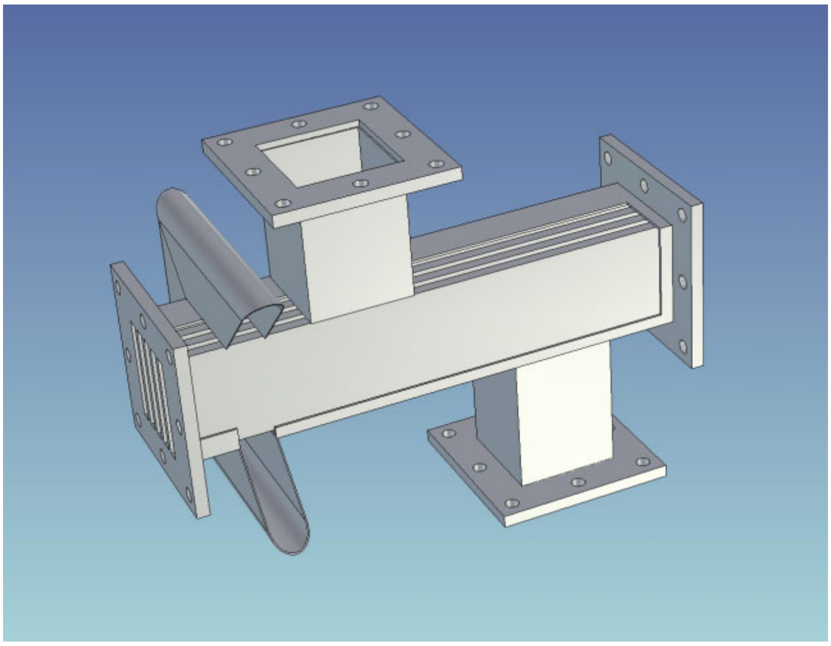
Rapport SGC 151

Reliability study of a small-scale fuel processor system (STUR-10 kWH_2)



Anna-Karin Jannasch & Fredrik Silversand
CATATOR AB

Rapport SGC 151 • ISSN 1102-7371 • ISRN SGC-R--151-SE

SGC:s FÖRORD

FUD-projekt inom Svenskt Gastekniskt Center AB avrapporteras normalt i rapporter som är fritt tillgängliga för envar intresserad.

SGC svarar för utgivningen av rapporterna medan uppdragstagarna för respektive projekt eller rapportförfattarna svarar för rapporternas innehåll. Den som utnyttjar eventuella beskrivningar, resultat e dyl i rapporterna gör detta helt på eget ansvar. Delar av rapport får återges med angivande av källan.

En förteckning över hittills utgivna SGC-rapporter finns på SGC´s hemsida www.sgc.se.

Svenskt Gastekniskt Center AB (SGC) är ett samarbetsorgan för företag verksamma inom energigasområdet. Dess främsta uppgift är att samordna och effektivisera intressenternas insatser inom områdena forskning, utveckling och demonstration (FUD). SGC har följande delägare: Svenska Gasföreningen, Sydkraft Gas AB, Sydkraft AB, Lunds Energi AB, Göteborg Energi AB, och Öresundskraft AB.

Följande parter har gjort det möjligt att genomföra detta utvecklingsprojekt:

Statens Energimyndighet
Catator AB
FMV
Sydkraft Gas AB
OptiCat International AB

SVENSKT GASTEKNISKT CENTER AB

Johan Rietz

Sammanfattning

Under år 2003 utvecklade Catator AB en ultrakompakt vätgasgenerator (nästan 1 Nm^3/h H_2 per liter reaktorvolym), den så kallade Ultraformern eller Single Train Ultraformer reaktorn (förkortas STUR). Målsättningen med detta arbete var att presentera en kompakt och skalbar reaktor design inkluderande reformering samt CO-rening med vilken man kan producera reformatgas av polymerelektrolytbränslecellskvalité (< 20 ppm CO). Enheten möjliggör reformering av ett flertal olika bränslen såsom biogas, gasol, alkoholer och tyngre kolväten. Den har även ett stort reglerområde (omkring 1:10), en hög termisk effektivitet (80 %) och möjliggör en snabb uppstart.

Detta arbete är en fortsättning på det tidigare avslutade arbetet. Projektet administrerades av Svenskt Gastekniskt Center (SGC AB) och finansierades av Sydkraft Gas AB, Försvarets Materialverk (FMW), Statens Energimyndighet (STEM), Catator AB (CAT) och OptiCat International AB. Arbetet har inkluderat utveckling och konstruktion av ett optimerat STUR-system designad för den nominella kapaciteten 10 kWH_2 (motsvarande ~ 3 Nm^3/h $H_2(g)$). I jämförelse med den tidigare utvärderade 30 kWH_2- STUR enheten har detta system optimerats med avseende på den integrerade brännarkonstruktionen, vilken förser ångreformerings-reaktionen med värme, samt med avseende på den totala värmeåtervinningen. Projektet innefattade en riskanalys av hela systemet samt implementering av ett säkerhetssystem för att möjliggöra automatisk, delvis obevakad, långtidsdrift. Det sistnämnda i sin tur för att möjliggöra en tillförlitlighetsstudie av systemet under en längre tid (~ 500 timmar). Under hela utvärderingen användes naturgas som reformerbränsle. Målsättningen med långtids-utvärderingen var att identifiera eventuellt existerande degraderingsfenomen och svagheter hos det optimerade STUR-systemet, relaterade till både de användna katalysatorerna och de olika reaktorkonstruktionerna. Därefter, med hänsyn till projektets kalendertid och budget, finna metoder som kan eliminera dessa svagheter och som kan bromsa observerade degraderingsfenomen.

Resultaten visade att lovande prestanda kan uppnås med det fullt automatiska 10 kWH_2-systemet. Systemet visade sig kunna starta upp relativt snabbt (~30 minuter vid ren ångreformering, ~ 20 minuter vid partialoxidation), samt möjliggöra stabila driftsbetingelser vid olika laster med avseende på både temperaturprofiler och emissioner (≈ 96-97 % i HC-omvandling, nästan 80 % i vätgasutbyte och < 20 ppm CO). Ett återkommande problem uppkom däremot under tillförlitlighetsstudien med, inom detta projekt, den första STUR-konstruktionen. Problemet var relaterat till hållbarheten hos ångreformerings/brännarkonstruktionen. Efter omkring 50 -60 h av stabil drift så uppkom sprickor i reaktorn, troligtvis på grund av en alltför styv konstruktion, vilket resulterade i luftläckage från brännaren in till reformatreaktionsgasen. Detta i sin tur ledde till allvarlig katalysatordeaktivering och omöjliggjorde genomförandet av hela den planerade tillförlitlighetstudien. För att lösa detta problem, utvecklades och konstruerades en ny förbättrad ångreformering/brännarreaktor. Samtidigt utfördes arbete för att hitta en mer aktiv och en mer stabil ångreformeringskatalysator. Tillsammans resulterade detta arbete i en ny driftsättning och en ny långtidsutvärdering av det nu ytterligare modifierade och optimerade STUR-systemet. Tack vare den nya, mer flexibla ångreforming/-brännarkonstruktionen visade det sig vara möjligt att genomföra en lyckad, kontinuerlig och fullständigt automatisk, långtidsdrift av STUR-systemet under mer än 500 timmar. Stabila emissioner och driftstemperaturer uppnåddes efter ca 50 timmar. Slutligen, under tillförlitlighetsstudien utfördes totalt 9 kalla uppstarter av systemet. Ingen deaktivering av prestanda kunde detekteras till följd av detta. Nästa steg i detta utvecklingsarbete är att driftsätta och utvärdera systemet med en bränslecell integrerad.

Summary

During 2003, Catator AB finalized the development of an atmospheric ultra compact hydrogen generator (close to 1 Nm^3/h of produced H_2 per liter gross volume), Ultraformer or Single-Train Ultraformer Reactor (abbreviated STUR). The overarching goal of this work was to present a compact and scalable reactor design including fuel processing and CO purification in order to reach low temperature fuel cell quality (i.e. < 20 ppm CO). The unit can run on a variety of feed stocks, i.e. biogas, natural gas, LPG, alcohols and heavier hydrocarbons. It also has a wide turn-down ratio (about 1:10), a high thermal efficiency (80%), and enables a rapid start-up. The evaluation of a fully integrated 30 kWH_2 STUR unit showed that the characteristics listed above could be reached.

This work is a following-up study of the previously concluded work. The project was administrated by the Swedish Gas Centre AB (SGC), and was financed by the companies Sydkraft Gas AB, Försvarets Materialverk (FMV), the Swedish Energy Agency (STEM), Catator AB (CAT) and OptiCat International AB. The work has involved the development and the construction of an optimized STUR-system designed for the nominal capacity of 10 kWH_2 (i.e. 3 Nm^3/h $H_{2(g)}$). Compared to the earlier evaluated 30 kWH_2 unit, this system has been optimized with respect to the design of the integrated catalytic burner, from which heat is supplied to the steam reforming reaction, and with respect to the overall heat recovery of the system. The project included a risk analysis of the system and implementation of a security system for enable fully automatic, partly non-supervised, long term testing. The latter was for enabling a reliability study of the STUR-system during a longer period of continuous operation time (~ 500 h). The feed stock used throughout this evaluation work was natural gas. The overall scope of the long time operation test was to identify any existing degradation phenomena and weaknesses of the optimized STUR-system, with respect to both the used catalysts and to the different reactor constructions. Then, with respect to the calendar time and budget of the project, to find methods to eliminate these weaknesses and to slow down any observed degradation processes.

The results showed that promising performance results could successfully be obtained with a fully automatic STUR 10kWH_2 system. The system enabled a relatively quick start-up (within 30 minutes in pure steam-reforming mode without any partial oxidation, 20 minutes with initial partial oxidation in the steam reforming reactor), stable operation conditions at various loads with respect to both temperature profiles and emissions (≈ 96-97 % in HC conversion, close to 80 % in H_2 efficiency and < 20 ppm CO). One returning problem was however encountered with, within this project, the first constructed STUR-design during the reliability study. The problem was related to the durability of the SREF/burner design. After about ~50-60 h of stable operation time, cracks occurred in the reactor, most likely due to a too stiff design, causing air leakage from the burner into the reformate reaction gas. This resulted in turn in a serious catalyst deactivation and precluded long-time reliability studies to be finalized. To overcome this problem, a new improved steam reforming/burner design was developed. In addition, efforts were simultaneously made to find a more active and a more stable SREF catalyst formulation. Altogether, this resulted in a new commissioning and a new long time evaluation phase of a further modified and optimized STUR-unit. Thanks to the new, more flexible SREF/burner design, it was found that it is possible to successfully run, continuously and fully automatically, the STUR-system for at least 500 h. Stable emission levels and operation temperatures were reached within about 50 h of operation time. Finally, in totally 9 shut downs and cold start-ups were made with the modified system. No influence on the performance could be detected. Furthermore, the next step in this development work would be to operate and to evaluate the system with a fuel cell (~2 kW_{el}) integrated in the system.

List of content

1. Background and aims of the work

In 2003, Catator AB (CAT) finalized the development of an atmospheric ultra compact hydrogen generator (close to 1 Nm^3/h of produced H_2 per liter gross volume), the so called Ultraformer or Single-Train Ultraformer Reactor (abbreviated STUR). In brief, that work resulted in the design, construction, commissioning, and experimental evaluation of a STUR unit with a capacity of 30 kWH_2 (i.e. 10 Nm^3/h $H_{2(g)}$).

The STUR unit is a totally integrated fuel processor system which comprises the following catalytic steps:

- Steam reforming (SREF)
- Water Gas Shift converter (WGS)
- Reactor for preferential oxidation of CO (PROX)
- An integrated catalytic burner for heating up the SREF.

The catalysts used in each reaction step listed above are based on CAT’s background knowledge in the area of steam reforming and downstream reactions for CO purification. This information originates in turn from a large number of experimental tests performed in micro-reactors, and through utilisation of CAT´s simulation code (Catalyst Explorer) results were implemented and evaluated in different simulations models.

The previously performed evaluation work has all together confirmed that this type of fuel processor can provide

- a design concept that can be easily scaled in hydrogen production.
- a fuel flexibility with respect to the feed stock (natural gas, LPG, alcohols and light/heavy naphta).
- a product gas with a CO concentration < 20 ppm, which corresponds to the fuel quality required for polymer electrolyte membrane fuel cell (PEFC) applications.
- a high thermal efficiency, i.e. > 80 % calculated on the LHV of the feed stock.
- a high turn-down ratio, i.e. 1:10.
- a quick thermal response, i.e. < 15-20 minutes for a 10 Nm^3/h of produced H_2.

The work presented in this report is a following-up study to the previously described work. This project has involved:

- development and construction of an optimized STUR-system designed for the nominal capacity of 10 kWH_2. This unit has been, compared to the earlier evaluated 30 kWH_2 unit, optimized with respect to the design of the integrated catalytic burner, from which heat is supplied to the SREF reactor, and with respect to the overall heat recovery of the system.
- a risk analysis of the system and implementation of a security system for enabling fully automatic, partly non-supervised, long term testing.
- a reliability study of the system by operating the system during a longer period of time (~ aimed at 500 h). The feed stock used throughout this project was natural gas.

The long-time testing is in turn aimed at examining and giving valuable input concerning the catalyst deactivation and other possible weaknesses / degradation phenomena in the optimized STUR design. Methods to eliminate observed degradation phenomena of the construction design and/or of the catalysts are suggested and further evaluated.

The project is administrated by the Swedish Gas Centre AB (SGC), and is financed by the companies Sydkraft Gas AB, Försvarets Materialverk (FMV), the Swedish Energy Agency (STEM), Catator AB (CAT) and OptiCat International AB.

2. Description of the STUR system

2.1 Description of the reactors included in the 10 kWH_2 STUR system

In this section, the different sections of the STUR unit will be described. As is well-known from the literature, there are a number of chemical reactions to take into consideration in the fuel processor´s different sections. The most important reactions are summarised in Table 1.

Table 1. Summary of the most important chemical reactions to be considered in the fuel processor.

Steam reforming reactions

$CH_4 + H_2O \leftrightarrow CO + 3H_2$
$C_nH_m + n\ H_2O \leftrightarrow n\ CO + (n+m/2)\ H_2$

Water gas shift reaction

$CO + H_2O \leftrightarrow CO_2 + H_2$

Oxidation reactions

$C + O_2 \rightarrow CO_2$
$2\ CO + O_2 \rightarrow 2\ CO_2$ (i.e. PROX)
$2\ H_2 + O_2 \rightarrow 2\ H_2O$
$CH_4 + 2O_2 \rightarrow CO_2 + 2\ H_2O$
$C_nH_m + (n+m/2) \rightarrow nCO_2 + m/2\ H_2O$

Soot formation reactions

$CH_4 \rightarrow C + 2\ H_2$
$2\ CO \rightarrow C + CO_2$

Figure 1 shows a photo of the STUR-10kWH_2 unit. Similar to the 30 kWH_2 prototype, the core of the fuel processor is built up by reactors and integrated heat exchangers. In each reactor section, CAT´s patented wire mesh catalysts, coated with formulations suitable for the different reactions, are packed according to the example illustrated in Figure 2. In order to enable inspection of and also, if needed, easy exchange of the catalysts, the prototype is flanged. The construction material of the reactors is Avesta 253 (S30815).

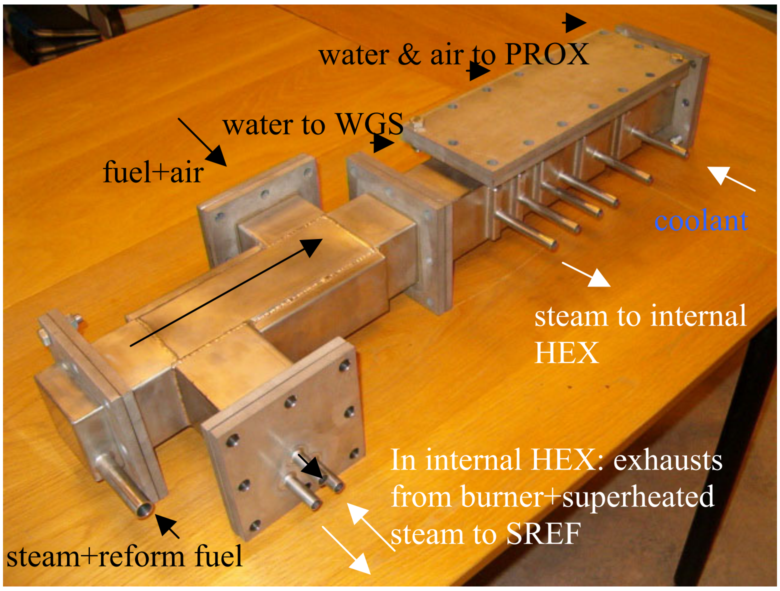


Figure 1. *A photo of the STUR-10 kWH_2 unit illustrating the different flow directions and the working principle of the fuel processor.*

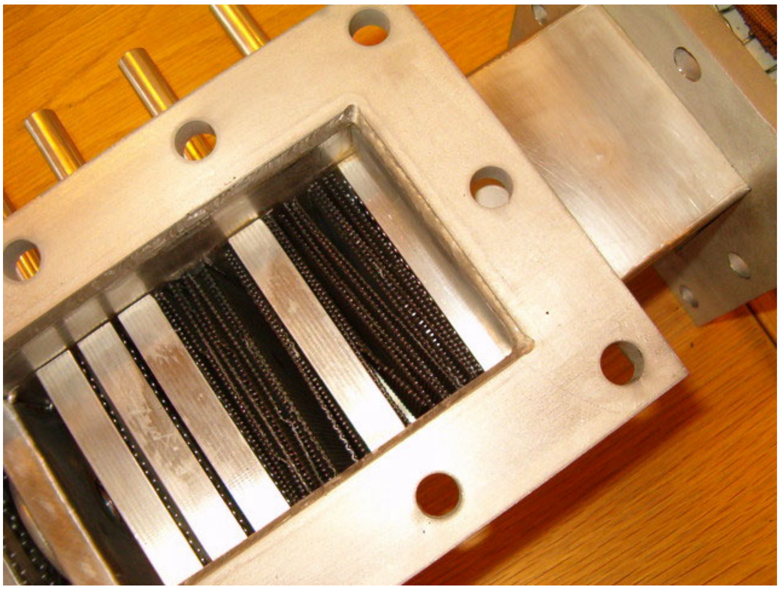


Figure 2. *A photo showing the principle of how the wire mesh catalysts are packed inside a reactor section. To be noted that the wire mesh catalysts were more carefully and closely packed on top of each other during the experimental evaluation. The photo shows a upper view of the two first PROX catalyst sections.*

As can be seen in Figure 1, the SREF is fed by fuel and steam, and steam is produced up-streams in the integrated heat-exchangers. The feed stock/steam mixture enters the SREF reactor at a temperature of about 200-350 °C, depending on the load and steam:carbon (S:C) ratio applied. Additional heat is supplied via the integrated heat-exchange burner, see 3D-drawing displayed in Figure 3, resulting in an exit temperature (out from SREF) of approximately 800-850°C. The first lower temperature part of the SREF-reactor (i.e. LT-SREF) provides for pre-reforming, which in turn reduces the problem of coke formation (due to an increase of the ratio between hydrogen and hydrocarbons).

To be noted that in the final section of the SREF reactor however, it is advisable to reach relatively high temperatures, preferably > 800°C, in order to minimise the methane residues.

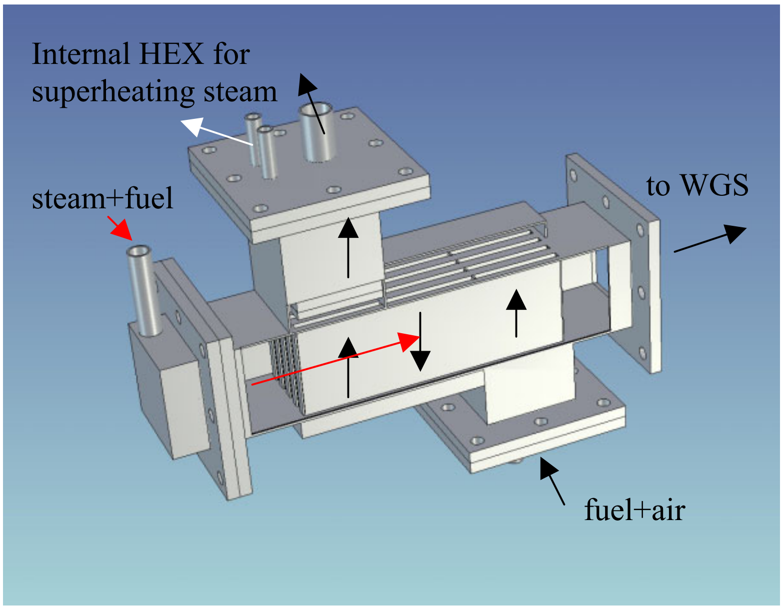


Figure 3*. A 3D drawing of the SREF/integrated heat exchanger burner reactor. The black arrows indicate the direction of the hot exhausts through the integrated heat exchanger, whereas the red arrows indicate the direction of the reaction gas along the SREF reactor. To be noted that the drawing shows the reactor without any wire mesh catalysts inserted.*

Figure 4a shows a photo of the catalytic burner section of the integrated heat-exchange burner (also partly shown in Figure 3), which is fed with a preheated fuel/air mixture. The combustion is started via a glow-igniter (24 V), which is inserted above the upper side of the wire mesh catalyst which is in turn attached in the burner. In order to enable for a good fuel distribution over the whole wire mesh catalyst shown in this figure (the burner includes 2 wire mesh catalysts), a fuel distributing nozzle is positioned in its inlet, Figure 4b. Moreover, in the outlet of the heat-exchange burner reactor, another heat exchanger is inserted, in here abbreviated as internal HEX, see Figure 1 and Figure 3. The latter unit enables the superheating of the steam by heat-exchanging the hot exhausts from the catalytic combustion with the steam produced up-streams in the cooling blocks.

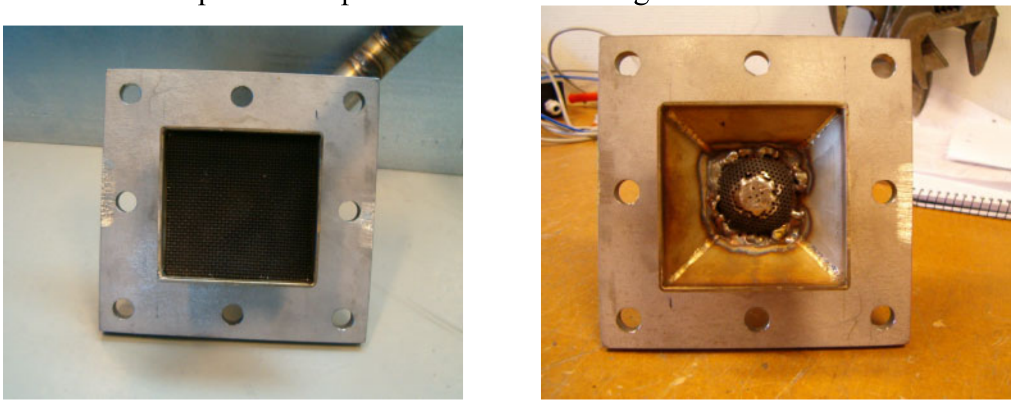


Figure 4. a) *A photo of the combustion zone section, i.e. the wire mesh catalysts, of the catalytic burner heat exchange reactor.* ***b)*** *A photo of the flow distributing nozzle positioned in the inlet of the reactor, below the wire mesh catalysts shown in a).*

The reformer gas leaving the SREF reactor will, according to our previous studies, typically contain around 10 vol% of CO. For utilising this reformer gas as fuel in low temperature fuel cells (PEFC), it is necessary to decrease the CO concentration to less than 20 ppm. For this reason, a WGS and PROX reactor are integrated in to the STUR-unit. As is well-known, the WGS equilibrium reaction is favoured by low reaction temperatures and high concentrations of water/steam, see results presented in Figure 5. Water is therefore injected to the gas mixture (corresponding to approximately 10-15 % of the total water supply to the system) prior to the first catalytic WGS section. A photo of the water distributor is given in Figure 6. As seen, the water is injected through and heated up in the coil positioned in the inlet reactor volume space and then fed to the reaction gas through small holes in order to provide for a well distributed water/steam supply. The resulting temperature of the reformate gas mixture entering the WGS reactor is about 450-500 °C. The reformate gas is then cooled down, by means of the integrated heat exchangers, see Figure 7, as is flows through the reactor, resulting in an average catalyst temperature of around 350-400 °C.

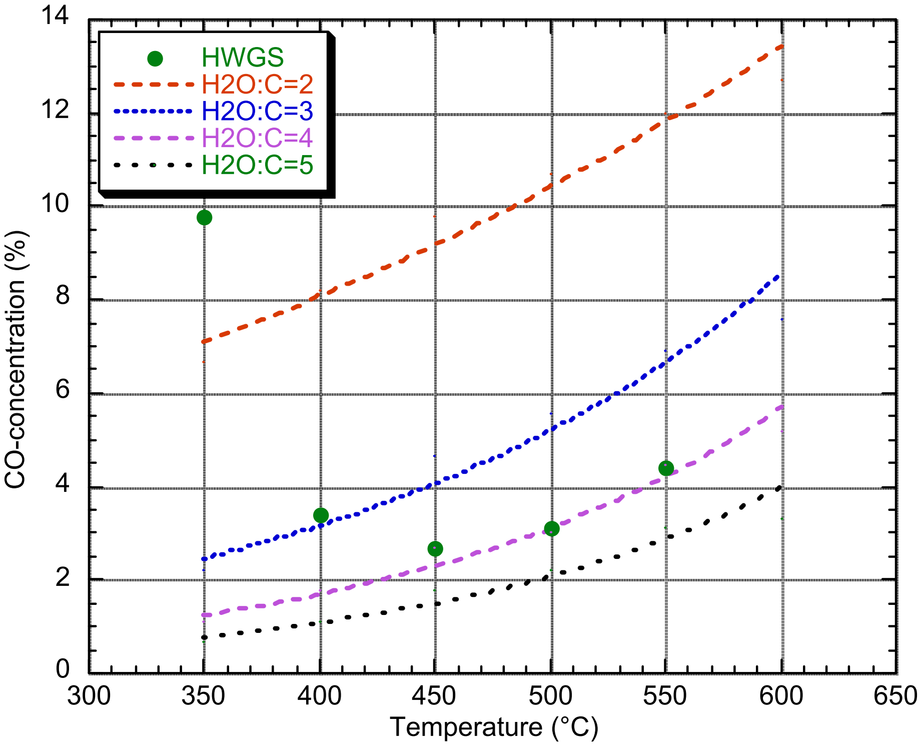


Figure 5. *Measured performance of Catators WGS-catalyst in the water-gas reaction at SV 200 000* h^{-1} *(dots). Gas composition corresponding to downstream conditions when reforming methane at steam:carbon=4:1. Catalyst Pt/ReMeOx on wire meshes (16 mesh/0.5 mm). Thermodynamic simulated data are given for different steam:carbon ratios.*

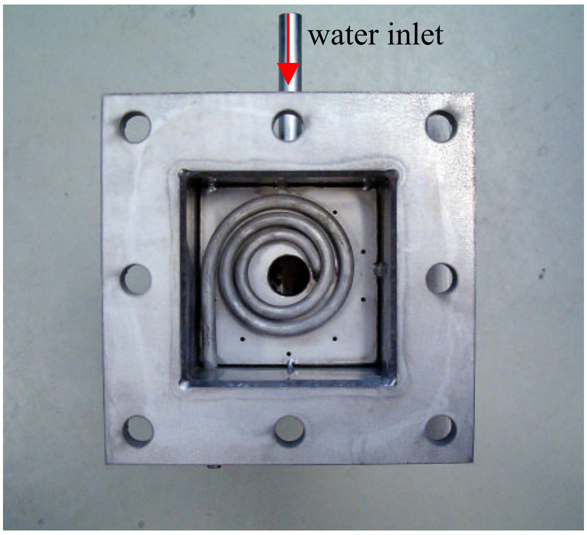


Figure 6. *A photo of the water distributor in the inlet of the WGS reactor. The water is injected through the coil and heated up prior to that it is fed to the reaction gas through the small holes for powering the WGS reaction.*

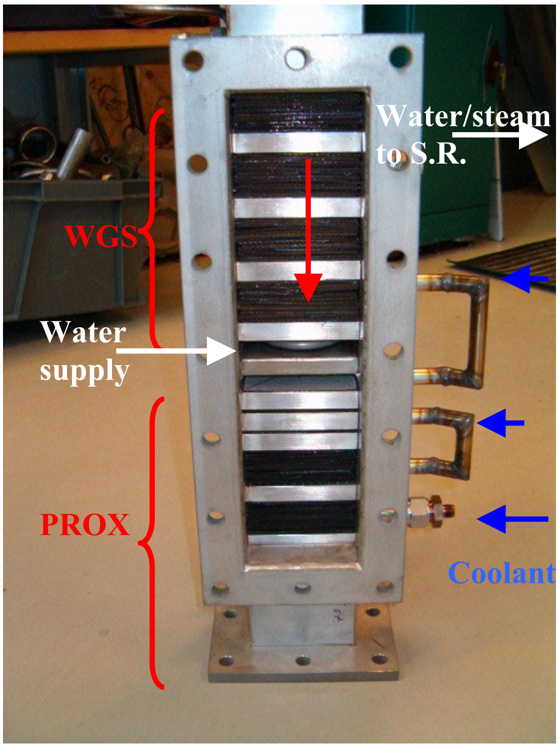


Figure 7. *A photo of the WGS and the PROX reactors with the integrated cooling blocks positioned in between the catalytic reactor sections. The red and blue arrows indicate the direction of the reformer reaction gas and the water coolant stream, respectively. To be noted that small amounts of water can also be added prior to the PROX reactor.*

The reformer gas will contain about 0.5-1 vol% of CO when leaving the WGS-reactor and when entering the PROX reactor. The performance of the PROX reaction is highly dependent on the temperature balance in the reactor. This is due to the fact that the PROX reaction is extremely quick, highly exothermic and shows a maximum in selectivity over the competitive H_2-oxidation in a rather narrow temperature window, i.e. 120-180 °C. In this prototype, overheating is avoided by intermittent cooling by the internal cooling blocks and by supplying the required oxygen amount in two separate steps. About 85 % and 15 % of the required air is injected in the first and in the second step, respectively. In addition, to ensure that the reformer gas does not have a too high temperature prior to this reactor, small amounts of water can be added to the gas in a mixing chamber positioned in between the WGS and the PROX reactor sections, indicated with a white arrow in Figure 7.

No HDS (i.e. hydrodesulphurisation unit) was included in the STUR-system. The reason for this is that natural gas with a moderate sulphur content was used in this case as reformer feed stock (i.e. < 5 ppm S) in combination with the fact that the catalyst formulations preferred by CAT are all containing precious metals as active phase. According to our previous investigations, catalysts containing precious metals have a significant increased sulphur tolerance. However, it should be noted that the presence of S will decrease the performance of the catalysts somewhat (even though completely reversible) and to compensate for this, the amount of catalyst must be increased. For more information about the choice of catalyst formulation and the catalyst volume/space velocity applied in the different reactors, see section 4. in this report.

2.2. Description of the implemented control system

To be able to perform a continuous long-time testing of the STUR-unit, a fully automatic control system was developed and implemented into the system. A complete P/I diagram of this system is presented in Figure 8, and will be described in the following. Explanations to all the abbreviations used in this scheme are given in Table 2. Views of the real experimental prototype set-up can be seen in Figures 9a-b.

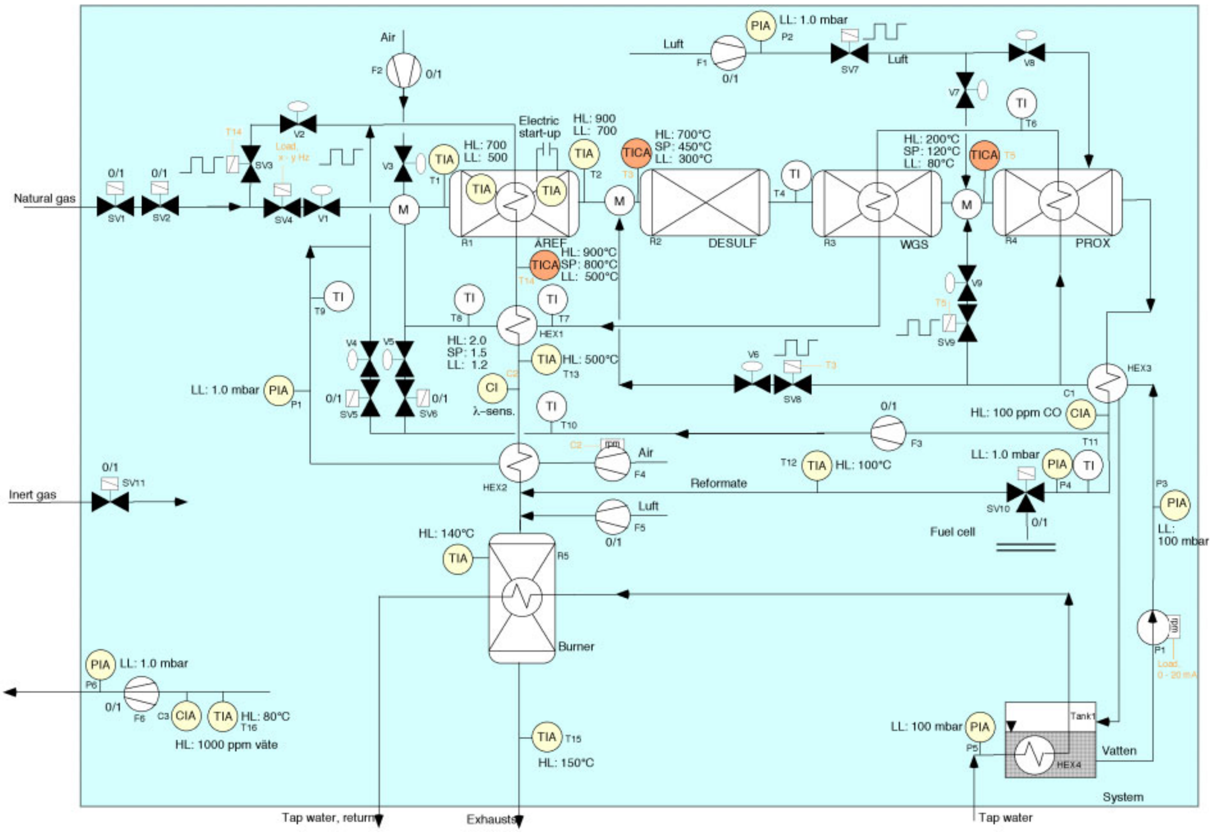


Figure 8. *P/I-diagram of the control & security system implemented into the STUR10kWH$_2$-system.*

Table 2. *Explanations to the abbreviations used in the P/I diagram in Figure 8.*

F1-F3	Membrane pump
F4-F6	Fan
P1	Pump
HEX1-HEX4	Heat exchanger
R1-R5	Reactor
SV1,SV2,SV5,SV6,SV11	Solenoid valve
SV3-SV4	Proportional valve
SV8-SV9	Pulse valve
SV10	Three–way solenoid valve
V1-V5, V7-V8	Rotameter (gas/air)
V6, V9	Throttle valves (water)
P1-P6	Pressure transmitter
C1	IR-sensor for CO
C2	Lambda sensor (indicator of oxygen excess in the catalytic combustion in the burner)
C3	Hydrogen, CO, and HC sensor
TIA	Temperature alarm
TI	Temperature measurement

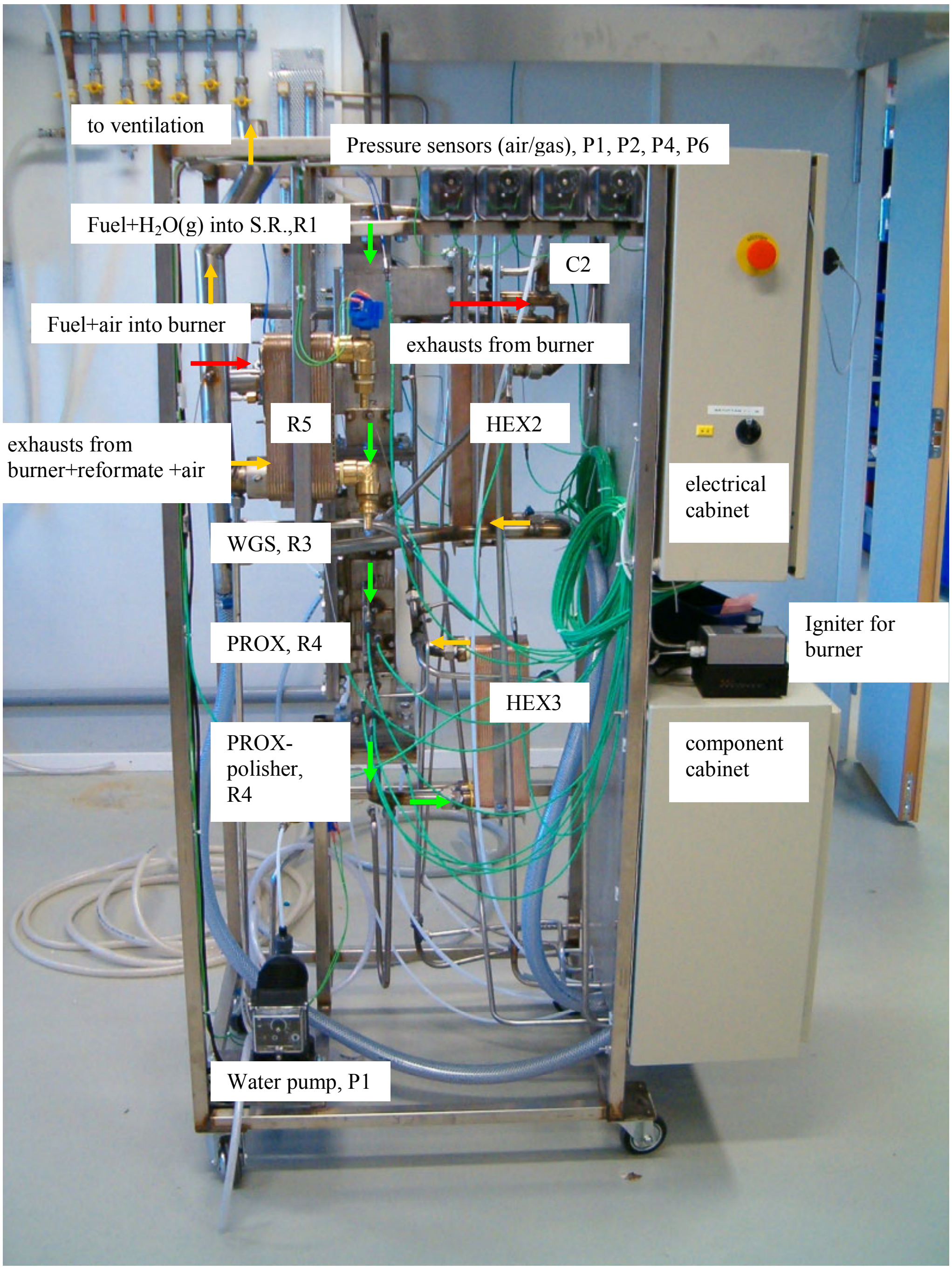

to ventilation
Pressure sensors (air/gas), P1, P2, P4, P6
Fuel+H$_2$O(g) into S.R.,R1
C2
Fuel+air into burner
exhausts from burner
R5
HEX2
exhausts from burner+reformate +air
electrical cabinet
WGS, R3
PROX, R4
Igniter for burner
HEX3
PROX-polisher, R4
component cabinet
Water pump, P1

Figure 9a).

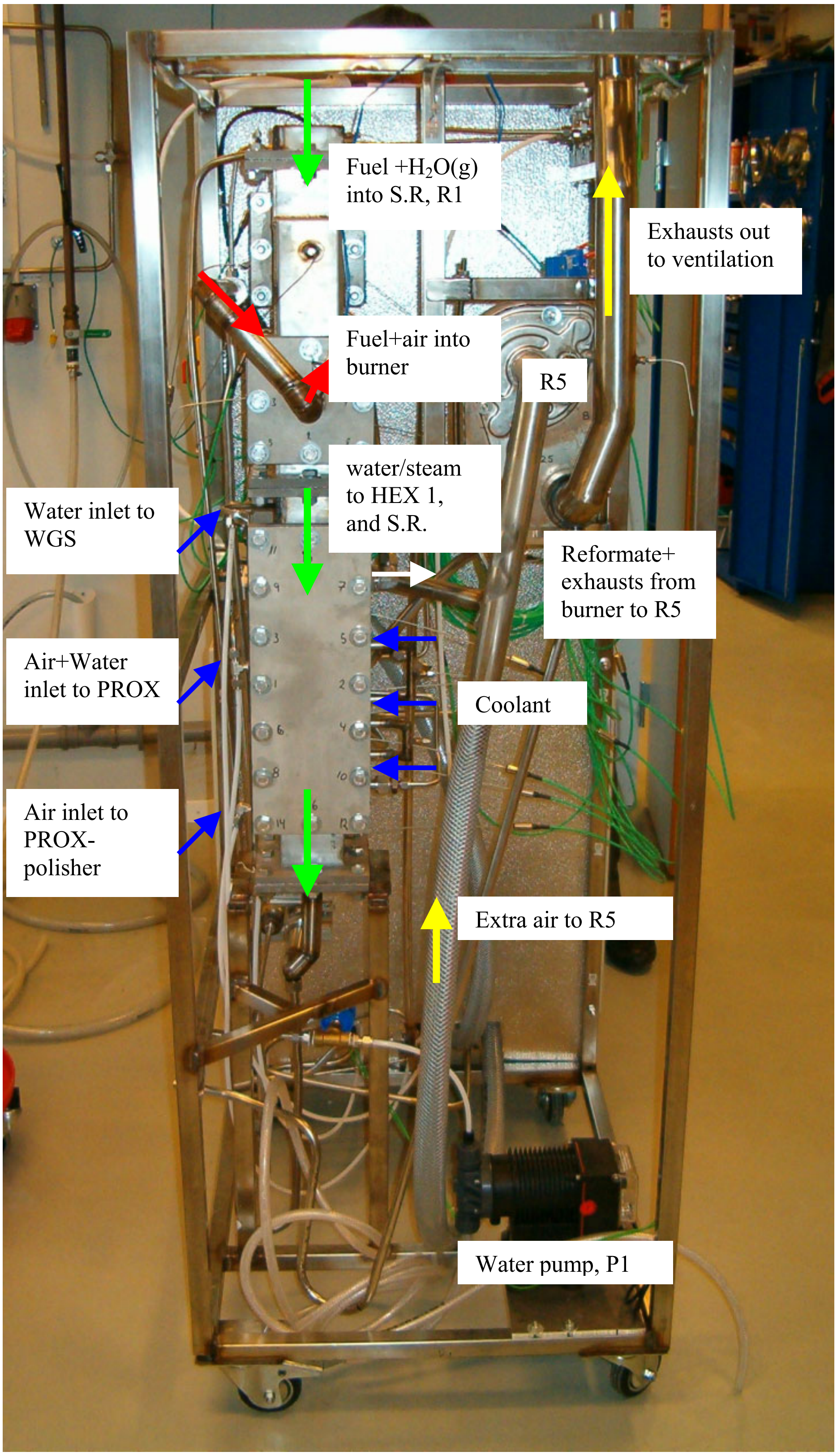


Figure 9b.

Figure 9. *Photos of the whole STUR10 kWH_2-system set-up viewed from different angles.*

Gas is fed to the system via the solenoid valves SV1 and SV2, respectively. The flow rate of the gas fed to the reformer is controlled by SV4 and into the integrated heating catalytic burner, the gas flow is controlled by SV3.

Water is supplied via a pump (P1) to the system from a tank (water quality: ≤1 μS/cm). This incoming water is fed into two separate lines: the cooling/steam generation line and the line for water insertion into the WGS and the PROX reactor, respectively. In contrast to what the P/I scheme indicates, water is in this case not re-circulated in the system, and consequently, no heat-exchanger (HEX4) is installed in this set-up.

As can be seen in Figure 8, a number of membrane pumps and fans are incorporated into the system, whose functions are listed in the following.

F1- membrane pump that supplies air in two separate steps to the PROX reactor.
F2- membrane pump that supplies air to the SREF-reactor. This may be used for enabling additional rapid heat supply (by partial oxidation) to the SREF which leads to a quicker start-up of the system.
F3 – membrane pump that enables re-circulation of reformate gas (H_2) to the SREF-reactor. This is used for suppressing coke formation when heavy feed stocks, e.g. diesel and kerosene, are processed. Thus, in this study, this option is not necessary to use, since only natural gas is used as fuel.
F4 – fan that supplies air to the combustion in the integrated catalytic burner.
F5- fan that supplies air to the catalytic combustion in the exhausts catalytic heat-exchange burner, R5.
F6- ventilation fan for the whole system.

As indicated in the P/I diagram, this system does also includes a number of temperature (TIA) and pressure alarm sensors (PIA). The temperature sensors are as seen positioned both in between the different reactor steps in the STUR- unit itself and in the exhaust tubes in order to prevent for that critical temperatures are exceeded in any part of the system. Besides the temperature alarm sensors, it should be underlined that the temperatures were under the evaluation work also measured in a number of other positions, where some of those are marked in this P/I-diagram by the abbreviation TI. For more details about the different temperature measurements, see Ch. 4. Moreover, the role of the pressure sensors are to control the functionality of the different fans and the different pumps used. Once any temperature or pressure sensor´s alarm is switched on, the valve SV1 and SV2 are closed and consequently, the feed of natural gas to the system is totally cut off. On the same time, all air supply, via the different fans and membrane pumps, is stopped. The water supply is however left on for some time in order to prevent overheating to take place.

Finally, since no fuel cell is integrated into the system in this project, the produced reformate gas has to be burnt off before entering the ventilation system. This is carried out in reactor R5. This gas-off burner is a water cooled catalytic heat-exchange burner, which has been developed within the framework of anther project performed at CAT.

3. Risk analysis

Prior to the commissioning of the STUR-system, a risk analysis of the entire system was performed. The aim was to identify hazardous deviations in the normal modes of operation and once identified, to describe methods to eliminate/reduce the potential risk of hazardous situations. The risk analysis was made according to the *what if*-method. In this analysis, all the incorporated components in the system are analysed in a structural manner. The focus is on different failure modes and the consequences associated with these events. The results of this analysis is summarised in the Appendix 1 included in this report.

4. Experimental

4.1. Experimental evaluation of STUR10kWH_2

Natural gas was used as fuel feed stock throughout this project. The composition of the gas is given in Table 3.

Table 3. *Gas composition of the natural gas used as feed stock in this project. The percentage is given in vol%.*

METHANE	88.16 %
ETHANE	6.49 %
PROPANE	2.70 %
n-BUTANE	0.57 %
i-BUTANE	0.41 %
n-PENTANE	0.09 %
i-PENTANE	0.11 %
HEXANE	0.05 %
NITROGEN	0.32 %
CARBONDIOXIDE	1.10 %

The commissioning of the STUR-10kWH_2 system was performed under continuous supervision. During this phase, flow rates of fuel, water and air, respectively, and so also the temperature profiles along the different reactor sections were calibrated and optimized.

The gas composition of the reformate gas was analyzed with NDIR (Electra control MGA 4000-T). To verify the gas analysis made by NDIR, some complementary gas measurements were also made by FID (Flame Ionisation Detector, Bernath Atomic (BA) Model 3006), photoacoustic IR (Brüel & Kjær Innova Multigas Monitor Type 1302) and GC (Varian CP-3800 GC). All gas analyses were performed with dry gas.

The substrate material of the catalysts consisted of a woven wire mesh (mesh number: 16), made of a high temperature resistant iron alloy (Kanthal AF). Prior to washcoating, the substrate was thermally sprayed with a porous layer of metal oxide according to CAT's patented technology. The latter is for increasing the surface area and the adhesiveness of the material. The choice of the catalyst formulations for the different reaction steps were based on the knowledge gained under the prevailing studies performed at CAT. The SREF and the WGS catalysts were washcoated with a ceramic layer containing a mixture of rare earth metal oxides and thereafter impregnated with precious metal.

This catalyst formulation has, in addition to the increased sulphur tolerance, been found to be oxygen tolerant and is able to suppress coke formation. Furthermore, the PROX catalysts were washcoated with an alumina based ceramic layer, and impregnated with precious metal doped with metal oxide. To compensate for the sulphur adsorption and the expected initial catalyst deactivation, the amount of catalyst in the SREF and the WGS reactor was overdimensioned with a factor of approximately 5.

The commissioning of the system proceeded very well. The start-up time, i.e. the time for reaching stable emission and temperature data, was found to be within 30-35 minutes. It should be noted that this start-up time can be significantly reduced by injecting small amounts of air (air:C≈ 1) to the SREF during the start-up, i.e. according to previous evaluation tests with the 30 kWH$_2$-system around 20 minutes.

The performance was evaluated for different loads, and some typical results are presented in Table 4. As seen, promising performance data could be obtained for all the tested input loads. The emissions were also measured after the SREF reactor and when no air was supplied to the PROX reactor, thus corresponding to the reaction gas composition right after the WGS reactor. Typical results (dry gas analysis) measured for the NG input load of 6-7 kW were after the SREF reactor: ≈8-10 % CO, 10-12 % CO_2, 1-1.5 % CH_4, 65-70 % H_2, and after the WGS reactor: ≈75-77 % H_2, 1-1.5 % CO, 21-22 % CO_2, 1-1.5 % CH_4.

Table 4. *Performance data measured at different loads with the STUR-unit 10 kWH$_2$. S:C≈3, O_2:CO in PROX≈2. SV (SREF) ≈ 5100 h^{-1}, SV (WGS)≈ 9800 h^{-1} at 9.9 kW NG input. The calculation of SV is based on the reactor volume in which the catalysts are placed and the total ingoing reaction gas to the specific reactor.*

Input capacity (kW NG)^1	Output capacity (kW H_2)^2	NG conversion (%)^3	H_2 efficiency (%)^4	CO (ppm)
3.5	3.2	98	78	< 20
6.9	6.4	96	77	< 20
9.9	9.0	91	76	< 20

1) based on the LHV of the natural gas fed to the SREF.
2) based on the LHV of measured H_2 produced.
3) defined as $(X_{NG(in)}-X_{NG(out)})/X_{NG(in)}*100$
4) defined as (measured prod. H_2/theoretical prod. H_2)*100

In addition to the emission analyses, the temperature profiles were measured. Table 5 displays a summary of temperature data collected for different loads under steady-state conditions. The temperature profiles measured over the wire meshes´ cross section surface areas in the WGS and in the PROX reactors, respectively, show that the gas flow is well distributed over the whole catalyst surface areas. In the hot section of the SREF reactor however, the equivalent temperature gradient seems to be larger. In this respect, it should however be underlined that temperature measurements over a non-homogenous surface, as in this case, is also difficult to perform. A significant temperature gradient may not necessary mean that the reaction distribution is poor. This can instead for example be a consequence of that the thermocouple itself is positioned more or less in contact with a wire mesh thread, and thereby is exposed to more or less radiation heat.

Table 5. *Temperatures (℃) as a function of input NG load (kW based on the LHV of NG fed to the SREF). The temperatures were measured with thermocouples (type K) inserted according to the positions shown in Figure 10 or explained in the following text.*

Temperature measurements along the WGS reactor (totally 4 reactor sections):

	Center of wire mesh	*Side of wire mesh*
Section no. 1/4	*T7*	*T8*
Section no. 3/4	*T9*	*T10*

Air is supplied in two steps to the PROX reactor, i.e. the main PROX reactor, which includes 2 catalyst package sections (with intermittent cooling) and to the Polisher PROX reactor, which includes only one catalyst section.

Main PROX reactor:		
	Center of wire mesh	*Side of wire mesh*
Section no. 1/2	*T11*	*T12*
Section no. 2/2	*T13*	*T14*
Polisher PROX reactor :	*T15*	*T16*

	T1	**T2**	**T3**	**T4**	**T5**	**T6**	**T7**	**T8**	**T9**	**T10**	**T11**	**T12**	**T13**	**T14**	**T15**	**T16**
3.5	799	799	779	839	872	805	433	435	363	358	133	125	104	102	133	143
6.9	720	720	676	816	822	708	431	442	402	392	186	167	118	118	128	138
9.9	735	737	715	813	835	706	401	428	365	368	187	172	121	119	134	154

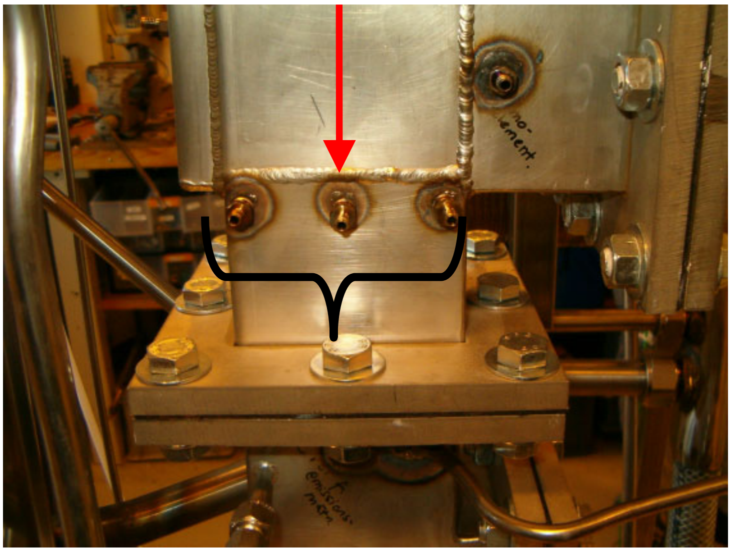


Figure 10a)

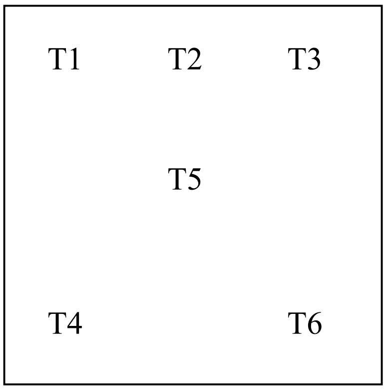


Figure 10b)

Figure 10a) *One side-view over the inlets for 3 out of the 6 thermocouples placed over a single wire mesh surface positioned according to Figure 10b in the hot section of the SREF reactor. The red arrow inserted in the figure shows the direction of the reaction gas along the SREF reactor.* ***b)*** *Schematic picture of the various positions of the thermocouples inserted over a single wire mesh surface.*

As planned for this project, the performance of the system was also measured as a function of operation time. Results obtained for ~6 kW input load during the first 120 h of operation time is shown in Figure 11. t=0 corresponds to the initial commissioning operation moment of this system with all the reactors steps included. It should be noted that the steam:carbon ratio in the SREF reactor and the O_2:CO ratio in the PROX reactor, respectively, varied somewhat during this series of measurements due the fact that calibrations of flow rates and temperature set-points were somewhat continuously made.

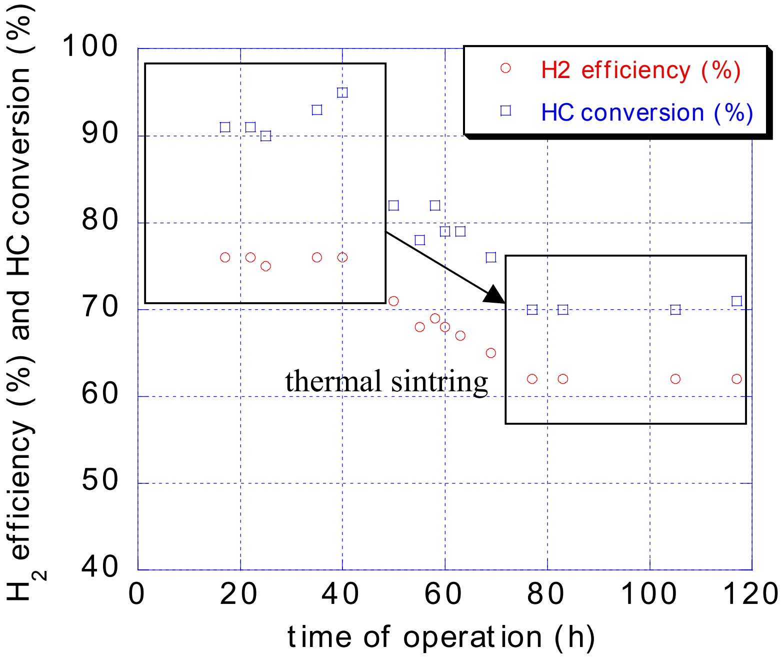


Figure 11. *Performance data measured with the STUR-10kWH_2 unit at the input load≈6 kW (based on the LHV of the NG fed to the SREF). S:C (SREF). =3-3.5, O_2:CO(PROX)≈2-2.5. Every mark in the plot corresponds to steady-state data measured after that a new start-up has been carried out. SV (SREF) ≈3500 – 4000 h^{-1}, SV (WGS) ≈ 6800 - 7500 h^{-1}.*

As can be seen in Figure 11, the performance was good and very stable until about 50 h of operation time. No deactivation of the system performance could be detected during this time. At about t= 50 h however, a crack arised in a welding positioned in the integrated heat exchange burner construction, which in turn resulted in that a significant amount of air was leaked from the burner section into the hot part of the SREF reactor during operation mode. The approximative position of the crack is indicated in Figure 12. After that the crack had been identified and repaired, it was seen that the performance of the system was continuously declining for every new start-up made. The observed phenomenon is most probably explained by thermal sintering due to that very high temperatures were obtained in the SREF reactor during the air leakage. After another 30 h of operation, a new crack was detected. The crack was also this time, even though it was smaller than the previous one and situated in another position, found to be in a welding in the SREF/burner reactor, Figure 12.

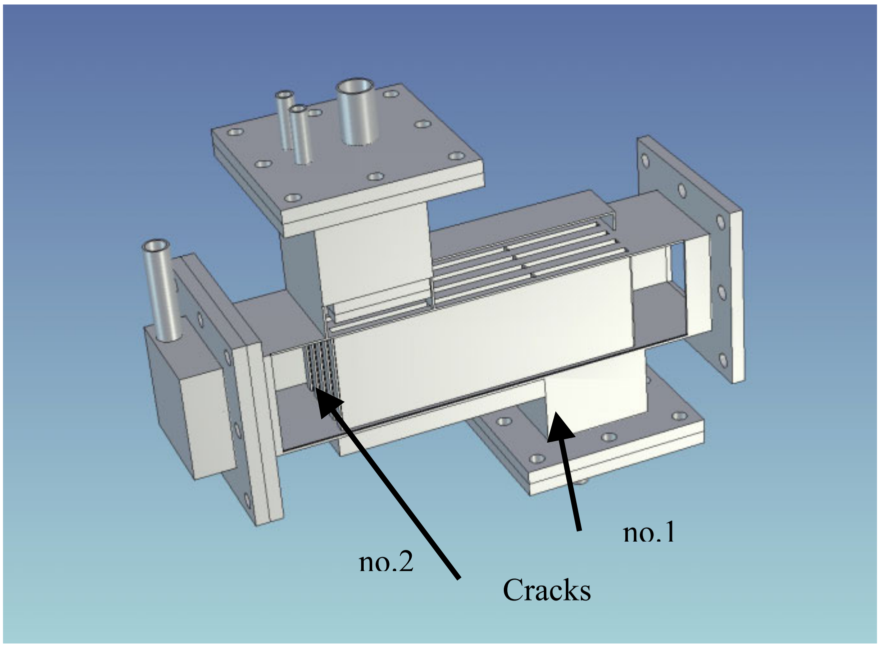


Figure 12. *A 3D-drawing of the evaluated burner/SREF reactor in which the positions of the identified cracks are indicated. Arrows also indicate the positions of the vulnerable dimension changes in the reactor construction. The same drawing is also displayed in Figure 3.*

After that the secondly appeared crack had been repaired, the performance of the SREF reactor was found to be stable but too poor, i.e. the HC conversion had decreased from being around 96-97 % (until t≈50 h) to a more or less constant value of about 70 %. Since the deactivation with time was observed to not behave as is expected for a normal catalyst deactivation process, and could instead be correlated to the air leakages, it was at t=120 h decided to stop the operation of the system. It was at this stage obvious that the catalysts needed to be exchanged into new, fresh ones before any fair reliability study could proceed. Thus, a second commissioning of the system was carried out. Likewise the first 50 h of the previous commissioning, the performance was established in this case to be very good with respect to both the stability and the emissions for all loads applied, see Figure 13. Unfortunately, at t=65 h after that the second commissioning had been initiated, a new crack appeared and it was identified to be in about the same position as the first one.

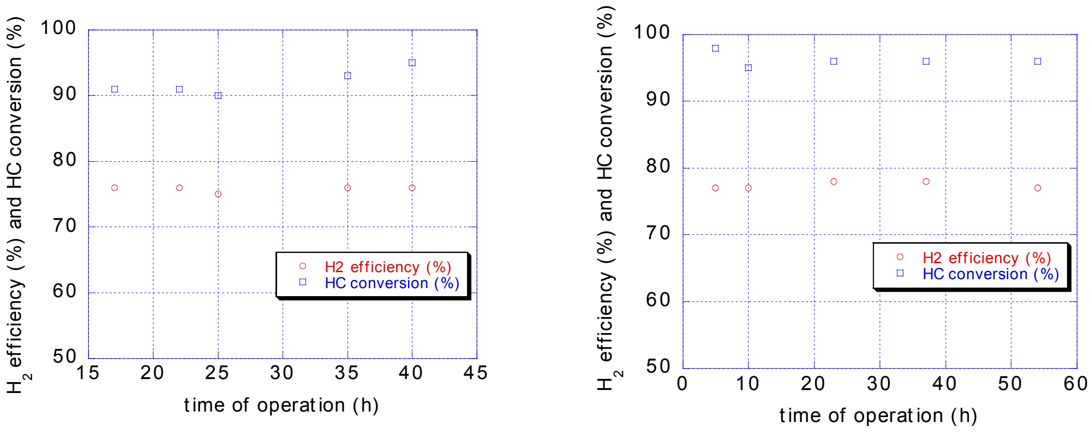


Figure 13a. *1st commissioning* ***Figure 13b.*** *2nd commissioning*

Figure 13a and b. *Performance data obtained with the STUR-10 kWH_2 unit during the 1st (a) and 2nd (b) commissioning phase. The data collected during the 2nd commissioning phase are measured at 6,6 kW input load (based on the LHV for NG fed to the SREF). Each mark corresponds to steady-state data measured after that a new start-up has been carried out. S:C≈3-4, O_2:CO≈2. SV (SREF) ≈ 3500-4500 h^{-1}, SV (WGS) ≈ 6800-8000 h^{-1}, temperature in the hot section of the SREF reactor ~800 °C (see Table 5). For the experimental conditions used under the 1st commissioning phase, see Figure caption to Figure 11.*

It is obvious that the weakness in this reactor design is a returning problem. As a consequence of this together with that fact that it was in turn precluding the evaluation of the long time operation to be continued and finalized, we decided at this point that a new burner/SREF design had to be developed and constructed before the reliability study could proceed. With respect to the positions of the observed cracks, we established that this observed durability problem was attributed to the fact that the SREF/burner reactor is rather stiff. Another weakness of the design could also be that it unfortunately includes relatively large changes in construction dimension in positions where very high temperatures are attained during normal operation conditions, see Figure 12.

The new improved SREF/burner reactor design had thus to be significantly less stiff and any large changes in the construction dimensions had to be avoided. Another additional way for improving the system was also of course to find and to exchange the SREF catalyst formulation to a more active one, which in turn makes it possible to operate the reactor at lower, less critical temperatures. A 3D-drawing of the new improved burner design that was evaluated in the project´s final phase is displayed in Figure 14. As can be seen, the construction is much less stiff thanks to a flexible joint construction between the inner and outer tube. The crucial dimension change in the original design has also been eliminated.

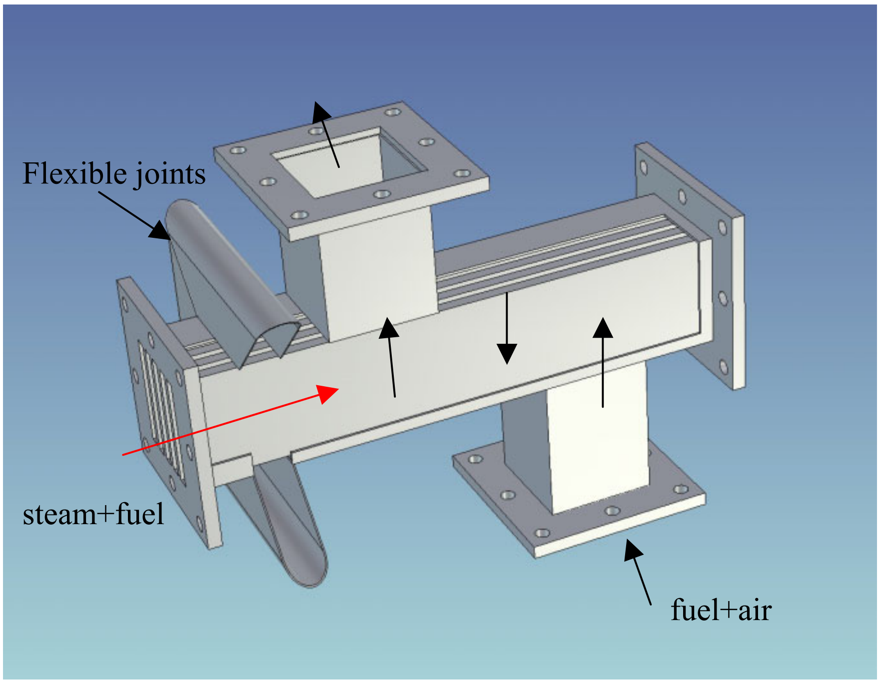


Figure 14. *A 3D-drawing of the new generation burner/SREF reactor evaluated during the project's second phase. The black arrows indicate the flow direction of the hot exhausts in the integrated heat-exchanger, whereas the red arrow indicate the flow direction of the reformate reaction gas.*

4.2. Long-time catalyst activity tests

As a complement to the improvements made of the reactor construction (as described in prevailing section in this report), catalyst activity tests were run in a fully automatic small-scale reformer set-up (designed for the nominal power output of about 1-1.5 kWH$_2$). In contrast to the STUR-system, the SREF-reactor consisted in this case of a simple reaction tube in which the wire mesh catalysts were positioned. The tube itself was inserted in a furnace, thus, no integrated burner reactor was needed. A photo of the experimental set-up is shown in Figure 15. The overarching purposes of these tests, performed within this project, were to

1) examine the activity and the stability of the catalyst formulation used in the SREF-reactor of the STUR-unit. The result of these tests gave valuable information about the SREF-catalyst performance which would be expected in the STUR-unit under normal operation conditions when no air leakages occur. This catalyst is herein abbreviated catalyst A.
2) investigate the activity and the stability of a somewhat modified SREF-catalyst formulation and to compare the performance with the non-modified one. The modification of the catalyst formulation was made with respect to the sintering procedure used in the preparation of the catalyst and also with respect to the active phase composition. This catalyst is herein abbreviated catalyst B.

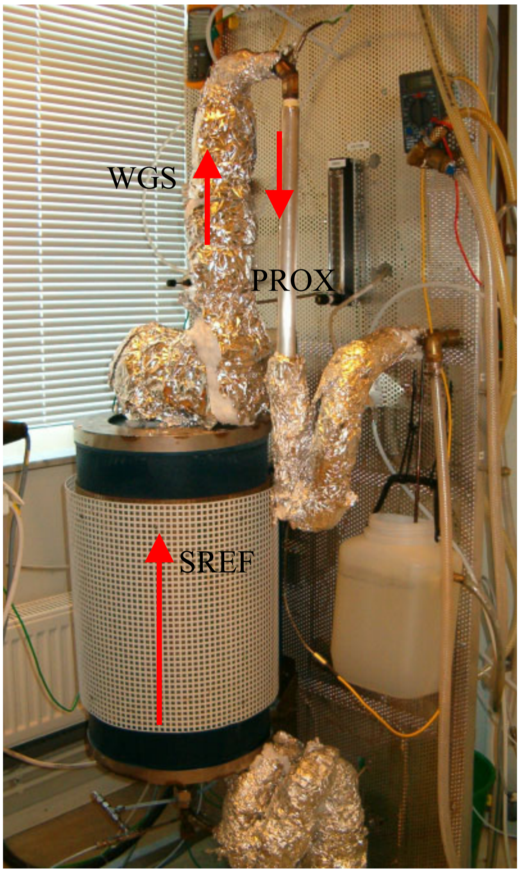


Figure 15. *A photo of the experimental for catalyst testing. The red arrows indicate the flow direction of the reaction gas.*

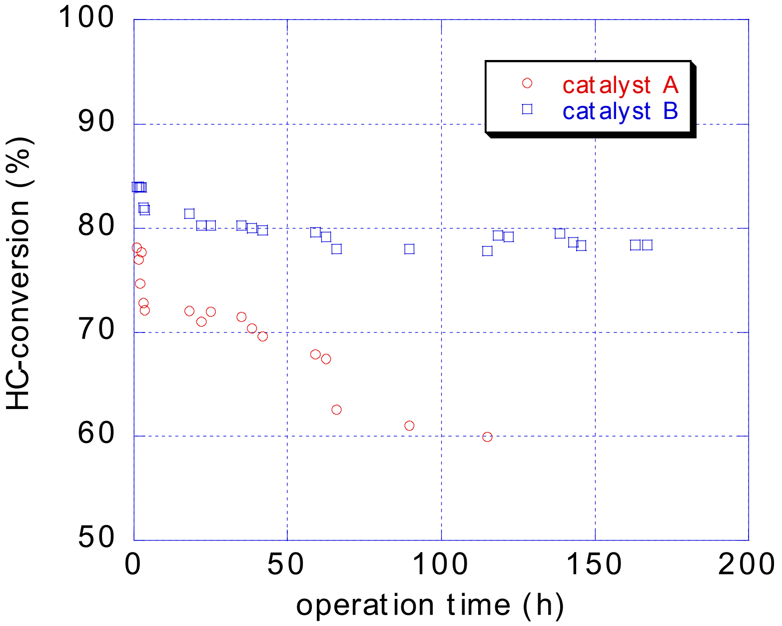


Figure 16. *Performance data measured with two different SREF-catalyst formulations. Catalyst A=SREF catalyst used in the STUR-10 kWH$_2$ unit during the commissioning no.1 and no.2 during the first phase of this project. Catalyst B= Modified catalyst formulation used in the new modified STUR-unit evaluated in the project's second phase. S:C≈3.5, SV=25 000 h^{-1}, temperature of the hot section of the SREF-reactor ≈700 °C. The substrate of the catalyst is the same thermally sprayed wire mesh substrate used for the catalysts inserted in the STUR-unit, see ch. 4.1.*

The results obtained for the two different catalyst formulations are presented in Figure 16 as HC-conversion plotted as a function of operation time. The results show clearly that

1) the activity of catalyst B is higher than the activity of catalyst A.
2) the stability of catalyst A worse than the stability of catalyst B. A significant decline in activity is observed with time.
3) the stability of catalyst B is very good. No difference in catalyst activity can be detected between t≈ 20 h and the time at when the series of measurements was stopped, i.e t≈180 h.

The results obtained with catalyst A can at first sight seem to be in contradiction to the equivalent results obtained with the STUR-unit (Figures 11 and 13) until the cracks and the air leakages began to appear. In the latter case, no deactivation could be detected up to t≈ 50 h. This divergence in results is attributed to the large difference in space velocity applied in the two cases, i.e. ≈ 4000 h^{-1} and 25 000 h^{-1} in the STUR-reactor and in the small-scale set-up, respectively. Anyway, it was obvious that the modified SREF-catalyst formulation, Catalyst B, should be preferred over Catalyst A in the evaluation work of the new, modified STUR-reactor.

4.3. Evaluation of the new, modified STUR-unit

Thanks to the improved, less stiff design, the long-time reliability study could be successfully accomplished with the STUR-unit including the modified SREF/burner. The SREF-catalysts used in this case were of type B, see Figure 16. The unit was operated more or less continuously, fully automatically, for 500 h at 6.9 kW input load without that any cracks were formed in the reactor. During this period of operation time, in totally nine cold start-ups were carried out. The efficiency as a function of operation time can be seen in Figure 17, here illustrated by the ratio between the produced power output (kWH$_2$) measured at t=t and what was initially measured at t=0. It was found that the HC-conversion and thereby the system´s efficiency declined during the approximately first 50 hours, but thereafter a rather stable condition, with respect to both emissions and temperatures, were obtained. The CO emissions were seen to be relatively stable during the whole evaluation, i.e. 0.5-1 vol% and 10-50 ppm after the WGS and the PROX reactor, respectively. Furthermore, the results also showed that shut-downs with following cold start-ups of the system, at pure steam reforming conditions, do not seem to have an impact on the performance of the system (see figure caption to Figure 17).

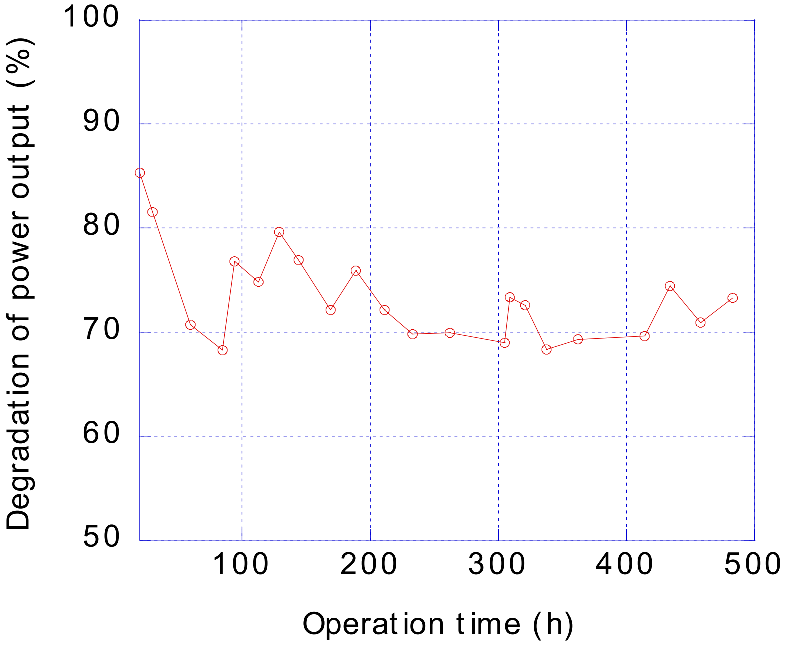


Figure 17. *Degradation of power output (referring to kWH$_2$ produced) measured as a function of time with the STUR-unit including the SREF/burner design shown in Figure 14, and the SREF-catalysts of type B discussed in section 4.2. The investigation were run at 6.9 kW power input at S:C ≈3. S.V (SREF) ≈ 5700 h^{-1}. S.V.(WGS) ≈ 6600 h^{-1}. Cold start-ups were carried out at 6.9 kW power input after the operation time =0, 4, 9, 20, 30, 95, 130, 320 and 484 h.*

Likewise the evaluation of the prevailing STUR-unit, this system was also investigated at different loads. Typical results measured after that the system had been operated for a few hours are given in Table 6.

Table 6. *Performance data measured at different loads with the new, modified STUR-unit 10 kWH$_2$. S:C≈3, O$_2$:CO in PROX≈2. SV (SREF) ≈ 7600 h^{-1}, SV (WGS)≈ 8400 h^{-1} at ~9.5 kW NG input. The calculation of SV is based on the reactor volume in which the catalysts are placed and the total ingoing reaction gas to the specific reactor.*

Input capacity (kW NG)[1]	Output capacity (kW H$_2$)[2]	NG conversion (%)[3]	H$_2$ efficiency (%)[4]	CO (ppm)
3.5	3.2	96	77	< 20
6.9	6.5	90	78	< 20
9.5	7.0	70	63	< 20

1) based on the LHV of the natural gas fed (≈11 kWh/m^3) to the SREF.

2) based on the LHV of measured H$_2$ (≈3 kWh/m^3) produced.

3) defined as $(X_{NG(in)}-X_{NG(out)})/X_{NG(in)}*100$

4) defined as (measured prod. H$_2$/theoretical prod. H$_2$)*100

In comparison with the results obtained with the prevailing SREF/burner design and SREF-catalyst of type A, the overall efficiency was established to be about the same at low power input, whereas at higher loads, the overall performance was established to be significantly poorer (e.g. HC-conversion 70 % instead of 91 % at 9 kW power input), see Table 6. This difference in results at higher loads is explained by the fact that it was not possible to reach, with the same type of air fan installed (F4 in Figure 8), as high temperatures in the hot section of the SREF-reactor as in the prevailing reactor design, i.e. ~700 vs. 800 °C. The latter is in turn a consequence of that the modified construction possessed a higher pressure drop, which limited the air flow and hence, the power input to the burner reactor. To demonstrate the strong affect of the temperature of the hot section of the SREF-reactor, the used air flow provided by fan F4 was after finalized reliability study exchanged with a higher air flow from a compressor. Comparative evaluation tests were thereafter run at 6.9 and 9.5 kW power input (to SREF), respectively. It was found that by solely increasing the temperature about 70-80 °C in the SREF reactor, the HC-conversion could be increased by a factor of as much as 30-40 %.

Furthermore, while discussing the strong affect of the temperature in the SREF reactor, it is important to note that it has recently been found, in other on-going projects at CAT, that the reforming of natural gas/methane requires significantly higher temperatures than the reforming of heavier fuels such as LPG, city-diesel, kerosene, gasoline and alcohols. As a matter of a fact, these parallel investigations have shown that SREF operation temperatures in the range of 750 °C would actually be sufficient for enabling complete conversion in the case of for example diesel reforming. In other words, altogether these results strongly indicate that the reliability results reported herein could also be assumed to be valid for the reforming of heavier hydrocarbons. In the latter case, the efficiency could, under the same operation conditions, also be expected to become significantly higher than what has been found for the natural gas reforming.

Finally, comparative cold start-up experiments with and without partial oxidation in the SREF-reactor were performed with this system. Similar to the results obtained with the 30 kWH$_2$-STUR system, the results showed also this time that the start-up time could be reduced from being around 30 minutes to become equal to about 20 minutes by initially supplying small amounts of air to the SREF-reactor (air:C ≈ 1).

Conclusions

An optimized STUR-prototype unit designed for the nominal capacity of $10kWH_2$ has by Catator AB been constructed and evaluated with natural gas as reformer fuel. The performance was measured as a function of load and operation time. For enabling the long-time tests, a completely automatic control and security system was successfully implemented into the system. The results show that promising performance data can be achieved with this fuel processor including downstream CO-purification. A relatively quick start-up could be obtained and stable temperature profiles and emission data could be measured for various input loads.

The long-time tests indicated that at SV (SREF)$\approx$ 4000 h^{-1}, no catalyst deactivation could be detected until at least 60 h of operation time. Evaluations for a longer operation time was with the initially, within this project, evaluated STUR system unfortunately precluded by returning crack formations in weldings positioned in the SREF/burner reactor. The latter was most probably due to that the reactor design was too stiff for coping with the high temperatures that were reached during the operation conditions. The arised cracks were found to result in air leakages from the burner into the reaction reformer gas, causing serious catalyst deactivation of the SREF catalysts. To overcome this problem, a new, less stiff SREF/burner design was developed and constructed. On the same time, efforts to improve the activity and the stability of the SREF catalyst formulations were carried out and performance tests were performed in a fully automatic small-scale reformer set-up. All together, this work resulted in a another commissioning- and long time evaluation phase of a modified STUR-system; this time including a SREF catalyst formulation of a somewhat higher activity but especially of an improved stability than the type used in the prevailing SREF-design. The tests showed that it is possible to successfully operate continuously, fully automatically, for at least 500 h with the latest STUR concept. Stable emissions and temperatures were reached within 50 h of operation time. Moreover, the results also pointed to that the system´s efficiency is not affected by shut-downs and followed cold start-ups. Finally, in similar to the results previously reported for the 30 kWH_2-STUR system, it was concluded that the start-up time can be reduced from ~30 to ~20 minutes by initially supplying small amounts of air (air:carbon=1) to the SREF-reactor.

Now, after finalized reliability study of the STUR-reactors, the next natural step of this development work would be to operate the system with a suitable fuel cell (~ 2 kW_{el}) integrated in the system. This should first of all include integration work of the two systems, and thereafter for investigating the interaction between the two systems, evaluations at transient and intermittent operation at different loads, and finally, further long-time operation tests.

Appendices

Appendix 1: Summary of the risk analysis

Appendix 1

Project ” Reliability study of a reformer-10 kWH_2-proj”

Risk analysis according to the model “*What if*”

* component will not be used in the case of that natural gas is used as fuel feedstock.

Component	*What if?*	*Consequence component*	*Consequence system*	*Preventive measures and other comments*
F1 (membrane pump)	Membrane damage Failure in control system	Incorrect airflow	Lower airflow results in lower combustion temperature in R4. Higher CO emissions. Higher airflow results in higher combustion temperature in R4. High CO emissions. Lower capacity (due to larger extent of H_2-oxidation)	The pressor sensor P2 will detect flow rates that result in pressure drops < 1 mbar and shut down the system. No fuel cell is integrated in this system. Thus, no damage of system will occur if the CO concentration out from R4 is high. However, if fuel cell (i.e. PEMFC) is integrated, a CO-detector C1 will be installed down streams R4 and if > 100 ppm CO, the system will shut down.
F2 (membrane pump)	Membrane damage Failure in control system	Incorrect airflow	Lower airflow results in lower combustion temperature in SREF, R1. Higher UHC emissions. Longer start-up time of the system. Risk for coke formation if heavier feed stocks are used. Decline in efficiency of the system.	Temperature alarms will detect too high or too low temperatures in SREF, R1 and shut down the system.

			Higher airflow results in higher combustion temperature in SREF, R1. Lower thermal efficiency (due to that larger amounts of fuel is oxidised in SREF).	
*F3 (membrane pump)	Membrane damage Failure in control system	Incorrect flow of re-circulated reformate gas.	No re-circulated reformate flow or lower reformate flow to SREF in R1. Coke formation if heavier hydrocarbons are used as feedstock. Higher UHC emissions. Lower capacity and efficiency of the system. Higher reformate flow to the catalytic burner, R1 results in a lower lambda value and higher combustion temperature in R1. Lower efficiency of the system.	Temperature alarms will detect too high or too low combustion temperatures in the catalytic burner, R1, and shut down the system.
F4 (fan)	Filter clogged (at inlet), leakage airline Control system failure	Incorrect airflow	Lower air flow results momentarily in a lower lambda value and a higher combustion temperature in the catalytic burner, R1. T14 will then compensate for the lower air flow with a lower fuel feed in order to retain the set-point of T14.	Temperature alarms will detect too high and too low temperatures in the catalytic burner and in SREF in R1, and shut down the system. The pressor transmitter, P1 will detect flow rates that result in pressure drops < 1 mbar and shut down the system.

			A lower fuel feed results in lower heat transport to the SREF reaction. Higher UHC emissions. Lower capacity of system. Very high temperatures in R1 may result in overheating of R1 , causing cracks and leakages between catalytic burner and SREF-reactor. Catalyst deactivation. Poor efficiency and capacity of the system. Higher airflow results momentarily in a higher lambda value and a lower combustion temperature in the catalytic burner, R1. Poor combustion, and low heat transfer to SREF.	
F5 (fan)	Filter clogged (at inlet), leakage airline Failure in control system/setting value	Incorrect airflow	Lower airflow results in a lower lambda value and a higher temperature in the exhaust heat exchange burner, R5. Risk for flashback in the inlet of R5.	Temperature alarm will indicate if the temperature of the exhausts out from R5 is ≥ 150 °C and the system will shut down. Thermostat positioned on the outside of the inlet tube (made of stainless steel) of R5 will detect flashbacks. The system will shut down if the temperature ≥ 140 °C.

			Higher airflow results in a higher lambda value and a lower temperature in the exhaust heat exchange burner, R5. Higher H_2-emissions out from the system to the ventilation system.	Hydrogen sensor (C3), positioned in the system box, will alarm if H_2-concentration ≥ 0.2 % and shut down the system.
F6 (ventilation fan)	Filter clogged (at inlet), leakage airline Hardware error	No or Incorrect airflow	No or Insufficient ventilation of system box if significant leakages of reformate occur. Critical amounts of reformate/H_2 can be enclosed inside the system box.	Hydrogen sensor (C3), positioned in the system box, will alarm if H_2-concentration ≥ 0.2 % and shut down the system. If critical amounts of reformate/H_2 gas is enclosed inside the system box, one side of the box (attached with magnets) will open and the system will be vented. If the presence of hydrogen, ouside the reactors, causes a fire inside the system box, a fire alarm (attached to the top ceiling inside the system box)) will shut down the system and for blowing out the fire, inert gas, via SV11, will be supplied to the system box.

				The functionality of F6 will be continuously verified by the pressor sensor P6. If the pressure drop > 1 mbar in the tube connected to the outlet of the fan, the system will shut down.
P1 (water pump)	Water line clogged, Leakage of water line. Failure in control system	Incorrect waterflow	**SREF** Lower flow rate of steam into SREF, R1, may result in coke formation. Higher UHC emissions. Lower capacity and efficiency of the system. Higher flow rate of steam into SREF, R1, results in a lower reforming temperature. Higher UHC emissions. Lower capacity and efficiency of the system. **WGS** Lower flow rate of water results in a higher temperature in R3. Poorer efficiency of the WGS-reaction. Lower capacity and efficiency of the system. Higher CO-concentrations. Higher flow rate of water results in a lower temperature in R3. If T<300-350 °C, Catalyst activity low.	Temperature alarm sensors (T1-T5) will control the temperature in each reactor step (R1, R3 and R4). If any temperature is measured to be outside the acceptable ranges, the system will shut down. The pressor sensor P3 will detect water flow rates that result in pressure drops < 100 mbar and shut down the system. If fuel cell is integrated in the system, C1 will shut down the system if CO emissions out from the STUR-system > 100 ppm CO.

			Higher CO emissions. But: if 350≤T≤450 °C, in combination with high flow rates of steam→ high efficiency of WGS. Low CO emissions. **PROX** Higher flow rate of water results in lower combustion temperatures in R4. Higher CO emissions. Lower flow rate of water results in higher temperatures in R4. If>180°C, higher CO-concentrations out from R4. Lower capacity and efficiency of the system (more H_2 is oxidised).	
HEX1 (heat-exchanger)	Catastrophic leakages	Failure	Catalytic burner and the integrated heat exchange surfaces will be filled with water/steam. Catastrophic leakage of air into SREF. Overheating and destruction of catalysts and reactors.	Too high or too low temperatures in catalytic burner and in SREF in R1 will be detected by temperature alarms and the system will be shut down.

	Corrosion	Minor leakages	Air leakage into SREF in R1, overheating in R1, catalyst deactivation. Problems with steam/gas leakage. Decrease in the thermal efficiency of the integrated heat-exchanger. Decreased amount of steam fed to the SREF, R1. Risk for coke formation. Decrease in efficiency of the system. Increase in UHC emissions. Lower capacity.	Deionised water is used in this process, which is from the viewpoint of corrosion the most aggressive water type. To minimise the risk for serious corrosion, the HEX1 and the ultraformer, respectively, are made of stainless steel.
HEX2 (heat-exchanger)	Leakage	Major leakage→ failure of component	No or poor preheating of the in-going air to the integrated catalytic burner, R1. Decreased thermal efficiency of the system	Temperature alarms in R1 will detect too high or too low temperatures in the catalytic burner and shut down the system.
		Minor leakage	Leakage of air in HEX2 results in a lower airflow to the catalytic burner, R1. Momentarily a lower lambda value and a higher combustion temperature. Overheating. Cracks in reactor.	A thermostat positioned on the outside of the inlet tube to R5 will detect flashback. If T≥ 140 °C.

			Leakage between catalytic burner and SREF. Catalyst deactivation. T14 will adjust for the setting temperature value by compensating the lower air flow with a lower fuel flow. Decreased heat transfer to the SREF reaction. Lower efficiency and capacity of system. Higher UHC emissions. Poor cooling of the exhausts from R1 into the heat exchange catalytic burner, R5. Larger risk for flashback in the inlet of R5.	
HEX3 (heat-exchanger)	leakages Corrosion	Major leakage→ failure of component Minor leakage	No or poor heat-exchanging between incoming water from Tank 1 and outgoing reformate gas from PROX. Larger probability for flashback in the inlet of R5. Lower thermal efficiency of the STUR-system.	Temperature alarm T12 will shut down the system if T12 ≥ 100°C. Concerning flashback in R5, see HEX2 above.
Catalysts in R1-R4	Overheating	Thermal deactivation (sintring)	Large emissions of UHC, CO. Low capacity and efficiency of the system.	If no fuel cell is integrated into the system, UHC and CO emissions will be burnt off in R5.

	Poisoning (Coke, S)	Deactivation		If fuel cell is integrated, UHC emissions (diluting) will go through the fuel cell resulting in low electrical efficiency. If CO concentration > 20 ppm, significant loss in electrical efficiency. If CO concentration> 100 ppm, system will shut down via C1. If the fuel feed stock contains high concentrations of S, a desulphurisation step will be installed, R2, which will prevent from downstream S-poisoning. Significant catalyst deactivation will influence the temperatures in R1, R3 and R4. Temperature alarms will shut down the system if too high or too low temperatures are reached.
SV1 (Solenoid valve)	Valve does not open on demand. Valve always open.	No flow of fuel Always fuel flow	No combustion in the integrated catalytic burner and no reformate gas will be produced. The flow will be stopped by SV2	The system will shut off via the control systems (via the low temperature alarms).
SV2 (Solenoid valve)	Valve does not open on demand. Valve always open.	No fuel flow Always fuel flow	No combustion in the integrated catalytic burner and no reformate gas will be produced. The system will proceed as normal, until any alarm shuts down the system.	The system will shut off via the control systems (via the high or low temperature alarms).

SV1 & SV2 (Solenoid valve)	Valves do not open on demand.	No fuel flow	No combustion in the integrated catalytic burner and no reformate gas will be produced.	The system will shut off via the low temperature alarm in R1.
	Valves always open.	Always fuel flow	Control system will be out of function. Overheating of system possible. High emissions of UHC.	The danger of this action is limited by the maximum allowed flow rate of fuel (natural gas) that is fed to the system, and to the room in which the system is placed. With respect to the double installed fuel gas supply valves, theirs diameters and the ventilation flow of the room in which the system is placed, the CH4 concentration can never become > 0.3 % (explosion level: 5%). If any fire is initiated outside the STUR-system, but within the system box, the fire alarm will start off and inert gas will be supplied via SV11 and blow out the fire. The SV11 and the fire alarm are hard ware wired (independent of PLC). The STUR system is positioned below a ventilation hood, and the emissions will be vented out.
SV3 (Proportional valve)	Valve does not open on demand.	No fuel flow	No heat will be produced in the catalytic burner, R1. No reformate gas will be produced.	Temperature sensors will detect too high or too low temperatures in the catalytic burner R1 and shut down the system.

	Leakage Failure of control system (T14)	Always fuel flow Incorrect fuel flow.	Too high or too low combustion temperatures. Too low combustion temperature may lead to that combustion is blown out. Too high combustion temperatures may lead to that cracks are arised in R1, leakage between catalytic burner and SREF, deactivation of catalysts. High UHC emissions. Lower efficiency and capacity of the system.	
SV4 (Proportional valve)	Valve does not open on demand. Leakage	No fuel gas flow Incorrect fuel gas flow.	No natural gas will be fed to the SREF (R1) and no reformate gas will be produced. Lower fuel gas flow results in lower H_2-production (m^3/h). With respect to the actual load, incorrect calibrated settings for the water/steam supply to the SREF and in the air supply to the PROX, R4.	Temperature sensors will detect too high or too low temperatures in the catalytic burner R1 and shut down the system. If CO concentration>100 ppm out from PROX/STUR-unit and fuel cell is integrated (PEMFC), C1 will shut down the system.

	Failure of control system (4-20 mA)		In PROX: Higher combustion temperature. Higher CO emissions. Lower capacity and lower efficiency of the system due to a larger extent of H_2-oxidation. In SREF: Higher reforming temperature (due to less heat needed for the endothermic SREF-reaction). Lower capacity of system. Higher fuel gas flow results in lower S/C-ratio. Coke formation more probable. Higher UHC emissions. Lower capacity and lower efficiency of the system.	
*SV5 (Solenoid valve)	Valve does not open on demand Valve always open	No flow of re-circulated reformate gas. Always flow of re-circulated reformate gas	No heat will be produced for the SREF, R1. No reformate will be produced. If higher fuel flow than expected to catalytic burner, R1: momentarily lower lambda value and higher combustion temperature in R1. Overheating possible. Cracks and leakage between catalytic burner and SREF possible. Catalyst deactivation.	Too high or too low temperatures in the catalytic burner, R1, will be detected by temperature alarms and shut down the system.

*SV6 (Solenoid valve)	Valve does not open on demand	No flow of re-circulated reformate gas	Coke formation probable if heavier hydrocarbons are used as feed stock. Higher emissions of UHC. Lower capacity and lower efficiency of the system.	Reformate gas will only be re-circulated to the SREF, R1, when heavier feedstocks are used as fuel. If fuel cell is integrated into the system, higher UHC emissions in the reformate will lead to lower electrical power efficiency.
	Valve always open	Always flow of re-ciculated reformate gas		
SV7 (Proportional valve)	Valve does not open on demand.	No air flow	High CO emissions.	If fuel cell (PEMFC) integrated into the system, and If CO concentration > 20 ppm, significant loss in electrical efficiency. If CO concentration> 100 ppm, system will shut down via C1.
	Failure in control system (4-20 mA)	Incorrect airflow	If too low airflow, high CO emissions. If too high airflow, high CO emissions and low capacity and efficiency of the system (due to larger extent of H_2-oxidation)	
SV8 (Pulsing valve)	Valve does not open on demand.	No water supply	If no water supply: High reaction temperature in R4 (T>480-500 °C). Poor efficiency of the WGS-reaction. High CO emissions. Low capacity and low efficiency of the system.	Temperature alarms will shut down the system if a too high or too low temperature is measured in the first WGS reactor compartment (totally four WGS reactor compartments).

	Valve always open	Always water supply	If always water supply: Possible too low temperature in R4 (<350-380 °C). Poor efficiency of the WGS reaction. Low capacity and low efficiency of the system. High emissions of CO.	If fuel cell (PEMFC) is integrated into the system, C1 will switch off the system if CO concentration> 100 ppm out from the STUR-unit.
	Failure in control system (T3). Incorrect calibration of water flow.	Incorrect water supply	See above.	
SV9 (Pulsing valve)	Valve does not open on demand.	No water flow	This may cause too high temperatures in R4 (>180 °C). Poor efficiency of the PROX reaction. Higher CO emissions and lower capacity of the system due to more $H2_{(g)}$-oxidation.	Temperature alarms will shut down the system if too high or too low temperatures are measured in the first PROX reactor compartment (totally three PROX compartments)
	Valve always open	Always water flow	Lower temperature in R4. Poor efficiency of the PROX reaction. Higher CO emissions.	If fuel cell (PEMFC) is integrated into the system, C1 will switch off the system if CO concentration> 100 ppm.
	Failure in control system (T5)	Incorrect water flow	See above	
SV10 (Three-way solenoid valve)	Valve does not open on demand.			Not installed since no fuel cell is integrated into the system.
	Valve always open			

SV11 (Solenoid valve)	Valve always closed.	No flow of inert gas possible	No fire can be extinguished by the inert gas supply.	If fire alarm, the system (SV1 and SV2) will shut down. Thus, any fire inside STUR-reactors will be put off.
	Valve always open	Inert gas always fed to the system until N_2-bottle (200 bar) is empty.	The amount of available inert gas will run out. The operation of the STUR-unit will proceed. If fire alarm turns on when no inert gas is available, the fire cannot extinguished by any inert gas supply.	The inert gas bottle pressure should always be checked to be at 200 bars before leaving the STUR-system on unsupervised.
	Failure in electrical supply.	Inert gas supply to the system until N_2-bottle is empty (200 bar)		SV11 is hardware wired (independent of PLC).
Rotameter V1	Leakage (major or minor)	Incorrect flow rate	High UHC emissions inside the system box/component cabinet. With respect to the actual load, incorrect calibrated settings for the water/steam supply to the SREF and in the air supply to the PROX, R4.	External emissions of UHC are collected in a hood placed above the system box and then vented out through the ventilation system. If too large volumes of gas is collected within the system box, one of the sides of the box will be opened (attached by magnets), and the system in this way itself vented.

			In PROX: Higher combustion temperature. Higher CO emissions. Lower capacity and lower efficiency (T>180°C in PROX), due to more H_2-oxidation. In SREF: Higher S/C-ratio. Higher reforming temperature, due to lower amount of heat needed for the endothermic SREF reaction. Lower capacity and lower efficiency of the system.	Temperature alarms will detect too high temperatures in R1-R4 and shut down the system. C3 is sensitive to CO, H_2 and UHC, thus, if too high concentrations of UHC (>> 1 %) is collected inside the system box (outside the STUR reactors), the system will shut down.
Rotameter V2	Leakage (major or minor) Incorrect calibration of flow rate.	Incorrect flow rate	High emissions of UHC outside the STUR system/inside the component cabinet. If lower flow rate: Higher lambda value and lower combustion temperature in R1. Combustion may blow out or poor combustion. Decrease in heat production for the SREF reaction. Lower temperature in SREF, R1. Higher emissions of UHC. Lower efficiency and capacity of the system.	External emissions of UHC are collected in a hood placed above the system box and then vented out through the ventilation system. If too large volumes of gas is collected within the system box, one of the sides of the box will be opened (attached by magnets), and the system in this way itself vented. Temperature alarms will detect too low temperatures in the catalytic burner, and in SREF, R1, and shut down the system.

Rotameter V3	Leakage (major or minor) Incorrect calibration of flow	No or incorrect air flow	Decrease in heat production in SREF. Increase in start-up time. If higher airflow: Increase in heat production in SREF. Decrease in start-up time. Decrease in capacity and efficiency of the system (due to more combustion of fuel in SREF). Destruction/overheating of reactor and catalysts.	Temperature alarms will detect too high or too low temperatures in R1-R4 and shut down the system.
*Rotameter V4	Leakage (major or minor) Incorrect calibration of flow	No or Incorrect flow of re-cicrulated reformate gas	Reformate/H_2 leakage to the system box/ component cabinet. If lower flow of re-circulated reformate to the catalytic burner, R1: a momentarily higher lambda value and a lower combustion temperature in the catalytic burner, R1. Combustion may blow out, if not, T14 will compensate for the lower fuel flow with a lower air supply in order to retain the set-point of T14. A lower fuel feed results in lower heat transport to the SREF reaction. Higher UHC emissions. Lower capacity.	A ventilation hole is positioned in the upper part of the component cabinet. The whole system box is placed below a ventilation hood. C3 will detect if hydrogen concentrations in the system box is ≥ 0,2 % and shut down the system. If fire is initiated, fire alarm will be shut off and shut down the system. Inert gas will be fed to the system box and the component cabinet via SV11. Temperature alarms will detect too high or too low temperatures in R1 (SREF+catalytic burner) and shut off the system.

			If higher flow of re-circulated reformate to the catalytic burner, R1: very high momentarily combustion temperatures in R1. Overheating of R1 possible , causing cracks and leakages between catalytic burner and SREF-reactor. Catalyst deactivation. Poor efficiency and capacity of the system.	
*Rotameter V5	Leakage (major or minor). Incorrect calibration flow	No or Incorrect flow of re-circulated reformate	Reformate/H_2 leakage to the system box/ component cabinet. Coke formation (if heavier feed stocks are used), resulting catalyst deactivation. Higher UHC emissions. Lower efficiency and capacity of the system. An increase in the refomate flow to SREF results in a decrease in the efficiency of the system.	V5 will only be used if heavier feed stocks are fed to the STUR-system. If significant H_2-leakage to the system box/component cabinet, see equivalent text for V4 above.
Throttle valve V6	Leakage (major or minor)	No or Incorrect water flow	If lower or no water flow to WGS: higher temperature in R3. Poor efficiency of the WGS reaction.	Too high temperatures R3 will be detected by temperature alarms and the system will shut down.

	Incorrect calibration of flow		Decrease in efficiency of the system. Increase in CO emissions. If increase in water flow to WGS: lower combustion temperature in R3. Poor efficiency of the WGS reaction. Decrease in efficiency of the system. Increase in CO emissions.	If fuel cell is integrated (PEMFC), C1 will alarm if CO concentration out from R4> 100 ppm and shut down the system.
Rotameter V7	Leakage (major or minor) Incorrect calibration of flow	No or Incorrect air flow	If decrease or no air supply to PROX in R4: lower combustion temperature in R4. Poor efficiency of the PROX reaction. Higher emissions of CO. If increase in airflow: higher combustion temperature in R4, poor efficiency of the PROX reaction, lower efficiency of the system (due to H_2 oxidation) and higher CO emissions.	Too high or too low temperatures in R4 will be detected by temperature alarms and the system will shut down. If fuel cell is integrated (PEMFC), C1 will alarm if CO concentration out from R4> 100 ppm and shut down the system.

Rotameter V8	Leakage (major or minor) Incorrect calibration of flow	No or Incorrect air flow	If decrease in air flow: lower combustion temperature in PROX polisher, R4. Poor efficiency of the PROX reaction. Higher emissions of CO. If increase of airflow: higher combustion temperature in PROX polisher, R4, lower efficiency of the system (due to H_2 oxidation), lower efficiency of the system (due to H_2 oxidation) and higher CO emissions.	If fuel cell is integrated (PEMFC), C1 will alarm if CO concentration out from R4> 100 ppm and shut down the system.
Throttle valve V9	Leakage (major or minor) Incorrect calibration flow	No or incorrect water flow	Decrease in water supply causes higher combustion temperature in PROX, R4, poor efficiency of the PROX reaction, decrease in efficiency of the system (due to H_2-oxidation), and increase in CO emissions. Increase in water supply may cause too low temperatures in R4, high CO emissions.	Too high temperatures in the inlet of R4 will be detected by temperature alarms and the system will shut down. If fuel cell is integrated (PEMFC), C1 will alarm if CO concentration out from R4> 100 ppm and shut down the system.

P1 (pressure transmitter, air)	Component failure	No signal on demand (=sensor break)	The system will not be able to start-up or if system already operating, the system will shut down.	Temperature alarms in R1 will detect too low or too high temperatures and shut down the system.
		Always signal	Natural gas supply possible to catalytic burner, R1, without any or at very low air supply. High UHC emissions out from system. No or low heat production in R1. No of low capacity of reformate produced.	
P2 (pressure transmitter, air)	Component failure	No signal on demand (=sensor break)	The system will not be able to start-up or if system already operating, the system will shut down.	If fuel cell is integrated (PEMFC), C1 will alarm if CO concentration out from R4> 100 ppm and shut down the system. Temperature alarm in R4 will shut down the system if too low temperatures are reached in R4.
		Always signal, signal without reason	No or a decrease in air supply to PROX reactor, R4. Low combustion temperature in R4, high CO emissions.	
P3 (pressure transmitter, water)	Component failure	No signal on demand (=sensor break)	The system will not be able to start-up or if system already operating, the system will shut down.	Temperature alarms will detect too high temperatures in the burner and in SREF in R1 and shut down the system.

		Always signal, signal without reason	Natural gas supply possible without any or at very low water supply to the system. If low water supply, S.:C ratio in SREF becomes very low. Coke formation possible. Catalyst deactivation. Low capacity and efficiency of the system. High UHC emissions.	
P4 (pressure transmitter, reformate)	Component failure	No signal on demand (=sensor break)	The system will not be able to start-up or if system already operating, the system will shut down.	
		Always signal, signal without reason	The system will continue operating.	
P5 (pressure transmitter, water)	Component failure	No signal on demand (=sensor break)	The system will not be able to start-up or if system already operating, the system will shut down.	Temperature sensor, T15, will detect too high temperatures of the exhausts out from R5 and the system will shut down.
		Always signal, signal without reason	Overheating in R5.	Any flashback in the inlet to R5 will be detected by the thermostat positioned outside the tube. If T≥ 140°C, the system will shut down.
P6 (pressure transmitter, air)	Component failure	No signal on demand (=sensor break)	The system will not be able to start-up or if system already operating, the system will shut down.	C3 (H_2-sensor) will detect if $H_{2(g\geq}0,2$ % and shut down the system.

		Always signal	Operation of the system possible even though no ventilation of the system box takes place.	Temperature sensor , T16, will alarm if $T_{system\ box} \geq 80$ °C and the system will shut down.
Pressure transmitter in ventilation hood	Component failure	No signal on demand (=sensor break)	The system will not be able to start-up or if system already operating, the system will shut down.	The pressure transmitted positioned in the ventilation hood is hardware wired (independent of PLC)
		Always signal	Operation of the system possible even though there is no forced ventilation flow out from hood.	
C1 (CO sensor)	Component failure	No signal on demand (=sensor break)	The system will not be able to start-up or if already operating, the system will shut down.	Component C1 not installed since no fuel cell is incorporated in the present system.
		Always signal, signal without reason	If fuel cell (PEMFC) installed, CO-poisoning of the anode electrode in the fuel cell possible, significant decrease in electrical efficiency of the system.	
C3 (H_2-sensor)	Component failure	No signal on demand (=sensor break)	The system will not be able to start-up or if already operating, the system will shut down	Temperature alarm (T16) will detect if too high temperatures are reached in the system box and shut down the system. Fire alarm will detect any fires, and inert gas will be supplied to the system and the fire will be put out.

		Alway signal, signal without reason.	The system will continue operating even though the $H_{2(g)}$-concentration in the system box≥.2 %. Critical, explosive, $H_{2(g)}$- concentrations can be reached.	One side of the box will be opened (attached with magnets) and thereby, vent the system if too large volumes of reformate gas are collected inside the system box.
TIA (temperature sensors)	Too low detection		Shut down via the control system	All the temperature alarm sensors (marked with TIA in P/I diagram) are included in the control algorithm. Temperature indications outside the normal window of operation will result in a shut down of the system.
	Too high detection		Shut down via the control system	
	Sensor fault		"infinite value" supplied, which shuts down the system.	
PLC-system	Software errors	Solenoid valves open without reason	If SV1 and SV2 open without demand, control system is out of order.	To be noted that fire alarm, ventilation fan (F6) and SV11 are hardwire wired and will thus function independent of the PLC system.
		Solenoid valves closed without reason	The system will shut down.	
Supply of electricity	No electricity (common cause failure)	All solenoid valves will be closed, except for SV11.	No natural gas will be fed to the system and hence, no reformate will be produced.	All solenoid valves are normally closed, except for SV11. Once electricity is cut off, SV11 will open and nitrogen will be supplied to the system box.

SGC Svenskt Gastekniskt Center AB

Hemsida www.sgc.se • epost info@sgc.se