less problems with condensing water. Indeed, the gas quality reaches fuel-cell quality 20 minutes after start-up in this case.

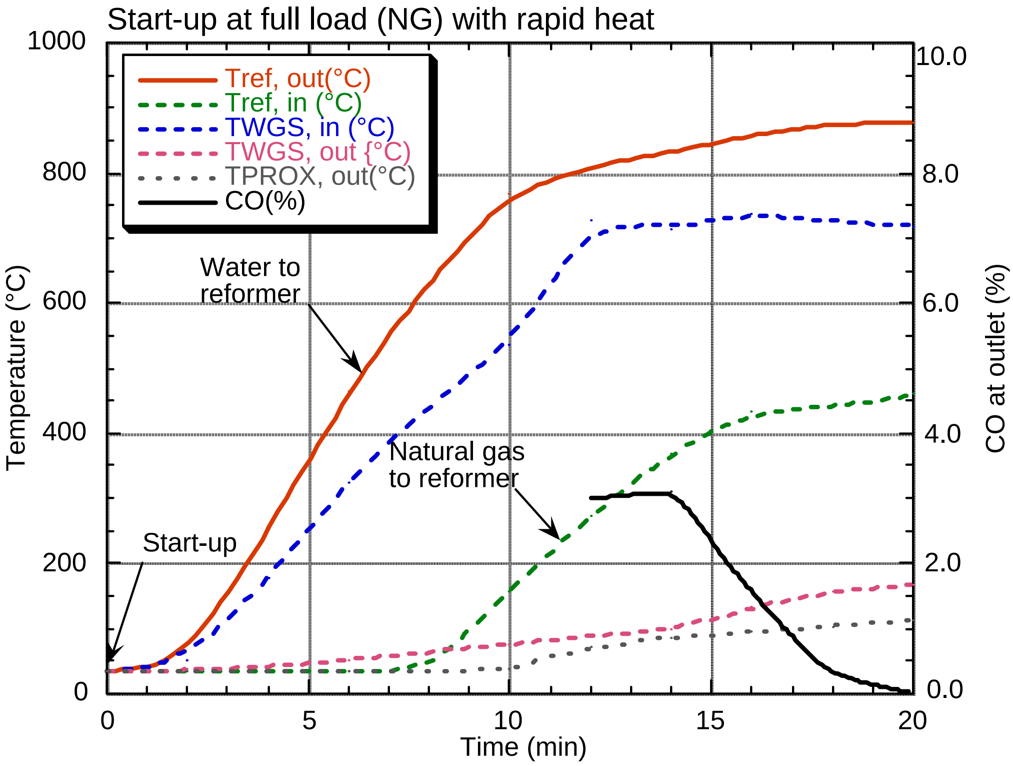


Figure 21 Start-up experiment with rapid heat (oxidation in the reformer). Temperature profiles given as a function of the time together with the CO-signal.

If the air:C-ratio is increased further we foresee positive effects in the start-up behaviour of the reactor. If some air also was introduced between the steam reforming reactor and the WGS-reactor, the heat-up of the downstream reactors would be favoured and the condensation phenomenon could be avoided completely.

It is estimated that the lag-time during start-up can be reduced to less than 10 minutes if these measures are followed. Further studies concerning the start-up behaviour should be performed in the proposed following-up projects.

Even if the Ultraformer concept works according to the specification in most senses and further optimisation/calibration is possible, it is important to summarise the technical risks with this and similar concepts in relation to the specification of demands. The most significant technical risks are summarised in the next chapter.

7. Technical risk evaluation and remaining problems

There are a number of potential technical obstacles and risks, which must be reviewed. The most evident risk is connected to catalyst deactivation & degradation. The catalysts included in the Ultraformer unit are oxygen resistant and can tolerate minor amounts of sulphur without deactivation. In cases were the feed stock carry excessive amounts of sulphur it is necessary to include a more efficient desulphurisation unit. However, implementation of HDS into the Ultraformer seems rather unrealistic since this would complicate the system and make it slow in response.

The best way is to bring up the reformer temperature (possible via air injection into the steam reformer) when processing feed stocks with a high sulphur content and to convert the complex heterocyclic sulphur compounds into hydrogen sulphide, which is easy to trap on zinc oxide. The water-gas catalyst has a tendency to sinter in the reformate gas stream. Two alternatives exist: over dimension the catalyst or improve its resistance to sintering. The PROX-catalyst is sensitive to poisoning since it operates at very low temperatures.

All catalyst deactivation will degrade the performance of the system and in time give a reformate mixture with poor quality. Also the operability of the unit might be affected in a negative way. Thus, it is important not only to improve the catalyst life, but also to find indicators for these degradation processes and to design the units for an easy catalyst replacement.

The stability of the system can be improved by replacing inherently unstable processes (e.g. PROX) with stable processes (membrane separation of hydrogen). Excessive recuperation also has a negative impact on process stability and tends to give a slow system response. However, process stability has not turned out to be a problem in the Ultraformer concept, provided the catalysts are fresh and all auxiliary components work according to the specification. By using components with a high reliability and by the use of redundant components it should be possible to overcome these problems.

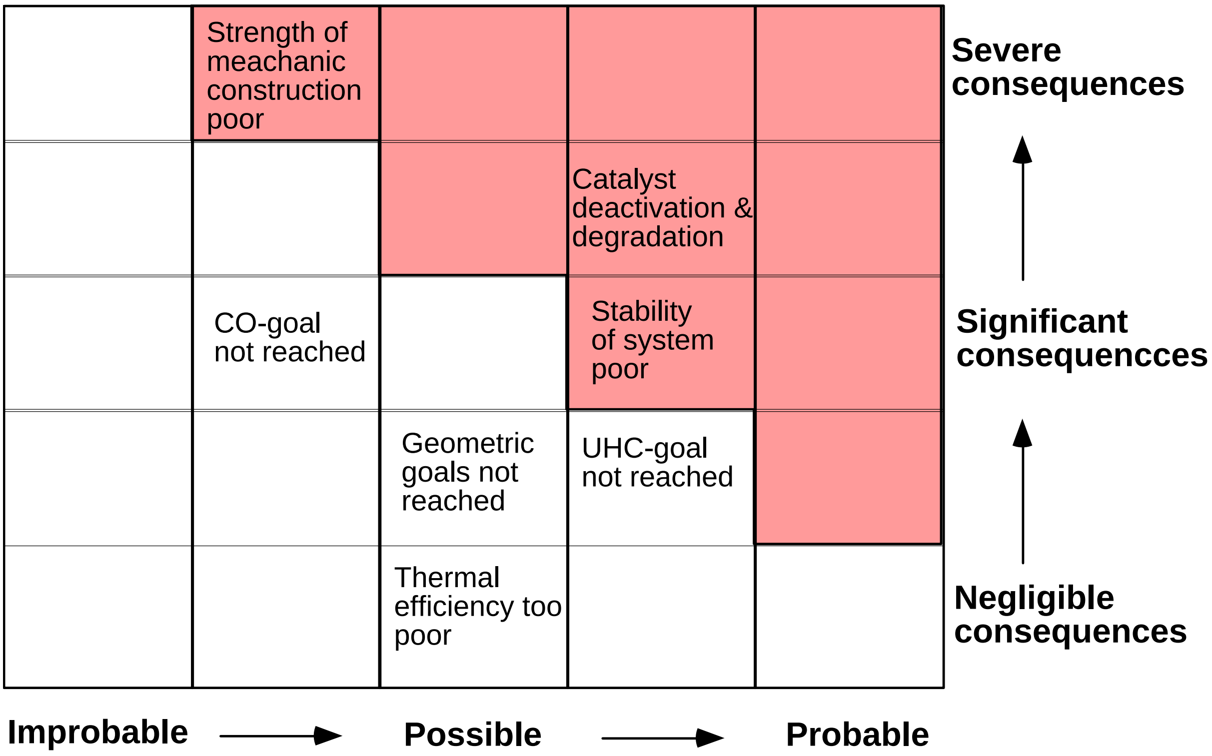
Some of the unit reactors in the Ultraformer concept are operated at very high temperatures. This might give rise mechanical problems like thermal fatigue and thermally induced corrosion. The reformate carries a lot of carbon monoxide, which is known to cause chemical corrosion (metal dusting) through carbide formation together with many materials. These processes can in time lead to a catastrophic failure of the system. Thus a careful review of the mechanic design and the material choice should be performed in order to highlight possible problems. Moreover, the surface temperature of the mechanic construction could be decreased through a more effective heat transfer.

The CO/UHC-goals can be reached as demonstrated in the experiments performed in this study. However, the figures are only reached in a narrow window with respect to operation parameters, which means that the system is sensitive to disturbances. This is perhaps not a catastrophic problem, but might affect the overall efficiency of an Ultrafomer + PEMFC-system. The window with acceptable concentrations of CO/UHC should be wider in order to make the process more stable.

The unit can be built in a very compact way, as demonstrated in this study. However, if it at the end of the day is necessary to increase the amount of catalyst and/or to increase the size of the reactors to avoid thermal fatigue, the size goals might be violated.

The thermal efficiency can always be improved. There exists a delicate trade off between the insulation work and the degree pf recuperation on one side and the compactness of the system on the other side. It is reasonable to believe that a suitable balance can be found, even if the thermal efficiency of the unit used in this study can be improved.

Figure 23 below tries to put the relevant risks into a matrix, shoving the likelihood and the consequence of different problems. The long-term goal is to try to decrease the likelihood for severe problems and to decrease the consequences for probable issues.



	Strength of meachanic construction poor			
			Catalyst deactivation & degradation	
	CO-goal not reached		Stability of system poor	
		Geometric goals not reached	UHC-goal not reached	
		Thermal efficiency too poor		

Figure 23 Relevant obstacles and technical risks.

8. Conclusions

The experimental study of the Ultraformer system shows that the expectations from the previous design study (appendix A) could be met. A single-train reactor with necessary auxiliary components can process a variety of fuels to give a reformate mixture with low concentrations of hydrocarbons and CO. The reactor concept is easy to scale and has a high thermal efficiency together with a wide turn-down ratio.

Start-up is quick and if the start-up sequence is optimised it would most probably be possible to generate reformate with fuel cell quality within 10 minutes.

A simple and reliable control algorithm was used in the automation of the system. The focuses were here to a find a cheap system with good enough performance for this application.

Optimisation should focus on measures to bring up the reformer temperature without violating the long-time durability of the mechanic construction. Moreover, activities should to be directed to catalyst deactivation and degradation processes. The fuel processor (Ultraformer) can easily be fitted with fuel cells for extended evaluations of a complete APU-system based on fuel processing and fuel cells.

9. Continued work

There are really a number of important and interesting areas for continued work. Some of the activities should be directed to the fuel processor itself (the Ultraformer unit) whereas other activities include the implementation of fuel cells into the Ultraformer concept in order to build compact APU-units.

First of all, it is clear that studies must be devoted to the reliability and possible degradation processes in the Ultraformer concept. These investigations should include extended catalyst deactivation studies together with system optimisation work. The robustness of the system to cope with degradation processes must be improved. The mechanic construction should be revised with respect to stress-strain analysis, thermal fatigue and material choice (thermal and chemical degradation including metal dusting).

When the robustness of the Ultraformer concepts has been verified, it is possible to include fuel cells into the system. It would then be interesting to operate a PEMFC together with the complete Ultraformer unit and to unify the control system of the fuel processor and the fuel cell. A slip stream of reformate could be used to power a SOFC and an evaluation of these two concepts could be performed (Ultraformer + PEMFC vs. Ultraformer + SOFC). The study should include different fuels as the feed stock, e.g. renewable fuels like biogas and alcohols, fossil fuels like natural gas, LPG and heavier hydrocarbons (including logistic fuels containing sulphur). Differences in the way of operating the systems with these different fuels should be highlighted and the best mode of operation should be found for each fuel.

These projects should be performed in a consecutive manner, starting by the autumn of 2003.

Fuel processor for small-scale production of hydrogen – Design study

Vätgasgenerator för småskalig vätgasproduktion – en designstudie

Lund 02-06-25

Catator AB
Fredrik A. Silversand, Ph.D., Chemical Engineering & Catalysis

SGC:s FÖRORD

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Följande parter har gjort det möjligt att genomföra detta utvecklingsprojekt:

Catator AB
Försvarets Materielverk
Sydkraft Gas AB
OptiCat International AB
ABB Group Services AB, Corporate Research
AB Fortum Värme samägt med Stockholm stad
Statens Energimyndighet

SVENSKT GASTEKNISKT CENTER AB

Johan Rietz

Summary

A design study concerning small-scale fuel processors for stationary applications has been performed on the request of Swedish Gas Centre AB (SGC). The catalyst formulations and the reactor designs are based on Catator ABs background information in the area of steam reforming and downstream reactions for CO-purification. Thus, a preliminary system-layout and detailed reactor designs are presented for a fuel processor with a capacity of 30 kWH_2. The fuel processor includes the following functional steps:
- Stem reforming (SREF)
- Water-gas-shift converter (WGS)
- Reactor for preferential oxidation of CO (PROX)
- Units for hydrogenolysis and sulphur trapping (DESULF)

The reactor designs are based on a large number of confirmatory experiments with different gas compositions when utilising different catalysts. The steam-reforming catalyst will be based on an alkaline formulation doped with precious metals. It is important that the alkaline component is matrix bound in order to avoid evaporation and catalyst deactivation. Catators formulations are not sensitive to coke formation and have an increased tolerance to sulphur.
The water-gas-shift catalyst will be based on a precious metal doped on to a rare earth metal oxide. This formulation shows an extremely high activity together with a good sulphur tolerance. Preferential oxidation of carbon monoxide is performed on a Pt/metal oxide catalyst, which operates at rather low temperatures (close to the boiling point of water).

Experimentally derived reaction data were implemented into our generic simulation model for chemical reactors, CatalystExplorer. The simulation code enabled us to dimension the catalyst need and the required heating/cooling in each catalytic step. Reactor simulations together with thermodynamic calculations (HSC to Outokompu) and mass- & energy balance calculations (Design II to WinSim) enabled us to present an overarching system lay-out.

All experimental data confirm the following expectations concerning the fuel processor:
- Scalable design for small-scale fuel processing (1 – 1000 nm^3/h of H_2)
- All-inclusive unit including feed stock purification and gas purification
- The product gas shall have fuel-cell quality (i.e. <20 ppm (v/v) of CO)
- The unit shall have a wide turn-down ratio, preferably, 1:10
- The unit shall be compact, < 2 litre per kWH_2 (gross volume)
- The thermal efficiency shall be high, preferably >80% calculated on the LHV of the feedstock
- The unit shall process different feedstocks: natural gas, LPG, alcohols and light/heavy naphtha
- The thermal response of the unit shall be high (start-up within 5 minutes)

The objective of the Realisation phase is to construct and evaluate a novel reactor design for hydrogen production @ 10 nm^3/h. This project phase, which will be initiated during the summer of 2002, can be divided into the following sub tasks:
- Detailed design including flow sheets and P/I-diagrams
- System construction and assembly
- Commissioning
- Experimental evaluations
- Possible system modifications to improve the performance
-Conclusions

Sammanfattning

En designstudie avseende små stationära anläggningar för vätgasproduktion har utförts på uppdrag av Svenskt Gastekniskt Center AB (SGC). Utnyttjade katalysatorformuleringar och principdesigner bygger på Catator ABs tidigare erfarenheter som har anpassats till aktuell tillämpning. I rapporten presenteras detaljerade reaktordesigner respektive ett flödesschema för en anläggning med en kapacitet på 30 kWH_2. Anläggningen innehåller en rad delsteg enligt:

- Ångreformer
- Vattengasreaktor
- Reaktor för selektiv oxidation av CO
- Enheter för avsvavling

De reaktordesigner som presenteras bygger på en rad verifikationsexperiment där olika gasblandningar fått reagera på en rad olika katalysatorformuleringar. Ångreformeringskatalysatorn kommer att baseras på en formulering innehållande ädelmetaller på en alkalisk bärare. Det är härvid av vikt att bärarens alkaliinnehåll är matrisbundet för att undvika förångning och katalysatordeaktivering. Catators katalysatorformuleringar uppvisar låg benägenhet till koksning samt har en god svaveltålighet. Vattengaskatalysatorn består av ädelmetaller som tillförts en bärare av sällsynta jordartsmetalloxider. Denna formulering uppvisar en mycket hög aktivitet samt har en god svaveltålighet. Selektiv oxidation av CO utförs på en ädelmetallbaserad katalysator vid låg temperatur, ca 100°C – nära vattnets kokpunkt.

Experimentellt härledda data implementerades i Catators simuleringsmodell för katalytiska reaktorer, CatalystExplorer. Utnyttjande av simuleringsmodellen möjliggjorde en dimensionering av katalysatorn samt av behovet av kylning/värmning i de olika katalytiska stegen. Genom reaktorsimuleringar, termodynamiska beräkningar (HSC, Outokompu) och processimuleringar (Design II, WinSim) kunde en övergripande systemdesign tas fram.

Experimentella data verifierar de förväntningar som finns avseende vätgasgeneretorn:

- Skalbar design (1 – 1000 nm^3/h av H_2)
- Totalintegrerad enhet som innehåller samtliga katalytiska steg
- Stort driftområde, 1:10
- Kompakthet, < 2 l/kWH_2
- Hög termisk verkningsgrad, >80% beräknat på bränslets effektiva värmevärde
- Enheten skall kunna utnyttja olika bränslen (bränslegaser, alkoholer, bensin, fotogen)
- Enheten skall ha en god termisk respons (korta starttider, ca 5 minuter)

Målsättningen med realisationsfasen av projektet är att konstruera, driftsätta och utvärdera en vätgasgenerator med en kapacitet av 10 nm^3/h av vätgas (30 kWH_2). Denna projektfas, som avses påbörjas under sommaren 2002, kan uppdelas i följande delmoment:

- Framtagande av detaljerade flödesscheman och P/I-diagram
- Konstruktion och sammansättning
- Experimentella utvärderingar
- Modifieringar och verifikationstester
- Slutsatser

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1. Introduction

There is a growing interest concerning hydrogen as a fuel on the market. Hydrogen is traditionally used as a reducing agent in the chemical industry but is increasingly considered as one of the major energy carriers for the future. Thus, large volumes of hydrogen are expected to be utilised as propellant on fuel cell powered vehicles beginning a few years ahead. Other interesting areas of applications might be small-scale heat-and power generation for domestic and industrial use, i.e. boilers equipped with fuel cells.

The route to hydrogen is normally over steps including fuel processing and gas purification. Pure hydrogen can also be produced via electrolysis. Future processes might also include renewable sources like wind, solar energy and biochemical methods. For the time being, however, these sources are far too expensive to be applicable candidates for massive hydrogen production.

In order to realise the hydrogen economy it is important to supply the increasing hydrogen market with cheap hydrogen. Fuel processing including hydrogen extraction from various fossil and renewable fuels is probably the most economic way of hydrogen production today. However, in order to reach low production costs also in minor production facilities it is essential to present compact all-inclusive reformers with a high thermal efficiency. Indeed, it is not suitable to miniaturise old-fashioned system designs to arrive at small units applicable for transient operation and rapid start-up.

Future reforming technology is associated with a novel reactor- and catalyst design with a maximum of integration to achieve compact, cheap and durable units for processing different feed stocks.

Catator AB (CAB) has over the years developed different novel reactor designs and catalyst formulations suitable also for small-scale fuel processing. This project was initialised to explore the possibilities to design a fuel processor with the following characteristics:

- Scalable design for small-scale fuel processing (1 – 1000 nm^3/h of H_2)
- All-inclusive unit including feed stock purification and gas purification
- The product gas shall have fuel-cell quality (i.e. <20 ppm (v/v) of CO)
- The unit shall have a wide turn-down ratio, preferably, 1:10
- The unit shall be compact, < 2 litre per kWH_2 (gross volume)
- The thermal efficiency shall be high, preferably >80% calculated on the LHV of the feedstock
- The unit shall process different feedstocks: natural gas, LPG, alcohols and light/heavy naphtha
- The thermal response of the unit shall be high (start-up within 5 minutes)

The total project is divided into two consecutive phases, a) Feasibility and Design phase and b) Realisation phase. This report covers the results obtained during the first project phase and function as background information to the second project phase, which includes design, commissioning and evaluation of a prototype reformer with said characteristics.

2. Scope and objectives

The overarching objective of the current project phase (Feasibility and Design phase) might be expressed as follows:

“To suggest a novel reactor concept for small-scale production of hydrogen based on experimental evaluations and existing background information”.

Project phase a) covers the following items:

- Design/erection/commissioning of test rig
- Catalyst preparation and characterisation
- Comprehensive experimental evaluation of unit-steps in the process
- Novel reactor design
- Design calculations (unit-processes and integral system)
- Design suggestion and expected features
- Conclusions

The objective of the Realisation phase is then expressed as:

“To construct and evaluate a novel reactor design for hydrogen production @ 10 nm^3/h”. This project can be divided into the following sub tasks:

- Detailed design including flow sheets and P/I-diagrams
- System construction and assembly
- Commissioning
- Experimental evaluations
- Possible system modifications to improve the performance
- Conclusions

The results of each project phase are concluded in comprehensive reports.

3. State of the art

Important reactions

There are a number of reactions to take into consideration in fuel processing. The highest hydrogen yield is obtained when using pure steam reforming where a mixture of the hydrocarbon feed stock and steam is reacted over a suitable catalyst. The hydrogen concentration might be as high as 60% or above whereas processes including autothermal or exothermal reforming (steam reforming conditions with addition of oxygen/air) give a lower hydrogen yield [1]. However, steam reforming with simultaneous oxidation gives a more compact reactor design since it is possible to simplify the heat transfer structure.

The most important reactions to take into consideration in steam reforming and/or partial oxidation of methane and higher hydrocarbons are given below. Steam reforming yield a mixture of hydrogen and carbon monoxide. Carbon monoxide will then in turn react with more steam to yield carbon dioxide and hydrogen. The exact composition of the reformate gas leaving the reactor is depending upon the feed stock composition, the temperature and the pressure. Hence, an increased temperature favours the conversion of hydrocarbons but result in a higher concentration of CO. A low reforming temperature will result in a mixture containing relatively high amounts of methane and carbon dioxide. The steam reforming reactions and the water-gas shift reaction are equilibrium reactions, which add limitations to the process.

Steam reforming is a highly endothermic process and large amounts of heat need to be supplied to the catalysts to power the reactions. One simple way of adding heat is simply by combusting a part of the flammable components in the mixture. Autothermal reforming is when there exists an accurate balance between the endothermic reforming reactions and the exothermic combustion reactions. Addition of oxygen might also have a merit in decreasing the coke formation.

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

$$CO + H_2O \longleftrightarrow CO_2 + H_2$$

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

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

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

The main problems associated with steam reforming are heat supply, coke formation and possible poisoning. Coke formation is normally through thermal cracking of hydrocarbons or through reactions between carbon monoxide molecules [2]. Extensive coke formation will result in pore blockage in the catalyst and increased resistance to pore diffusion. In addition, coke formation will also result in an increased pressure drop. The tendencies for coke formation can be influenced by a number of catalyst- and process parameters.

The reformer gas will carry high concentrations of CO and formation of metal carbonyls is possible under some reaction conditions. Such reactions might result in catalyst corrosion and metal dusting.

Example of compact reformers

A number of compact reformers have been presented over the years [3-4]. Haldor Topsøe A/S was one of the first companies to present a reactor design for “compact reforming”, see Figure 1 below. The reactor consists of a number of tubes creating annular volumes where a standard pellet catalyst is put. Heat is supplied by means of a burner, located in the centre of the reactor. The flue-gases will heat the annular reforming section via convective heat transfer. The feedstock/steam is led in two passes through the reformer catalyst. The temperature is rather low in the first pass to enable some pre-reforming. The second reformer step is closer to the burner and operates at a higher temperature to arrive at a high overall conversion of hydrocarbons (especially methane).

Although the design might look complicated it is a rather innovative design, especially in comparison to traditional tube reformers. The capacity of the Topsøe compact reformer is in the neighbourhood of 0.1 kWH_2/litre. The Topsøe concept is built on true steam reforming and the hydrogen yield is consequently high. The design is suitable in stationary applications with modest demands concerning thermal response and a quick start-up.

A couple of years ago, Johnson Matthey demonstrated a design, which later on was going to be called the “hot spot” reformer, see Figure 2 below. This concept is built on autothermal or exothermic reforming, where air is added to the feed stream. A suitable gas, preferably hydrogen, is added on start-up. When the catalyst is hot enough, the start-up fuel is replaced with the hydrocarbon to be processed. The thermal balance of the reactions and consequently the catalyst temperature are controlled by the amount of air added. The hydrogen yield is lower than in true steam reforming but the reactor design is much simpler. The “hot-spot” reformer is especially assigned for automotive applications where compactness is an important demand.

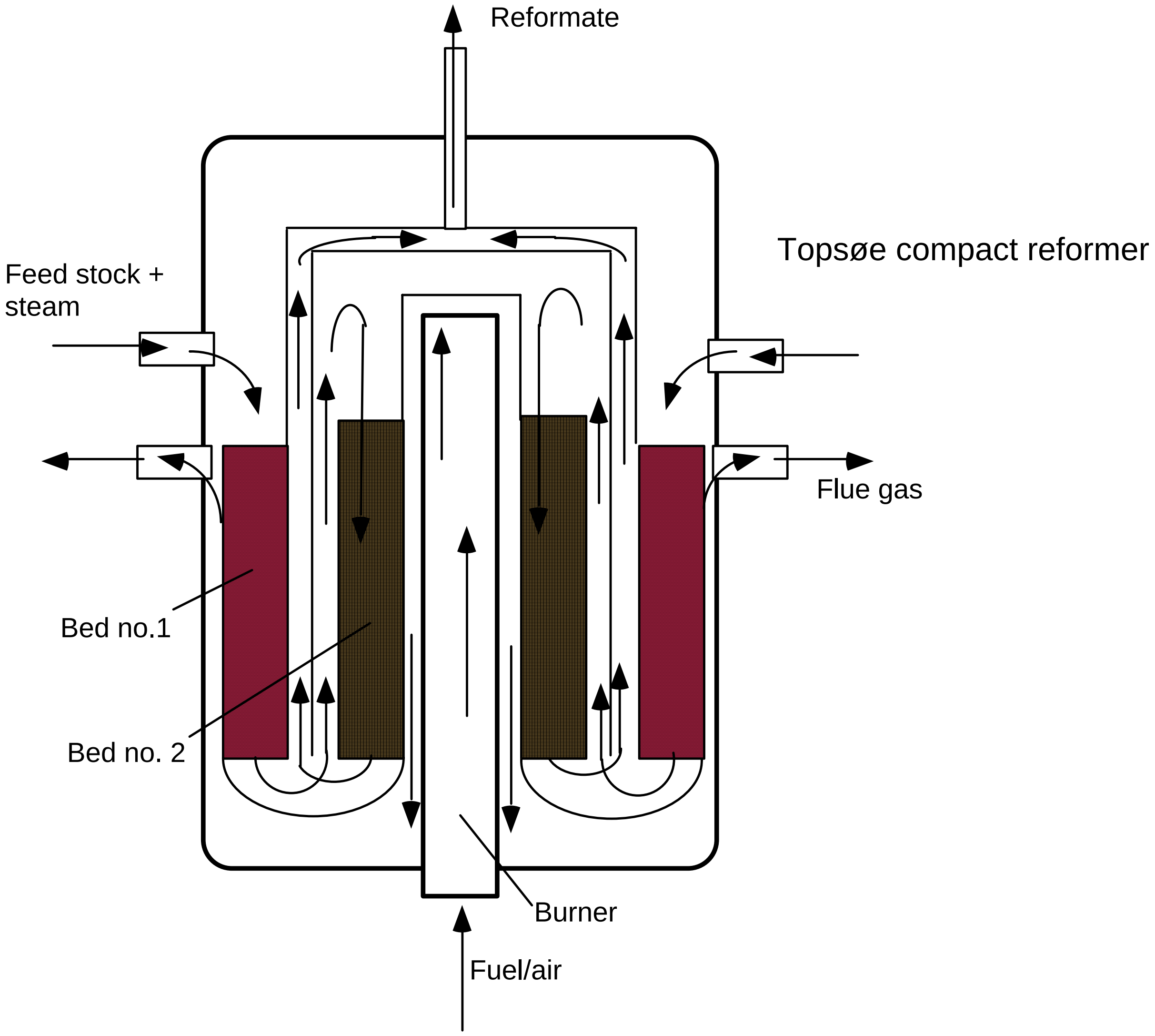


Figure 1 Topsøe compact reformer.

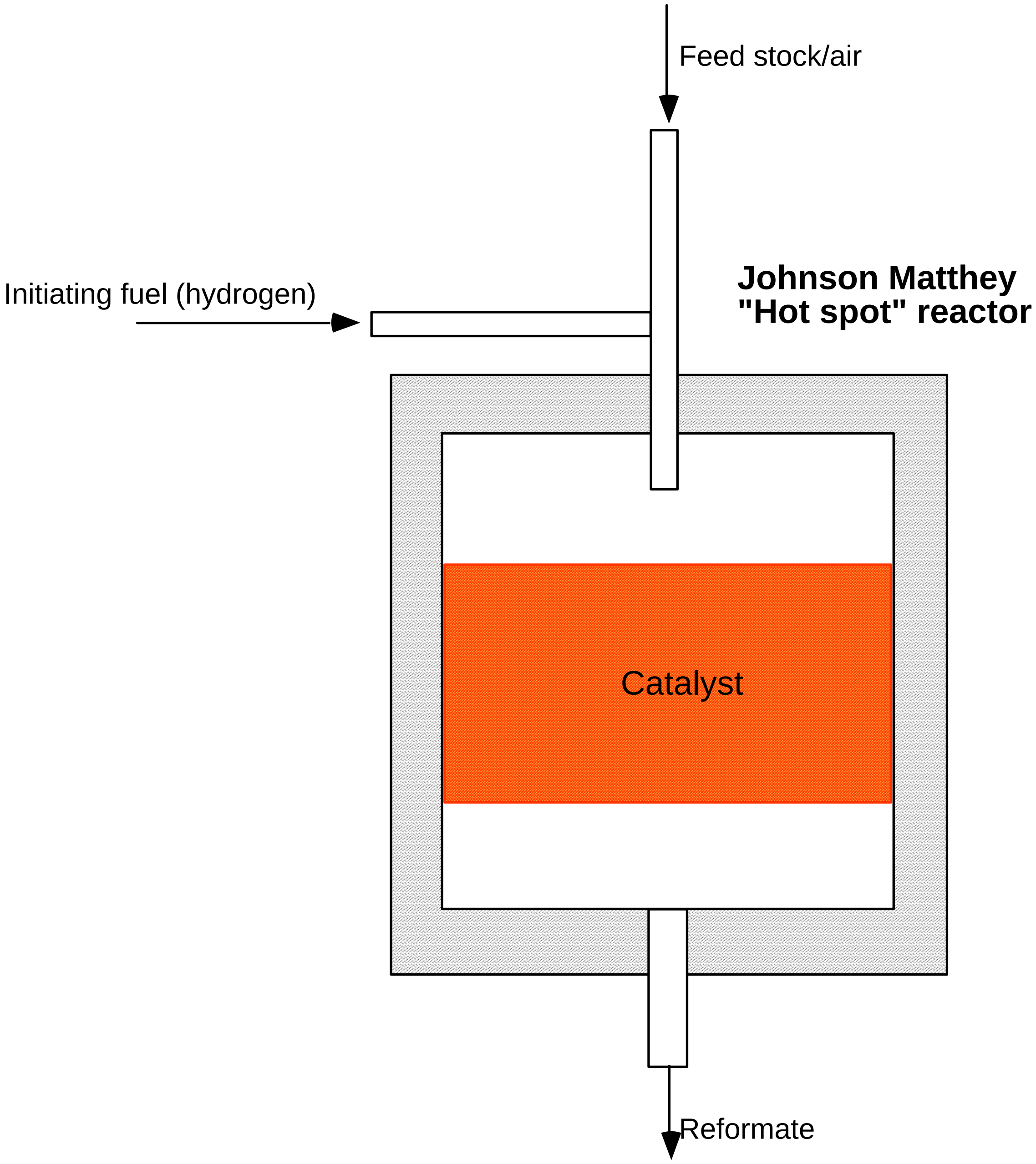


Figure 2 Johnson Matthey “hot-spot”-reformer.

Advantica (formerly British Gas) has demonstrated a heat-exchanger reactor for steam reforming. The basic idea is to coat one side of a plate with a reforming catalyst and the other side with a combustion catalyst, see Figure 3 below. The intimate coupling between the exothermic combustion reaction and the endothermic reforming reactions enable them to arrive at a compact reactor design. The capacity is about 10 kWH_2/litre, which is extremely high. The Advantica-concept is an innovative design, which might show merit in automotive applications since it produces a more hydrogen rich gas than the “hot-spot”-reformer. The adhesion of the catalyst to the surfaces is, however, a crucial problem in this design.

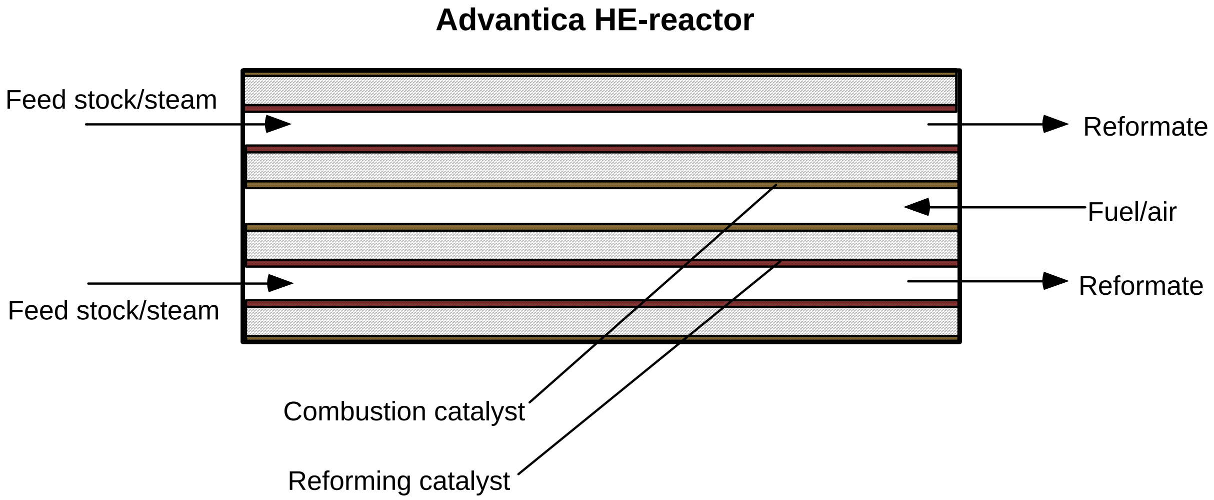


Figure 3 Advantica heat-exchanger reformer.

Catator has designed a heat-exchanger reactor for autothermal reforming including downstream reactions for carbon monoxide removal [5]. The reactor design is based on a brazed plate-type heat exchanger. Catalytic cylinders are located at the inlet and the outlet sections of the heat exchanger. In addition, the plates are coated with a catalyst for CO-removal. The catalyst is based on Catators novel methods for catalyst preparation including modified thermal spraying. The catalyst cylinders consist of wire-mesh catalysts whereas the catalyst on the plates is a body-fitted catalyst. The capacity is about 10 kWH$_2$/litre. The Catator-SWEP design includes all necessary steps for the production of a suitable reformer gas for fuel-cell applications. The Advantica concept only includes the first step, i.e. the reformer reactor.

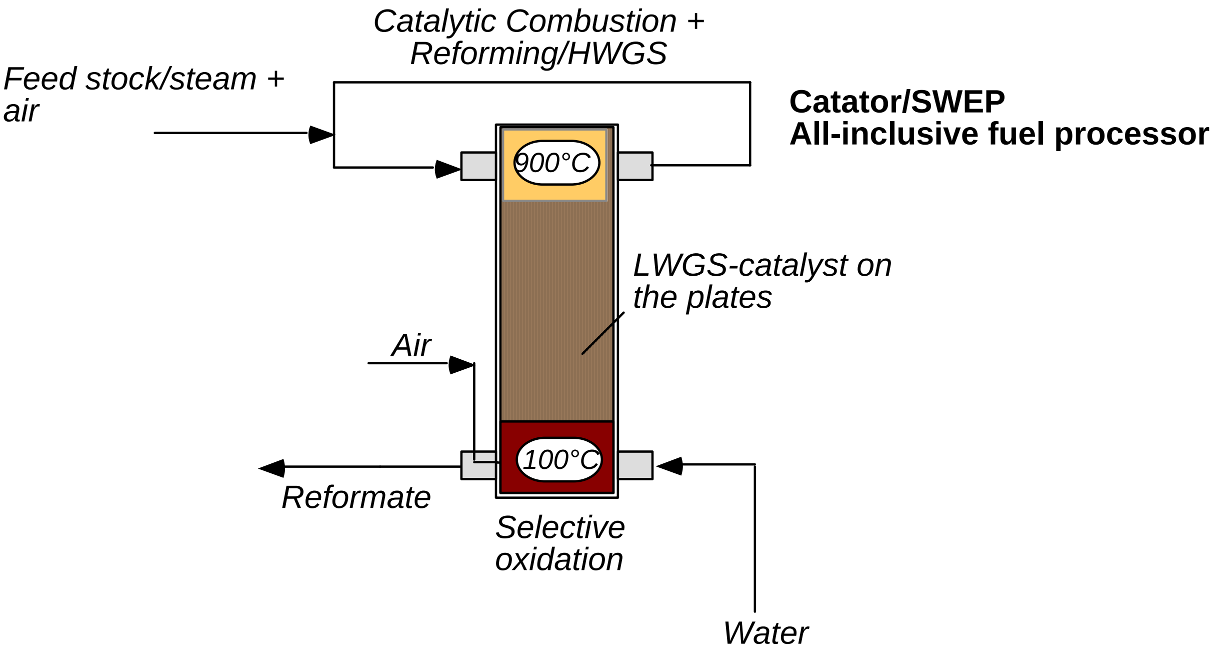


Figure 4 Catator/SWEP all-inclusive fuel processor.

However, the Catator-SWEP concept contains some difficult parts for continued studies. The problems are associated to material choice, method/materials in the brazing process and expected problems with thermal fatigue on transient operation. Even if this concept is interesting from a technical point of view, this project will focus on other design alternatives.

The above examples show some major design principles to comply with future demands concerning compactness, thermal response and hydrogen yield/quality.

Problems associated to steam reforming

Even if the reactor design is crucial for the function & operability of the fuel processor, it is also essential to choose applicable catalyst formulations to avoid problems arising from coke formation and sulphur poisoning.

Indeed, even if steam reforming as a process was invented almost a decade ago, it was not until the 50s it was possible to process heavier feed stocks like naphtha [6]. The main reason was extensive coke formation in the catalysts utilised at earlier stages and a lack of fundamental understanding of the processes giving rise to coke. The development of alkaline catalysts together with an increased understanding of the influence of different process parameters led to major breakthroughs during the 50s and 60s. Figure 5 below indicates the limits for coke formation in methane reforming. If the temperature is too high at the inlet together with a too low partial pressure of hydrogen, coke will form due to thermal cracking. Consequently, pre-reforming at rather low temperatures is conventional to increase the partial pressure of hydrogen at the inlet section. An alternative way is to re-circulate some hydrogen to the reactor inlet. These two reaction routes are shown in Figure 5 below. In addition, an increase in the steam:carbon ratio at the inlet will favour the coke removal reactions. The steam:carbon ratio is normally chosen to values above 3 in order to reduce the coke formation.

In this project we intend to include a number of measures to reduce/eliminate the problems with coke formation. The catalyst formulations will include novel compositions containing matrix bound alkaline compounds like Ba or Sr. Also, the active phase will consist of precious metals, which will not dissolve carbon. Formation of carbon whiskers is favoured by a high solubility of carbon in the active phase, e.g. in Ni. The process design includes pre-reforming and hydrogen re-circulation. The steam:carbon-ratio will also be set to an applicable value, generally above 3:1.

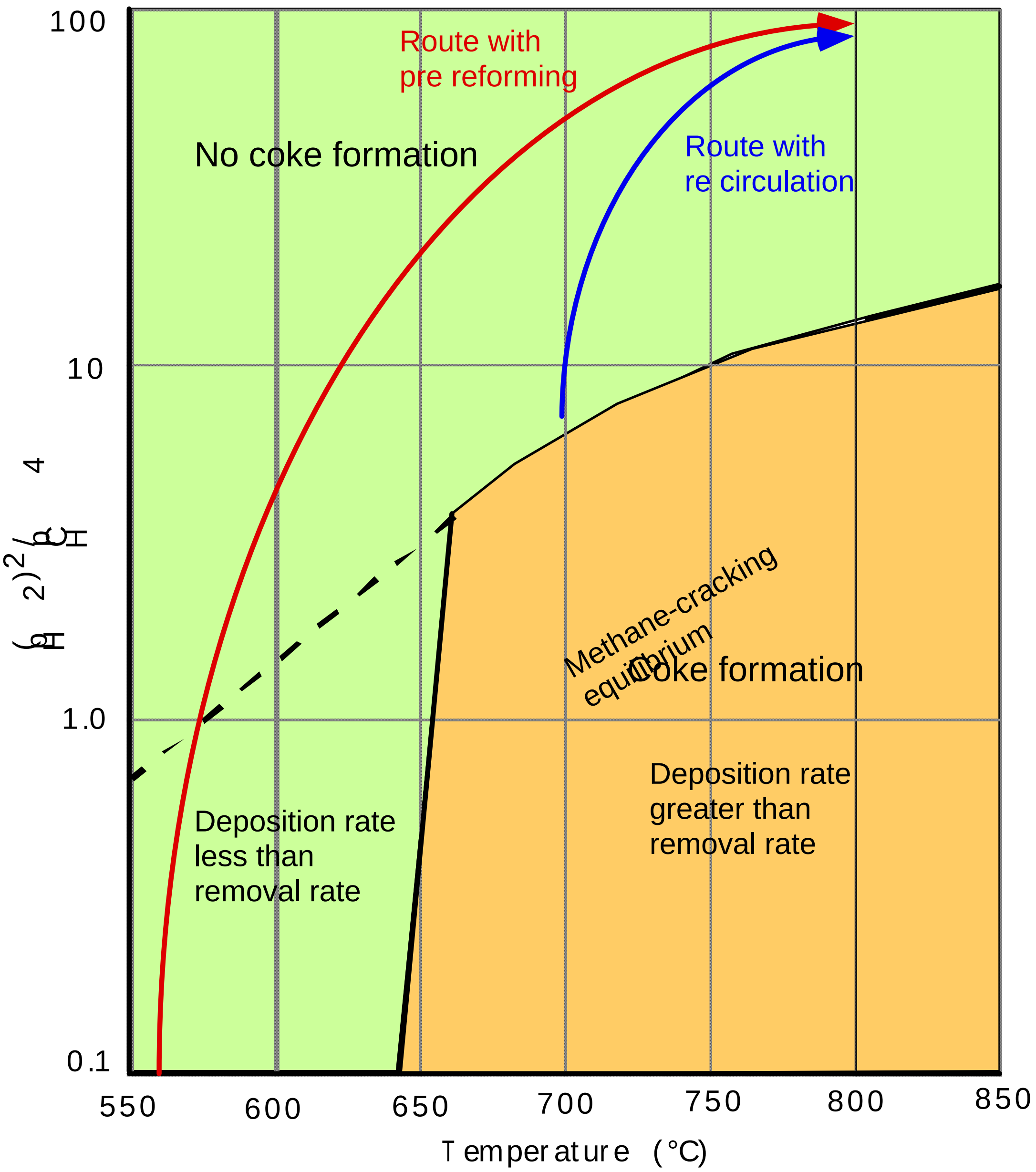


Figure 5 Coke formation in steam reforming of methane, different process routes including pre-reforming and re-circulation.

The expected problems clearly associate to the feed stock quality. The heavier the feedstock is, the more problems might be expected. From this point of view, alcohols are the least cumbersome feeds to process. They are rather easily reformed, show a low tendency to coke formation and do not contain any sulphur. Traditional fuel gases like natural gas and LPG contain sulphur since such compounds are added to enable leakage detection. Some kind of desulphurisation is thus necessary to include in order not to poison the catalysts. Fuel gases show a low to moderate tendency to coke formation. Naphtha might be split into virgin naphtha (normally gasoline) and heavy naphtha (kerosene and diesel). Virgin naphtha contains a mixture of hydrocarbons, also aromatic and unsaturated. Unsaturated and aromatic compounds show high abilities for coke formation [7]. In addition, the sulphur content is normally somewhat higher than in fuel gases. However, environmentally rated gasoline has low sulphur content since the desulphurisation is completed at the refinery.

The composition of heavy naphtha varies to an even greater extent with respect to the composition and the sulphur content. Consequently it is important to derive a specification for the feedstock of interest.

Figure 6 indicate the location of different possible feedstocks with respect to the molecular weight and the sulphur content. The most cumbersome feedstocks are likely to be fractions in the group “heavy naphtha”, i.e. diesel and kerosene.

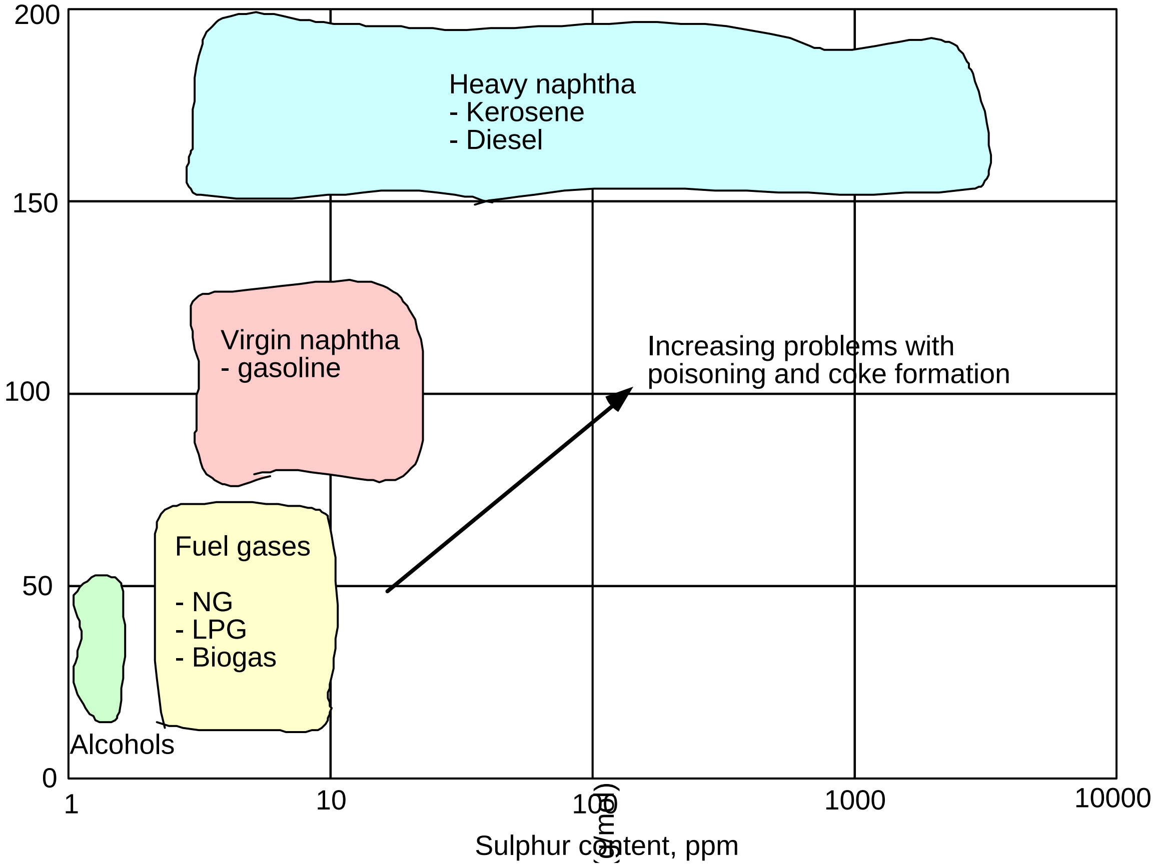


Figure 6 Problems associated with different feedstocks.

The overarching conclusion is that the reactor design together with the formulation and operation of the catalysts are important factors, which influence the overall performance of the fuel processor. Also, the feed stock quality is crucial for the operability & performance of the reactor system. Catator’s background knowledge and methods to avoid process & catalyst problems are described in the next chapters.

4. Catator's background knowledge

Novel reactor designs

Catator has over the years developed a number of catalyst formulations and novel reactor designs suitable for steam reforming and downstream reactions. Our patented methods for catalyst preparation enable us to produce a number of interesting catalytic structures, e.g.:
- Wire-mesh catalysts
- Body-fitted catalysts
- Catalytic heat exchangers
- Electrically heated catalyst structures
- Membrane catalysts

One concept is to combine chemical and physical steps, e.g. chemical reaction and heat transfer. Figure 7 shows different types of EndEx-tubes, both straight flow and recuperative alternatives. The basic idea is to use a catalytically coated coil as a combustion catalyst. The effect density is varied by means of adjusting the coil density along the tube. The heat is transferred to the outer tube where a second catalyst layer is located, e.g. a reformer catalyst.

EndEx-tubes may also be used for pure heating, e.g. for pre-heating other catalyst structures.

EndEx-tubes have successfully been used in fuel processing, i.e. steam reforming of feedstocks ranging from C_1 to C_{12}+.

The idea is to use the EndEx-principle in the steam reformer, which will be designed in this project. The EndEx-concept enables us to build an extremely compact heat-exchanger reactor with an accurate temperature control for said application.

In order to increase the amount of catalyst available in the EndEx-tubes, it is possible to squeeze wire-mesh catalysts on the EndEx-tubes to obtain a finned EndEx-structure.

Catator has also developed a heat-exchanger structure suitable for intermediate cooling/heating in catalytic processes. The CatHex-structures comprises pair of brazed plates, which have a dense pattern of holes where the gas is led through the structure, see Figure 8. Cooling is by means of a suitable cooling media, which is led in a cross-flow pattern in relation to the gas flow. It is also possible to heat the structure by means of utilising hot oil, steam, hot gases or even catalytic combustion (i.e. a combination between CatHex and EndEx).

Wire-mesh catalysts are sandwiched between the CatHex-structures and heat is transferred to the wire meshes by means of an extremely effective convective heat transfer. The heat is then transferred to the CatHex-structures, primarily by means of conduction.

CatHex-structures enable us to include an accurate temperature control in a catalyst package and to carry out intermediate cooling.

CatHex-structures will be used in the reformer- and the WGS-sections of the reactor proposed in this project. In the reformer section the CatHex-structure will be combined with catalytic combustion whereas the CatHex-structures in the WGS-section is for pure cooling.

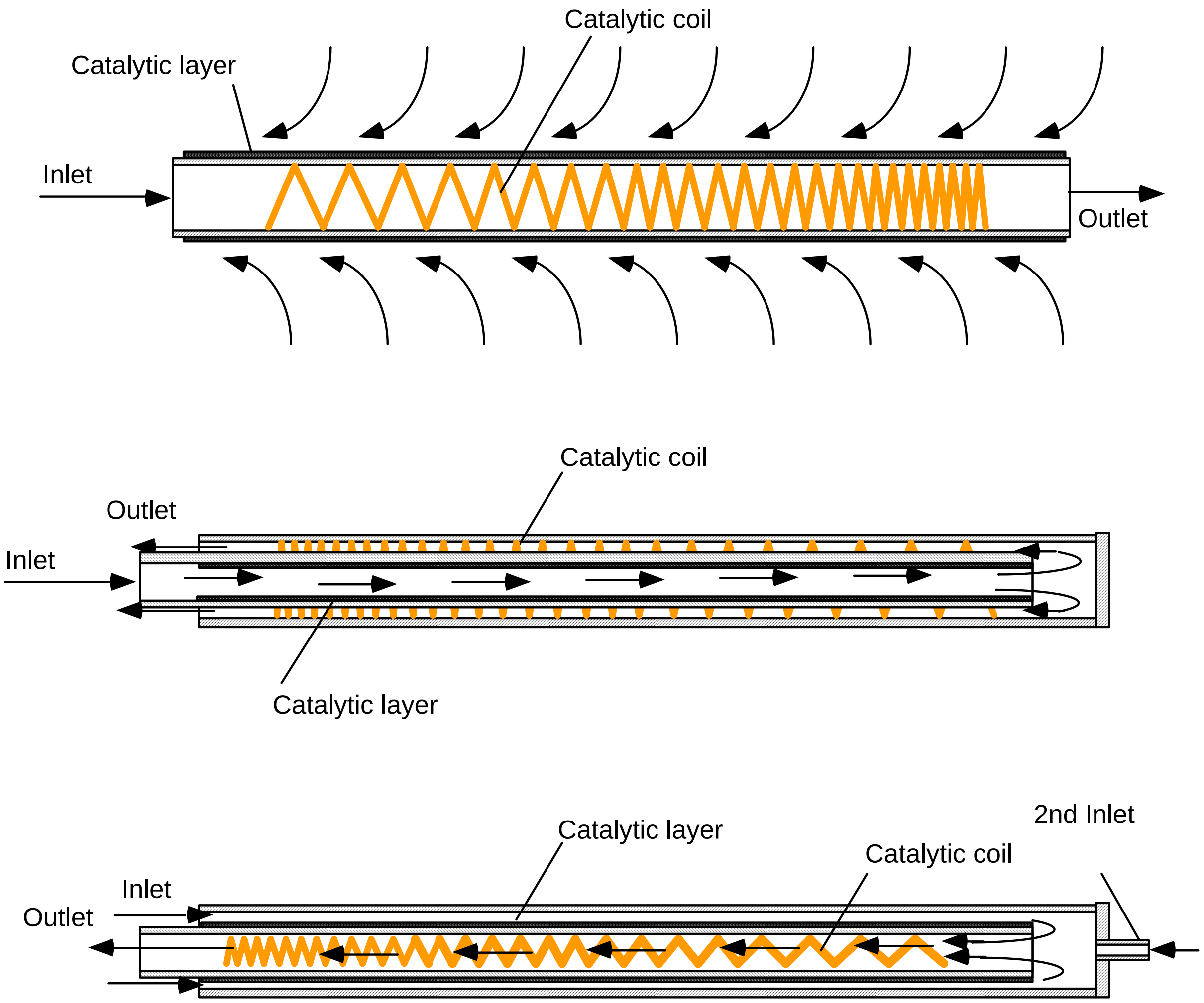


Figure 7 The EndEx-concept; straight flow and recuperative design alternatives.

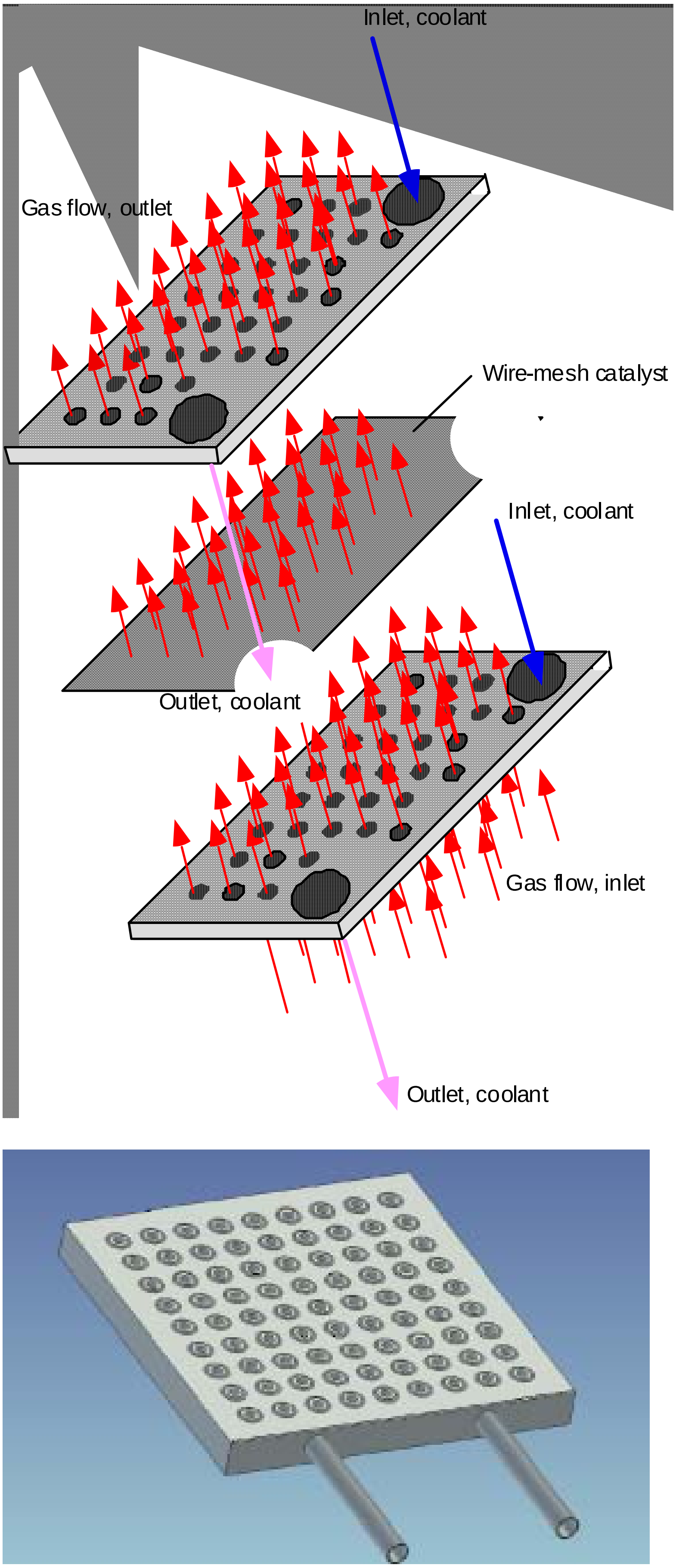


Figure 8 CatHex-structures.

The EndEx- and/or CatHex-structures might be coated with an adhesive catalytic layer, i.e. bodyfitted catalysis. Figure 9 shows an EndEx-tube in operation where catalytic combustion is on the catalytic coil inside the tube. The outside of the tube is coated with a reforming catalyst. This design is suitable for micro reformers (a few nm^3/h of hydrogen) whereas the CatHex-alternative (heated with catalytic combustion) is more suited for larger appliances and is easier to scale.

Catator’s technology also opens up for design/production of catalysed impellers and fan wheels as well as reactive distillation on catalytic active sieve bottoms.

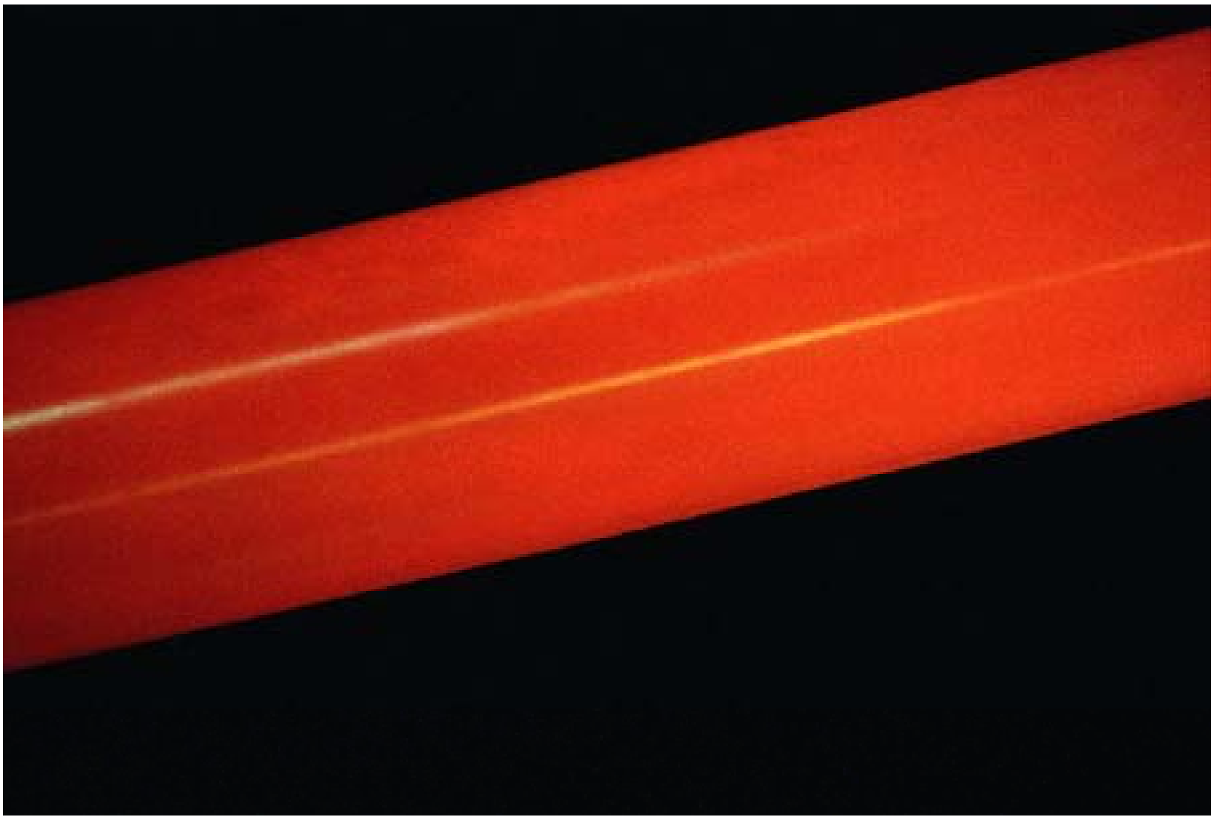


Figure 9 Body fitted catalysis on the outside of a tube.

One area of concern is usually associated with start-up of chemical reactors from cold conditions. Since it is possible to use a wire material with a rather high thermal resistance, it is also possible to pre heat the catalyst by means of electricity, see Figure 10 below where a catalytic wire mesh is pre heated with electricity. It is also possible to pre heat the catalytic coils in the EndEx-tubes with electricity to enable an extremely quick start-up.

Apart from pre heating the catalyst, it is also possible to support an endothermic reaction with energy to avoid catalyst cooling.

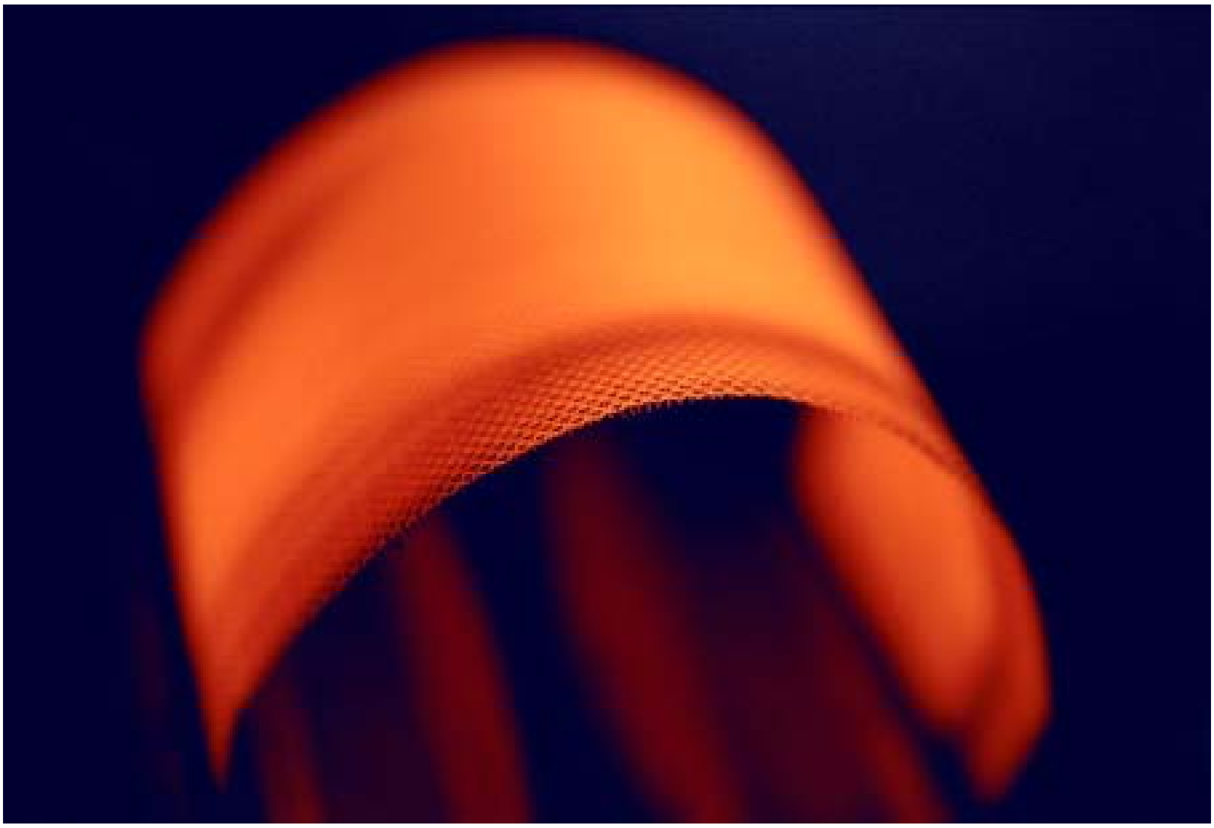


Figure 10 Electrically pre-heated catalyst element.

Catator’s coating methods also give the opportunity to produce membrane structures where the pore structure and the pore-size distribution can be varied in order to control the flow through the membrane. The flow through the membrane can be either diffusive (concentration gradient) or convective (pressure gradient). Catalytic membranes have been used in diffusive catalytic burners as well as in reactors where a dispersed supply of a component is applicable, e.g. in preferential oxidation of CO (PROX) to enhance the selectivity. Catalytic membranes might be used in the PROX-design.

Wire-mesh catalysts and active phases

Wire meshes or wire gauzes have previously been used as geometric supports. The mesh or gauze is normally woven directly from an active metal, e.g. Pt/Rh (ammonia oxidation) or Ag (methanol oxidation). The surface area of such metal structures is low and they can only be used to catalyse extremely quick reactions. The activity can be enhanced if the wire mesh is coated with a porous ceramic layer through a wash-coating procedure. Thermal spraying is a suitable method for producing ceramic layers with superior adhesion to the metal substrate. It is also possible to produce rather thick ceramic layers with this technique. The surface area and the porosity of as-sprayed ceramic layers are low. To increase the porosity and the specific surface area, a modified spray technique has been developed by Catator. There are several advantages of catalytically active wire meshes. The mass- and heat-transfer characteristics are excellent, the pressure drop is low, the geometrical flexibility is high and the active material is effectively utilised. The major drawback is attributed to clogging effects at high dust concentrations, e.g. in solid fuel combustion.

Figure 11 indicates the advantages of wire-mesh catalysts over pellet and monolith structures. Space velocity and pressure drop have been calculated for a number of catalyst alternatives in a fully mass-transfer controlled reaction (1st order, irreversible). From the Figure it is obvious that the SV can be increased to extremely high values when wire-mesh catalysts are used. 90% conversion is obtained at SV 100 000 h^{-1} for pellets with a diameter of 2 mm where the corresponding value for a wire-mesh catalyst with mesh no. 60 is around 2 000 000 h^{-1}. The pressure drops of wire-mesh structures are also extremely low in comparison to pellet catalysts, generally a factor 5 – 10 less for the same conversion. The main merit of monolith reactors is attributed to the low-pressure drop, which is important in some applications. However, the monolith catalysts must generally be operated at rather low space velocities.

The wire-mesh approach also gives a unique geometric flexibility in reactor design since the mesh structures can be fitted into almost any vessel or pipe system.

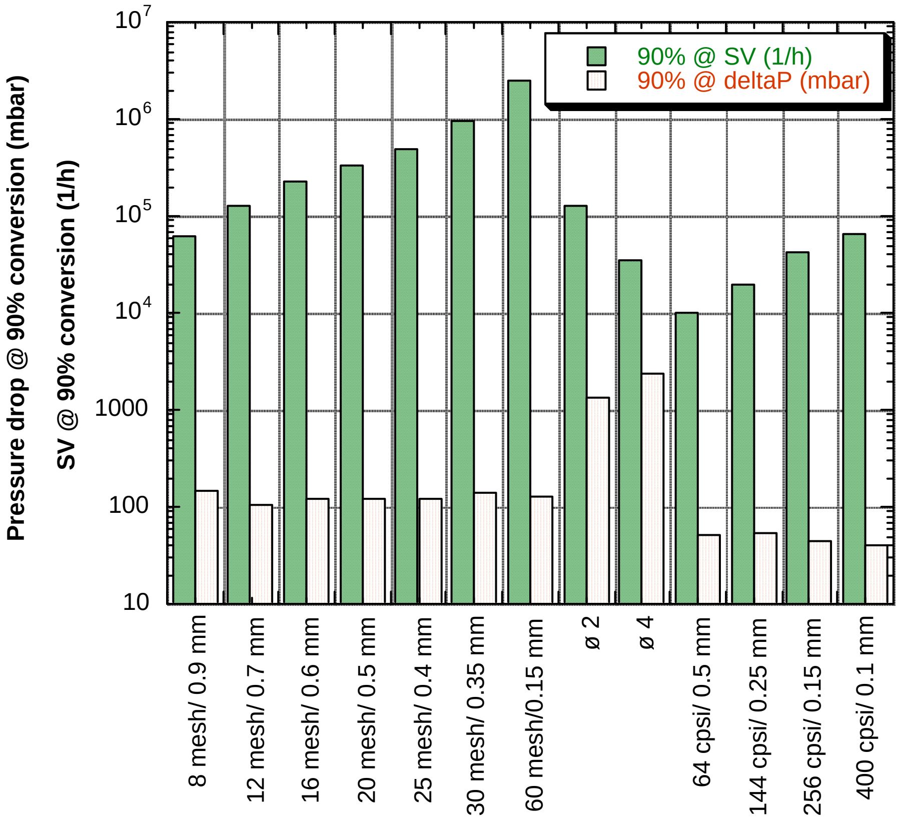


Figure 11 Performance comparison between different catalysts in a first order irreversible reaction. Space velocity and pressure drop are given for 90% conversion.

The porous layer can contain a variety of materials ranging from ceramic materials to metals and semi-metals. It is also possible to produce porous layers of polymer material and graphite.

CAB has over the years developed a number of active phases for a variety of reactions:
- Oxidation of volatile organic compounds
- Catalytic combustion of different fuels
- Two-and three-way catalysts for emission abatement
- Selective Catalytic Reduction of nitrogen oxides with ammonia
- Ammonia oxidation
- De-odorisation, nitrogen-, oxygen- and sulphur containing compounds
- Hydrogenation/dehydrogenation
- Steam reforming (C1 – C12+)
- Water-gas-shift (WGS, low-temperature/high-temperature)
- Preferential oxidation (PROX)
- HDS catalysts and H_2S-trap

Catator has previously explored different compositions of active phases to be used on wire-mesh structures in steam reforming, WGS, PROX and methanation. The following figures will give an indication of the performance of the catalysts, which have been investigated over the years.

Catator has developed a number of different phases for steam reforming of hydrocarbons, ranging from light feed stocks to rather heavy ones. By applying these phases to wire-mesh catalysts it is possible to use quite high space velocities. Figure 12 shows the performance of a wire-mesh catalysts (16 mesh/0.5 mm) in steam reforming of methane and hexane at a steam to carbon ratio of 3:1. The yield is defined as the ratio between the observed and theoretical production of hydrogen.

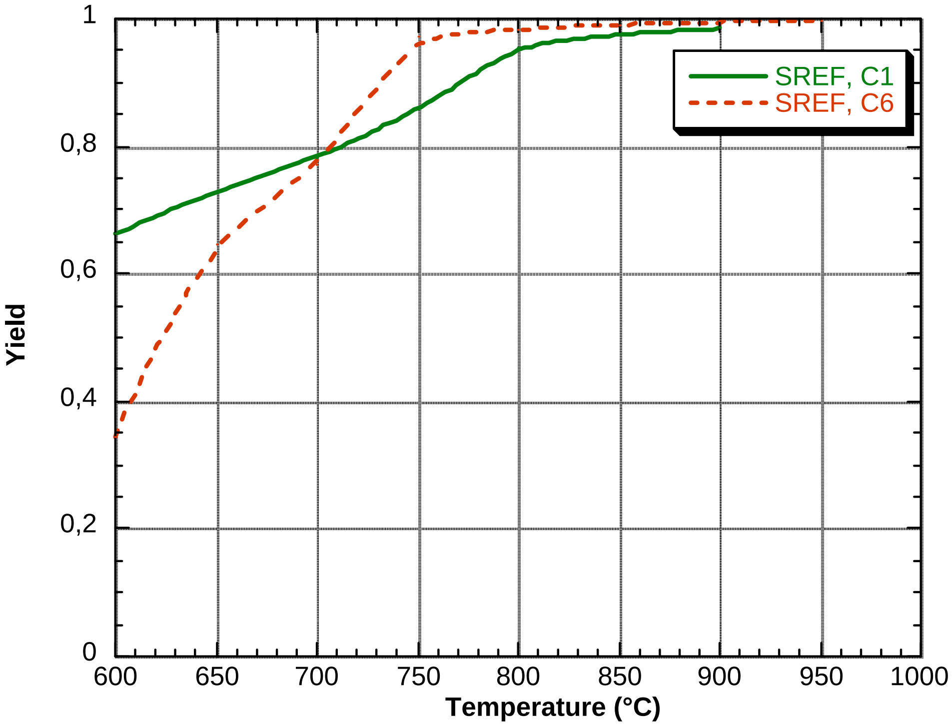


Figure 12 Steam reforming of methane and hexane over a wire-mesh catalyst at space velocity 100 000 h^{-1}. The hydrogen yield (related to the theoretical yield) is given as a function of the temperature at a steam:carbon ratio of 3:1.

A standard Ni-phase was used in methane reforming whereas a novel catalyst formulation (alkaline catalyst formulation with precious metals as active phase) was utilised in hexane reforming to avoid coke formation. The conversion of hydrocarbons is close to thermodynamic equilibrium at high temperatures, thus indicating an extremely high intrinsic activity in combination with excellent mass-transfer characteristics.

The reformer gas normally carries 10 – 12% (v/v) of CO downstream the reformer. By installing a water-gas-shift converter, it is possible to reduce the CO-concentration to levels below 1% (v/v). Catator has developed a number of active phases for the WGS-reaction. The WGS-catalysts have an increased sulphur tolerance and contains small amounts of precious metals (preferably Pt) on a high-surface material comprising rare earth metal oxides. Depending on the stabilisation of the high-surface material, these catalysts split into two major groups: high-temperature WGS (HWGS) and low-temperature-WGS (LWGS).

The high-temperature version tolerates temperatures as high as 500 – 600°C and is not susceptible to sintering on activation (reduction). The low-temperature version can be used at temperatures between 200 and 400°C.

CAB has also studied conventional active phases like mixtures of oxides of iron and chromium and formulations based on copper and zinc. The Fe/Cr-type of catalysts shows a far too low intrinsic activity for this application. The Cu/Zn-containing catalysts, although much more active, suffer from a high sensitivity to sintering phenomena (thermal deactivation).

For extremely high sulphur concentrations in the feed stream (% by volume), we have also developed a sour-shift catalyst, which needs to be in the form of a sulphide to be active. During sulphur free conditions the sulphides will decompose and the corresponding oxides will be formed. During that process the catalysts also looses its activity.

Figure 13 below shows the performance of the HWGS- and the LWGS-catalysts under normal downstream reformer conditions (reforming at steam:carbon=3). The inlet-CO-concentration to the HWGS-step was about 16% (v/v, dry gases). The balancing compounds were water, hydrogen and carbon dioxide.

Additional water was added prior to the LWGS-step to speed up the reaction and to make the thermodynamics more favourable. Depending on the amount of water added, it is possible to decrease the CO-concentration to extremely low values, i.e. to values below 5000 ppm (v/v).

Comprehensive studies concerning the sulphur tolerance of CABs WGS-catalysts, indicate a weak inhibition (1 – 10 ppm of H_2S added) at temperatures between 300 – 400°C, although completely reversible. Formulations containing Cu will be severely poisoned by sulphur present in the feed gas stream.

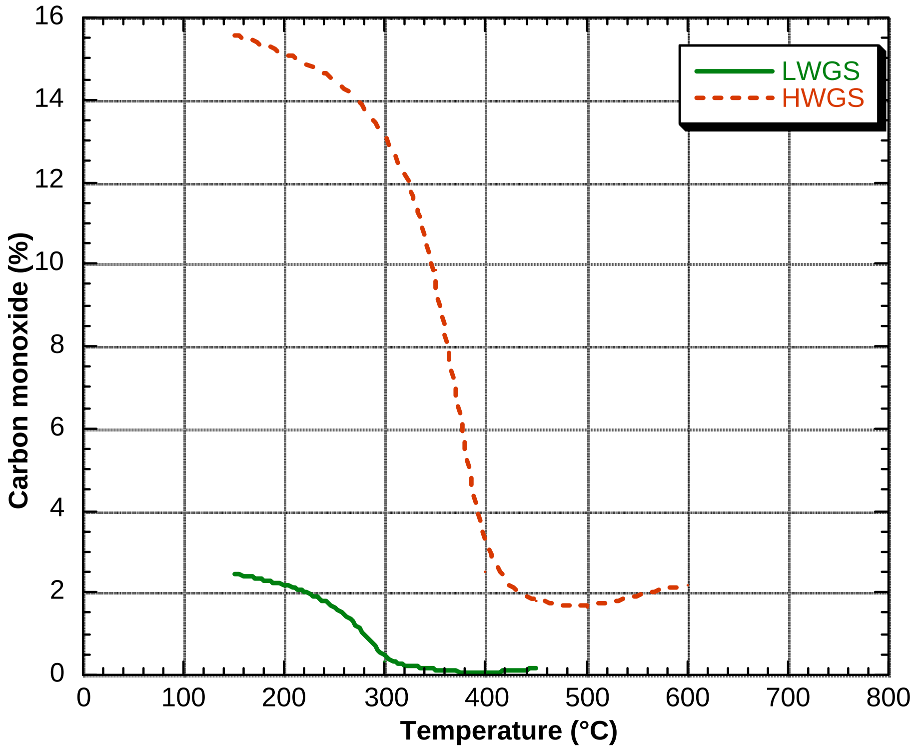


Figure 13 Catators WGS-catalysts (low and high temperature verisons) based on precious metals on rare earth metal oxides, SV≈ 200 000 h^{-1}.

In order to reach fuel-cell quality [10 – 20 ppm CO (v/v)], it is necessary to add a catalytic step including preferential oxidation of CO. PROX is a competitive reaction between oxygen and carbon monoxide and oxygen and hydrogen. The CO-removal shows a maximum at a specific temperature. At higher temperatures, oxygen is consumed by hydrogen, thus leaving CO. CAB has a number of formulations suitable for PROX. They show a high selectivity for CO-removal if runaway conditions can be avoided with respect to the temperature. Hence, the temperature control is crucial for the PROX-step since the oxidation reactions are extremely quick and highly exothermic. In order to control the process, it is essential to add effective cooling to the catalyst and preferably to supply the necessary oxygen in steps. The best result is obtained with dispersed oxygen supply on a cooled catalytic membrane. Under such circumstances it is possible to arrive at selectivities above 70 – 80%.

Figure 14 below shows CO-removal on a LPROX-catalyst comprising precious metals and metal oxides at a O_2:CO-ratio of 1:1. The inlet concentration of CO was about 2000 ppm (v/v) and maximum CO-removal was obtained at 100°C. The performance of the PROX-step can be improved further in a number of ways:

- Accurate temperature control throughout the catalyst bed
- Dispersed oxygen supply
- Structured catalysis where different compositions are used along the reaction pathway

We intend to use a reactor design with an accurate temperature control and a dispersed oxygen supply along the reaction pathway. The exact design of the PROX-reactor will be discussed more in detail further on in the report.

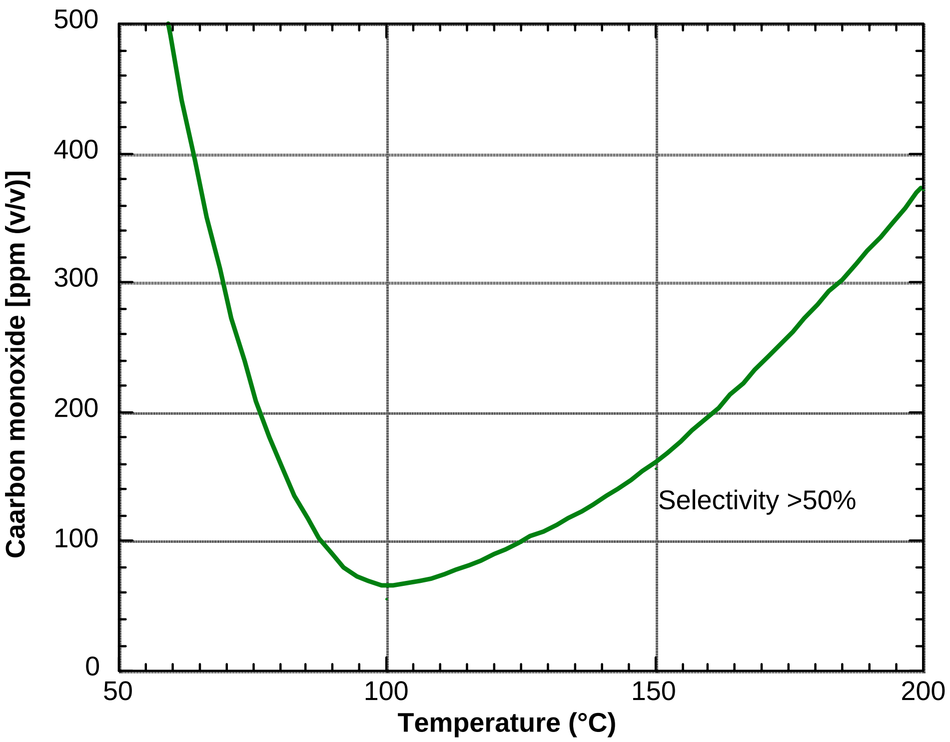


Figure 14 Catators LPROX-catalyst operated at SV 200 000 h^{-1} and an inlet concentration of 2000 ppm (v/v) of CO. O_2:CO=1:1.

Apart from preferential oxidation it is also possible to reduce the CO-content by means of methanation (usually on a Ni-based catalyst). In order to reduce the hydrogen consumption it is necessary to separate the carbon dioxide upstream this step since also CO_2 will react to yield CH_4. Figure 15 below shows one example of the performance of Catator's methanation catalyst at an extremely high gas load. The catalyst consists of Ni/alumina supported on a wire mesh structure. The gas mixture contains reasonable amounts of CO/CO_2 following gas absorption with respect to CO_2 downstream a steam reformer and a WGS-converter. From the Figure it is obvious that the carbon oxides are quantitatively converted into methane at temperatures in the region of 500 – 600°C and that CO is more readily reacted than CO_2.

Absorption of CO_2 is an expensive and cumbersome process to incorporate into small fuel processors. Consequently, methanation is not considered as a suitable process for CO-removal in this project.

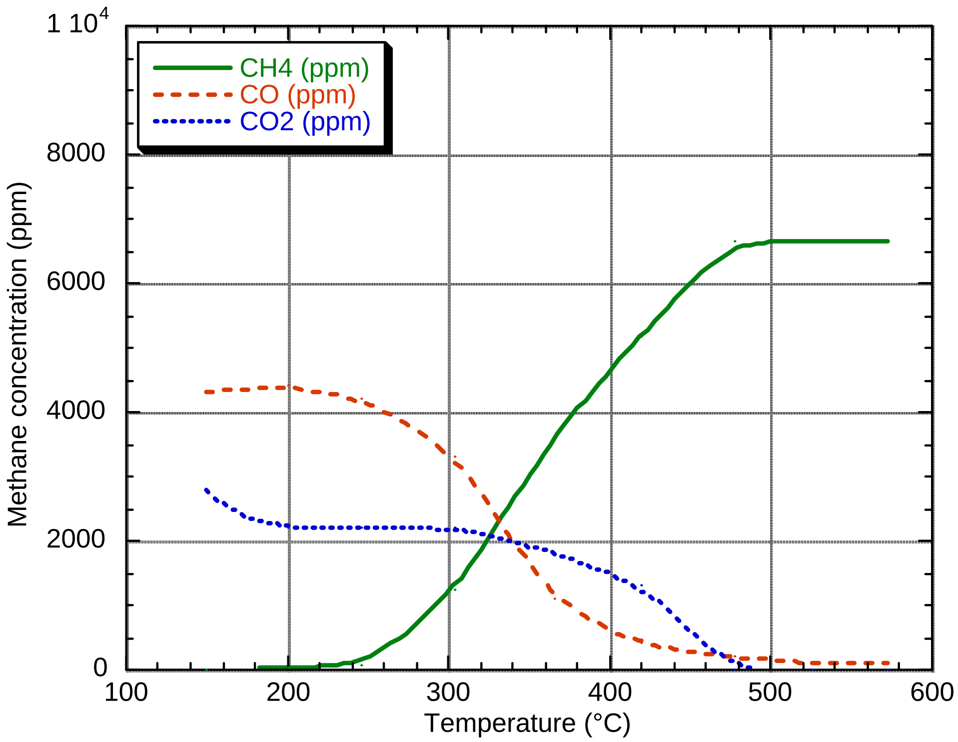


Figure 15 Methanation on wire-mesh catalyst at SV≈100 000 h^{-1}.

A large number of confirmatory tests have been performed on Catator's catalyst formulations in order to obtain applicable data for design/dimensioning of a small-scale stationary fuel processor. These data are presented further on in the report.

5. Development work and project phases

The Feasibility- and Design phase is divided into a number of sub tasks according to:

- Design/erection/commissioning of test rig
- Catalyst preparation and characterisation
- Comprehensive experimental evaluation of unit-steps in the process
- Novel reactor design
- Design calculations (unit-processes and integral system)
- Design suggestion and expected features
- Conclusions

The first task was to erect and commission a suitable rig for catalyst testing. A schematic diagram showing the design and the function of the rig is shown in Figure 16 below. A number of gases are mixed by means of mass-flow controllers to yield a suitable gas composition for the investigation. Liquid components can be added via a liquid mass flow controller or via a syringe pump (not shown in the Figure). The gas composition is then led through the reactor containing a catalyst or through a reference tube without any catalyst. The catalyst might be a monolith, a pellet catalyst or a wire mesh catalyst. The product gas is then cooled downstream the reactor and possible condense water is removed. The system pressure might be varied between ambient conditions and 10 bar(a).

Analysis is performed with a number of techniques depending on applications. Analysis methods available are:

- Gas chromatography
- GC-MS
- Photo acoustic IR
- NDIR
- Chemiluminiscence
- FID-instrumentation

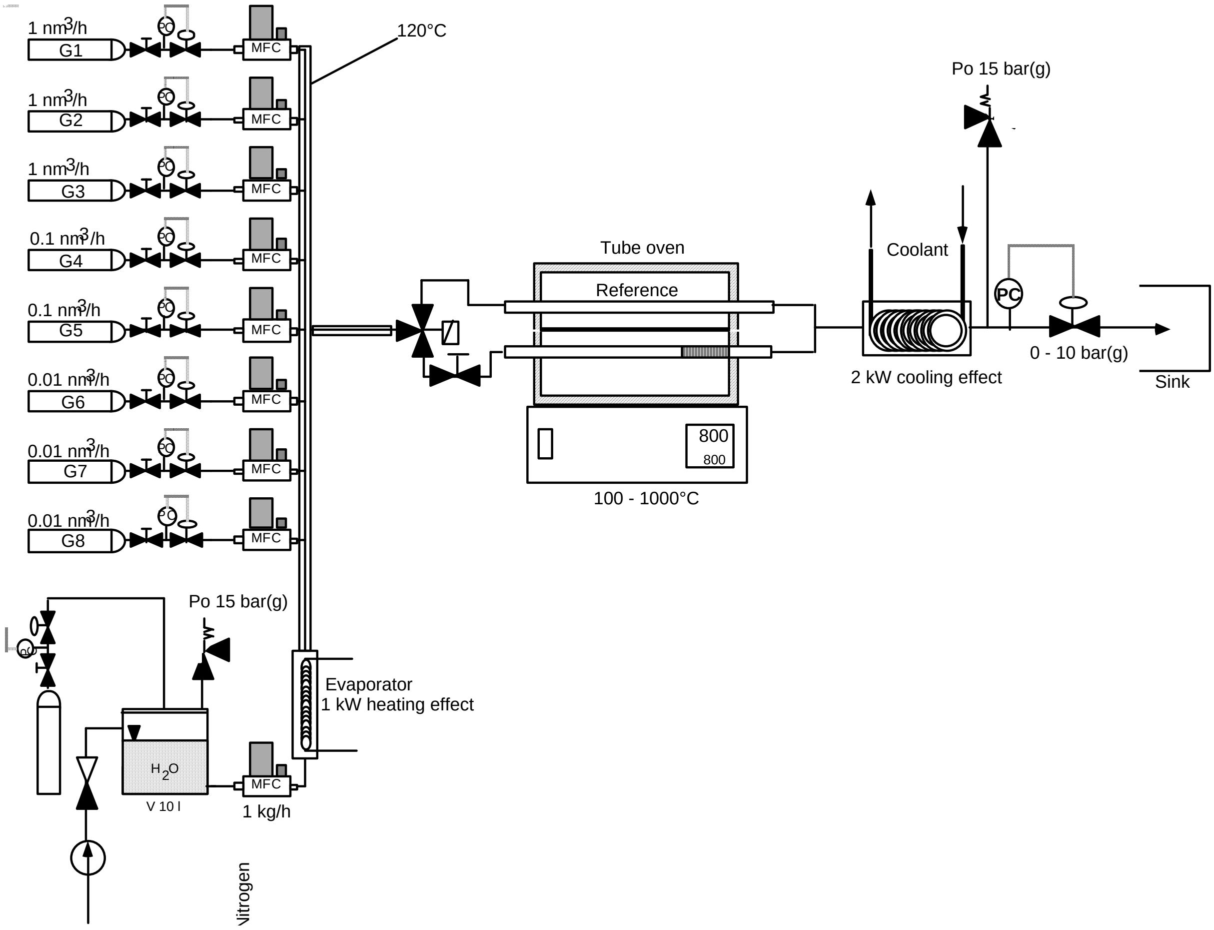


Figure 16 Experimental set-up for micro-reactor testing.

Activity tests have been performed for a number of catalyst formulations in the relevant reactions included in steam reforming and downstream reactions. i.e.:

- Steam reforming of different feed stocks (pure feed stocks & commercial feed stocks)
- The water-gas-shift reaction
- Preferential oxidation
- Methanation

The comprehensive experimental evaluations were boiled down into kinetic expressions, which were implemented into our generic simulation code for catalytic reactors, CatalystExplorer.

The Feasibility- and Design phase also included design work concerning the unit-reactors as well as process simulations for dimensioning purposes. These calculations enabled us to suggest suitable reactor- and system lay-outs. The expected features of the integral system are also presented in this report.

The next project phase (Realisation phase) will be based on the information given in this report and includes the following major sub tasks:
- Detailed design including flow sheets and P/I-diagrams
- System construction and assembly
- Commissioning
- Experimental evaluations
- Possible system modifications to improve the performance
- Conclusions

Complete and detailed flow sheets and diagrams showing all components and the control strategy will be presented during the initial phase of phase 2. These documents will be open documents since modifications might be necessary to include following the evaluation phase. The intention is also to develop a dynamic simulation model for the system to enable predictions of transient and intermittent operation.

The system is then constructed and commissioned. A comprehensive evaluation of the performances of the system is then conducted. Different modes of operation will be mapped and a number of different feedstocks will be tested.

Some design modifications are expected to increase the performance of the system further. Additional evaluations are performed following possible design modifications.

The aim is to present the functioning fuel processor during the spring of 2003.

6. Fuel processor design and elementary steps

This chapter summarises the important steps in ordinary steam reforming and gas purification with respect to carbon monoxide, see Figure 16. The feed stock (natural gas) usually contains unacceptable amounts of sulphur compounds in the form of hydrogen sulphide, mercaptans, thiophene etc. In order not to deactivate the catalysts in the system it is necessary to remove the sulphur. Since some of the sulphur containing compounds are rather stable it is necessary to include a catalytic step where the sulphur containing compounds are converted to hydrogen sulphide through reaction with hydrogen. The process is catalysed by metal sulphides and is called hydrogenolysis [8]. The hydrogen sulphide formed in the process is then quantitatively removed downstream the HDS-unit through reaction with ZnO to yield ZnS and water. Steam is then added to the feed, preferably so that the steam:C ratio is above 3. The reforming reactions normally start at a rather low temperature to yield enough hydrogen to avoid coke formation further downstream the reactor. The outlet temperature should be as high as possible to reduce the methane concentration to low levels. Methane is always formed in steam reforming for thermodynamic reasons. The outlet concentration of methane will decrease with the reactor temperature.

Steam reforming is endothermic and thermal energy must consequently be added to the process, normally in the region of 600 W per nm^3/h of hydrogen produced. In ordinary tube reforming, the catalyst is contained in tubes and heat transfer is by means of gas flames on the outside of the tubes. In novel reactor engineering, the aim is to combine catalysis and heat transfer in order to increase the thermal efficiency and to decrease the reactor size. Formulations based on Ni as active phase are always used in large-scale units.

The reformate gas is then cooled to a temperature of about 350°C and is fed into the HWGS-converter. The water-gas-shift reaction is exothermic and results in a temperature rise through the reactor. In order to get a more favourable equilibrium position it is optional to install intermediate cooling prior to the LWGS-converter. The HWGS-catalyst usually contains a mixture of Fe and Cr, whereas the LWGS-catalyst usually is Cu-based. The CO-concentration downstream the LWGS-converter is normally below 1 % (v/v). The final steps to upgrade the reformer gas might include a PROX-reactor (preferential oxidation) and membrane separation. The PROX-catalyst operates at a low temperature in order to obtain a high selectivity for CO-oxidation over hydrogen oxidation. The catalyst normally consists of a precious metal on a hydrophobic carrier.

Membrane separation can be performed on metallic or polymer membranes to yield essential pure hydrogen [9]. The off gases from the membrane can then be burned catalytically, preferably in the reformer to supply thermal energy.

It is not necessary to add membrane separation in fuel-cell applications since all gases (apart from CO, which must be removed) only causes a dilution of the hydrogen. In other applications, however, it is essential to obtain pure hydrogen. In such cases it is possible to include membrane separation.

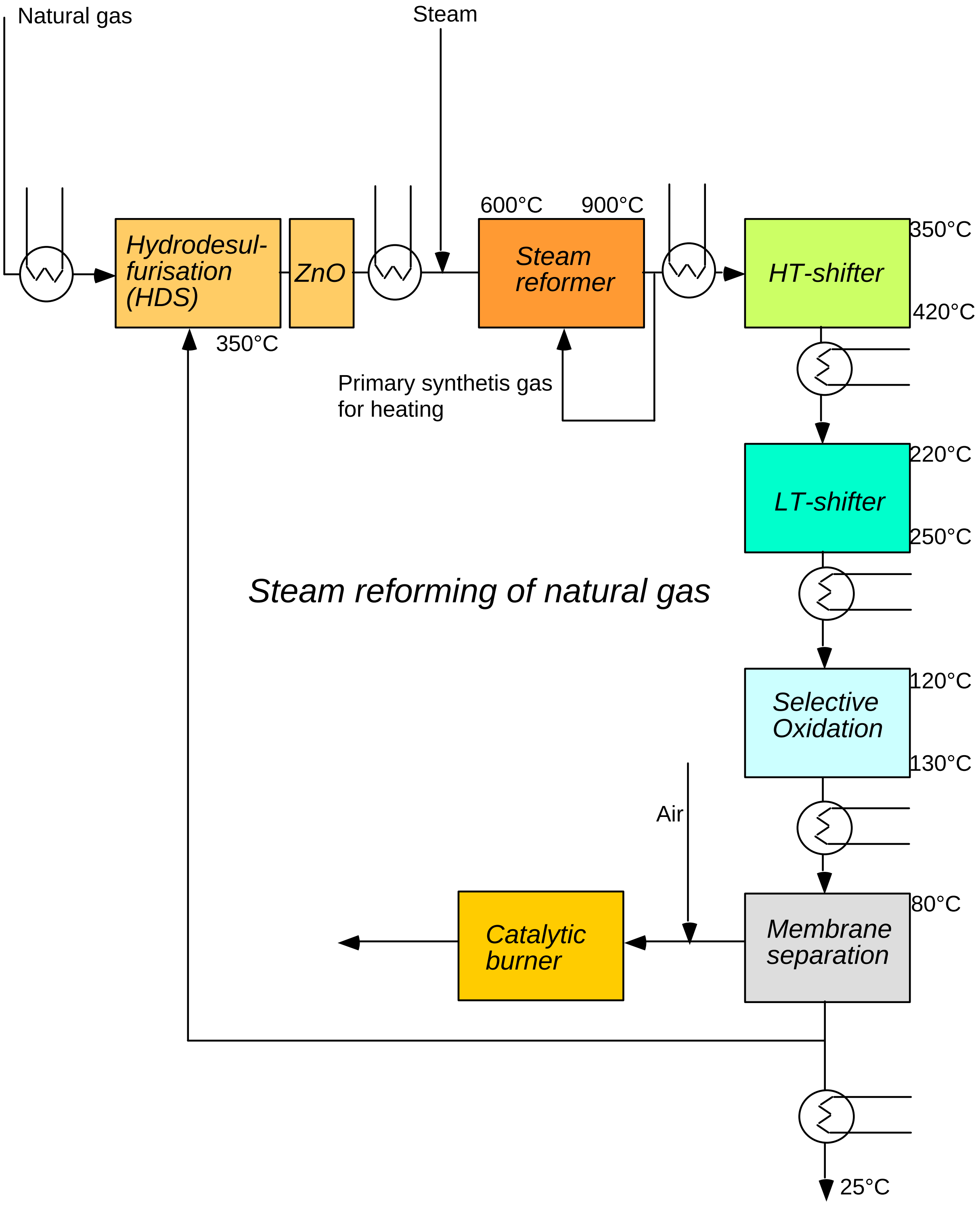


Figure 16 Block diagram showing steam reforming of methane & gas purification.

Figure 16 shows all relevant parts of an industrial steam reformer. The aim is now to integrate different functions and to simplify the lay-out. The design approach chosen in this project is described further on in the report.

7. Confirmatory tests of active phases

Steam reforming

One important part of the Feasibility and Design phase was to verify the activity of Catator's catalysts under conditions prevailing in the fuel processor and to derive kinetic data for catalyst- and reactor dimensioning. The studies were focused on three major catalytic steps:
- Steam reforming (SREF)
- The water-gas-shift reaction (WGS)
- Preferential oxidation (PROX)

Pure hydrocarbons as well as commercial feed stocks were studied. Special attention was directed to studies concerning sulphur poisoning and coke formation. To really power the coke formation reactions, additional experiments were performed with steam reforming of ethylene and toluene. Unsaturated and aromatic hydrocarbons are known to form coke more readily than aliphatic hydrocarbons.

All activity tests were performed in the test rig, previously described. A synthetic gas mixture of the desired composition was led through a number of catalytic active wire meshes, placed in the reactor. The gas load was extremely high in comparison to the amount of catalyst in the reactor. The gas load normally corresponded to 100 000 – 200 000 catalyst volumes per hour (SV= 100 000 – 200 000 h^{-1}). Since so high gas loads were utilised, possible deactivation phenomena will be observable quickly during the tests. Steam reforming was directed to two group of feed stocks, pure and commercial:

a) Pure feed stocks
- methane
- propane
- hexane
- do-decane
- methanol
- ethanol

b) Commercial feed stocks
- natural gas (Danish quality), ≈ 5 ppm (v/v) of sulphur compounds
- LPG, ≈ 5 ppm (v/v) of sulphur compounds
- environmentally rated gasoline, ≈ 5 – 10 ppm (w/w) of sulphur compounds
- environmentally rated kerosene, ≈ 5 – 10 ppm (w/w) of sulphur compounds
- JetA1, aircraft fuel, ≈ 100 ppm (w/w) of sulphur compounds

Commercial feedstocks contain aromatic and unsaturated compounds to some extent, especially the liquids. However, it is generally not possible to obtain a detailed specification of these feedstocks.

The steam reforming experiments were normally performed at a steam:carbon-ratio of 3:1 except in cases where excessive coke formation was desired. Hydrogen was normally added to the inlet stream in order to simulate reformer-gas re-circulation. The re-circulation ratio was normally set to 1:1. Re-circulation is important when reforming heavy feed stocks like kerosene and diesel in order to suppress the coke formation.

The gas mixture was led through the catalyst at different temperatures and the gas mixture at the outlet was analysed by means of NDIR and gas chromatography. The hydrogen yield was calculated and related to the theoretical value, obtained from thermodynamic calculations (HSC to Outokumpu). The theoretical hydrogen yield is a function of the temperature, since the steam-reforming reaction and the water-gas-reaction are equilibrium reactions.

Figure 18 shows the hydrogen yield as a function of the temperature when reforming pure feed stocks on a wire-mesh catalyst (16 mesh/0.5 mm) at a space velocity of 200 000 h^{-1}. It is obvious that all feedstocks will be totally converted to reformer gas at temperatures above 900°C. However, if the gas load is decreased it will be possible to reduce the reformer temperature to about 700 – 800°C to add durability to the system. Methanol is the easiest feedstock to decompose but methane is formed at temperatures around 600°C on this catalyst (a minimum in the graph showing the yield).

All experiments with pure feedstocks were performed with Pt/alumina-catalysts. In cases where Pt was replaced with Ni, we obtained problems with coke formation for the heaviest feedstocks. The coke formation is attributed to the solubility of carbon in the Ni-phase. Coke formation via carbon dissolving in the active phase is not possible when Pt is used as the active phase. The Pt-content in the steam reforming catalyst is normally 3 – 5 g/m^2.

Kinetic studies indicated a weak inhibition of hydrogen but essential first-order behaviour concerning the hydrocarbons. Hence, the reactions were modelled with first-order kinetics and the correlation between experimental and forecasted data was generally very good.

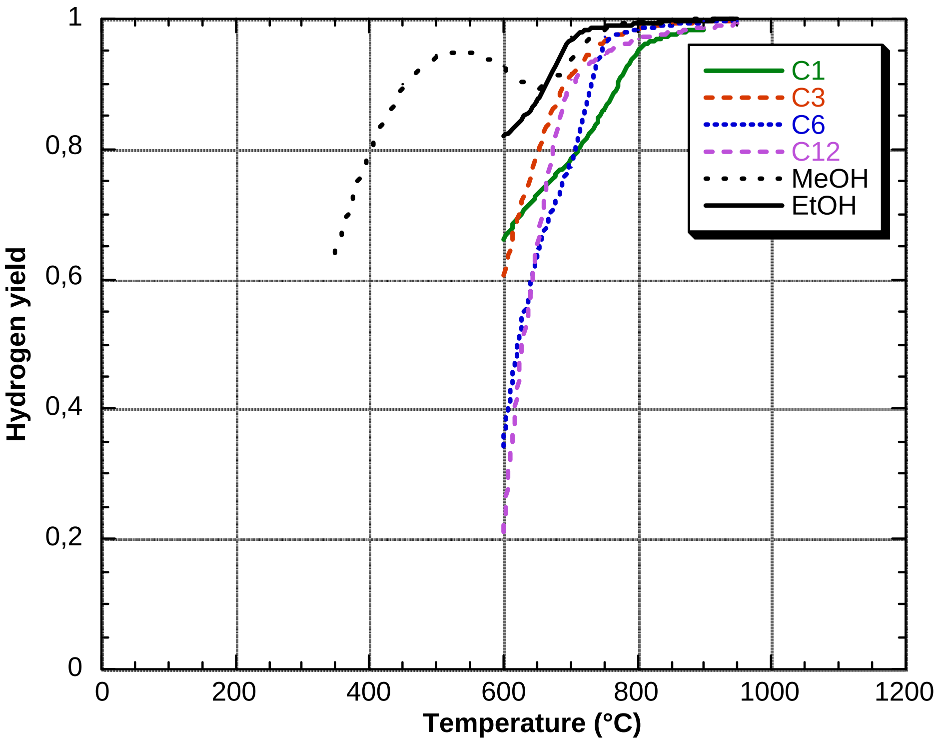


Figure 18 Steam reforming of pure feedstocks. SV≈200 000h^{-1}. Steam:carbon=3:1. Catalyst: Pt/alumina on wire meshes (16 mesh/0.5 mm).

In order to explore the effects of sulphur, a number of additional experiments were performed with kerosene containing different amounts of sulphur, see Figure 19 below. From the Figure it is obvious that sulphur causes a significant retardation of the steam-reforming reaction, especially at low temperatures. The effect of sulphur inhibition follows a classic Langmuir-Hinshelwood expression with the partial pressure of sulphur sulphide in the denominator. In order to steam reform fed stocks with high sulphur contents it is thus necessary to add more catalyst to the reactor to compensate for these inhibition effects. Again, Ni is much more sensitive than Pt for S-poisoning. Even if the inhibition is reversible, the recovery is extremely slow in the case of Ni. The reason is that Ni forms bulk sulphides whereas Pt only forms surface sulphides, which readily decomposes [10].

A sulphur content corresponding to 10 ppm (w/w) is applicable for environmentally rated commercial feed stocks whereas 100 ppm (w/w) or above is typical for ordinary heavy feed stocks like jet fuel and diesel. The sulphur containing compounds is a cocktail of aliphatic, aromatic and cyclic compounds like mercaptans, thiophene etc. These compounds will decompose into hydrogen sulphide during steam reforming conditions and it is necessary to trap the hydrogen sulphide prior to downstream process steps (WGS/PROX).

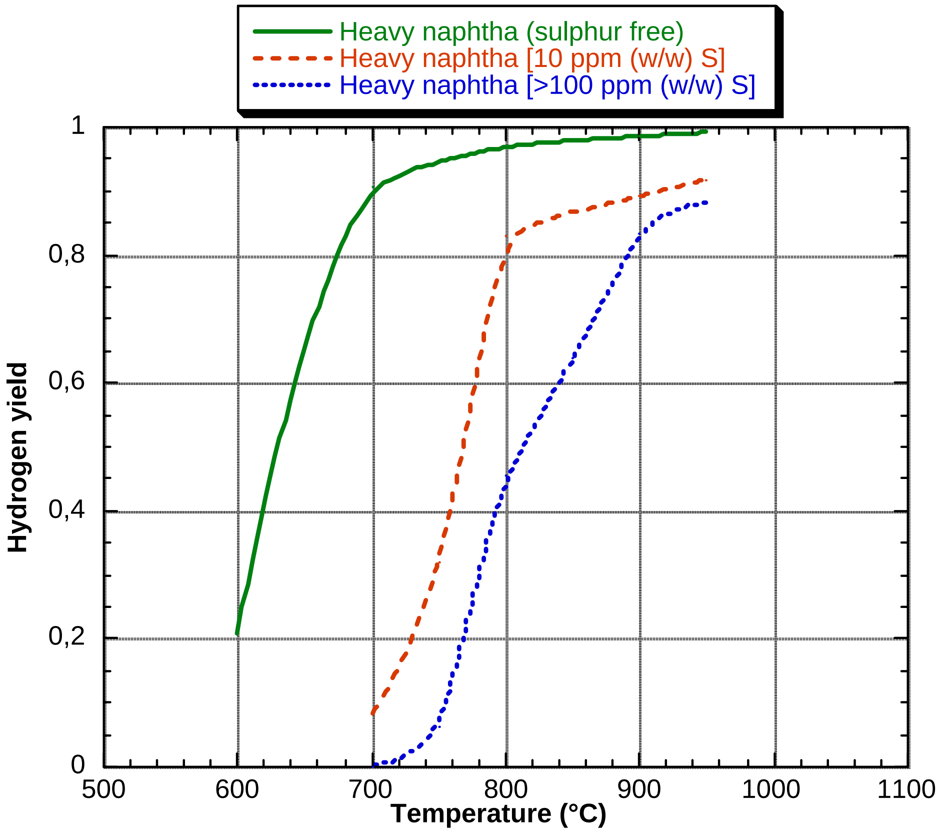


Figure 19 Steam reforming of heavy naphtha containing different amounts of sulphur. Data taken at SV≈200 000h^{-1} and at a steam:carbon ratio of 3:1. Catalyst: Pt/alumina on wire meshes (16 mesh/0.5 mm).

Figure 20 shows the performance of two alkaline reforming catalysts (barium-hexa-aluminate) containing Ni and Pt as active phases in methane reforming. The equilibrium concentration of CO is also given in the diagram. It is obvious that the catalysts show an extremely high activity in the steam reforming reaction since the outlet concentration of CO is close to equilibrium also at this extremely high gas load (400 000 h^{-1}). 10 ppm H_2S is added to the gas mixture after 1 minute and we can see a sudden decrease of the catalyst activity, especially for the Ni-catalyst. The H_2S-injection is stopped after about 25 minutes and the catalysts recover. The recovery of the Pt-catalyst is almost momentary whereas the recovery of the Ni-catalyst is much slower (decomposition of bulk sulphides). The conclusion is that Pt has a much higher sulphur tolerance than Ni. In order to use Ni, it is essential to desulphurise the feedstock upstream the steam reformer.

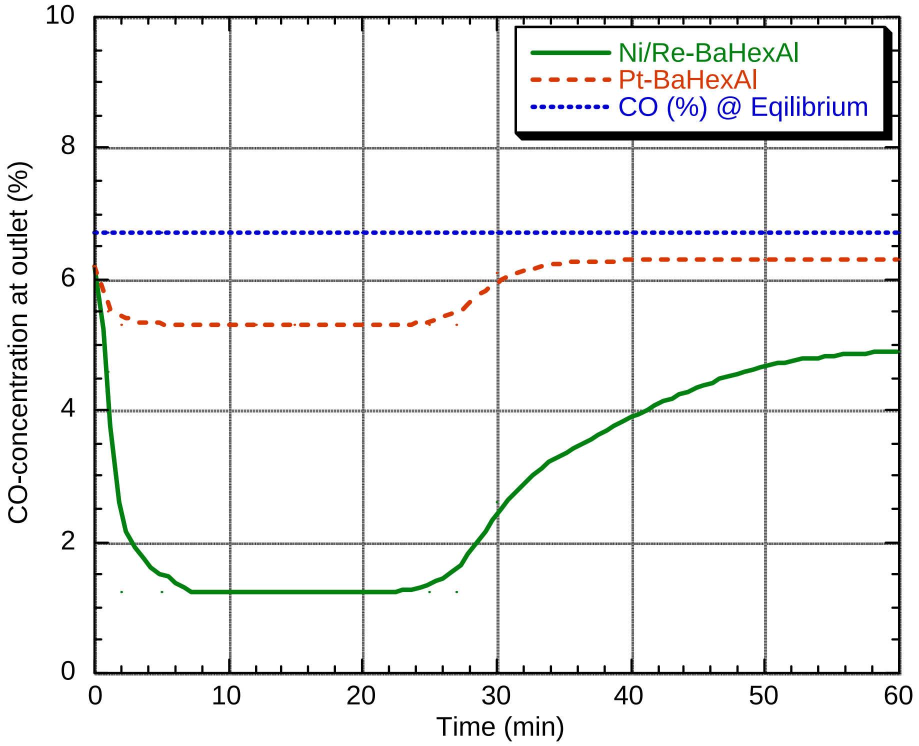


Figure 20 Influence on addition of 10 ppm (v/v) H_2S during steam reforming of methane at SV≈400 000h-1 (steam:carbon=3:1) at 800°C. CO-concentration at the reactor outlet is given as a function of the time on stream. H_2S-addition removed after 25 minutes.

A number of comparative experiments were performed with Catator's Pt-catalysts when reforming pure and commercial feed stocks. The ratio between the hydrogen yield obtained for the commercial feed stock and the hydrogen yield obtained for the corresponding pure feedstock is given as a function of the temperature. The hydrogen yield is lower in cases with commercial feedstocks. This observation is attributed to the sulphur content of commercial feedstocks. Also, the commercial feed stocks might contain unsaturated and aromatic compounds, which can affect the problems with coke formation.

Even if there is a difference in the hydrogen yields obtained for pure feedstocks and commercial feedstocks, the catalyst activity is still extremely high. To compensate for the somewhat lower activity, it is possible to add more catalyst to the reforming reactor. As an alternative way, it is possible to include a desulphurisation step in the system to decrease the impact of sulphur compounds on the catalysts in the fuel processor.

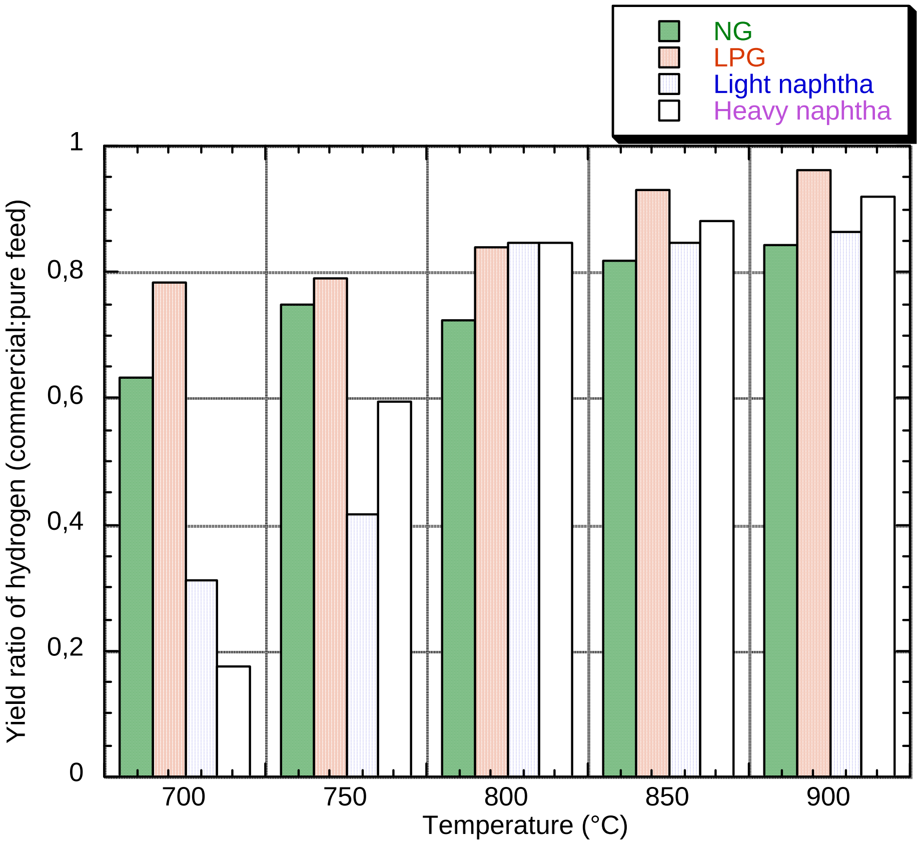


Figure 21 Ratio between hydrogen yield obtained with commercial and pure feed stocks. Methane-natural gas, propane-LPG, hexane-gasoline, Do-decane-kerosene. SV≈ 200 000 h^{-1} on a Pt/alumina-catalyst applied to wire meshes (16 mesh/0.5 mm).

The investigations have provided the project enough information to enable design and dimensioning of a reactor for steam reforming of different feedstocks, pure as well as commercial. Deliberate tests with coke formation (ethylene and toluene reforming at low steam:carbon ratios) show that Catators alkaline catalyst formulations with precious metals are superior to conventional Ni/alumina-catalysts. The alkaline compounds are incorporated into the catalyst matrix in order to obtain a stable composition (alkaline compounds are sensitive to evaporation if not matrix bound). Best results were obtained with formulations involving Pt on spinels and heaxaaluminates. Indeed, these formulations resisted coke formation even in ethylene reforming at a low steam:carbon-ratio.

The water-gas reaction

The reformer gas leaving the reactor will typically contain some 10% (v/v) of carbon monoxide. In order to utilise the gas in a fuel cell (proton-exchange-membrane cell) it is necessary to decrease the content of CO to less than 20 ppm (v/v). CO-reduction is accomplished in two steps, WGS + PROX. Traditional catalysts for the water-gas-shift reaction contain base metals. They show a modest intrinsic activity or/and are extremely sensitive to sulphur poisoning and thermal deactivation. Catator has developed a catalyst formulation including precious metals on a rare earth metal oxide. This catalyst can tolerate rather high temperatures and has a higher sulphur tolerance than the conventional catalysts.

Figure 22 shows the influence of 15 ppm H_2S on the activity of Catator's WGS-catalyst. By placing Zn-coated wire meshes upstream the WGS-catalyst it is possible to decrease the impact of sulphur on the WGS-catalyst. Addition of 15 ppm H_2S will cause a significant decrease in the catalyst activity, i.e. the amount of WGS-catalyst needs to be increased by 100% to compensate for the inhibition by H_2S. Installation of Zn-wire meshes decreases the H_2S-concentration of the gas entering the WGS-step. The trapping efficiency of the Zn-wire meshes is about 80% at a space velocity of 400 000 h^{-1} and above 98% at a space velocity of about 100 000h^{-1}. Consequently, by placing wire meshes coated with Zn downstream the steam reformer it is possible to eliminate the negative effects caused by H_2S in downstream reactions.

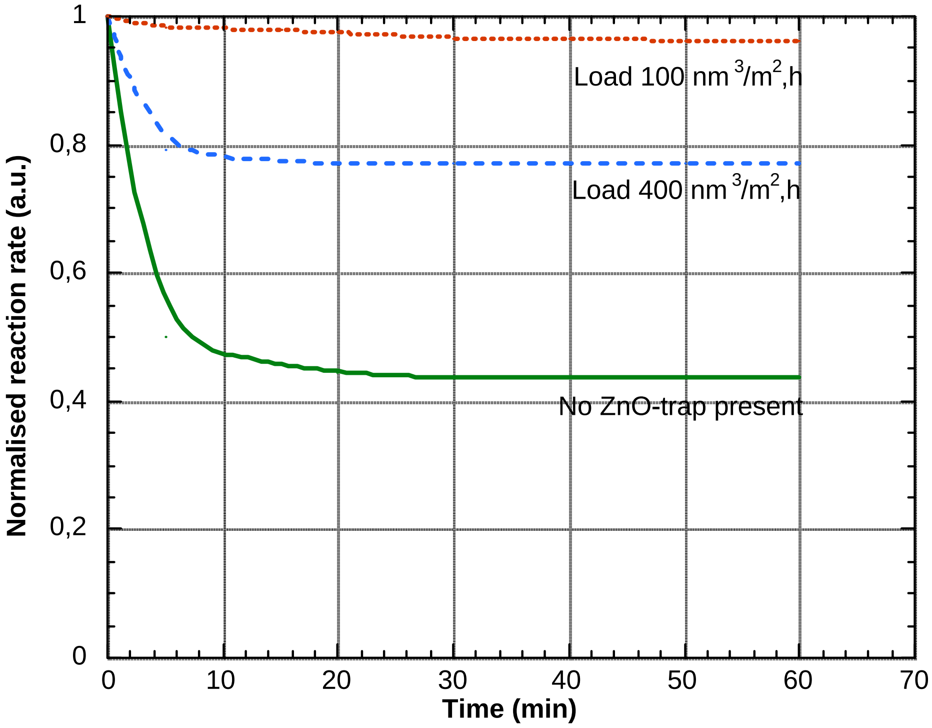


Figure 22 Effects of a sulphur trap installed upstream the WGS-catalyst. Reaction rate in the WGS-reaction when placing Zn-wire meshes Upstream the WGS-catalyst. A gas load of 100 000 h^{-1} corresponds to 100 nm^3/m^2, h.

It is possible to obtain a more favourable equilibrium position by increasing the water content of the gas mixture. The CO-concentration at equilibrium is affected by the temperature, thus decreasing with a decreasing temperature, see Figure 24. The performance of Catator's WGS-catalyst (HWGS) is shown in the Figure together with thermodynamic data (equilibrium concentrations of CO). Thermodynamic equilibrium is reached at temperatures about 450°C. In order to approach equilibrium at lower temperatures it is necessary to increase the amount of catalyst in the WGS-reactor. Also, the low-temperature version of Catator's WGS-catalysts shows a higher activity but has a lower stability to thermal deactivation.

The experimental data clearly verifies the possibilities to reach the desired activity and stability of the catalyst for this application. The WGS-reaction is modelled with first-order kinetics and yield an accurate prediction of the experimental data under different conditions with respect to the temperature and the concentration of different gases.

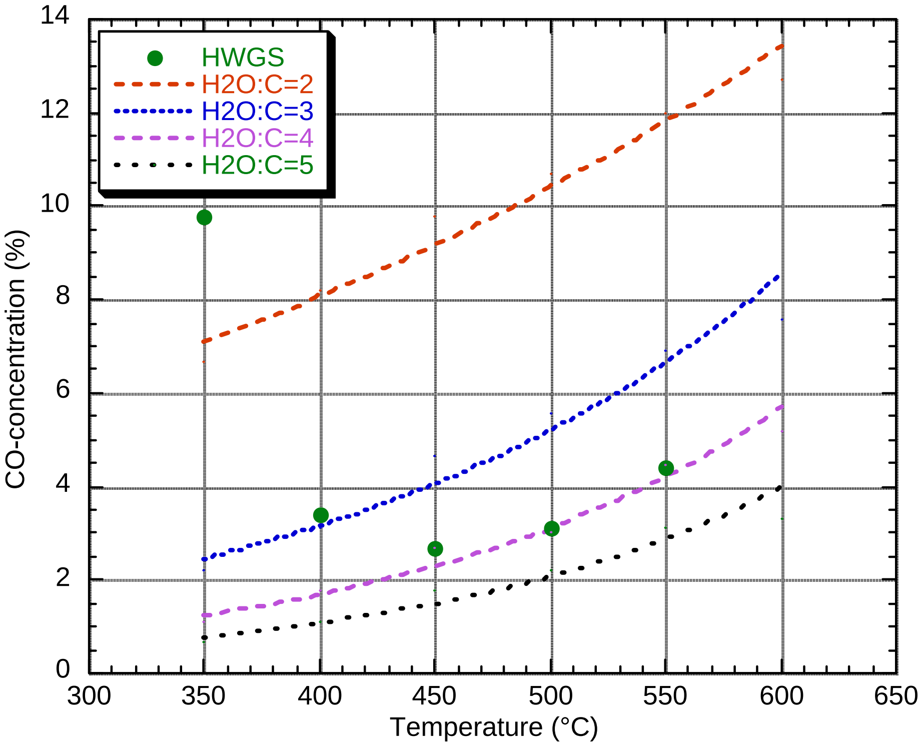


Figure 23 Performance of Catator's HWGS-catalyst in the water-gas reaction at SV 200 000 h^{-1}. Gas composition corresponding to downstream conditions when reforming methane at steam:carbon=4:1. Catalyst Pt/ReMeOx on wire meshes (16 mesh/0.5 mm). Thermodynamic data are given for different steam:carbon ratios.

Preferential oxidation of CO

The final step of the gas purification prior to the fuel cell includes preferential oxidation of CO in the presence of H_2. This reaction is extremely quick and shows a maximum in selectivity in a specific window with respect to the temperature. Catator has developed a number of suitable phases, which have different temperature windows for maximum selectivity. The catalysts utilise combinations of precious metals and metal oxides as the active phase. Since the oxidation reactions are highly exothermic, an accurate temperature control is crucial for the performance. The reformer gas will contain about 1% (v/v) of CO when leaving the WGS-reactor. A similar amount of oxygen (as air) is injected upstream the PROX-reactor and CO is converted to CO_2. The conversion degree is shown as a function of the temperature in Figure 24, when utilising extremely high gas loads (400 000 h^{-1}). The low-temperature versions show maximum performance at a temperature between 120 and 180°C whereas the high-temperature version has its performance maximum shifted to higher temperatures.

In order to avoid overheating, runaway reactions and a lost selectivity, it is possible to add the necessary oxygen in steps, still under a careful temperature control.

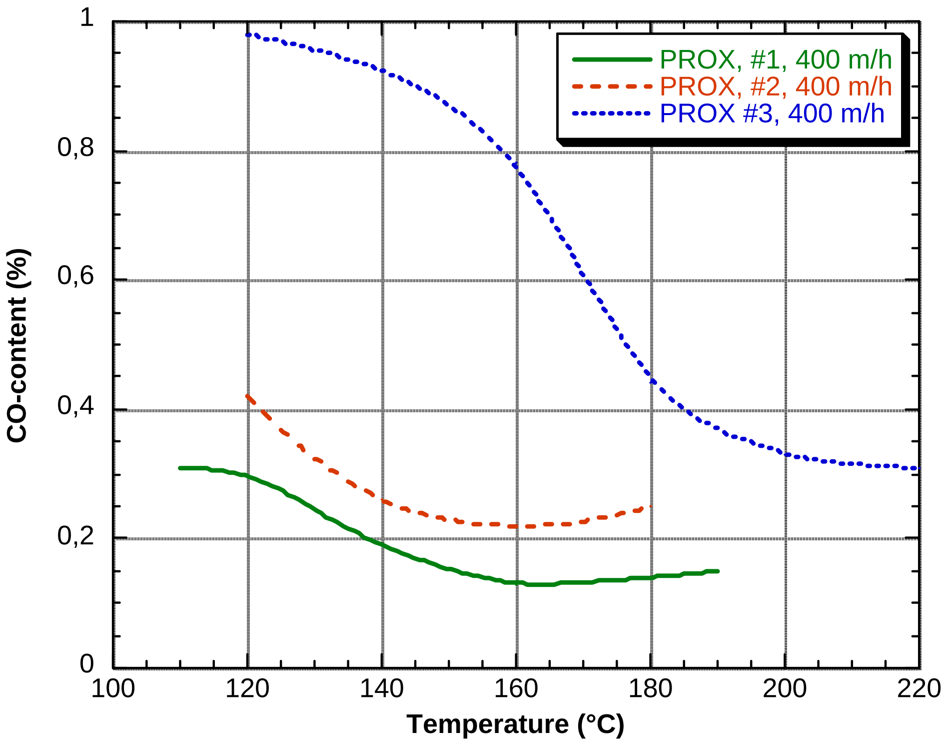


Figure 24 Different PROX-catalysts for CO-removal. The catalysts are operated at SV= 400 000 h-1 and the inlet concentration of CO corresponds to 1% (v/v).

Figure 25 shows the performance of a LPROX-catalyst when oxygen is supplied in four steps. The inlet concentration of CO is 1% (v/v) and the overall conversion degree is 99.6%. Careful temperature control/cooling together with multiple oxygen inlets are important factors when designing the PROX-section of the reactor.

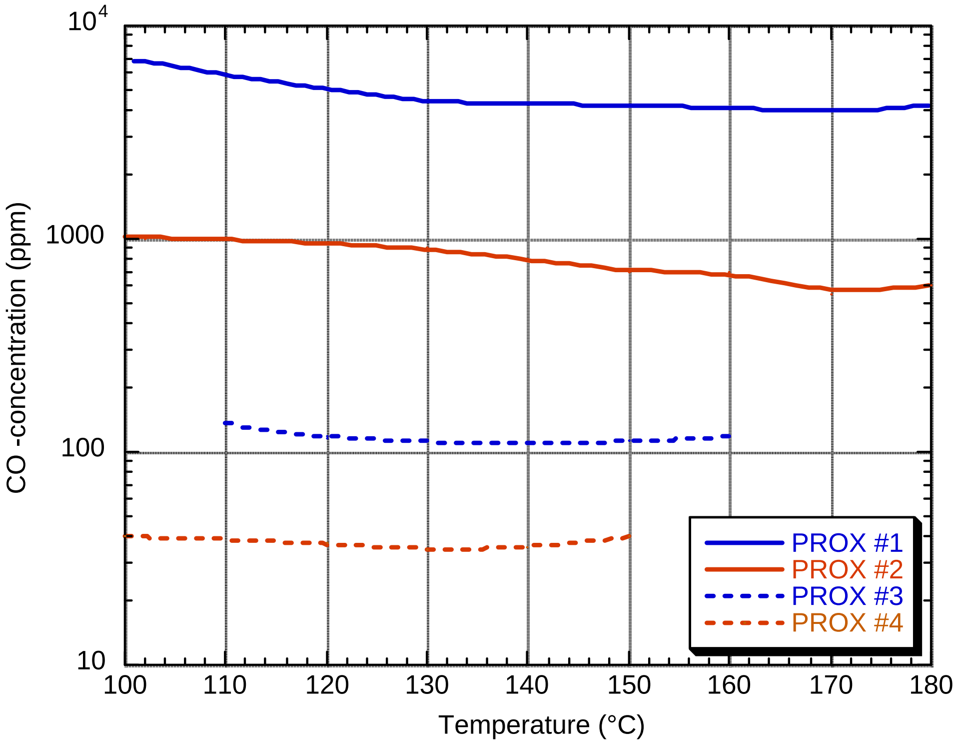


Figure 25 The effect of multiple air-inlets and intermediate cooling in the PROX reaction. Each step is operated at SV 400 000 h^{-1}. Inlet CO-concentration was 1% /v/v).

The PROX-reaction is modelled as a competitive reaction between CO and H_2 with first order kinetics in oxygen and CO/H_2. The kinetic model describes the influence of the temperature on the selectivity and can be used for dimensioning purposes. The PROX-catalysts are sensitive to sulphur poisoning since they are operated at relatively low temperatures. Consequently, total desulphurisation is necessary upstream the PROX-step.

Sulphur removal

Desulpurisation is preferably performed through hydrogenolysis of the sulphur compounds in the fuel. The sulphur containing compounds are reacted with hydrogen over a catalyst to yield H_2S, which then is trapped in ZnO.

The HDS-unit (hydrodesulphurisation) as well as the S-trap can be operated at temperatures ranging from 200°C to 400°C or above. The limits are set by the efficiency of the HDS-catalyst to hydrogenate some difficult S-containing compounds (e.g. thiophene). In order to treat such stable compounds it might be necessary to increase the reactor temperature to 350°C. Hydrogenolysis is performed on a pre-sulphidised wire-mesh catalyst containing sulphides of Co, Mo and Ni.

Figure 26 indicates the H_2S-yield for easily decomposed S-compounds over a typical HDS-catalyst. The load is given as a liquid space velocity. The design/dimensioning of a possible desulphurisatuion unit is covered further on in the report.

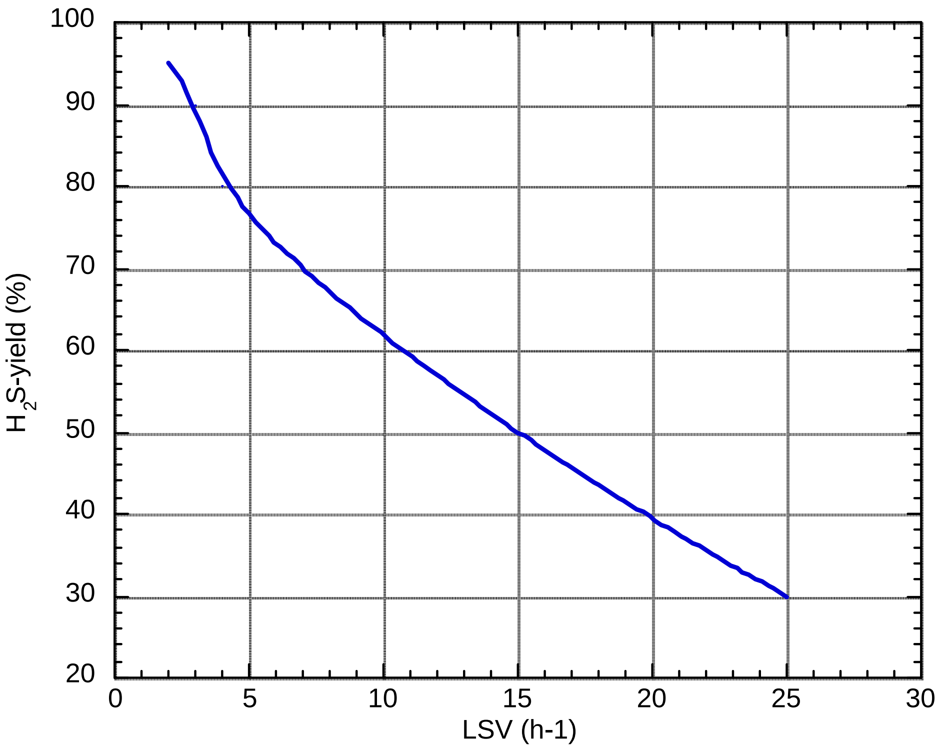


Figure 26 Forecasted yield of H_2S in hydrogenolysis of S-compounds in naphtha on Catators HDS-catalyst based on wire meshes.

8. Reactor design and dimensioning background

Steam reformer

The steam reformer will be based on CatHex structures heated by means of catalytic combustion, see Figure 27. Catalytic coils are inserted into the tubes of the CatHex-structure. The coil density might be varied to obtain an even heat flux along the combustor tubes in the CatHex-structures. The catalytic coils are pre heated with electricity on start up. Since the coils are coated with a ceramic layer we will obtain a good electric isolation from the CatHex structure. The electric resistance can be dimensioned for a variety of voltages but 12 or 24 VDC are optional.

The steam reformer catalyst is divided into three sections, each with intermediate heating by means of CatHex-structures. The total amount of heat necessary to add in the reformer section corresponds to about 600 W per nm^3/h of hydrogen produced.

The CatHex-plates will be produced from high-temperature stable steel where a large number of holes are drilled through the plate structure to enable gas transport. The plates will be in close thermal contact with the wire-mesh catalyst and the majority of the heat is transferred to the wire-mesh catalyst via thermal conduction and radiation. Since the thermal diffusion in the wire-mesh catalyst is high and the thermal length is short, we will obtain a close thermal coupling between the endothermic reforming reaction and the exothermic combustion.

The reactor will have a square geometry with a side length of approximately 80 mm (30 kWH_2). The thickness of the CatHex plates will be in the neighbourhood of 10 mm and each catalyst section will be about 20 mm.

Heat is generated by means of catalytic combustion of reformer gas, anode off gas or feed stock. The most realistic fuel to utilise in a fuel-cell application is anode off gas, which is a low-BTU gas carrying low concentrations of hydrogen. In other applications it is possible to heat the reformer section by combustion of reformer gas or the feedstock itself.

The off gases from the combustor tubes of the CatHex-structure are hot (about 900°C) and the heat will be recovered to arrive at an overall high thermal efficiency of the unit. The principle of heat recovery and the consequences on the thermal efficiency are discussed in detail in the next chapter.

All reactors and consequently also the reformer have been dimensioned utilising the experimental data obtained in the confirmatory tests, previously described. These data have been implemented into Catator’s simulation model to enable predictions of the temperature and conversion profiles throughout the reactor. Results from these simulations are described further on in the report.

Reformer gas re-circulation is optional when processing heavy feedstocks like gasoline and kerosene. However, in cases with light fuels like alcohols and fuel gases it is probably not necessary to re-circulate reformer gas to suppress the coke formation. The idea is to use a low inlet temperature to the reformer (500 – 600°C) to enable some pre reforming to avoid coke formation further downstream. Hence, the exact strategy of operation will vary depending on the feed stock quality.

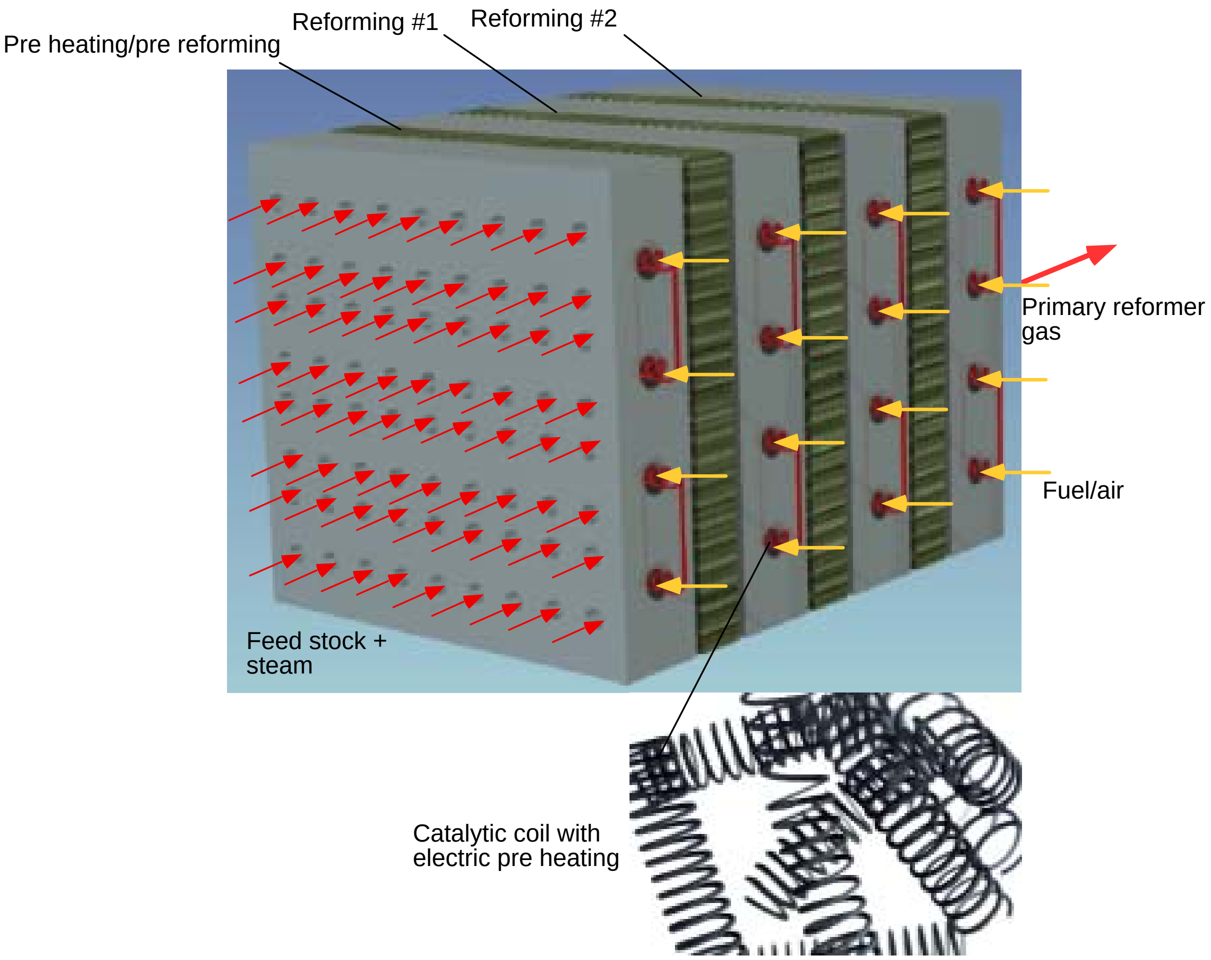


Figure 27 Close view of the reformer section.

The primary reformer gas will leave the reformer reactor at a temperature of about 800°C and it is necessary to cool the gas mixture before entering the water-gas-shift converter. It is possible to add liquid water to cool the reaction mixture and to further power the water-gas-shift reaction.

Water-gas-shift reactor

The WGS-reactor comprises three cooled sections of WGS-catalyst. Intermediate cooling is performed through a cooled version of CatHex-structures, see Figure 28 below. The primary reformer gas entering the WGS-reactor will have a temperature between 400 and 800°C, depending on if liquid water is injected upstream the reactor or not.

Cooling in the cooling tubes of the WGS-reactor is by means of a water/steam mixture. The WGS-reactor has a square geometry with the side 80 mm (30 kWH_2). The CatHex-structures are produced from solid metal plates fitted with appropriate drilled holes. The thickness of the CatHex-structures is 10 mm and each catalyst section will add another 20 mm to the package. The CatHex-structures in this reactor can be manufactured from aluminium, since the plate temperature is low enough. Cooling is primarily via conductivity in the package of wire meshes and to some extent via convection.

The water-gas reaction is an exothermic reaction and heat is consequently generated in the process. The generated heat corresponds to an increase of the gas temperature by 10°C per % (v/v) of CO converted.

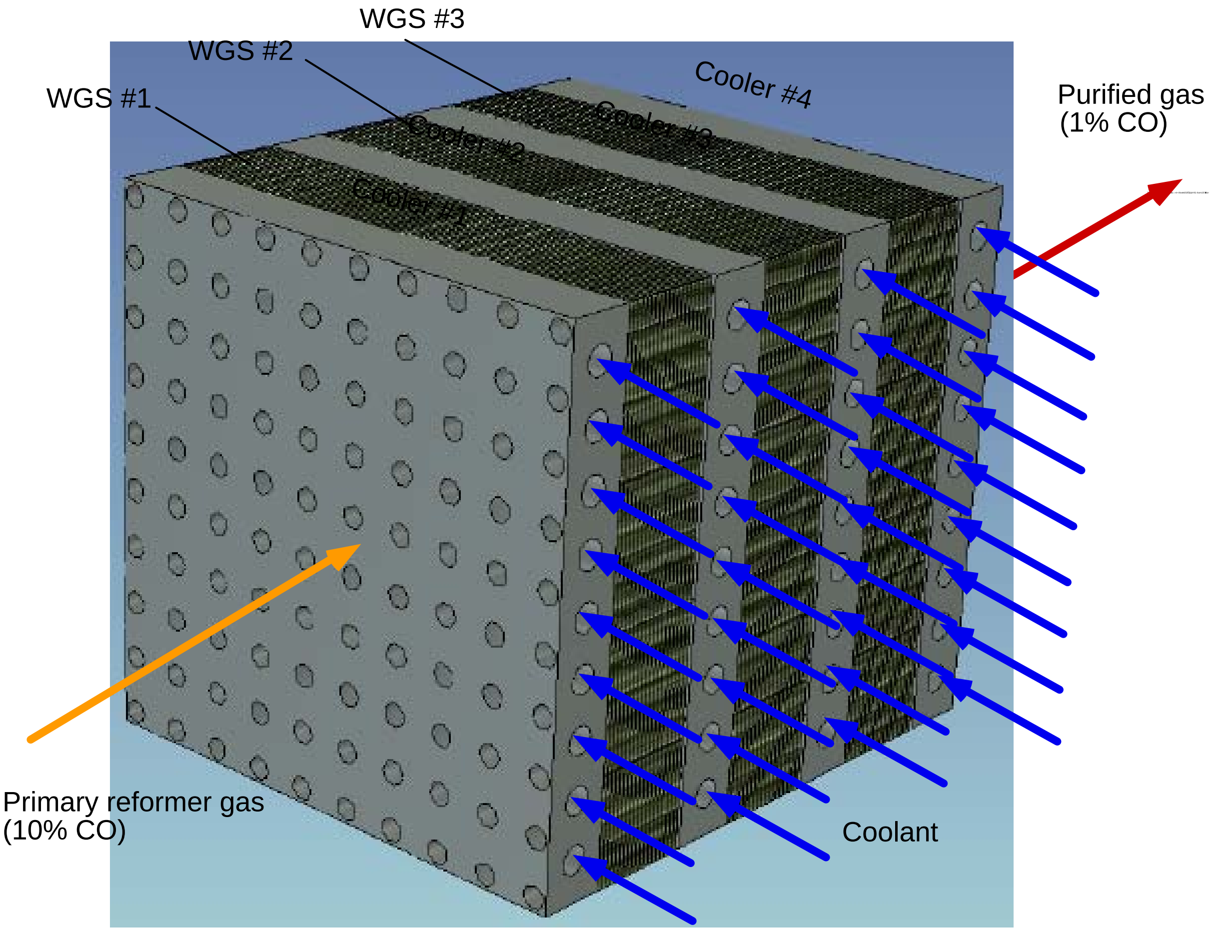


Figure 28 Close view of WGS-section.

The outlet temperature of the WGS-reactor will be in the neighbourhood of 150°C. The gas mixture is then fed into the PROX-reactor further downstream.

PROX-reactor

The CO-concentration of the gas mixture entering the PROX-reactor is about 1% (v/v) and an corresponding amount of oxygen (as air) is injected to power the preferential oxidation of CO. The PROX-reactor is a isothermal reactor, operated at a temperature between 100 and 150°C to obtain a high selectivity for CO-removal. Temperature control is via CatHex-structures, which are cooled with water. The first section of the PROX-reactor comprises a membrane catalyst for dispersed oxygen supply under an accurate temperature control. The membrane catalyst is in close thermal contact with the cooled CatHex-structures and the length of the catalytic membrane will be about 50 mm. The spacing between consecutive layers of membrane catalyst will be 5 mm.

The second part of the PROX-reactor consists of a package of wire mesh catalysts sandwiched between two consecutive CatHex-structures, see Figure 29 below. As for the other reactors, the PROX-reactor has a square section with a side of 80 mm (30 kWH_2). The total length of the reactor will be about 100 mm.

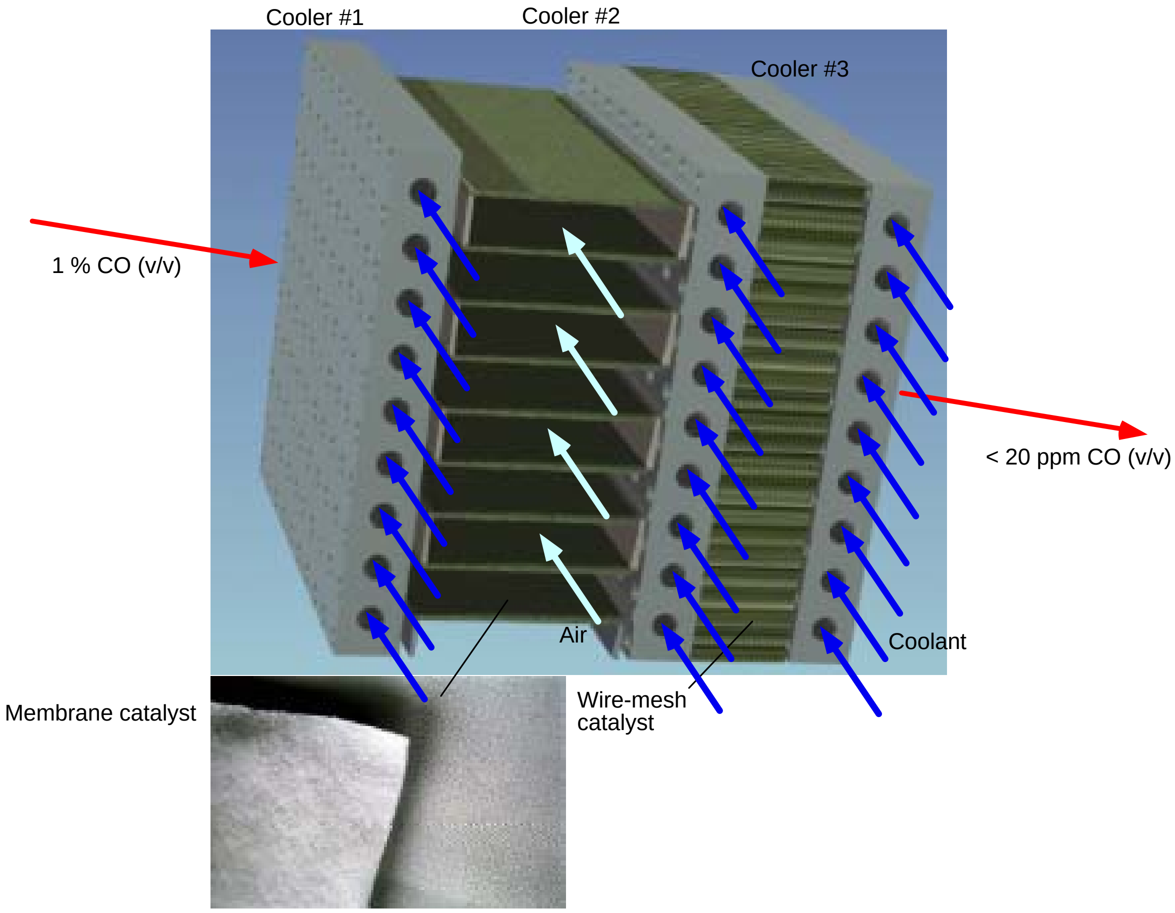


Figure 29 Close view of PROX-section.

The gas leaving the PROX-reactor will carry about 20 ppm (v/v) of CO at 80°C and can be fed directly to a fuel cell.

Desulphurisation unit

Desulphurisation is performed by means of catalytic hydrogenolysis of sulphur containing compounds. The HDS-reactor is (HDS=hydrodeslphurisation) is directly linked to the H_2S-trap further downstream, see Figure 30.

The volume of the H_2S-trap depends on the sulphur content of the feed stock and the time interval between consecutive replacements. However, at full-load operation (30 kWH_2) the following amounts of sulphur need to be separated utilising different feed stocks:

- alcolhols (sulphur free), 0 kg/yr
- fuel gases (5 ppm), 0.14 kg/yr
- gasoline (10 ppm), 0.16 kg/yr
- kerosene (30 ppm), 0.49 kg/yr

The trapping capacity of ZnO corresponds to 30% (w/w), which would mean a ZnO-consumption of about 1.5 kg/yr for kerosene. We intend to use wire meshes coated with porous Zn, which will be converted slowly into ZnO at stream conditions. Introductory experiments verify the function and capacity of these Zn-structures.

The HDS-unit as well as the S-trap can be operated at temperatures ranging from 200°C to 400°C or above. The limits are set by the efficiency of the HDS-catalyst to hydrogenate some difficult S-containing compounds (e.g. thiophene). In order to treat such stable compounds it might be necessary to increase the reactor temperature to values above 250°C. Hydrogenolysis is performed on a pre-sulphidised wire-mesh catalyst containing sulphides of Co, Mo and Ni.

Hydrogen rich gas (taken from the reformer circuit) is added to the evaporated feed stock. The reactor is pre-heated to its operating temperature by means of electricity, since the thermal energy carried by the hydrocarbon vapour is rather low. Consequently, without electric pre-heating, start up would take a long time.

The HDS-reactor has a length of 100 mm and an outer diameter of 100 mm and is operated adiabatically. If olefins are present, these will be hydrogenated under heat production. H_2S is then absorbed by ZnO in the sulphur trap downstream the HDS-reactor. The exact dimensions of the ZnO-trap will be settled during the Realisation phase.

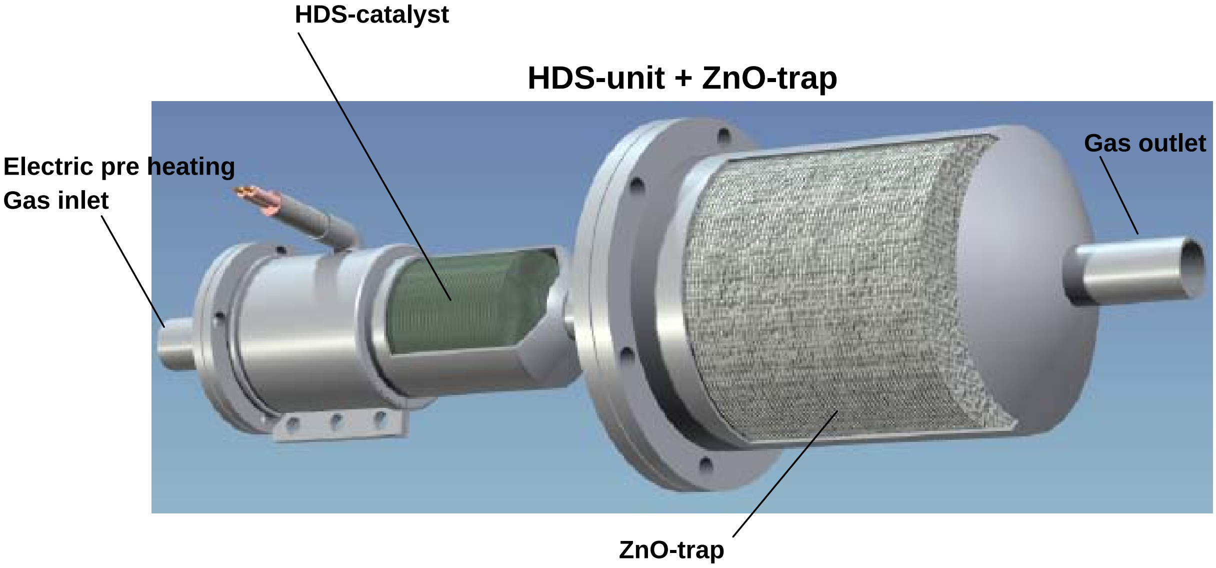


Figure 30 Close view of desulphurisation unit.

Integrated reactor structure (SREF + WGS + PROX) and reactor calculations

Depending on the rather innovative CatHex-concept, it is possible to integrate the unit reactors to an all-inclusive design, se Figure 31 below. The capacity of the unit will be about 10 kWH_2 per litre of gross volume. The corresponding weight will be in the neighbourhood of 10 kg.

A mixture of steam and feed stock is fed to the reactor inlet and the purified reformer gas is obtained at the outlet. Further efforts might be to try to integrate also the HDS-unit and the ZnO-trap into the unit. For the time being, however, the HDS/ZnO-units are considered to be separate units.

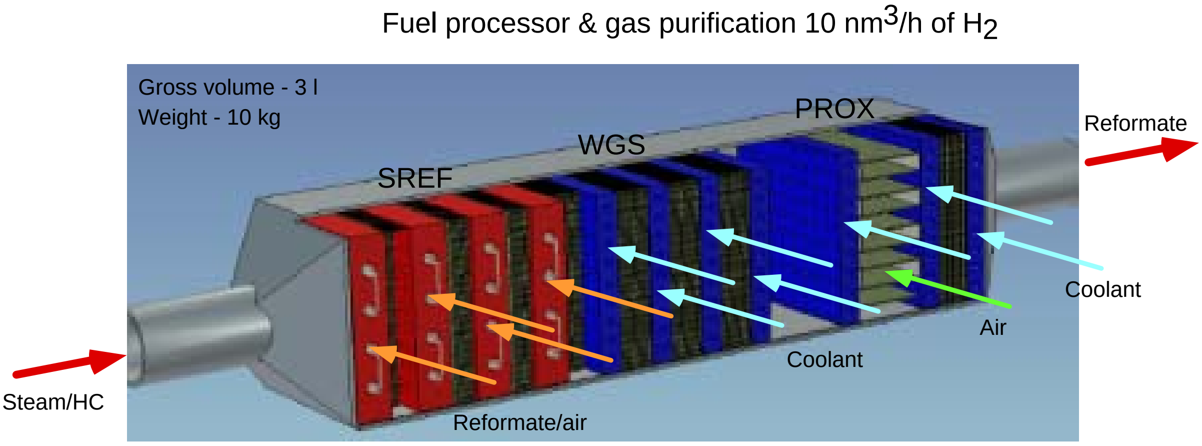


Figure 31 All-inclusive reactor; SREF+WGS+PROX.

Realisation of the all-inclusive unit presented in Figure 31 will indeed enable us to present a fuel processor in the research frontline world wide when it comes to compactness.

The intention is to construct the above design suggestion and to evaluate its performance during the Realisation phase of this project.

Extensive reactor simulations were performed for dimensioning purposes. The calculations were performed with Catator’s generic simulation code for catalytic reactors, CatalystExplorer. The results of these simulations can be presented as a number of diagrams showing the temperature profile and the conversion of important components (especially CO). Simulations have been performed for different feedstocks but the results from methane reforming are shown below.

Beginning at the inlet of the Steam reformer, the gas will be heated to a temperature of about 800°C in the first heated CatHex-section (Figure 32). The temperature will then decrease along the reaction pathway in the first catalyst section due to the endothermic nature of steam reforming. The conversion in the first catalyst section will be about 50% (Figure 33). The gas mixture is then heated to about 800°C in the second CatHex-structure before it enters the second catalyst sections. The second catalyst section enables us to reach an overall methane conversion of about 80%. The third step, involving intermediate heating and reaction, let us arrive at an overall conversion of 96% of methane and an outlet temperature of 800°C. It is possible (although not shown) to include a fourth catalyst layer downstream the last CatHex-structure to complete the reforming reaction and to cool the gas mixture somewhat (endothermic cooling).

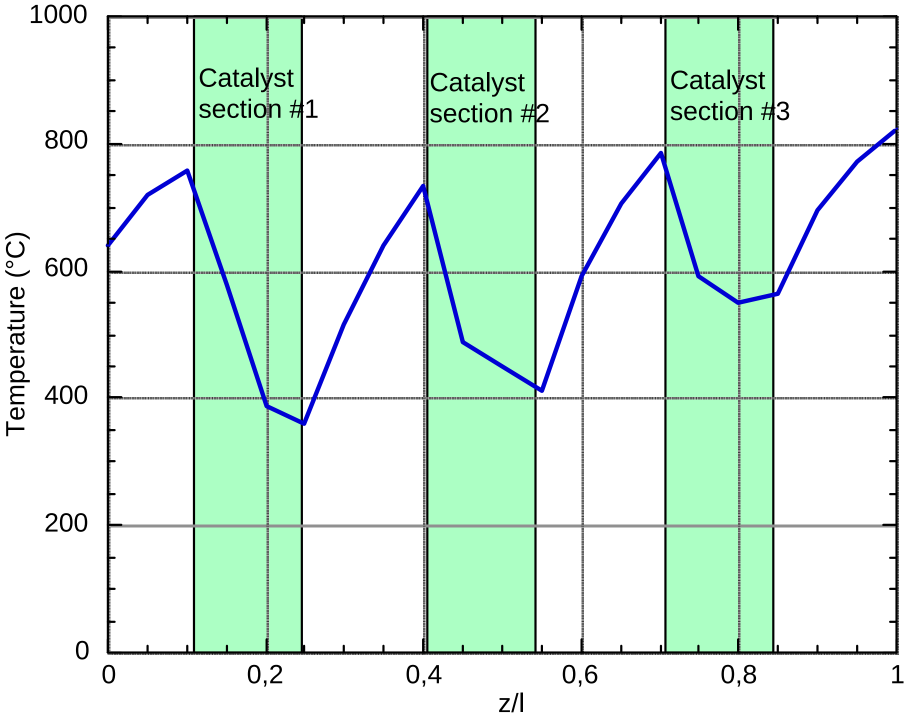


Figure 32 Temperature profile along the reaction pathway in the reformer section at full load.

Since the first part of the reforming reaction is accomplished at a rather low temperature, the reforming reactions will yield enough hydrogen to suppress the coke formation further downstream the reactor. In cases with heavy feedstocks it might, however, be necessary to re-circulate some of the reformer gas.

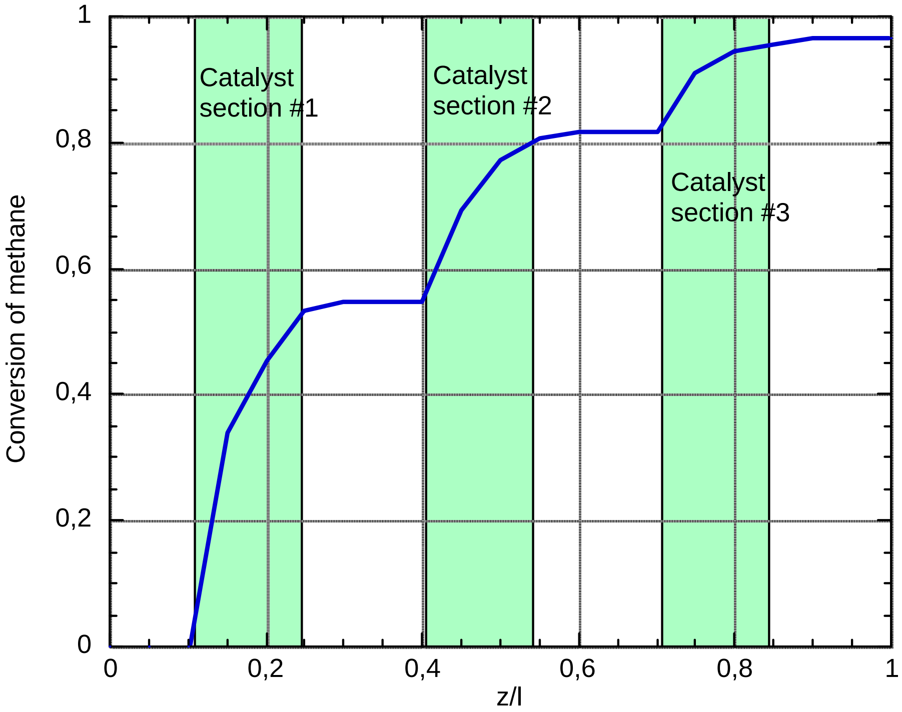


Figure 33 Conversion of methane along the reaction pathway in the reformer section at full load.

Figure 34 and 35 show the corresponding temperature- and conversion profiles through the WGS-reactor. The inlet temperature in the simulation was about 500°C (some water addition upstream the WGS-reactor was included to cool the gas mixture and to power the WGS-reaction). The consecutive cooling (CatHex-structures) and heating (WGS-reaction) can be followed through the reactor. Most of the CO-conversion is obtained in the first catalyst section, which operates at a high temperature. Consequently, thermodynamic equilibrium is established in this step and further cooling is necessary to reduce the CO-concentration further. The CO-concentration of the gas leaving the reactor will be about 1 % (v/v), which is an applicable inlet concentration to the PROX-section.

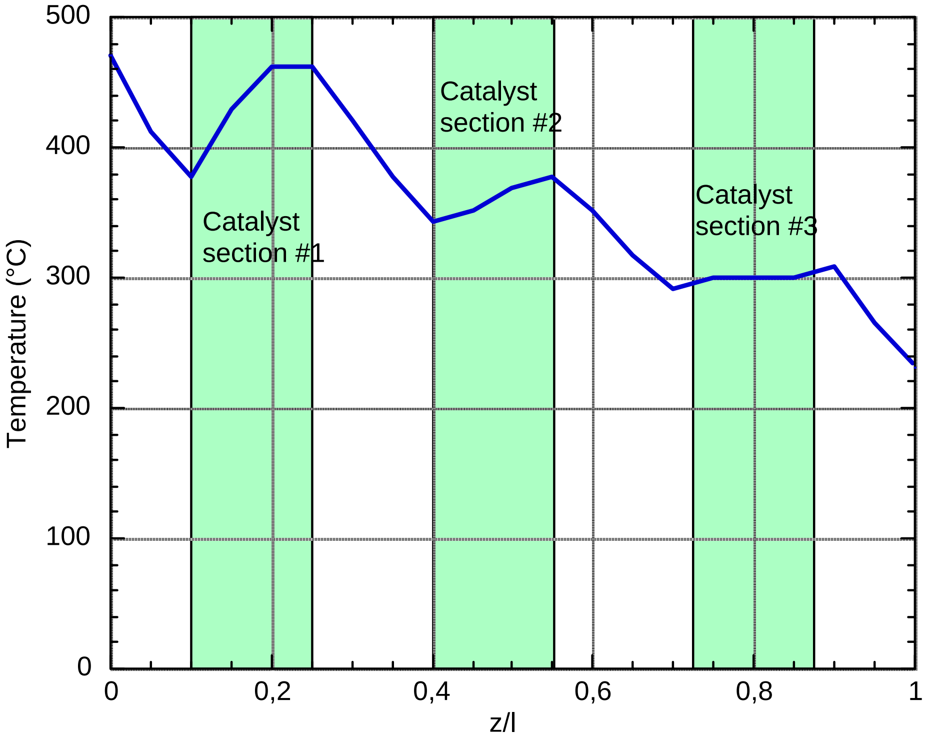


Figure 34 Temperature profile along the reaction pathway in the WGS-section at full load.

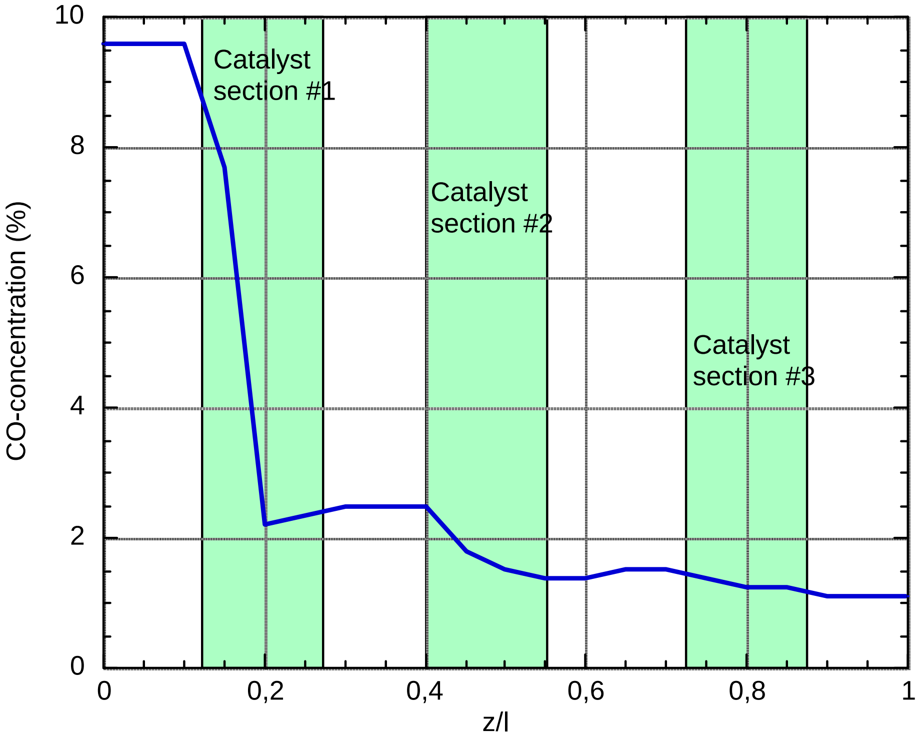


Figure 35 CO-concentration along the reaction pathway in the WGS-section At full load.

The PROX-section operates isothermally at 150°C and the CO-concentration along the reaction pathway is shown in Figure 36. The CO-concentration is decreased to about 1500 ppm in the membrane section whereas complete conversion (<10 ppm CO) is accomplished in the downstream package of catalytic wire meshes.

Thus, the CO-concentration of the gas leaving the reactor will be low enough for direct utilisation of the purified reformer gas in PEM-cells.

The above simulations are only example of calculations, which have been performed with CatalystExplorer, starting with kinetic data obtained in the extensive verification tests.

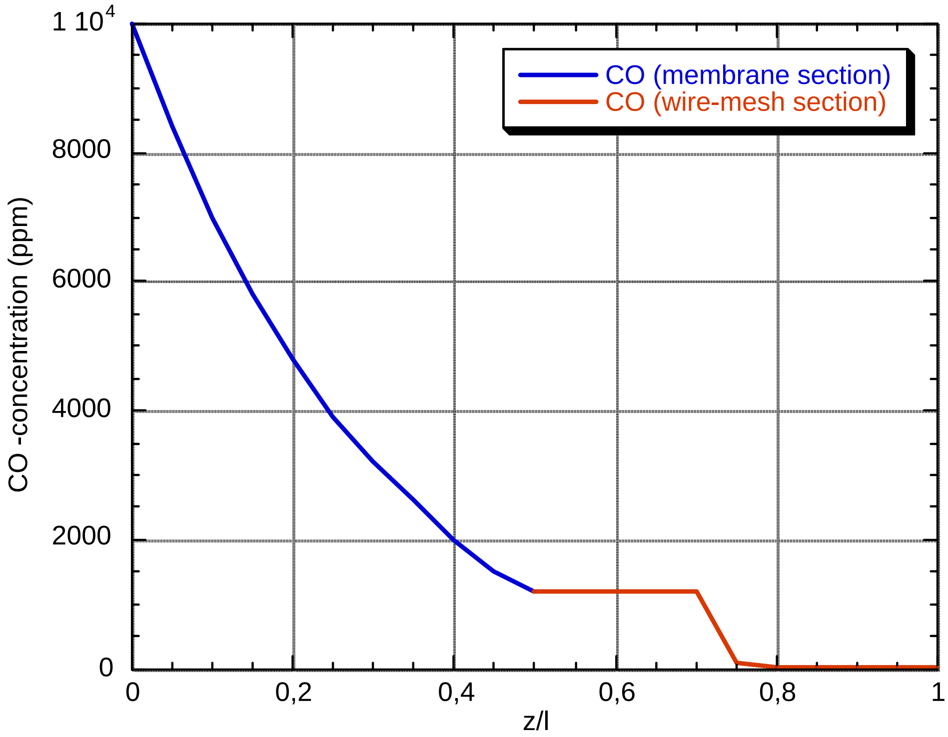


Figure 36 CO-concentration along the reaction pathway in the PROX-section at full load.

9. System lay-out

The total system will consist of a number of chemical reactors, heat exchangers and necessary components for gas supply/transport. Figure 37 below is a preliminary system lay-out and the intention is to forward a detailed system lay-out during the beginning of the Realisation phase of the project. The material- and energy balances have been calculated for methane reforming at a steam:carbon ratio of 3:1. Additional calculations will be performed also for other feedstocks during the next project phase.

The feedstock is led through the HDS-unit to convert all sulphur compounds to H_2S, which then is trapped in the ZnO-unit. These reactors are placed in an isothermal block, operated at a temperature between 250 and 300°C. The HDS-process/S-trapping is energy neutral and the added heat is to increase the temperature of the feedstock to the necessary reaction temperature. The sulphur free feed stock is then mixed with steam to obtain a steam:carbo ratio of 3:1 at the inlet to the steam reformer. The inlet temperature is set to about 600°C and some pre-heating/pre-reforming will take place at the inlet section of the reactor. Heat supply is by means of catalytic combustion of a fuel with air. It is possible to use the feedstock itself as the fuel but it is more reasonable to use either reformer gas or anode off gas (from the fuel cell stack). The outlet temperature of the reformer is 800°C in order to arrive at low residual concentrations of methane. In the lay-out shown below, however, the fuel is used as heating source.

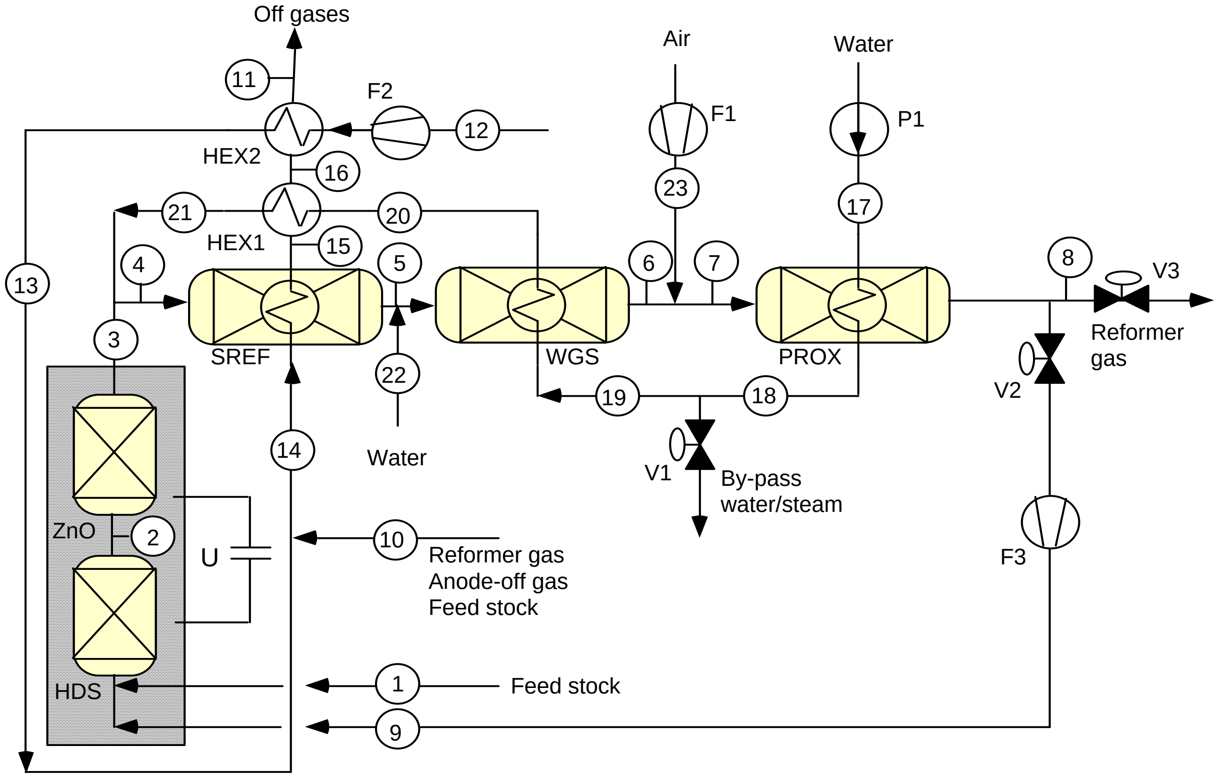
The heat of the off gases is recovered in the steam entering the steam reformer and in the air necessary for combustion. The primary reformer gas is then led into the water-gas-shift converter where a large portion of carbon monoxide is converted into carbon dioxide and hydrogen. The exit temperature of the WGS-reactor is set to 150°C. The water-gas-shift converter is cooled by water/steam. Air is injected to the reformer gas downstream the water-gas-shift converter to enable preferential oxidation. The cooling of the PROX-reactor is by means of water at a relatively low temperature 25 – 50°C.

Some of the purified reformer gas can be re-circulated to the HDS-reactor to promote the hydrogenolysis reactions. Also, by increasing the re-circulation ratio it is possible to suppress the coke formation reactions (especially for heavy fed stocks).

The combustion process in the reformer is initiated by means of electrically heated catalyst elements, previously described.

The data given in Figure 37 have been derived from thermodynamic calculations (HSC to Outokumpu) and mass- & energy balances (Design II to WinSim). Reactor modelling (differential mass- & energy balances) has been performed with CatalystExplorer (Catator AB).

When the system lay-out is settled (during the initial phase of the Realisation phase), a dynamic process simulation will be performed for the entire system in order to study transient operation and to map the robustness of the system (effects of disturbances).



No	T (°C)	P (kPa)	m (kg/h)	H_2 (vol%)	CO (vol%)	CO_2 (vol%)	H_2O (vol%)	CH_4 (vol%)	O_2 (vol%)	N_2 (vol%)
1	25	110	2.41	N/A	N/A	N/A	N/A	100	N/A	N/A
2	250	109	2.42	Trace	N/A	N/A	N/A	75	N/A	N/A
3	250	107	2.42	N/A	N/A	N/A	N/A	100	N/A	N/A
4	600	107	10.7	N/A	N/A	N/A	75	25	N/A	N/A
5	800	105	10.7	53.8	9.2	6.3	30.7	Trace	N/A	N/A
6	150	103	13.0	53.6	1.0	12.4	32.9	Trace	N/A	N/A
7	145	103	14.4	51.1	0.96	11.9	31.4	Trace	0.096	3.6
8	80	102	14.4	50.7	10 ppm	13.0	32.7	Trace	0	3.6
9	80	110	<0.1	50.7	10 ppm	13.0	32.7	Trace	0	3.6
10	25	105	0.98	N/A	N/A	N/A	N/A	100	N/A	N/A
11	300	101	17.5	N/A	N/A	9.5	19.0	0	0	71.4
12	25	106	16.5	N/A	N/A	N/A	N/A	N/A	21	79
13	200	105	16.5	N/A	N/A	N/A	N/A	N/A	21	79
14	175	105	17.5	N/A	N/A	N/A	N/A	9.5	19.0	71.4
15	900	104	17.5	N/A	N/A	9.5	19.0	0	0	71.4
16	475	102	17.5	N/A	N/A	9.5	19.0	0	0	71.4
17	25	112	8.2	N/A	N/A	N/A	100	N/A	N/A	N/A
18	100	110	8.2	N/A	N/A	N/A	100	N/A	N/A	N/A
19	100	110	8.2	N/A	N/A	N/A	100	N/A	N/A	N/A
20	210	109	8.2	N/A	N/A	N/A	100	N /A	N/A	N/A
21	650	107	8.2	N/A	N/A	N/A	100	N/A	N/A	N/A
22	25	105	2.5	N/A	N/A	N/A	100	N/A	N/A	N/A
23	25	103	1.4	N/A	N/A	N/A	N/A	N/A	21	79

Figure 37 Schematic system lay-out and MB & EB.

Based on the system lay-out and the detailed reactor designs it is possible to estimate the technical/economical performances of the system. The accuracy in these estimations will be improved once the detailed lay-out is settled.

10. Expected features and economic evaluation

The chemical reactors will be built in an extremely compact manner, as previously discussed. The total reactor volume will be less than 10 l (10 kWH_2). The gross volume of the fuel processor is expected to be below 40 l for a unit capable of producing 10 nm^3/h of hydrogen. The corresponding weight will be below 50 kg.

The fuel processor is built to enable utilisation of a number of commercial relevant feedstocks, e.g. natural gas, biogas, LPG, alcohols and light and heavy naphtha. The overall thermal efficiency is calculated to values between 70 and 80% of the lower heating value of the feedstock. The turn-down-ratio is expected to be at least 10:1.

Since the unit is characterised by a high degree of compactness and includes effective methods for pre-heating, the start-up time will be short, possibly below 5 minutes.

The unit operates under ambient conditions with respect to the pressure and the pressure drop of the system is low (< 5 kPa at full load).

The design of the fuel processor is applicable for large-scale production and the price is expected to be low. The life-time of the fuel processor is set to 16 000 hrs at full load, and the investment cost is estimated to about 0.30 SEK/nm^3 of hydrogen produced.

The price of the feedstock is the most important factor for the overall production cost of hydrogen. The feedstock alone stands for 0.60 – 1.30 SEK per nm^3 of hydrogen produced. Figure 38 below, indicates the production cost of hydrogen with the proposed design. It is obvious that electrolysis is a very expensive method of hydrogen production, whereas fuel processing is a method to produce rather cheap hydrogen [11]. Large-scale production of hydrogen is based on traditional steam reforming or partial oxidation.

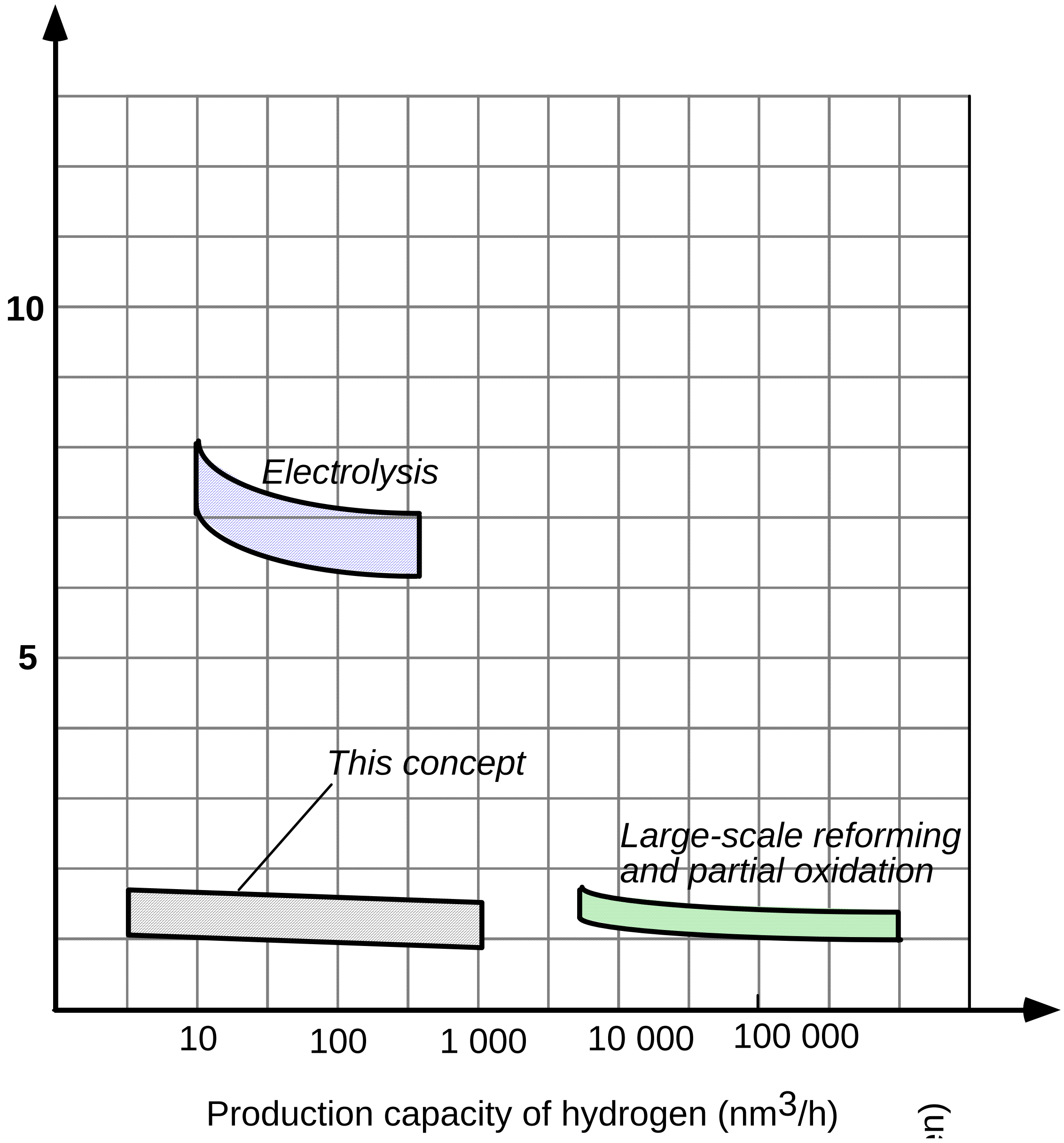


Figure 38 Estimated production price.

The design concept proposed in this report is easy to scale and units will be available with a production capacity ranging from <10 nm^3/h to about 1000 nm^3/h. The CO-concentration of the reformate will be below 20 ppm(v/v) to enable direct utilisation in PEM-cells.

11. Conclusions

The results obtained during the Feasibility- and Design phase clearly confirm the possibility to reach the design goals concerning the reactor system. A number of suitable catalyst formulations have been proposed for the unit-processes in the reactor system (SREF, WGS, PROX, DESULF). The experimental evaluations indicate an extremely high intrinsic activity of the active phases in the different reactions.

Through utilisation of Catator's novel heat-exchanger reactors (EndEx and CatHex), we have also demonstrated the possibilities of integrating catalytic steps and heat transfer structures. Thus the proposed all-inclusive reactor including SREF, WGS and PROX is really extremely compact, 10 kWH_2 per unit litre of reactor, which is a value in the frontline of research and development worldwide. Thus, the integral system (including supply systems and insulation) will also be compact and light, which is important in many applications. Also, this unit is a multi-feed unit, where a number of different feedstocks can be processed in the same unit. This feature certainly widens the area of application of this novel system design.

The high overall thermal efficiency together with electrically heated catalyst elements enables us to arrive at a quick thermal response and a high fuel economy.

The investment cost of the unit corresponds to about 0.30 SEK/nm^3 of hydrogen produced. The production price per nm^3 of hydrogen produced is typically around 1 SEK when utilising fossil fuels as feed stock. Renewable feedstocks like alcohols are currently somewhat more expensive and the production price is typically 1.50 SEK per nm^3 of hydrogen. Thus, the expected hydrogen production price with the novel reactor system is considerably lower than the corresponding production price with electrolysis.

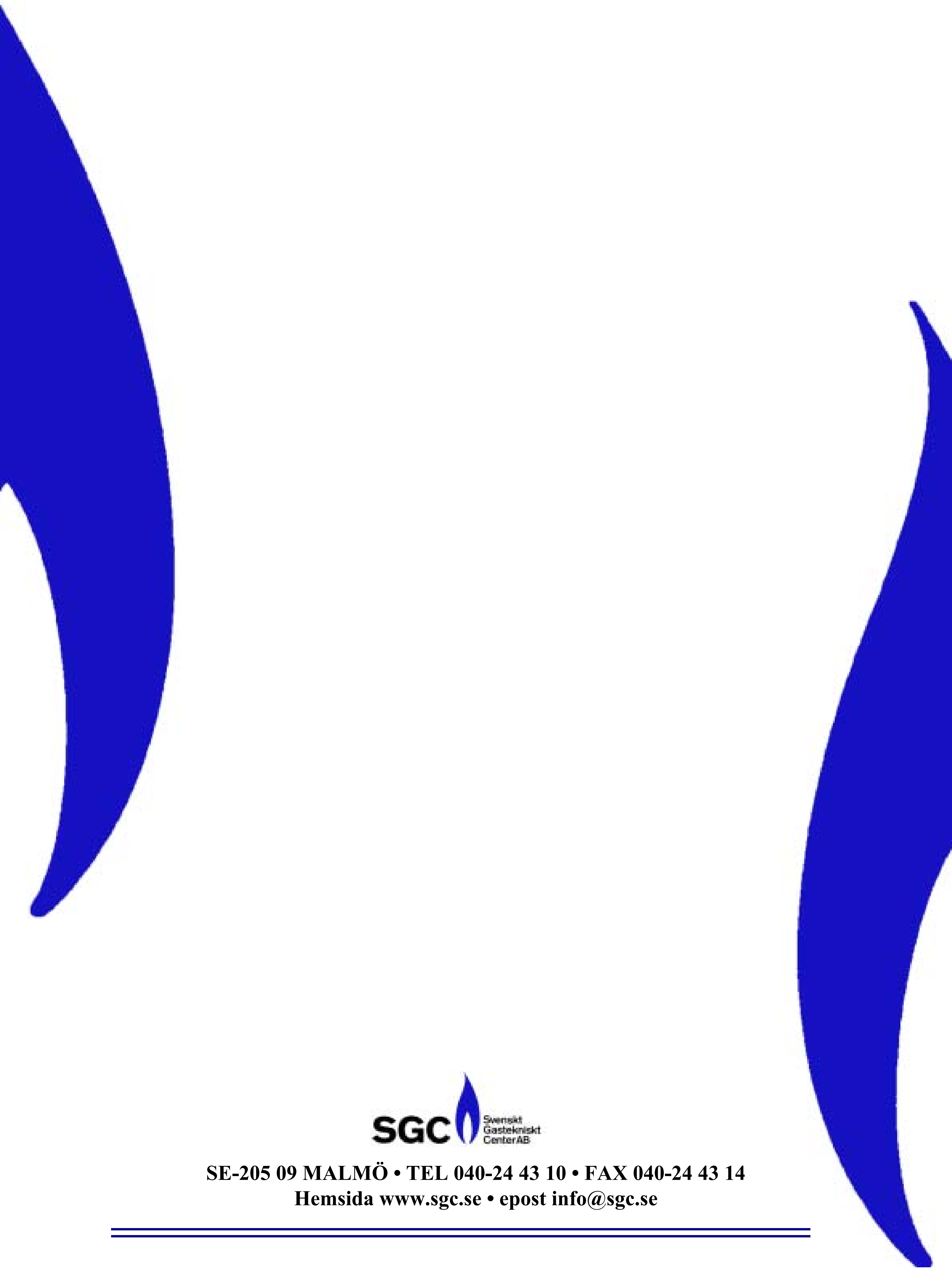
The main areas of problems are associated with catalyst deactivation through sulphur poisoning and coke formation. We intend to include a step with hydrogenolysis of S-containing compounds to decrease the impact of sulphur in the fuel processor. Also by choosing applicable conditions of operation and suitable catalyst formulation, it is possible to avoid sulphur poisoning and coke formation. The problems arising from sulphur and coke will, however, be in focus during the realisation phase.

12. Literature

1. M.V. Twigg, "Catalyst Handbook", Manson Publishing Ltd, London 1996, p 238.
2. C. N. Satterfiled, "Heterogeneous Catatlysis in Industrial Practice", McGraw-Hill, New York 1991, p 421.
3. J. M. Ogden, "Review of small stationary reformers for hydrogen production", Report to the International Energy Agency, Princeton University, March 2001.
4. A.L.Dicks, S. L. Jones, R. Judd, K. Pointon and A Gough, "Assessment of advanced catalyst performance and fabrication options for a compact steam reformer", ETSU F/02/00180/Rep, Crown Copyright 2001.
5. F. Silversand, "Catalytic Heat Exchangers for small-scale production of hydrogen – feasibility study", SGC report No. 129, Malmö 2002, p. 25 – 27.
6. M.V. Twigg, "Catalyst Handbook", Manson Publishing Ltd, London 1996, p 226.
7. C. N. Satterfiled, "Heterogeneous Catatlysis in Industrial Practice", McGraw-Hill, New York 1991, p 422.
8. G Ertl, H. Knözinger and J. Weitkamp, "Handbook of Heterogeneous Catalysis",VCH Verlagsgesellschaft mnH, Weinheim 1997, p 1909.
9. R. H. Perry and D. W. Green, "Perry´s Chemical Engineers´ Handbook – 7th ed.", McGraw-Hill, New York 1997, p22-61.

10 E.E. Petersen and A. T. Bell, "Catalyst Deactivation", Marcel Dekker Inc, New York, 1987, p.152.

11 F. Silversand, "Catalytic Heat Exchangers for small-scale production of hydrogen – feasibility study", SGC report No. 129, Malmö 2002, p. 32.



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