
Rapport SGC 152

Upgrading of reformat gas for different applications with focus on small-scale hydrogen production

©Svenskt Gastekniskt Center – December 2004

Anna-Karin Jannasch & Fredrik Silversand
CATATOR AB

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.

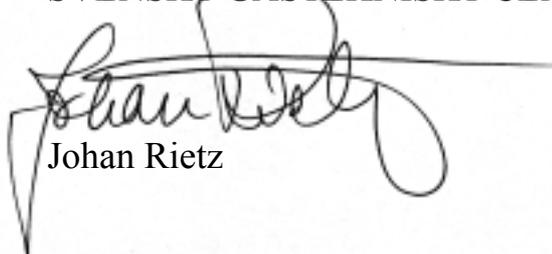
En förteckning över hittills utgivna SGC-rapporter finns på SGC's hemsida www.sgc.se.

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

SVENSKT GASTEKNISKT CENTER AB



Johan Rietz

Sammanfattning

Vätgas eller vätgasrika gasblandningar används idag i många olika tillämpningar, t ex som bränsle till bränsleceller eller som additiv till fordonsbränsle (sk hythane) och som reagent eller reduktant i olika produktionslinjer. Majoriteten av den vätgas som används produceras antingen via elektrolys eller via reformering, vilket det senare alternativet är det sätt som detta arbete har behandlat.

Detta arbete har finansierats av Svenskt Gastekniskt Center (SGC), Försvarets Materialverk (FMV) samt Sydkraft Gas AB. De övergripande målen för projektet var att demonstrera behovet för reformatupprening för olika användningsområden, och därefter undersöka olika tillgängliga gasreningsmetoder som kan användas för att uppnå den behövliga renhetsgraden. Olika gasreningsmetoder har undersökts med avseende på behövligt arbetsvillkor (temperatur, tryck), gifttolerans, storlek, vikt och kostnad. Ett annat mål med projektet var att undersöka hur valet av reformerbränsle påverkar reformatkvaliteten och således också vilken rening som krävs innan gasen kan användas i t ex en låg temperatur bränslecell (PEMFC). Denna kunskap har skaffats genom, inom ramen för projektet, utfört experimentellt arbete: Bränslena naturgas, gasol, bensin, diesel, fotogen (lågsvavlig (lysfotogen) och högsvavlig flygfotogen (JP8)) reformerades och den resulterande reformatgassammansättningen analyserades. Reformeringen utfördes i ett småskaligt reformersystem ($\sim 1 \text{ kWh}_2$) innehållande Catators utvecklade katalysatorformuleringar för ångreformerings- (SREF), vattengas- (WGS) och selektiva oxidationsreaktionen (PROX). Verifikationstester med en kommersiell 4-cell PEMFC stack (3-5 W) utfördes därefter med syntetisk reformatgasblandning innehållande olika potentiella reformatföroreningar samt med verklig reformatgas. Till sist undersöktes och till viss del utvecklades även Catators existerande gasreningsmetoder innefattande kemiska (WGS, PROX) och de fysikaliska (regenerativ adsorption) metoder.

Hög temperatur Pd-membran verkar vara det bästa gasreningsalternativet för tillämpningar som kräver extremt hög gasrenhet, som t e x elektronik och metallurgiska industrin som kräver $> 99.999 \%$ $\text{H}_2(\text{g})$. För de industrier som accepterar en något lägre renhet, t e x vissa tillämpningar inom läkemedels- och den kemiska industrin ($\geq 99.5 \%$ $\text{H}_2(\text{g})$) så kan även PSA vara en lämplig gasreningsmetod.

Enligt detta arbetets uppmätta resultat så krävs rening av de eventuellt förekommande komponenterna S, CO, halogener, ammoniak och oxygenerade kolväten innan reformatgasen kan användas i PEMFC-applikationer. För att åtminstone eliminera S, CO och de oxygenerade kolvätena så verkar gasrening m h a Catators regenerativa adsorbenter uppströms en PROX reaktor vara ett effektivt, kompakt och billigt alternativ. För att även eliminera komponenter såsom CO_2 , N_2 och CH_4 så krävs ett Pd-membran eller en PSA-enhet. I de fall de sistnämnda metoderna används så kan PROX reaktorn elimineras. Nackdelen med att rena m h a ett Pd-membran eller en PSA är däremot att trycksatt reformering krävs, vilket i sin tur leder till att reformersystemets vikt markant ökar. I fall av att PSA beaktas, så rekommenderas att en sk Fast Cycle PSA enhet används, eftersom de konventionella PSA systemen idag är alltför stora och tunga för att kunna vara av intresse för småskalig vätgasproduktion. Tyvärr finns det ännu inte några kommersiella Fast Cycle PSA enheter på marknaden för just reformatrening och de prototyper som finns tillgängliga på marknaden är således dyra. Till sist, för att få vidare information kring Pd-membranets lämplighet för reformatrening så har Catator nyligen beställt ett relativt billigt Pd-Cu membran från företaget ATI Wah Chang. Membranet kommer att utvärderas i kombination med Catators reformerteknologi i början av år 2005.

Koks och S är de föroreningar som är kritiska för SOFC. Koksbildningen kan undertryckas genom att för-reformera bränslet (intern reformering antas). Systemet kan också bli mer koks-tolerant genom att byta ut anodens katalysator (vanligtvis Ni) till exempelvis Pt. En Pt-baserad anod skulle även markant öka S-toleransen hos systemet (enligt våra tester, till åtminstone 100 ppm H₂S). S kan även lätt uppströms elimineras med hjälp av katalysators regenerativa adsorbenter.

Slutligen, i det fall då reformatgasen skall användas som additiv till fordonsbränsle så verkar det som om endast utspädande komponenter såsom CO₂ och N₂ behövs elimineras. Detta kan göras genom installation av relativt enkla och billiga lufttorknings PSA enheter. Ett projektförslag för design och installation av en lämplig reformer-anläggningen (10-20 Nm³/h H₂(g)) vid en tankstation finns inkluderat i denna rapport.

Summary

Hydrogen gas or hydrogen rich gas is today used in many different applications, i.e. as fuel in fuel cells or additive in vehicle fuel (i.e. hythane) and as reagent or reducing agent in different industrial product lines. The majority of the hydrogen is produced either via electrolysis or reformation, where this work has entirely been focused on the latter alternative.

This work has been financed by the Swedish Gas Centre (SGC), the Swedish Defence Material Administration (FMV), and Sydkraft Gas AB. The overarching aims of this project have been to demonstrate the need for reformat purification for different applications, and then, to investigate different available methods that can be used in order to enable the requested gas clean-up. The different purification methods have been examined with respect to parameters such as operating conditions (temperature, pressure), impurity tolerance, size, weight and cost. Another goal of the project has been to investigate how the reformer fuel type used influences the reformat gas quality and hence, the need for gas purification before the reformat can be fed to e.g. a low temperature polymer membrane fuel cell (PEMFC). For this reason, some experimental work has been performed. First, analysis of the reformat gas composition when natural gas, LPG, gasoline, diesel, kerosene (low and high S-concentration (i.e. JP8)) and ethanol have been processed. The reformation tests were carried out in a small-scale reformer unit ($\sim 1 \text{ kWh}_2$) including Catator's catalyst formulations developed for the steam reforming, the water gas shift and the preferential oxidation reaction, respectively. Verification tests, with synthetic gas blends, including different potential reformat impurities, and with real reformat gas were thereafter performed with a commercial 4-cell PEMFC stack (3-5 W). Finally, some examination and also to some extent further development of Catator's existing gas purification units were made, i.e. chemical (WGS, PROX) and physical (regenerative adsorption).

The Pd-alloy membrane seems to be the obvious choice of purification technique for applications that demand extremely high purity grades, i.e. $\geq 99.999 \%$ $\text{H}_2(\text{g})$, such as for example the electronic industry and the metallurgic industry. For the chemical and the pharmaceutical industry, for which the purity grade demand is somewhat lower (i.e. $\geq 99.5 \%$ $\text{H}_2(\text{g})$), PSA may also be a choice of consideration.

According to the results obtained in this work, S, CO, halogens, ammonia and oxygenated hydrocarbons seems to be the impurities of concern in the case of PEMFC applications. To remove at least S, CO and oxygenated hydrocarbons, Catator's regenerative adsorbents, installed upstreams a PROX reactor, seems to be an efficient, compact and non-expensive way for gas-clean-up. For also eliminating components such as CO_2 , N_2 and CH_4 , a PSA or a Pd-alloy membrane have to be used. In the latter cases, the PROX reactor can be eliminated. A disadvantage of using PSA or Pd-alloy membrane units is however that the reformation needs to be carried out at an elevated pressure which in turn results in that the weight of the fuel processor significantly increases. In the case of PSA, a compact so called Fast Cycle PSA is recommended, since conventional PSA systems are today way to large and heavy for being of interest for small-scale hydrogen production. However, Fast Cycle PSA systems for reformat purification are still not commercially available and therefore, still expensive. Furthermore, in order to further examine the suitability of using a Pd-alloy membrane for reformat purification, a relatively non-expensive Pd-Cu membrane has been ordered from the company ATI Wah Change. The membrane will be evaluated in combination with Catator's reformer technology in the beginning of 2005.

Coke and S are the critical impurities in the case of SOFC applications.. The coke formation can be suppressed by the use of pre-reforming (internal reforming is assumed). The system can also become more coke-tolerant by exchanging the anode electro-catalyst material (commonly Ni) to e.g. Pt. A Pt-based anode would also lead to a significant increase in S-tolerance of the system (according to our tests, at least up to 100 ppm H₂S). Sulphur impurities can also be easily removed upstreams by the use of Catator's regenerative adsorbents.

Finally, in the case of using the reformat gas for filling station applications (i.e. as additive to natural gas), it seems as the only components that needs to be removed are CO₂ and N₂. This can be made by the use of relatively non-expensive air-dryer PSA systems. A project suggestion for designing and to install a reformer system (10-20 Nm³/h H₂(g)) at a filling station is suggested in this project.

List of Content

	Page
1. Introduction	1
2. Gas quality requirements for different user categories	2
3. Description of different gas purification techniques	5
3.1. Pressure Swing Adsorption	5
3.2. Temperature Swing Adsorption	9
3.3. Membranes	10
3.3.1. <i>Low temperature polymer membranes</i>	10
3.3.2. <i>High temperature metal membranes</i>	11
3.4. Solvent Absorption	13
3.5. Chemical methods	14
3.5.1. <i>Water Gas Shift Reaction (WGS)</i>	14
3.5.2. <i>Preferential Oxidation Reaction (PROX)</i>	16
3.5.3. <i>Methanisation</i>	17
4. Experimental work performed at Catator	17
4.1. Reformation of different feedstocks	17
4.2. Verification tests with fuel cells	19
4.3. Adsorption tests	25
5. Conclusive discussion (incl. project suggestion for continuation work)	30
6. References	34
Appendices 1 and 2	

I. Introduction

During 2003, Catator AB (CAT) finalized the development of an atmospheric ultra compact hydrogen generator (close to 1 Nm³/h of produced H₂ per litre gross volume), Ultraformer or Single-Train Ultraformer Reactor (abbreviated STUR). The STUR-unit, which is a scalable and fully integrated fuel processor design with downstream CO purification, can be run on a variety of feed stocks, i.e. biogas/natural gas, LPG, alcohols and heavier hydrocarbons. It has a wide turn-down ratio (about 1:10), a high thermal efficiency (80 %) and it enables a relatively quick start-up (i.e. 15-20 minutes to reach fuel cell quality gas ≤ 20 ppm CO). Recently, a reliability study of a fully automatic 10 kWh₂ STUR-system was finalized. The system was operated for more than 500 h and it was found that stable emission levels and operation temperatures were reached within about 50 h of operation time (1).

Hydrogen gas or hydrogen rich gas is today used in many different systems/ applications. For example, hydrogen gas/hydrogen rich gas is needed as fuel in fuel cell systems (for stationary and automotive applications), as additive to fuel (i.e. hythane) or as fuel in vehicle engines, as reducing gas or carrier gas in the electronic industry, or as reagent in the pharmaceutical and chemical industry. This project was aimed at investigating different methods for reformat purification in order to enable usage of this hydrogen rich gas mixture for the different application categories. The investigation was divided into the following steps:

1. By means of literature studies and by contact with gas suppliers, map out the gas purity grades required for different hydrogen/hydrogen rich gas user categories.
2. By means of literature studies and by contact with different manufacturing companies, investigate the availability, the performance and the cost of different gas purification methods.
3. Based on the knowledge in the prevailing steps 1 and 2, judge the consequences of integrating and using different purification techniques with a hydrogen fuel processor. Parameters such as operating conditions, size (weight and volume), and cost, etc, were discussed.

It was in this project of special interest to examine how the type of reformer fuel influences the product gas quality and possibly also, the choice of gas purification needed before the reformat/hydrogen can be fed to e.g. a fuel cell. For this reason, some experimental work was included in this project. This included:

1. Analysis of the reformat gas composition when the following feed stocks were processed:
 - natural gas
 - ethanol
 - gasoline
 - kerosene (with low and high sulphur content (i.e. JP8))
 - diesel.
2. Evaluation of CAT's state-of-the-art gas purification units. This involved examination of both the chemical (water gas shift, preferential oxidation and methanisation reactor) and the physical (physisorption) downstream gas purification steps. These gas-clean steps may all be integrated in the STUR-unit.
3. Verification tests with fuel cells. In this work, the focus has been on PEMFC.

2. Gas quality requirements for different user categories

The quality requirement of the reformat/hydrogen gas depends strongly on the industrial process/application for which the gas should be used. Here follows a brief summary of the industry sectors which uses hydrogen in their production lines, and also the related purity grade of the hydrogen or hydrogen rich gas required for the specific applications.

- Electronic industry

Hydrogen is in the electronic industry typically used as reducing agent, or carrier gas in for example circuit manufacture, semi quartz melting, polysilicon production, and fiber optic production. These processes all require extremely high purity hydrogen gas, e.g. for semiconductor production that is $>99,99990\% \text{ H}_{2(g)}$ (2).

- Metallurgic industry

In the metallurgic industry, hydrogen is mostly used as reagent in heat treatment and bright annealing processes in the stainless steel production. The purity of the gas required for these processes is $>99.9990\% \text{ H}_{2(g)}$ (2).

- Fats and oils

Hydrogenation of fats and oils, i.e. converting liquid oils into semi solid, plastic fats, is the largest single reaction in the edible oil and oleochemical industries. The demanded purity grade depends somewhat on the final product, but for edible fats $>99.5\% \text{ H}_{2(g)}$ is required (2).

- Pharmaceutical industry

Hydrogen is used in the production of a variety of pharmaceuticals such as vitamins, steroids, hormones, antibiotics, and other kinds of different drugs. The purity grade varies but is in general in the order of $>99.98\% \text{ H}_{2(g)}$ (2).

- Chemical industry

Hydrogen is a common reagent in the chemical industry. For example, it is used for the production of many different organic compounds, e.g. alcohols, amines, tetrahydrofuran, but also inorganic products such as hydrogen peroxide. The purity grade depends somewhat on the specific process, but is for the majority of the processes around $>99.8\% \text{ H}_{2(g)}$ (2).

- Float glass

Hydrogen is used as a scavenging agent to ensure an oxygen-free environment in the float glass manufacture. To ensure high quality regular glass, the quality of the gas needs to be as high as $>99,9990\% \text{ H}_{2(g)}$ (2).

- Fuel cell industry

Two types of fuel cells have been of interest in this study, i.e. the polymer electrolyte membrane fuel cell (PEMFC) and the solid oxide fuel cell (SOFC). Below follows a short literature review of the impurity tolerance of these two systems.

PEMFC: Previous studies of reformat tolerance in PEMFC mainly address CO poisoning, since this contaminant is well-known to affect the performance of the fuel cell in a significant negative way even at very low concentrations in the anode gas stream. The exact CO tolerance depends on the fuel cell operation conditions such as the temperature and the pressure, but also strongly on the anode electro-catalyst used. For pure platinum catalysts, tests indicate that CO concentrations as low as 10 ppm in the gas stream begins to impact the cell performance, whereas a catalyst made of a PtRu, PtMo, and PtPd, have been reported to be tolerant up to 50 ppm (3,4). It is important to note that the CO tolerance concentration has also been found to depend on the hydrogen dilution, thus, the overall reformat gas composition. The lower the hydrogen partial pressure of reactants in the anode gas stream, the more CO sensitive the catalyst becomes as a consequence of that the already impaired CO hydrogen adsorption in this case becomes more retarded on the catalyst surface (5). One approach for reducing the losses from CO-poisoning is air-bleeding (3,6), where air is supplied to the anode side in order to facilitate the oxidation of CO on the catalyst surface. CO levels as high as 100 ppm has been shown to have negligible effect on the performance using this method of CO management. The drawback of the oxygen bleeding is however that it appears to cause sintering of the anode catalyst and may also result in accelerated aging of the fuel cell membrane (7). However, Ballard has run endurance tests in excess of 20 000 h with air bleeding without observing any deactivation of their fuel cell stack (8).

Another component that is well-known to cause severe poisoning effect in PEMFC at very low concentration levels is sulphur in the form of H₂S, SO₂ and COS (9,10). The sulphur tolerance of both Pt/C and Pt-Ru/C anodes, respectively, has been reported in the literature. For example, tests performed by Los Alamos National Laboratory showed that concentrations as low as 0.2 ppm H₂S adversely affect the performance of a Pt/C anode. The effect appears to be cumulative and causes severe deterioration of the fuel cell's performance. The results also indicated that regardless H₂S concentration and running time, replacing the contaminated fuel stream with pure hydrogen does not allow for any recovery (11). Further, results reported by de Wild et al. (11) have shown that the exchange of Pt/C anodes to Pt-Ru/C anodes does not lead to a lower sulphur sensitivity. Similar to the tests carried out with the Pt/C anode, it was found that the recovery with hydrogen was impossible. It was however seen that exposing the Pt-Ru/C anode to air during a couple of minutes resulted in a significant restoration of the original performance. Finally, considering the composition and the working temperature of the water gas shift catalysts (350-500 °C) and especially the preferential oxidation catalysts (120-180 °C), it should be noted that sulphur is not only a poison for the anode catalyst in the fuel cell unit, but also for the catalysts positioned in the prevailing reformer reactor steps. Thus, S should preferably be eliminated already upstreams the WGS and PROX reactors by for example installing a complete hydrodesulphurisation unit (HDS) prior to the inlet of the SREF reactor, or, if S-tolerant SREF catalysts are being used, by installing S-traps downstream the SREF-reactor, see section 4.3.

Even though not as severe as the effect of CO and S, CO₂, at the level present in the reformat gas, has also been reported to be a potential contaminant for PEMFC (12, 13, 14). While CO₂(g) itself is regarded as inert, CO can be formed *in situ* in the fuel cell, most likely via the reverse water gas shift reaction ($\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$) on the catalytic active sites. Thermodynamic calculations show that the reverse water-gas shift reaction can lead to equilibrium concentrations of CO of 20-100 ppm depending on operation conditions such as reformat gas composition (i.e. CO₂ and H₂-concentration), temperature and water content, etc (14). The type of electro-catalyst and the morphology of electrode used have also been shown to have an influence on the CO concentration produced. Results presented by de Bruijn et al. (14) evidence that the addition of ruthenium seems to suppress the reverse water gas shift reaction, and thus, justifying the use of Pt-Ru for being a reformat tolerant electro-catalyst. This group also reports that thin-film electrodes with high electrochemical utilization are much more tolerant towards CO₂ than more porous electrodes, irrespective of the noble catalyst used. This is explained by the fact that the reverse water gas shift reaction seems to be preferably catalyzed by sites that are uncovered by nafion, which, as a consequence of the fabrication method, exist to a larger extent in more porous electrodes.

While traces of methane are considered as being only dilutant, there are other organic compounds that most recently have been reported as potential PEMFC contaminants. These are water dissolvable compounds such as methanol, methyl formate, acetone, formaldehyde, and formic acid (7). Among those, Amphlett et al. established that formic acid is the impurity that causes the most severe and irreversible degradation of the fuel cell performance (Pt-C-anode) (7). The other contaminants were reported to cause only minor loss in fuel cell performance (at > 5000 ppm) and the effects were reversible by purging the anode with oxygen. However, Watanabe et al. (10) recently reported on observed losses due to the latter contaminants at significantly lower concentrations, i.e. methanol (> 2500 ppm), formaldehyde (>20 ppm) and acetone (> 250 ppm). Furthermore, the same group has also investigated the influence of impurities of the un-saturated hydrocarbons ethene and hexene. The tests indicated that ethene may have a small voltage lowering effect at concentrations > 5 %, whereas hexene may lower the voltage already at levels > 1000 ppm.

Finally, also trace amounts of halogens (<0.1-1.0 ppm) (9), hydrogen cyanide and ammonia have been reported as PEMFC impurities (14). Watanabe et al. reported on voltage drop due to presence of ammonia already at concentrations as low as 0.3-1 ppm (10). Uribe et al. reported on the effect of high NH₃ concentrations. They concluded that levels of around 100-300 ppm NH₃ can degrade the steady-state performance. It was however found that with short exposure times (1-3 h), the original performance can be recovered. But for longer times of exposure, the performance decreases to levels that cannot be recovered even with several days with pure H₂ operation (15).

SOFC: As a consequence of the high operation temperature (> 500 °C), the SOFC is significantly more poison tolerant than the PEMFC. However there are some poisons to be considered also in this case.

Of impurities in fuels, sulphur containing compounds, which are primarily represented as hydrogen sulphide (H₂S) under fuel electrode environment, has been reported to have the greatest impact on the SOFC performance. The actual performance loss due to S-poisoning has been found to be strongly dependent on the operation temperature and the total sulphur content in the fuel, but as a general rule, concentration levels > 0.05-1 ppm H₂S should be avoided (16). It should be underlined that the studies reporting on the sulphur tolerance of the

SOFC have been made with SOFC:s including conventional Ni-based anodes. This low tolerance could be significantly improved by replacing the Ni-anodes by for example Pt impregnated anodes. The reason for the latter is that Ni forms bulk sulphides whereas Pt only forms surface sulphides, which in contrast to the bulk sulphides, readily decomposes (17).

The high-operating temperature of SOFC may allow for direct oxidation of hydrocarbon fuels. One problem that is related to direct oxidation of the fuel at the anode may be the formation of coke, especially if heavier hydrocarbons are used as reformer fuel. In similar to the steam reforming reaction, the probability of and the tolerance towards coke formation depends on several parameters such as fuel type, temperature and the catalyst formulation used in this case as anode material. Likewise Ni-based reforming catalysts (18), the conventionally used Ni-based SOFC-anodes are relatively sensitive to coke formation. This is in turn due to the high solubility of carbon in Ni. Again, by replacing Ni by precious metals or Cu-Ceria, the tolerance towards coke formation may be significantly increased (19).

- as vehicle fuel

Hydrogen is a potential alternative to fuels such as gasoline and diesel for automotive applications in the future. Its use in conventional lean-burn combustion engines has generally shown decreased pollutant emissions primarily due to lean-burn characteristics of hydrogen and a reduction of carbon in the fuel (20). However, hydrogen is currently a rare commodity when compared to hydrocarbon fuels mainly due to a lack of a distribution infrastructure and thus, its introduction is a long-term prospect. Current use of hydrogen is probably limited to the role of a fuel additive. Natural gas vehicles (NGVs) are potential alternatives to gasoline vehicles in the short term. They are less pollutant, and the fuel is widely available. However, for reducing the emissions further, NGVs have been run on Hythane®, i.e a mixture of 20 vol% H₂ and CH₄ and trademarked by Hydrogen Consultants Inc. Besides the reduction in emissions, the addition of hydrogen results in advantages such as improved thermal efficiency and decreased fuel consumption in lean-burn engines. Tests have also shown that the fuel mixture can be used in normal NGVs vehicles without that any or only small modifications of the engine are needed to be carried out (21).

There are today a number of hydrogen filling stations in existence worldwide. The majority of the stations are situated on the premises of automotive companies, where the high qualitative hydrogen is produced by electrolysis. The hydrogen is either used as additive to natural gas/biogas or as fuel for fuel cell driven buses and cars. The quality of the hydrogen gas is therefore dependent on the application. For fuel cell driven buses or automobiles (PEMFC), the quality required is of course set by the impurity tolerance of the fuel cell used. However, for use as additive in natural gas for NGVs vehicles, the purity grade is different. In gas engines, trace amounts of CO, hydrocarbons and sulphides will not cause any detrimental effects. In this case it is more important to remove components with diluting effects, i.e. nitrogen and carbon dioxide. In addition to diluting the combustible gases, it should also be mentioned that carbon dioxide can cause corrosion in high-pressure tanks and in the compressor system.

3. Description of different gas purification techniques

3.1. Pressure Swing Adsorption

Conventional Pressure Swing Adsorption (PSA) technology has been used to separate and to purify industrial gases in more than 35 years. The technology is based on the principle that adsorbents, typically alumina, silica gel, activated carbon or molecular sieves, are capable of adsorbing more impurities at a higher gas-phase partial pressure than at a lower gas-phase partial pressure. Hydrogen is essentially not adsorbed, which makes it a suitable technique for reformat/H₂ -purification.

- *Working principle of PSA*

A complete pressure-swing cycle consists of five basic steps, which are briefly described in the following and also schematically illustrated in Figure 1 (22, 23).

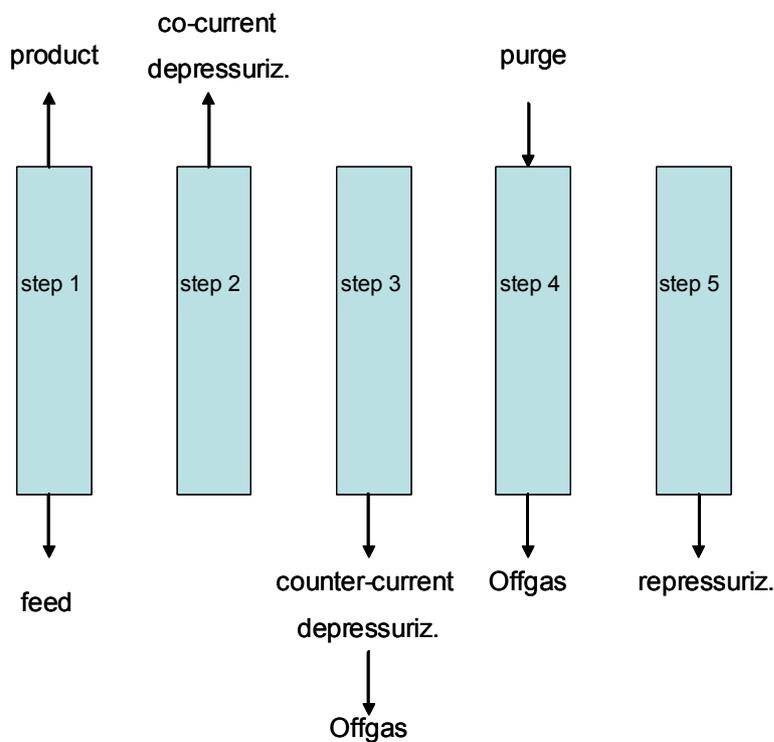


Figure 1. A schematic description of the five basic steps of the PSA technology.

Step 1. Adsorption

The feed gas, in this case the reformat gas, is at high pressure introduced into a vessel containing adsorbent beds. Impurities of the gas adsorb onto the internal surfaces of the adsorbent, leaving purified hydrogen gas in the void spaces of the vessel. The product gas is then withdrawn from the top of the vessel under pressure.

Step 2. Co-current depressurisation

To recover the hydrogen gas remaining in the void spaces of the vessel, the pressure is reduced from the product side in the same direction as the feed flow (co-current), and high purity hydrogen gas is withdrawn.

Step 3. Counter-current depressurisation

The saturated adsorber is partly regenerated by depressurizing towards the feed end (counter-current), and the desorbed impurities are rejected to the PSA off gas.

4. Purge at low pressure

The adsorber is purged with high-purity hydrogen (taken from another adsorber on co-current depressurization) at constant offgas pressure to further regenerate the bed.

5. Repressurisation

The adsorber is repressurized with hydrogen to the adsorption pressure used in step1, and the cycle has then been completed. The hydrogen is provided from the co-current depressurization and with a slip stream from the hydrogen product.

Since each cycle is essentially a batch process, multiple pressure vessels are used together in a sequence to provide a semi-continuous flow of product gas. In addition, large surge tanks are used to dampen variations in flows of feed, product and exhaust streams. To improve the product gas quality, more complex PSA-cycles than described above are needed involving more intermediate steps such as co-current and counter-current depressurization. For determining the optimum process cycle for a given gas purification requirement, an economic trade-off must thus be made between increased efficiency and higher capital cost.

- Key parameters for the design and the performance of PSA

The design and the performance of the PSA unit depend on parameters such feed gas composition, required product purity, feed and off gas pressure.

The PSA process can handle feed gas with a variety of impurities. The nature of the impurities determine in turn the selection of choice of adsorbent material.

PSA enables a high purity product grade to be achieved, i.e. 99.9-99.9999 % H₂. It should however be noted that a higher purity grade is always at the expense of hydrogen recovery and investment costs. In general, by changing the product specification by an order of magnitude, for example from 10 to 1 ppm, the hydrogen recovery changes by about 1 % (22).

The adsorption pressure can be fixed either by available feed pressure or the required product pressure. It is always preferred to have a high feed gas pressure for obtaining high hydrogen recovery and low investment costs. The pressure drop from feed to product is relatively small and consequently, the product is available at a pressure about 0.5 bar lower than the feed. The feed gas pressure most commonly ranges between 5-50 bars.

Off gas pressures ranges between atmospheric and 10 bars. This parameter has its strongest influence on the hydrogen recovery. The lower the off gas pressure, the higher the hydrogen recovery possible, and the lower the investment costs for a fixed flow rate.

- Disadvantages of conventional PSA

Despite the widespread use of PSA in industry, this technique has some inherent disadvantages.

First, the cycle time of conventional PSA systems, i.e. the time for an adsorbent vessel to complete the 5 operation steps described in Figure 1, is relatively slow, about 2-20 minutes. Faster cycle speeds/gas flow speeds are limited by the fluidization velocity of the adsorbent beads, which causes bead abrasion and destruction. These slow cycle speeds of conventional PSA systems means that individual pressure vessels have to be extremely large, leading to high costs and a large number of footprints (i.e. valves, etc). Furthermore, the fluidization constraint also limits the minimum adsorbent bead size that can practically be used, i.e. normally about 2 mm (23). Larger adsorbent bead sizes means slower mass transfer between the bulk gas and the adsorption sites, which in turn must be further compensated by larger amounts of adsorbent and slower cycle speeds.

Then, in conventional PSA installations a complex and expensive network of solenoid valves, with associated instrumentation, is used to switch gases between the adsorbent beads. In addition, this complex network required to link the array of valves adds dead volume to the overall PSA process, which in turn results in reduced product yield and overall process efficiency.

- Market availability of PSA

As said in the introduction of this section, PSA is a well-established technology for gas purification, mainly used in refinery plants and in the petrochemical industry. The technology was first developed by Exxon Air and Air Liquide in the late 1950s. Some major designers and manufactures of conventional PSA units are today Air Liquide, Aga Linde, Norsk Hydro and Catalyst and Chemical Europe. All these companies design units for very large capacities, i.e. from 100-100 000 Nm³/h of H₂, and the physical dimension of the systems are in general very bulky.

To our knowledge, there are today two companies that design more compact PSA-units for small scale gas purification. These are Sequel Technologies and Quest Air.

The Quest-Air H-3200 system, introduced in 2003, utilizes an optimized PSA-cycle with conventional beaded adsorbents in combination with a, by the company, patented rotary valve technology. According to Quest Air's homepage, this system requires approximately only one-tenth of the space of conventional PSA, but still, the unit is relatively large and especially, extremely heavy (i.e. in the range of 2-3 tons for a unit designed for the production capacity 5 Nm³/h H₂(g)). Detailed data for the H-3200 system is given in Appendix 1.

Currently, a new PSA technique, called Fast Cycle PSA, is also under development at QuestAir. According to their web-page, it can operate up to 100 times faster than conventional PSA, resulting in much more compact energy efficient systems, i.e. the module size can be up to one-fiftieth the size of traditional PSA. The principal key for this breakthrough is, except for the exchange of solenoid valves with integrated rotary valves, the replacement of the conventional beaded adsorbents with structured adsorbents. The structured design of the adsorbent allows for significantly larger gas flows mainly due to that it provides for a higher adsorbent surface area and that the fluidization limit associated with the adsorbent beads are eliminated. However, like any other technology, there are always some drawbacks that come with the advantages, so also for the fast cycle PSA process. The reduction in adsorbent amount makes the fast cycle PSA more vulnerable to contamination by liquid water or other condensable liquids. Another issue related to the fast cycle speed is the increase in cyclic loading stress of the adsorbent pressure vessel.

These facts require careful design of feed-processing equipment such as additional condenser steps up-stream the PSA unit, in combination with selection of proprietary adsorbents. Moreover, before this product is ready to be released as a commercial product, performance standard tests in terms of reliability, product purity, hydrogen recovery and pressure drop are planned to be carried out. The tests are planned to be completed within another year (24).

In contrast to QuestAir, Sequel Technologies claims that they already have a fully developed commercial fast cycle PSA system. However, the company is more focused on oxygen regeneration for medical applications and until now, they have only built prototype demonstration units for reformat purification which are capable of providing up to 6 Nm³/h H₂(g) (25). For more details, see Appendix 1.

Finally, to be noted that conventional air dryer systems, based on pressure swing adsorbents, could eventually also be an option for reformat purification. For example, Donaldson Company sells relatively cheap systems that can readily remove the water, CO₂, SO₂ and the hydrocarbon impurities in the reformat gas. The disadvantage of these units in their present form are however that they do not remove CO, unless oxygen is added (26). Kaeser is another company that manufactures desiccant air dryers.

3.2. Temperature Swing Adsorption

The temperature swing adsorption (TSA) technology is based on the principle that adsorbents are capable of adsorbing more impurities at lower temperatures than at higher temperatures at a constant pressure. Likewise for PSA, hydrogen is in this case not adsorbed, which in turn indicates that this technique could for some applications be suitable for reformat purification.

As regards the commercial market, different adsorbents, that can be incorporated in TSA-units for capture components such as H₂O, HC and S, etc, are available from most of the larger chemical manufacturing companies. The adsorbents suitable for a TSA-unit are in general the same type of adsorbents that are suitable for a PSA-unit. For example, silica gel, activated alumina or hydrophilic zeolites are most commonly used for removing water/moisture. HC, CO₂ and CO, respectively, can in general be adsorbed by activated carbon or by different kinds of zeolites, whereas H₂S and other sulphur containing compounds can be removed by for example activated carbon impregnated with KI (9).

The use of systems that contain combinations of different adsorbents and metallic catalysts such as Ni/NiO and TiO₂ is another alternative "TSA-like" technology. In this case, the reactions that remove the impurities include not only simple physisorption, but also chemisorption and oxidation reactions. These combined units are able to remove gaseous components such as H₂O, CO, O₂, and non-methane hydrocarbons at ambient temperatures at low pressures. The systems can, in similar to pure adsorptive TSA units, be periodically regenerated by heating, in this case up to about 180-200 °C in hydrogen or in a mixture of hydrogen and inert gas. Examples of manufactures of such type of purifiers are Johnson-Matthey, Aeronex Mykrolis and SAES Pure Gas. It should be noted that purifiers including metallic catalysts such as Ni/NiO is mostly used in the semiconductor industry where the purpose is to improve the gas quality from 99.999 to 99.9999 %. The purification unit is thus in this case only exposed to feed gas mixtures of very high purity grades. According to Dr. Tom Purcell at Johnson-Matthey, these catalyst purifiers are not practical to use with low purity gas mixtures such as reformat gas, mainly due to the Ni's pyrophoric nature, which may in turn generate a severe exotherm and consume the catalyst too quickly.

Compared to the regeneration of a PSA, the TSA- regeneration is in general time-consuming. Although the cleaning effect of TSA is effective, it has the disadvantage that the number of cycles obtainable in any given time is limited by the relatively slow heating and cooling process steps. For this reason, the TSA can be limited to the removal of small quantities of strongly adsorbed species (22). However, the advantage of this technique relative to the PSA is that no elevated pressure is needed.

In this work, different adsorbers were put onto CAT' patented wire mesh substrates and evaluated as regenerative TSA-components for reformat purification. For more details, see section 4.3.

3.3. Membranes

Membrane based purification techniques can be divided into high temperature metallic and low temperature polymer membranes, respectively.

3.3.1. Low temperature polymer membranes

Low temperature permeation through a polymer membrane is, similar to PSA, a technology that is used in the petrochemical industry for hydrogen recovery and purification. The technology is based on the difference in permeation rates between hydrogen and impurities across a gas-permeable polymer membrane.

Monsanto commercialized the use of membranes in gas separations in the mid-1970s with the development of the so called hollow fibre Prism system. With this system, pressurised feed gas enters and flows up a package of parallel polymeric fibres that are contained inside a vessel. The driving force for the diffusion is the partial pressure difference across the membrane between the feed and the permeate side. Fast gas components, such as hydrogen, permeates through the membrane and becomes enriched at the inside of the hollow fibers. The product, purified gas is thus collected at a lower pressure than the feed gas. Gases with lower permeability however enrich on the non-permeate side of the membrane at a pressure close to the feed gas pressure.

The polymer composition and the dimensions of the fibres are generally designed for each application. The product purity is then dependent on the feed purity, the available differential partial pressure and the desired recovery level. In similar to PSA, a higher purity grade is always obtained on the expense of a lower recovery degree.

Today, Ube Industries, Air Products and Chemicals, and Air Liquide are the major designers and suppliers of hollow fibre membranes for hydrogen purification. The systems that have until now been designed and installed are in general large, i.e. 50 up to several hundreds of Nm³/h H₂(g), and can operate over a wide range of pressures, i.e. ~10 – 120 bars. In contact with these companies, we have been informed that the technology is however not suitable for reformat purification if high purity grades, i.e. > 85-90 % H₂, is desired (27-29). The primarily reason for this low purity grade is the large amount of CO₂ in the gas stream, which will most probably co-permeate with the hydrogen through the membrane. Other impurities that may also easily be carried over to the product gas are C₃+ and H₂S. In overall, it seems as this technique is significantly less selective than for example PSA or high temperature metal membranes (see below) and that this technology should only be considered if a general, poor selective, up-grade of the reformat gas is desired (30).

The advantages of this technology relatively to other existing is however the poison tolerance. In contrast to PSA, there is in this case no problem with traces of condensable liquids present. Water can be accepted at any level up to saturation without any pre-treatment. Besides water, the compatibility against different chemicals given e.g. Ube Industries' membranes are: H₂S:5 %, NH₃:100 ppm, C5+ HC: saturated, methanol: 5 %, acetone: 5 %.

Finally, it should be mentioned that we have not succeeded in getting any information about the cost nor physical dimensions/weight for a commercially available membrane hollow fibre unit, suitable for small-scale hydrogen production, even though requests about these pieces of information have been sent out to all the major suppliers. A complete comparison including all the necessary aspects could therefore unfortunately not be made within this work.

3.3.2. High temperature metal membranes

The most popular metal used for membrane based hydrogen separation has been, and continuous to be, palladium and its alloys. In similar to low temperature polymer membranes, this gas purifier operates via pressure driven diffusion (~7-21 bars) across the membrane. The working principle of the technique is illustrated in Figure 2. When the hydrogen gas molecule comes into contact with a heated up (~300-400 °C) palladium membrane surface, it dissociates into mono-atomic hydrogen and thereafter diffuses as H⁺ through the membrane. At the exit surface, the reverse process occurs, i.e. the mono-atomic hydrogen is recombined into molecular hydrogen gas. Assuming no pinholes or micro-cracks in the membrane, investigations have shown that it can be assumed that only hydrogen can diffuse through the membrane, and in this way, ultra pure hydrogen gas can be produced, i.e. < 1 ppb purity with any inlet gas quality with impurities such H₂O, CO, CO₂, N₂ and hydrocarbons.

The throughput of a palladium based membrane is a function of surface area, membrane thickness, operating temperature, and differential membrane pressure. To enable a high diffusion rate across the membrane, it is desired to have a high differential pressure, a high temperature, a large membrane surface and a small membrane thickness, respectively.

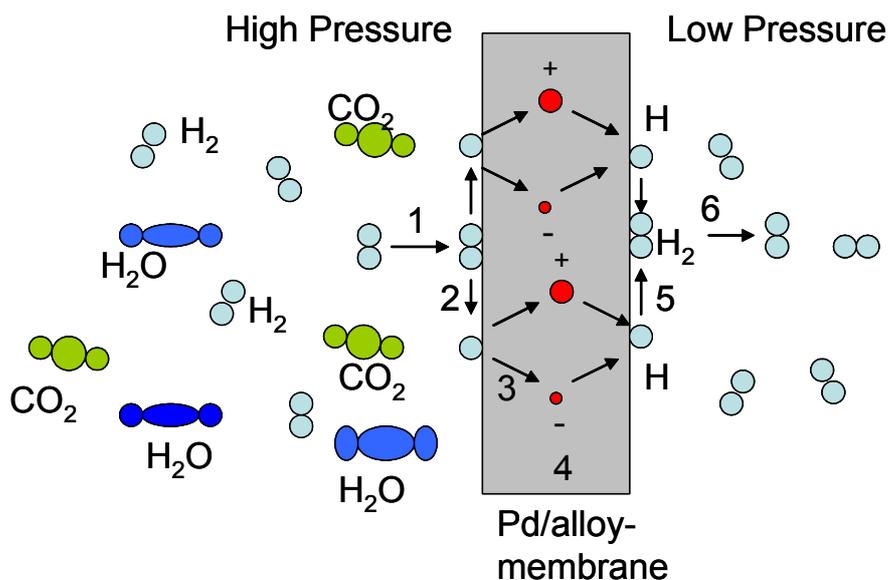


Figure 2. Schematic illustration of the working principle of a Pd/Alloy- membrane purifier. 1) adsorption 2) dissociation 3) ionisation 4) diffusion 5) recombination 6) desorption.

- Remaining problems with the Pd-Ag alloy membrane

One critical problem of palladium based membranes is that the palladium undergoes irreversible structural phase transformations on repeated cooling and heating in hydrogen environment. The latter leads in turn to embrittlement and fracture of palladium. Some control of this problem has been gained by alloying the palladium with silver. The silver addition does however increase the cost, which is another problem of palladium based membrane systems. Another way of avoiding the destructive phase transformations is, which is also recommended by the suppliers, to couple efficient purge systems to the purifier so that all hydrogen can be removed before any cooling of the system is carried out (i.e. $T < 300\text{ }^{\circ}\text{C}$).

One way for reducing the cost of palladium based membranes is of course to decrease the thickness of the membrane. A decrease in thickness would also favour the H^+ transport rate through the membrane. Thin films are however more fragile and hence, pin-holes and micro-cracks are relatively easily formed. Another problem encountered with thin films is that they have been found to easily de-laminate (the Pd-Ag comes off) within a few weeks of operation. Moreover, another way for reducing the cost of the membrane would be to replace the palladium metal with cheaper metals such as zirconium, niobium, tantalum, and vanadium. The latter mentioned metals also have the advantage of having higher bulk hydrogen permeabilities than palladium. This direct replacement is however hindered because these metals passivate to form surface oxide layers, which in turn limit the hydrogen flux. The problem with oxide formation could eventually be solved by using membranes built up by composite structures: very thin films of palladium are placed on each side of a thin foil of for example zirconium. Research efforts are today also put into investigating the latter (31).

Finally, since the palladium is catalytic in nature, Pd based membranes can, in contrast to low temperature polymer membranes, relatively easy be permanently destroyed or temporary poisoned by the presence of different contaminants. The membrane is sensitive to (32, 33):

- small concentrations of oxygen ($> 50\text{ ppm}$). Oxygen can in presence of palladium react with hydrogen to form water. The reaction is exothermic and may generate local hot spots leading to premature failure. To solve this problem, the feed gas is in general passed an oxygen removing guard bed prior to being in contact with the membrane.
- halogens and their compounds at as low concentrations as $> 10\text{ ppb}$. Presence of this impurity may lead to permanent failure of the membrane.
- metals of low melting point, high volatile metals (e.g. mercury), semi-metals (e.g. arsenic, phosphorous) and silicon ($> 10\text{ ppb}$). These components may react with the palladium, which reduces the permeability of the membrane locally. This creates stress sites on the membrane and leads to premature failure.
- sulphur and its compounds at a concentration level $> 200\text{ ppb}$, which may cause temporary poisoning of the membrane, which in turn leads to reduced throughput.
- $> 500\text{ ppb}$ of unsaturated hydrocarbons which may cause temporary poisoning of the membrane, which in turn results in reduced throughput.

- Market availability of Pd/Pd-Alloy membrane hydrogen purifiers

The first commercial version of a Pd-membrane purifier was developed by Johnson & Matthey in the 1960s and this company is still today the world leader in the manufacturing of this type of hydrogen purifier. Their purifiers may provide extremely high purity hydrogen, i.e. up to 99.999999 % in one step.

95 % of their sales go to the semiconductor industry where they are used to upgrade 99.9 % H₂ to 99.999 % or better. The units are tubes of Pd-Ag alloy, about 60-70 μm thick, and hence, the cost of the metal itself is very high and thereby also, the cost of the purifiers themselves, see Appendix 1. The membranes have a life time of approximately 2-4 years at continuous operation, significantly shorter if the feed gas is highly impure (34).

Another manufacture of Pd-based (in this case Pd/Cu) membranes is ATI Wah Chang. They claim that their membranes can very well purify reformat feed stocks, typically consisting of 65-70 % hydrogen, into levels exceeding 99.999 %. According to their homepage, their membranes have been operated under steady-state hydrogen flux for more than 10,000 h with no degradation in performance or failure. Compared to the Pd-Ag membranes supplied by Johnson-Matthey, these membranes are significantly less expensive, see Appendix 1.

Power and Energy is another company who is for more than 10 years now producing commercial Pd-based purifiers, from lab scale purifiers (> 0.06 Nm³/h) up to large scale industrial systems (78 - 625 Nm³/h). More details of their systems can be found in Appendix 1.

Furthermore, in correspondence with Dr Dave Edlund at Idatech, we have been informed that Idatech can in general design and supply Pd-Alloy membrane purifiers for the production of > 99 % pure hydrogen for flow rates in the range of 5-500 Nm³/h. It should be noted however that no one-off samples for this flow rate range can today be offered without a commercial agreement between the buying company and Idatech. What they can offer today without any agreements made is to lease out a small standard membrane module (0.03 Nm³/h H₂) that is intended to be used only for experimental evaluations in the laboratory, see Appendix 1. From experimental evaluation with this small unit, optimal working conditions (pressure, temperature) for the buyer's specific application can be found and this information can then be the basis for the design of a larger unit.

Finally, another company that is today, likewise Idatech, at the stage of producing relatively small capacity purifier prototypes (i.e. ≈0.7 Nm³/h) based on Pd-membranes is REB Research & Consulting. Their concept combines the water gas shift reactor (CO+ H₂O = H₂+CO₂), that generates the product, with a Pd-alloy membrane. The use of such a system would result in a significantly more compact fuel processor design (no external WGS nor PROX reactor would be necessary) plus greater conversion, since the removal of the H₂, via the Pd-alloy membrane, from the reactor drives the equilibrium-limited water gas shift reactor towards completion. Scale-up tests for enable manufacturing of units designed for larger capacities (≈ 5 Nm³/h) are planned to be performed at the company within the near future (35).

3.4. Solvent absorption

Solvent absorption for the removal of various impurities is quite commonly in the chemical process industry. The basic principle is to dissolve undesired components into the solvent at high pressure and low temperature leaving the wanted components in the gas phase. In a separate step, the solvent is regenerated by stripping off the impurities at low pressure and high temperature. For removing CO and CO₂ from reformat gas, monoethanolamine can be used as solvent (7). An advantage of using solvent absorption compared to other techniques is that the operating pressure is lower than PSA or polymer membrane separation. Another positive thing is that the H₂ is produced at the higher pressure.

The major drawback is that a complex solvent circulation and recovery system is required, which makes this technique un-suitable for small-scale H₂-production, where the external size of the purification unit is of crucial concern, and this is also why we have not investigated this purification alternative any further in this work.

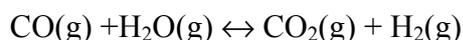
3.5. Chemical methods

The chemical methods that will be considered herein are those for CO-elimination. As described in section 2.1, the importance of removing CO depends strongly on the final application the reformat/H₂ should be used for, but since one of the major focus in this work is the PEMFC-application, the CO elimination becomes one of the major concerns.

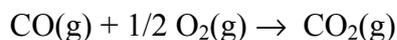
The exit from the steam reforming reactor contains about 10-12 % CO. This concentration needs to be reduced to approximately ≤ 50 ppm CO before the reformat can be used as a suitable fuel for PEMFC. This low CO-levels can be reached by leading the reaction gas through one or several water-gas- shift reactor(s) (WGS) and thereafter through a preferential oxidation reactor (PROX). An alternative to the PROX reaction is methanation. The schemes for these reactions are given in Table 1 below.

Table 1. Schemes describing reactions used for CO-removal

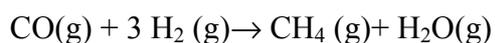
WGS



PROX



METHANATION



3.5.1. Water Gas Shift Reaction (WGS)

The traditional WGS reactions that are today used in industrial- and so also in small-scale hydrogen production can be divided into high temperature (HT-WGS) and low temperature WGS (LT-WGS) reactions. The conventionally used HT-WGS catalyst is based on Fe-Cr (≈ 350 - 550 °C), whereas catalysts based on Cu, Zn and Al are used for the LT-WGS-reaction (≈ 200 - 350 °C). The reason for driving this reaction in a high and a low temperature step is the thermodynamic limitations of this reaction. The WGS reaction is exothermic and the equilibrium is favoured by low temperatures, whereas the rate of the reaction, i.e. the kinetics, is favoured by high temperatures. By at first leading the gas through a HT-WGS reactor, the reaction can be driven at a relatively fast rate to about 3-5 % CO simultaneously as the H₂ content increases. In the LT-WGS- step, the CO concentration can then, but at a slower rate, be further decreased, i.e. 0.5 %. It should be noted that the optimal way would be to find a LT-WGS catalyst as active as the catalyst working at higher temperatures.

Much research is going on this area and the focus during the last years has been on precious metal activated Ce-based catalysts, which have been shown to have high initial activity at relatively low temperatures. Other advantages of this type of catalyst is its high tolerance against S-poisoning and that it is, in contrast to Cu-Fe based catalysts, non-pyrophoric, and thereby oxygen tolerant (36, 37). The disadvantage of these catalysts is the relatively fast deactivation rate. The reason for this instability is today not clarified, even though several theories have been suggested in the literature such as sintering of the precious metal (38), deposition of coke (39) and irreversible overreduction of the ceria carrier (40). Moreover, recently published results have indicated that the stability of this type of catalysts can be improved by doping the active phase with small amounts of other metals, e.g. Re. (41, 42). Other reports indicate that some improvements of the stability can also be obtained by using a zirconium doped ceria as carrier (43).

Motivated by its high sulphur and oxygen tolerance, CAT has during the past few years used precious metal activated ceria/alumina based WGS catalysts. Efforts for improving the activity and especially, the stability of these catalysts are continuously made. Most recently, the effect of promoting the active phase with a large number of different metals were carried out, e.g. Co, Re, Mo, W, K and Mn. In contrast to some literature (41, 42), it was found that among all the different promoters tested only the addition of wolfram resulted in an increased activity. Moreover, in accordance with reference R.R. Willigan (43), the evaluation tests also showed that further improvements can be achieved by using a carrier including, except for ceria and alumina, significant amounts of zirconium. The results are summarised in Figure 13, where the activity is illustrated by the temperature measured at 25, 50 and 75 % CO-conversion (i.e. the lower the temperature, the higher the activity). Besides improving the activity, the carrier including Zr was also seen to somewhat improve the stability, Figure 4. Further evaluation tests with this carrier material in combination with W-promoted Pt will be made within the next few weeks.

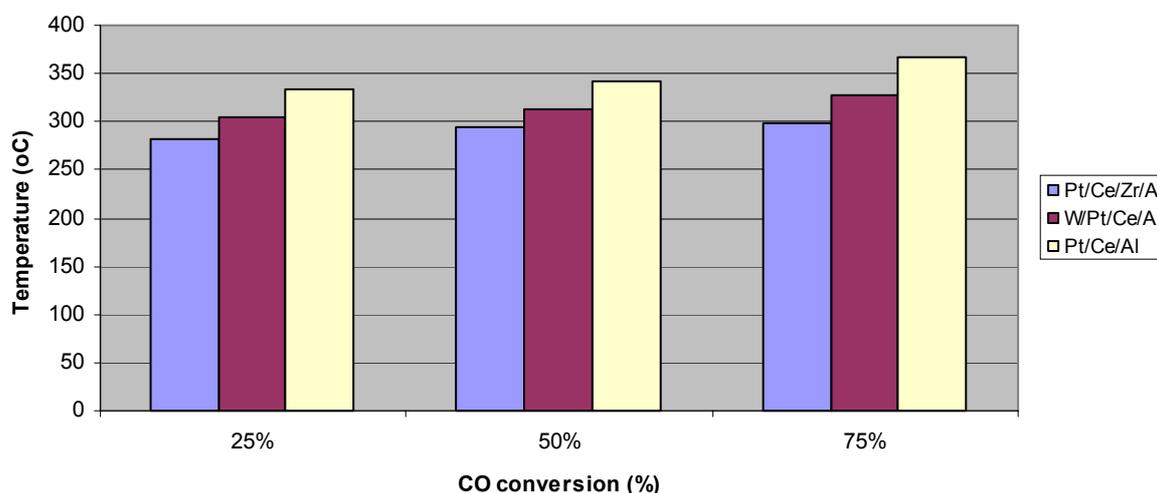


Figure 3. Activity data measured with CAT's un-modified state-of-the-art WGS catalyst (i.e. Pt/Ce/Al), Wolfram promoted Pt-catalyst (i.e. W/Pt/Ce/Al) and zirconium stabilized carrier (i.e. Pt/Ce/Zr/Al) WGS catalyst. The activity data is in the figure illustrated as temperature measured at which 25, 50 and 75 % of CO-conversion is achieved at $SV= 100\ 000\ h^{-1}$. All the catalyst samples have been deactivated for 45 h prior to activity test was performed.

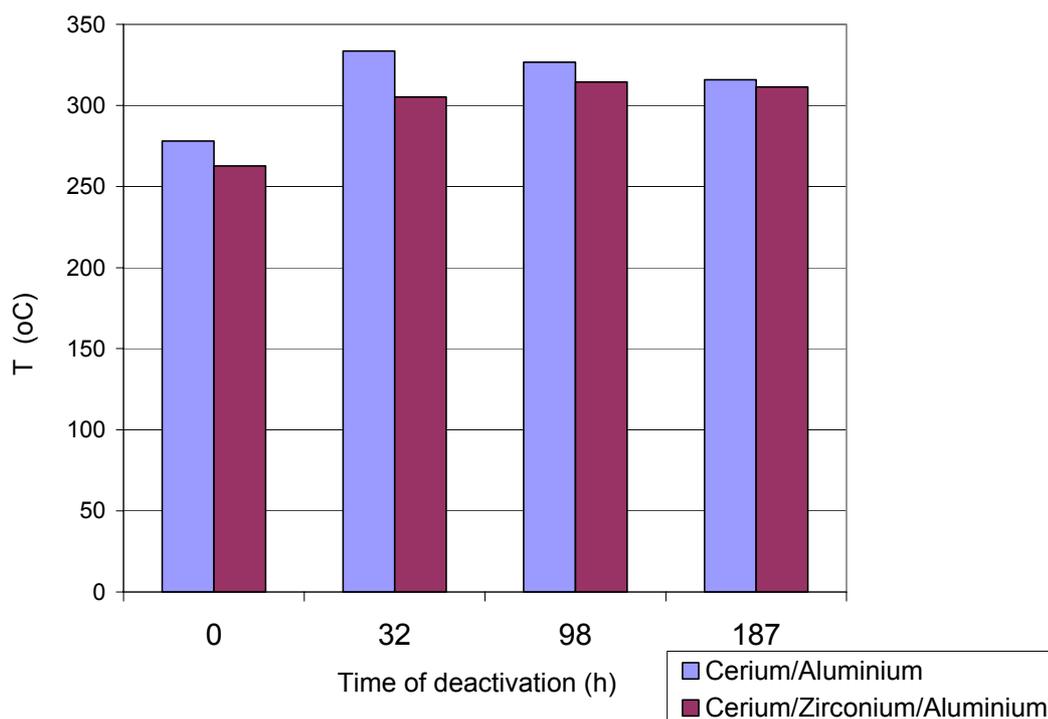


Figure 4. Activity data measured as a function of deactivation time at CAT with WGS catalysts of two different carrier materials. The activity is here illustrated by the temperature measured at which 50 % of CO-conversion is obtained at $SV = 100\ 000\ h^{-1}$.

3.5.2. Preferential Oxidation Reaction (PROX)

The exit concentration of CO from the WGS reactor is from 0.5 to 1.5 % CO depending on the operating conditions. As described previously, it is essential to remove CO to $\leq 100\text{-}50$ ppm level (depending on if air-bleeding is used or not) before it can be used as fuel for PEMFC. The most effective mechanism for removing CO from reformat gas is PROX. As can be seen in Table 1, this process requires that a small amount of air is added to the fuel gas stream. A fixed bed of precious metal activated catalyst then selectively catalyses the oxidation of CO while consuming a minimum amount of H_2 . The temperature control is critical for the selectivity. It has been shown that the selectivity for preferentially oxidising CO over H_2 is significantly reduced at higher temperatures ($>180^\circ$). Since both the oxidation of CO and H_2 are highly exothermic it is therefore important to remove heat from the reactor in an optimal way.

The PROX catalyst formulation includes most commonly a promoted precious metal dispersed on various supports such as alumina and ceria. The major drawback of using PROX as purification technique relatively to the other previously mentioned techniques is the fact that it is only removing CO. Other disadvantages are the addition of air to the reactor which results in a dilution of the fuel and the fact that the reaction is highly exothermic which in turn leads to a loss of fuel. One advantage is that no pressurisation of the system is required, and hence there are no moving parts involved, as in PSA units, that may break down. PROX is also a relatively non-expensive technology that is easy to scale, see Appendix 1.

The state-of-the-art PROX catalyst of CAT is based on an alumina carrier impregnated with metal-oxide doped platinum. The optimal working temperature window has for this catalyst formulation been shown to be in the range of 150-170 °C. The long time stability of the catalyst has been evaluated for about 1000 h of continuous operation at moderate space velocities ($\sim 30\text{-}40\ 000\ \text{h}^{-1}$) and the results verified its high stability.

3.5.3. Methanisation

As an alternative to PROX, methanisation can be used for removing CO from the reformat gas. In this case, the CO is reacted with hydrogen according to the reaction scheme shown in Table 1. The obvious disadvantage of this process is that H₂ is consumed, another drawback is that CO₂ may also react and form methane (43). Due to the latter, CO₂ is in this case needed to be removed prior to that efficient CO removal by methanisation can be performed. Thus, methanisation might be a technology of choice under the assumption that it is combined with another CO₂ removing technique such as one of the cheaper PSA alternatives suggested in section 3.1.

4. Experimental work performed at Catator

4.1. Reforming of different feed stocks

To investigate the composition of the reformat gas produced from various feed stocks with the use of CAT's catalyst formulations, reforming, including downstream CO-purification, of the following fuels were carried out:

- natural gas
- ethanol
- LPG
- gasoline
- diesel
- kerosene (with low and high sulphur content)

The investigations were performed in a small-scale, fully automatic, experimental set-up (nominal capacity $\sim 1\ \text{kWh}_2$) including SREF, WGS and PROX reactors, respectively. A photo of the set-up is shown in Figure 5. As can be seen in the figure, the steam reforming reaction is taking part in a reactor positioned in an electrical furnace, thus, no burner is integrated in this set-up. The catalysts inserted in the different reactors were of the same type as were used and previously evaluated in the STUR-10 kWh₂-system (operated for more than 500 h) (1). In brief, the substrate of the catalysts consisted a thermally sprayed wire mesh (Kantahl AF, mesh number: 16) prepared according to CAT's patented technology. The substrate had thereafter been washcoated with for the reaction a suitable metal oxide formulation and finally impregnated and activated with precious metal or precious metal doped with metal oxide. Moreover, the gas composition of the produced reformat gas was analyzed with NDIR (Electra control MGA 4000-T) and by GC (Varian CP-3800 GC). All gas analyses were performed on dry gases.

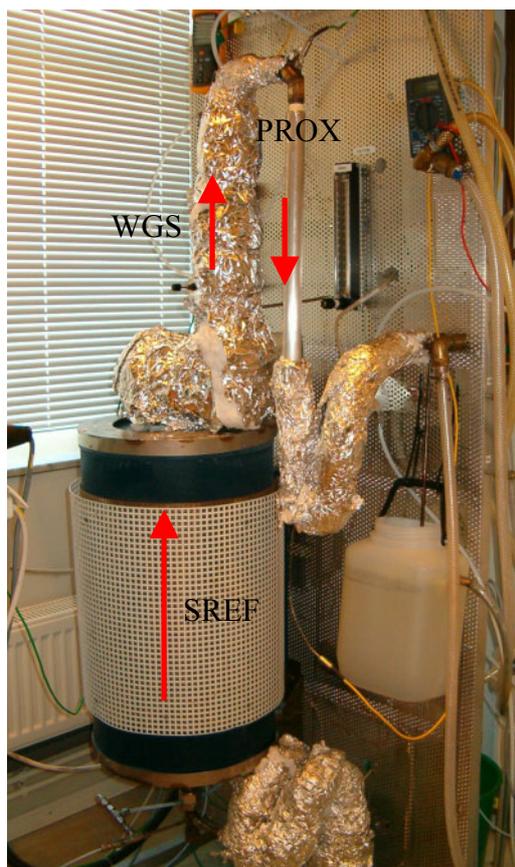


Figure 5. A photo of the experimental set-up for reforming various types of reformer feedstocks. The arrows indicate the flow direction of the reaction gas.

The reformate gas composition analysed for the various feed stocks are summarised in Table 2. The results were found to be very good for all the tested reformer fuels. Except for some small amounts of methane, no hydrocarbons (including saturated and un-saturated) could be detected in the reformate gas for any of the fuels reformed. The small concentrations of HC in the gas means in turn that the HC-conversion was throughout the series of measurement very good, i.e. about 90 % for natural gas reforming and close to 100 % for the other heavier hydrocarbon feed stocks tested. The somewhat lower conversion for the natural gas reforming is a consequence of that methane (natural gas consists of $\approx 88\text{-}90\%$ of methane) is a more stable molecule than the heavier hydrocarbon molecules, and as a result, it requires a higher activation energy, and thus a higher reforming temperature, for enabling full conversion. In this set-up, the reforming temperature was limited by the maximum furnace temperature and for this reason, a higher HC-conversion than 90 % could not be reached for the natural gas reforming. Furthermore, gas analyses were also made after the SREF and WGS reactors, respectively. Likewise the analyses after the PROX reactor, no HC concentrations could be measured up-streams, except for some traces of propane (C_3H_8) after the SREF reactor in the case of natural gas reforming and some traces of ethene (C_2H_4) after the WGS reactor in the case of LPG reforming.

For examining if the reformate gas contained any condensable hydrocarbons (could potentially result from fuel leakage through the reactors), the product gas was prior to the gas analysis cooled down, via a heat-exchanger, to about $50\text{ }^\circ\text{C}$ and the condensed water was then throughout measurement checked.

No smell of condensed hydrocarbons could at this temperature be felt and no phase separation could be detected in the condensed water for any of the experiments. It can thus be concluded that the reformat gas produced within the frame work of this project does not seem to contain any hydrocarbons that may possibly condense and consequently cause a detrimental effect in for example a PEM fuel cell.

Finally, no affect on the performance attributed to the sulphur content in the reformer feed stock could in this work be detected, even though the jet fuel, i.e JP8, contained as high concentrations as 112 ppm (analysed by Saybolt Sweden AB). The high sulphur tolerance observed hereby is mainly due to the fact that, as has been described in prevailing reports (1, 18), platinum is used as the active phase of the catalysts, but also to some extent due to the relatively low space velocity applied. It should also be noted that attempts to measure the concentration of H₂S in the product gas was in this case made by the use of a Drägerrör, but no H₂S could be detected. This result strongly indicates that the H₂S formed in the SREF reaction step has most probably in downstream reaction steps been adsorbed to the inner surfaces of the fuel processor and/or became oxidised to SO₂/SO₃.

Table 2. Reformate gas composition analysed after the PROX reactor for a variety of different reformer feed stocks. The analysis were made after that the reactions have reached steady-state. *SV (SREF)* ≈ 17 000-19 000 h⁻¹, *SV (WGS)* ≈ 25 000 – 30 000 h⁻¹. *S:C* ≈ 3-4. The estimation of *SV* is based on the to the reactor in-going reaction gas flow and the total catalyst volume positioned in the reactor.

	Natural gas (S ≈ 5 ppm)	LPG (S ≈ 10 ppm)	Gasoline (S = 1 ppm)	Diesel (S= 1 ppm)	Kerosene (S < 5 ppm)	Kerosene (jet fuel, JP8) (S = 112 ppm)	Ethanol, no S
H ₂ (%)	73-74	68-70	65-70	63-67	65-66	65-66	63-65
CO ₂ (%)	~21	~24	~25	~27	~26	~25	~27
N ₂ (%)	2-3	4-6	5-10	6-10	8-9	9-10	8-10
CO (ppm)	< 50	< 50	< 50	< 50	< 50	< 50	< 50
CH ₄ (%)	1.5-3	1.25	-	-	traces	0.3	-

4.2. Verification tests with fuel cells

To gain more knowledge of the impurity tolerance of fuel cells, especially of the PEMFC, and to verify the reformat quality produced at CAT as fuel for fuel cell applications, a series of verification tests with a commercial PEMFC were carried out.

The PEMFC used in this project is a convective 4-cell stack with the nominal capacity of 3 W 2.5 V, 5 W 2.2V, produced by BCS Fuel Cells and supplied by FuelCellStore®, see Figure 6. The stack is self- humidifying and hence, it requires no external humidification of the reactant gases to be made. The air was fed to the cathode side via natural convection, thus, no forced air-flow was in this case applied. The stack is specified as being a reformat tolerant fuel cell, thus, it can be assumed that the anode electrode most probably is based on Pt-Ru/C.



Figure 6. A photo of the fuel cell stack used for the PEMFC verification tests performed within this work.

As described in section 2.1., the impurity tolerance of a PEMFC depends strongly on the operation conditions (temperature, pressure, humidity of reactant gases, etc) and the type of fuel cell components used (electrode morphology, catalyst type, membrane type, etc). For facilitating the analysis of results, we therefore believed that it was necessary to systematically investigate the tolerance of different potential impurities for this specific fuel cell type, for a specific operation condition, separately before the verification tests with “real” reformat gas were performed. Different synthetic gas blends were therefore prepared inside- and then fed to the fuel cell from a gastight bag. The concentrations of the different impurity components were chosen according to what levels that could possibly be found in the reformat gas when produced from different feed stocks. The concentrations of the added hydrocarbons and CO impurities in the gas blends were controlled by NDIR (Electra control MGA 4000-T) and FID (Flame Ionisation Detector, Bernath Atomic (BA) Model 3006). The flow rate fed to the fuel cell was in turn controlled by a rotameter. In order to ensure that the fuel cell could be treated as a differential reactor for all loads applied, and hence, that the number of H₂-molecules could be assumed to always be non-limiting, a relatively large excess of fuel was used (H₂-stoeciometric ratio >>1.2). All the fuel cell measurements were made at approximately 40°C and at ambient pressure.

Figure 7 shows polarisation curves obtained for pure H₂(g) and a synthetic reformat gas blend of 20/80 % CO₂(g)/H₂(g), respectively. As seen, no influence of the CO₂ could in this case be detected. Tests with a 25/75 % CO₂(g)/H₂(g) blend was also made, but likewise the 20/80 % CO₂(g)/H₂(g) –mixture, no impact of any CO₂ poisoning or more correctly expressed, in-situ formation of CO via the reverse gas shift reaction, could be observed.

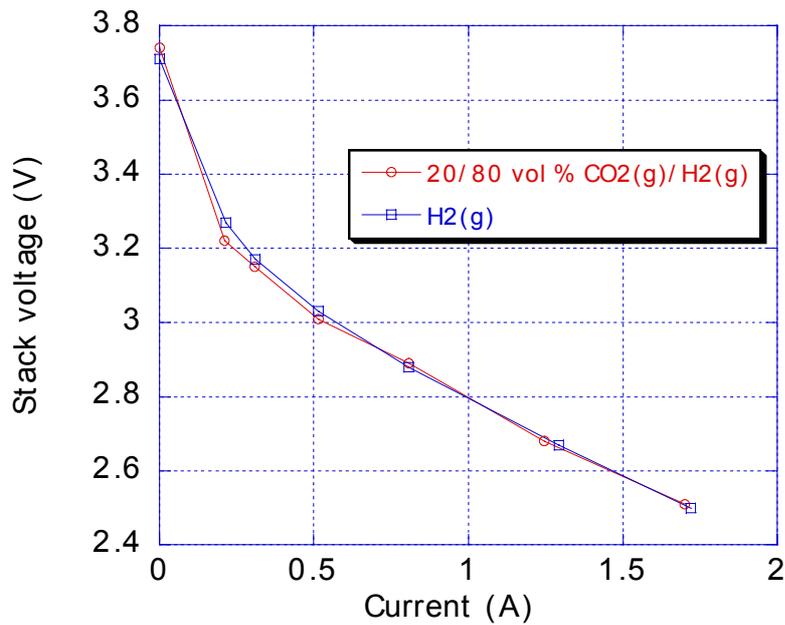


Figure 7. Polarisation curves obtained for pure $H_2(g)$ and a 20 % $CO_2/80\%$ H_2 –mixture, respectively.

As expected, CO was found to strongly poison the fuel cell, see Figure 8. The results clearly showed that the higher the concentration of CO, the larger decline in voltage drop. When the fuel was switched over to reformat gas without any CO content for some time, the voltage surged back to the initial level, indicating, as expected, that CO-poisoning is a reversible phenomenon.

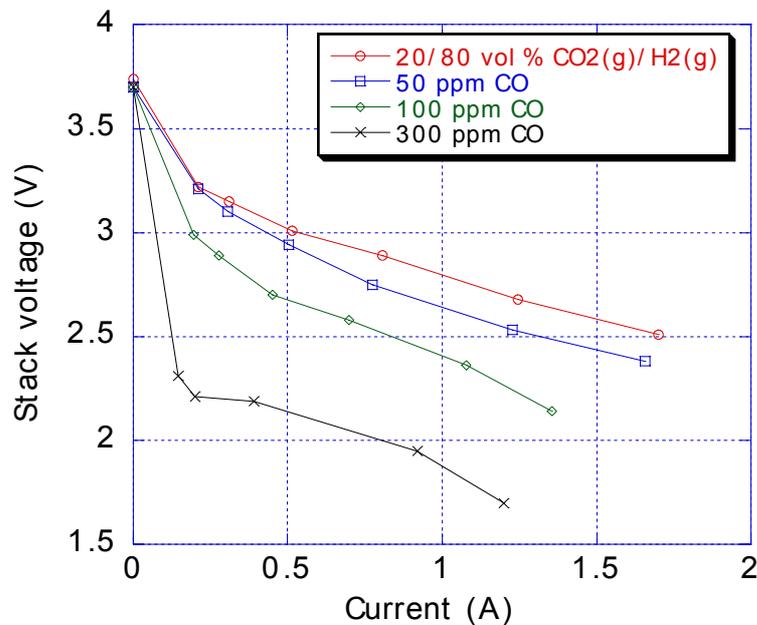


Figure 8. Polarisation curves obtained for synthetic reformat gas mixtures (20/80 % $CO_2/H_2(g)$) with various concentrations of CO.

The influence of various hydrocarbon impurities were also examined, see Figure 9. The results showed, as is also in line with the literature, that saturated hydrocarbons such as methane (CH_4) and propane (C_3H_8) were seen to have no poisoning effect on the performance. Likewise, the un-saturated hydrocarbons, i.e. ethene (C_2H_4) and propene (C_3H_6), were concluded to be only dilutant. The decline in voltage that can be seen for propene at currents < 1 A was thus established to be insignificant, since this deviation was found to be within the accuracy of the measurement.

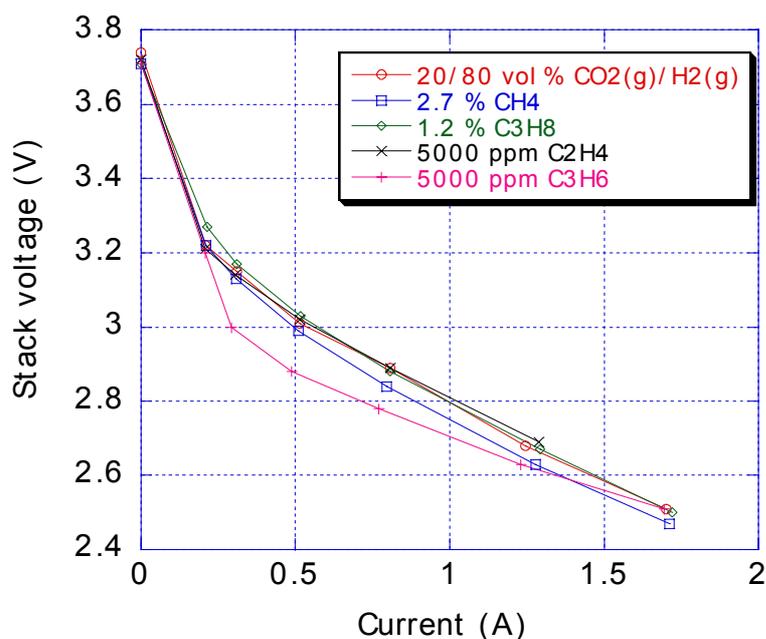


Figure 9. Polarisation curves obtained for synthetic reformat gas mixtures with various saturated and un-saturated non-condensable HC-impurities.

Finally, the impact of impurities of different condensable hydrocarbons, i.e. diesel (C_{14}), gasoline (C_6 - C_7) and ethanol ($\text{C}_2\text{H}_5\text{OH}$), were investigated. Even if there were not detected in the reformat gas produced within this project, see section 4.1., these components could potentially be expected to be found in the product gas leaving the fuel processor as a consequence of fuel slip and/or due to catalyst deactivation following long-time operation. The results are displayed in Figure 10 and 11, respectively. Impurities of diesel and gasoline do not seem to have any effect on the performance, at least not for short time operation (operation time < 1 h). In contrast, ethanol was established to cause a significant voltage drop, and the higher the concentration, the larger drop was obtained. This poisoning effect is most probably explained by the fact that ethanol is water dissolvable and can therefore be transported through the membrane to the cathode electrode surface where it is oxidised to acetaldehyde (CH_3CHO) and/or acetic acid (CH_3COOH). It should be mentioned that the characteristic odour of acetic acid could even be felt during the measurements. The phenomenon is thus similar to the well-known “methanol-cross over”-problem observed in direct methanol fuel cells (DMFC) (3). Moreover, in similar to a CO-poisoned fuel cell, it was also in this case possible to return to the initial performance by operating the fuel cell with pure hydrogen /reformat gas for some time. The recovering time was however seen to be significantly longer than for a CO-poisoned fuel cell, i.e. a few hours, since the formed acetaldehyde/acetic acid were in this case needed to be leached out.

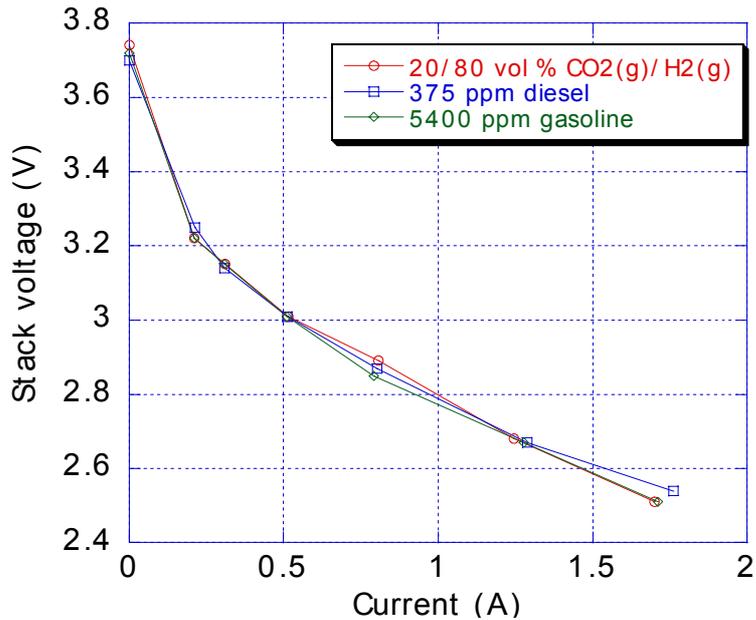


Figure 10. Polarisation curves obtained for synthetic reformat gas mixtures with impurities of heavier (condensable) hydrocarbons, i.e. gasoline and diesel.

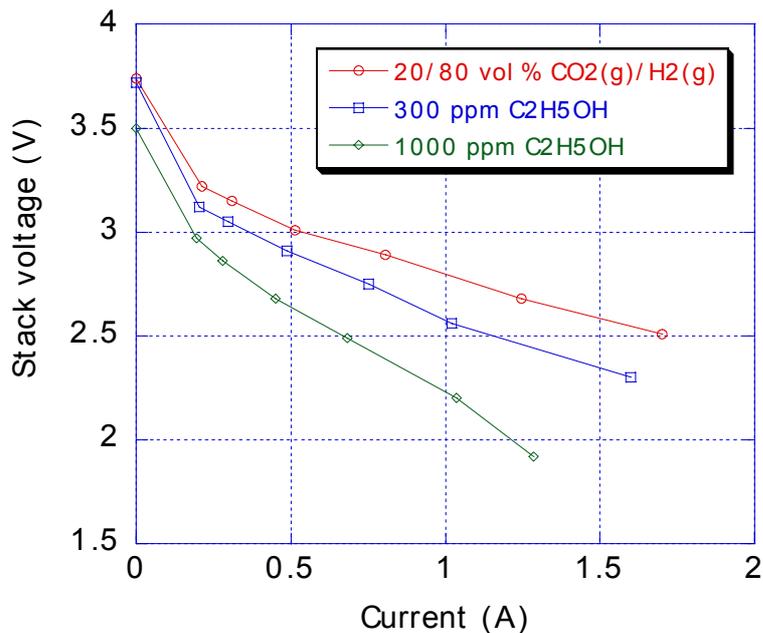


Figure 11. Polarisation curves obtained for synthetic reformat gas mixtures with impurities of ethanol.

The effect of sulphur impurities on the PEMFC's performance has not been evaluated within this work. The reason for this is twofold. First, it is well-documented that this is a serious fuel cell poison, even at extremely low concentrations (a few hundreds of ppb level) and second, it is an irreversible phenomenon (if no air purging is used, see section 2.1). In all cases, it is evident that a HDS-unit or at least a regenerative S-trap needs to be incorporated prior to the PEMFC. More information of the latter will be gained during the beginning of year 2005, when long-time operation tests (i.e. a few hundred hours) of a PEMFC integrated with CAT's reformer will be carried out.

As a final step, the fuel cell was operated with “real” reformat gas. As a consequence of that the degree of *formed* impurities in the reformat gas had been found to not differ to any extent between the used feed stocks (excluding the difference in S-content), it was decided that it would be sufficient to carry out verification tests with reformat gas produced from only one of the reformer feed stocks presented in Table 2. In this case, reformat gas produced from diesel was chosen. The results are given in Figure 12. The polarisation curve obtained for diesel reformat was seen to follow the synthetic reformat gas very closely up to around 0.8 A. At higher currents, the power efficiency was seen to drop. This performance drop at higher currents is here attributed to some CO-poisoning. The CO-concentration in the diesel reformat gas was measured to be around 50 ppm, which is also rather well agrees with the results obtained for the synthetic gas blend containing approximately 50 ppm CO, see Figure 12. It should be noted that no additional poisoning effect due to S could be distinguished under the applied experimental conditions, even though the diesel used contained about 1 ppm of S. This could eventually indicate that the sulphur had been adsorbed to any inner surface of the fuel processor and/or dissolved (as SO₃) in the condenser in which the product gas is cooled down before the reformat gas for fuel usage was collected (see section 4.1).

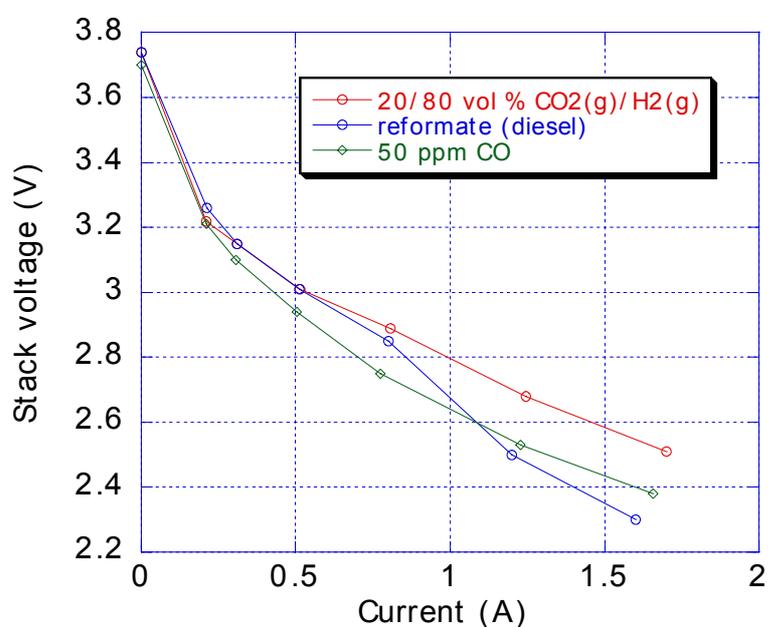


Figure 12. Polarisation curves obtained for reformat gas (reformer feed stock: diesel). As a comparison, the equivalent polarisation curves measured for synthetic reformat gas mixture without any CO and with around 50 ppm CO have also been inserted.

Verification tests were also planned to be carried out with a SOFC. As a consequence of that no SOFC was available for a, with respect to the project’s budget, reasonable cost, no measurements with a commercial SOFC could within this project be performed. It should be underlined though, in contrast to the PEMFC, that there are very few impurities that may have a poisoning effect on the SOFC. According to the literature, only sulphur and coke need to be considered (see section 2.1.). As already mentioned, the low tolerance against these impurities are related to the fact that commercial SOFC include Ni-based electrodes and that this tolerance could be significantly improved by exchanging the Ni to Cu or a precious metal, e.g. platinum. To illustrate the effect of the improved sulphur tolerance when Pt is used, some preliminary verification tests were run with a lambda sond (type: Bosch LSM 11).

As a matter of fact, the working principle of the lambda sond is the same as for a fuel cell (designed for measuring the oxygen concentration in a fuel-air mixture) and in addition, it is built up by about same material components as commercial SOFC, except for that Pt is used as active catalytic phase instead of Ni. In this case, the lambda sond was placed inside a tube in which a constant synthetic reformat stream was flowing. The working temperature of the lambda sond is around 350-400°C, thus, lower than the average working temperature for commercial SOFCs, and thus becomes theoretically even more S-sensitive than a real SOFC. In similar to the PEMFC-experiments, different loads were applied to the lambda sond and the corresponding voltage and current data were measured. Measured data collected for pure reformat gas were then compared to data obtained for reformat gas containing different concentrations of H₂S (10-100 ppm). The results indicated no poisoning effect, not even for the highest S-concentration applied, i.e. 100 ppm H₂S. This S-tolerance is an extreme improvement compared to the Ni-based electrodes where negative effects have been reported for as low concentrations as > 0.05-1 ppm H₂S (see section 2.1.).

4.3. Adsorption tests

The experimental evaluation tests with PEMFC have shown negligible impacts of reasonable amounts (> 0.1 %) of hydrocarbons in the fuel stream. The only compounds, which showed detrimental effects on the fuel cell performance were oxygenated hydrocarbons (alcohols) and, as expected, CO.

In parallel to the reforming evaluation tests presented in section 4.1, we also performed comprehensive studies of the reformat gas composition when steam reforming different fuels (no alcohols included) for a longer operation time (i.e. more than 500 h). The results showed that when using reasonable space velocities in the system, only light aliphatic hydrocarbons can be found downstream the PROX-reactor. Consequently, no, with respect to PEMFC-usage, harmful HC-components will be found during the initial phase of operation (when the catalysts are fresh). It was however seen that the catalyst degradation will be accompanied by increasing amounts of intermediate products like the olefins ethene and propene, in a position upstreams the WGS and PROX reactors. These compounds will then be hydrogenated to yield the corresponding aliphatic hydrocarbons in the WGS/PROX-reactors. Fuel slip could also be observed if the steam reforming temperature was decreased to levels below approximately 680°C. Again, the compounds which might be found following catalyst deactivation for a longer period of time are not harmful to the fuel cell according to our evaluations (to be noted that this excludes the case of alcohol reformation!). Consequently, the need for a hydrocarbon trap seems to be more psychological than real.

If a hydrocarbon trap should be necessary to install, it should be designed as a thermally regenerative trap, i.e. a TSA-unit. One approach for this would be to use CAT's patented wire meshes coated with different suitable adsorbers. To investigate the potential of this concept, a series of regenerative adsorption tests were performed within this work. Tests to adsorb the following impurities were made: CO, ethene, propene, slip of diesel, gasoline and ethanol. Evaluation of potential S-traps have been performed previously at CAT, and will also be discussed in the following.

- Adsorption of CO and various hydrocarbons

The different experiments and the related results performed in this work are listed in Table 3. All the coatings/adsorbents were prepared onto thermally sprayed wire meshes (Kanthal, mesh no. 16). For each adsorption test, 20 equally coated wire meshes were placed on top of each other in a reactor tube positioned inside a furnace. A dry synthetic reformat gas mixture containing the different impurities, was fed to the inlet of the reactor tube. The concentration of each impurity was measured prior to the adsorbent package and then, as a function of time, after the adsorbent package. Mass flow controllers were used for mixing the actual gas blends containing impurities of ethene, propene and CO, respectively. For obtaining the mixtures with impurities of gasoline and diesel however, a small part of the CO₂ gas stream was prior to the mixing with the final reactant gas flow, bubbled through a container (heated up to 40°C) including the condensable component. The adsorption experiments were carried out at around 35-40 °C. After each finalized adsorption test, the adsorbents were regenerated at 200 °C with pure synthetic reformat gas. The adsorption capacities for condensable and non-condensable hydrocarbons, respectively, were estimated from the amount of desorbed impurity. The concentration of HC was measured by a FID (Flame Ionisation Detector, Bernath Atomic (BA) Model 3006), which signal was plotted as a function of time on an X-Y-writer. The capacity for CO adsorption was measured by the use of a NDIR (Electra control MGA 4000-T).

Table 3. Summary of the adsorption tests.

Impurity component	Inlet concentration (ppm)	Load (Nm ³ /h·m ² wire mesh)	adsorbent	Estimated adsorbent capacity (mg/gram adsorbent)
gasoline (C ₇)	150	25	hydrophobic zeolit (CBV 780)	3.7
diesel (C ₁₄)	40	25	hydrophobic zeolit (CBV 780)	7.3
ethanol (C ₂ H ₅ OH)	170	25	hydrophobic zeolit (CBV 780)	10
ethene (C ₂ H ₄)	420	25	activated alumina/ hydrophobic zeolit (CBV 780)	No adsorption
propene (C ₃ H ₆)	300	25	activated alumina/ hydrophobic zeolit (CBV 780)	No adsorption
CO	300	33	activated alumina	1.4

As can be seen in Table 3, significant amounts of condensable HC and ethanol can be adsorbed by the use of hydrophobic zeolite. In contrast, it was found that it was not possible to remove any of the un-saturated, non-condensable HC such as ethene and propene by either hydrophobic zeolite or activated alumina. The tests indicated however that some CO can be eliminated by activated alumina.

To summarise, the adsorption tests have shown that it is possible to remove fuel slip of ethanol and heavier HC such as gasoline and diesel, but also to some extent detrimental components such as CO by the use of CAT's regenerative adsorbers. By adsorbing some of the CO, the PROX reactor will be relieved and could thereby be simplified and its operation would be more stable. Furthermore, if the regeneration cycle is short, the amount of wire-mesh adsorber can be decreased to a very small amount. With the adsorption capacities obtained, the HC/CO-trap could indeed be designed in a very compact manner. If the regeneration cycle is set to 1 hr, the amount of wire-mesh adsorber will typically be 1 – 2 m² for a unit producing 10 nm³/h of hydrogen. This amount of adsorber can be contained in a vessel with a size of less than 5 litres.

- Sulphur adsorption

CATs basic idea is to utilise catalyst formulations with an increased sulphur tolerance. However, in the case of heavy naphtha reforming (kerosene), the impact of sulphur will be so high that it is worth installing a catalytic step for hydrogenolysis of sulphur containing compounds to H₂S and to trap H₂S in a ZnO-adsorber. As an alternative solution it is possible to convert the sulphur-containing compounds into H₂S in the steam reformer and to trap H₂S on a suitable adsorber downstream the steam reformer. In order to compensate for the sulphur, either the amount of steam-reforming catalyst or the reaction temperature can be increased. For instance, when processing feed stocks with a sulphur content of more than 100 ppm of S, it is applicable to use reaction temperatures exceeding 850°C, see Figure 13. The results shown in Figure 13 were obtained for extreme space velocities in order to enable kinetic evaluations. In normal operation, the space velocity should be around 10 000 h⁻¹, i.e. the amount of catalyst will be 20 times higher.

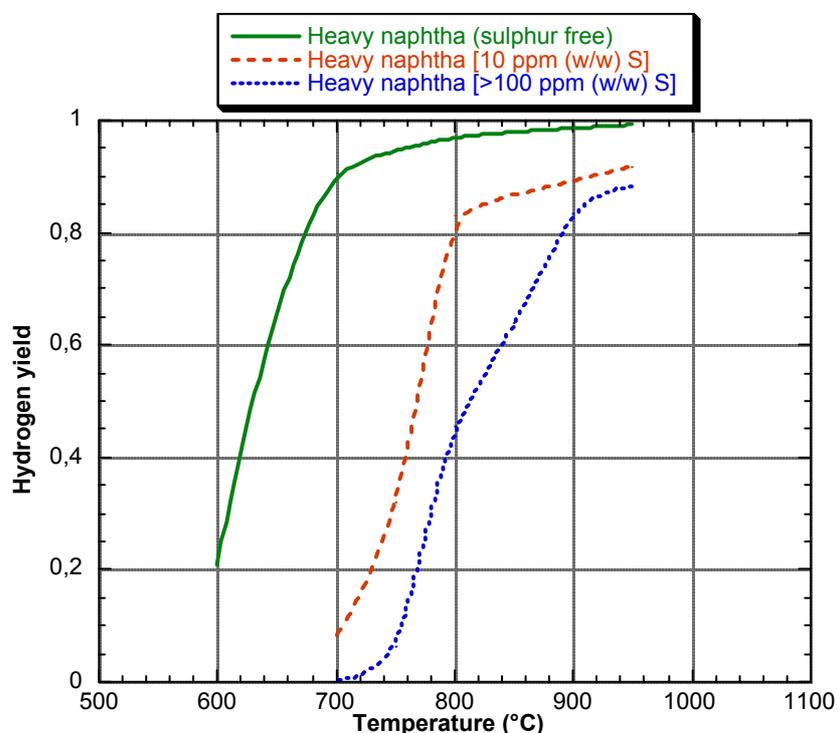


Figure 13. Steam reforming of commercial feed stocks containing sulphur ($SV \approx 200\ 000\ h^{-1}$).

CAT has developed a method to coat wire-meshes with porous zinc, Figure 14. The metal is slowly converted into ZnO in the reformer gas stream by uptake of oxygen from water and carbon oxides. The ZnO formed will then effectively react with H₂S to form ZnS. We are currently exploring this method to be used together with our sulphur tolerant reforming catalyst. In Figure 15, the effects of Zn-wire meshes are shown when placing a package of such wire meshes upstream the water-gas-shift reactor. The influence on the reaction rate in the reversed water-gas reaction is shown as a function of the time. The inlet concentration of H₂S was 15 ppm (v/v) in a gas mixture containing 10% CO₂, 10% H₂ and balance N₂. The formation rate of CO in the consecutive tests is shown when placing different numbers of Zn-wire meshes in the reactor. From the figure it is evident that the trapping efficiency of the Zn-wire meshes is rather high. The investigations indicate a H₂S-removal of 80% at a gas load of 400 nm³/m², h of Zn-mesh and a value of >99% at gas load of 100 nm³/m², h. The ZnO-wire meshes will enable a compact and effective design of the H₂S-trap. As an alternative to these Zn/ZnO-wire meshes, it is also possible to use wire meshes coated with promoted metal oxides. Although showing less sulphur-removal capacity, these structures can be thermally regenerated and re-used, i.e. they are suitable for thermally regenerative sulphur-traps (i.e. a TSA unit).

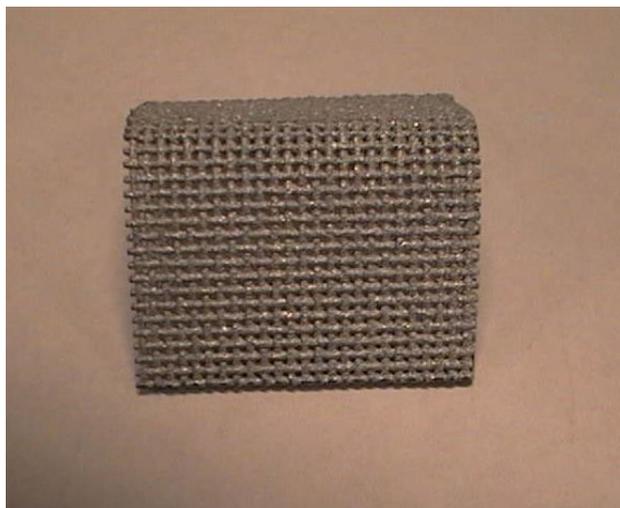


Figure 14. *Wire mesh coated with porous Zn/ZnO.*

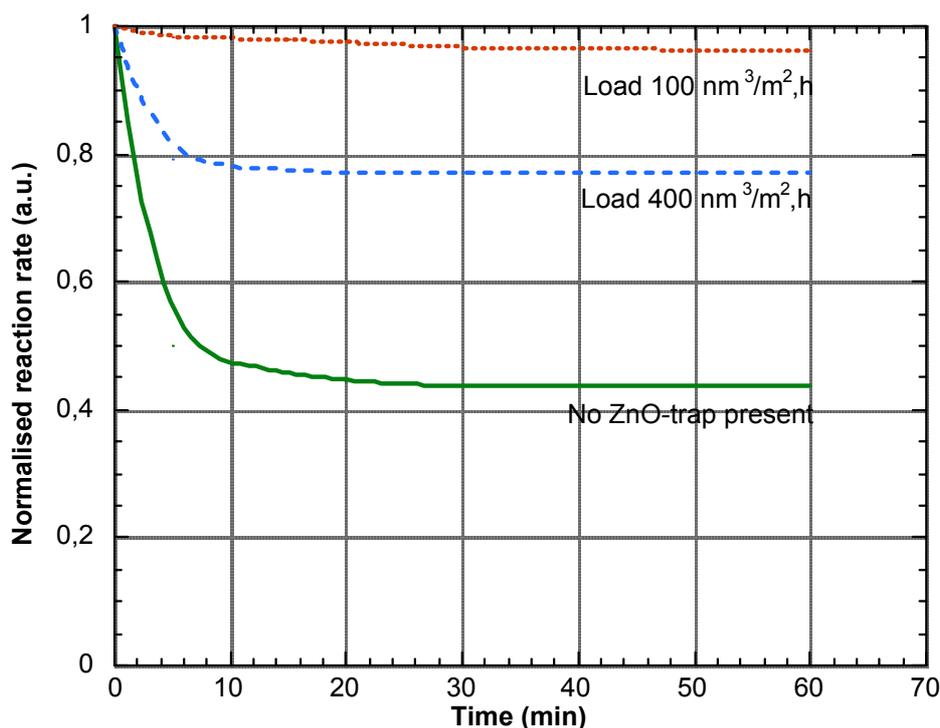


Figure 15. Catalyst methods of desulphurisation. A number of Zn-coated wire meshes were placed upstream the WGS-catalyst. The effects on the reaction rate of the reverse WGS-reaction is shown for different gas loads on the Zn-meshes. The inlet H₂S-concentration was 15 ppm (v/v). Normalised reaction rate for CO-production vs. time.

A typical small-scale hydrogen generator will produce 10 nm³/hr of hydrogen. The amount of ZnO-adsorber necessary on a yearly basis is shown in the Table 4 below for different fuels. The S-adsorption capacity of ZnO was set to 20 weight%. The amount of Zn/ZnO on a wire mesh substrate can range between 300 and 600 g/m².

Especially in cases with high S-contents it is advisable to use the regenerative S-trap in order to simplify maintenance and to save space.

Table 4. The estimated amount of ZnO-adsorber necessary on a yearly basis for a STUR-30 kWh₂ (10 nm³/hr H₂) system for a variety of reformer fuels. The estimation is based on the adsorption capacity measured for CAT's thermally sprayed wire meshes coated with Zn/ZnO.

Natural gas, 5 ppm S (v/v) => 140 g S/yr (≈0.7 kg ZnO/yr)
 LPG, ≈ 10 ppm S(v/v) => 280 g S/yr (≈1.4 kg ZnO/yr)
 Naphtha, 5 ppm (w/w) => 80 g S/yr (≈ 0.4 kg ZnO/yr)
 Kerosene, 100 ppm (w/w) =>1600 g S/yr (≈8 kg ZnO/yr)

5. Conclusive discussion

CAT has during the last two years designed, constructed and evaluated compact and fully integrated fuel processor(s), including downstream CO-purification, for small-scale hydrogen production (i.e. STUR). Most recently, a reliability study of a fully automatic optimised STUR-10 kWh₂ system was successfully finalized. Likewise in all technology development, the development of the complete STUR system has been performed step-wise, which work until today have been financed by the Swedish Gas Centre (SGC), the Swedish Defence Material Administration (FMV), and Sydkraft Gas AB, see Figure 16. Furthermore, the study reported herein has now moved this development work another step forward. It has demonstrated the need for reformat purification for various hydrogen applications, and also given more insight into different, today available, gas purification units/systems. From now on, the work is planned to be concentrated on two different hydrogen user categories, i.e. fuel cell applications (including PEMFC and SOFC) and hydrogen production for filling stations. Some continuation work on the first mentioned user category (fuel cell applications) will be initiated already in the beginning of 2005, and will be financed by FMV. As regards the work on the filling station application, a project proposal is presented in the end of this section. Before this proposal, some conclusive remarks regarding the herein reported work will be outlined.

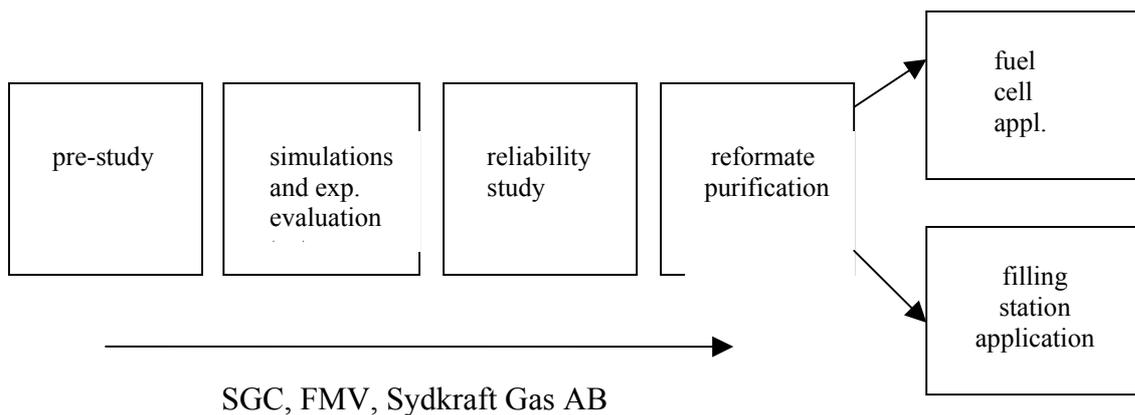


Figure 16. A Schematic illustration of the step-wise development work performed and planned at CAT within the field of reformer prototypes for small-scale hydrogen production.

For choosing a suitable purification technique for meeting up with a purity grade demand for a specific application, parameters such as hydrogen recovery, impurity tolerance, life time, size and cost of the totally integrated system (fuel processor + purification unit) have to be taken into consideration. In Appendix 2, a summary of advantages and disadvantages of each technique are listed. Another aspect to take into account before a purification unit can be purchased is also of course the market availability of the purification technology, here with focus on small scale hydrogen production. An idea of the current (summer/autumn-2004) market availability and cost of different units/systems can be gained from Appendix 1.

With respect to the extremely high purity grade required for the electronic industry, the metallurgic industry and for the float glass manufacturing industry ($> 99.999 \text{ H}_2(\text{g})$), respectively, the Pd/alloy membrane seems to be the obvious technology of choice. For the chemical industry and so also the pharmaceutical industry, however, PSA may also be a good alternative. For both Pd-alloy membranes and PSA, an elevated pressure of the reformat gas is required. A general drawback of producing reformat at an elevated pressure is that the weight of the fuel processor increases as a consequence of that the walls of the reactors have to be significantly thicker. The overall size of the fuel processor however tend to significantly decrease if it is integrated with a Pd-alloy membrane or PSA since these purification units allow the PROX/methanisation reactor to be removed.

According to the literature and the evaluation results obtained in this work, it seems as the most crucial components that need to be removed before the reformat gas can be fed to a PEMFC is S, CO, halogens, ammonia and oxygenated hydrocarbons. One compact and relatively non-expensive way for at least removing S, CO and oxygenated hydrocarbons is to install CAT's regenerative adsorbent reactors up-stream the PROX reactor. The disadvantage of using this approach is that relatively small amounts or even none of the diluting components N_2 nor CO_2 are eliminated, where the latter component could, even though not detected in this work, may have an indirect poisonous effect on the fuel cell. For also eliminating CO_2 , the installation of a PSA downstreams the WGS reactor seems to be the most advisable choice. In this context, it should be underlined that the use of PSA for this application has even been recommended by the manufacturers of both polymer and Pd-alloy membranes (27,33). To avoid too large and especially, too heavy systems, a fast cycle PSA unit is of course preferable. Unfortunately, this technology has not yet reached commercial status, and is therefore still relatively expensive. Furthermore, another approach for obtaining a very high purity grade is to install a Pd-alloy membrane. For enable an appropriate cost and size/weight estimation, it is in this case important to also consider the relatively high impurity intolerance of the Pd-alloy. In order to avoid reduction in the membrane's throughput, it seems, considering the experimental evaluation results of this work, to be advisable to combine the membrane with upstream traps for both S and unsaturated hydrocarbons. Anyway, to gain more knowledge about the suitability of the Pd-alloy membrane technology for reformat purification, CAT has most recently ordered a Pd-Cu membrane from the company ATI Wah Chang. Evaluation tests with their membrane type in combination with CAT's reformer technology are planned to be launched in the beginning of 2005. Further work will also be put into evaluating the impurity tolerance of the PEMFC at long-time "real reformat" operation.

In comparison to PEMFC, SOFC is a very impurity tolerant system. As discussed in section 2.1., only S and coke (in the case of internal reforming) seem to be cumbersome. While S can be removed by up-streams installed regenerative adsorbent, coke formation has to be avoided by other means. One possible way for reducing the risk of coke poisoning is, as previously mentioned, exchange the commercial Ni-based electrodes into for example precious metal activated electrodes. Another approach is to pre-reform the feed stock before it is entering the SOFC. The hydrogen formed during the latter will in turn suppress the *in situ* coke formation.

Finally, in the case of that the reformat gas is to be used as additive in natural gas for driving NGV vehicles, small amounts of CO, hydrocarbons and sulphides will in contrast to the other H_2 -using systems/industries not cause any detrimental effects. In this case, it is more important to remove components with diluting effects, i.e. nitrogen and carbon dioxide.

In addition to diluting the combustible gases, carbon dioxide can also cause corrosion in high-pressure tanks and in the compressor system. Consequently, the system used in fuel-cell application shall, be stripped from the PROX-reactor where air (nitrogen) is injected. Carbon dioxide can be removed by means of a simple PSA-device normally found in systems for drying compressed air, e.g. from the company Donaldson, see Appendix 1. In order (if necessary) to remove CO, a methanisation reactor can be implemented into the system. Methanisation is a quick exothermic reaction, accomplished at rather low temperatures in the presence of hydrogen, CO being more reactive than CO₂. Figure 17 below, indicates the performance of CAT's wire-mesh catalyst for methanisation at extremely high space velocities.

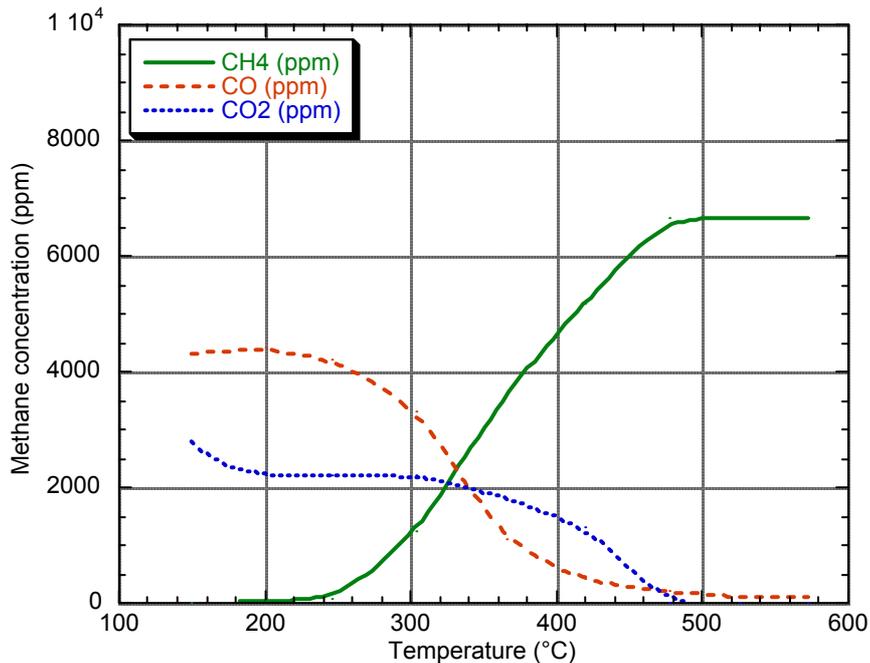


Figure 17. Methanation on wire-mesh catalyst at $SV \approx 100\,000\ h^{-1}$.

Consequently, a suitable system would consist of the following unit-reactors, see also Figure 18:

- A) Steam reformer reactor
- B) WGS-reactor
- C) PSA-unit for removal of carbon dioxide and water
- D) Methanisation reactor for CO_x-removal
- F) Applicable heat exchangers, pumps and blowers

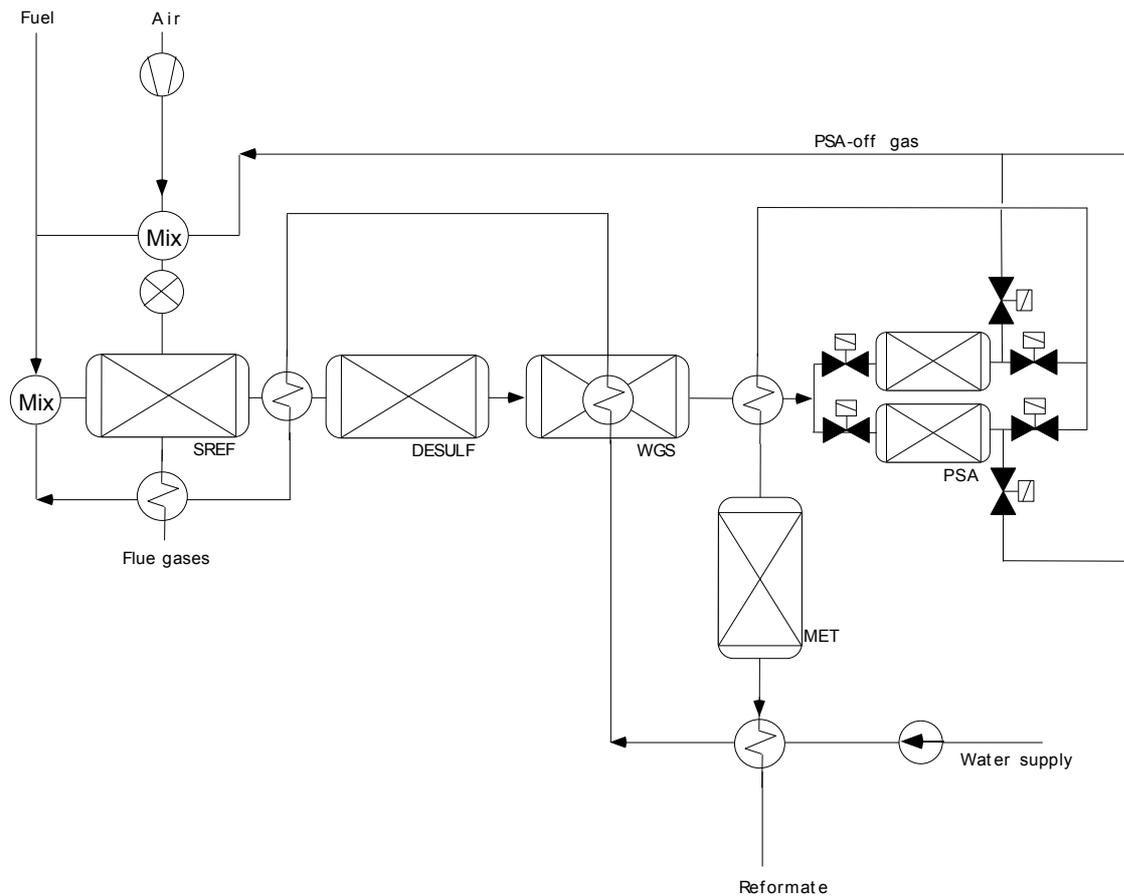


Figure 18. System overview for a filling station.

The reformat gas leaving the unit described above will contain hydrogen and methane and only very small amounts of trace components like carbon oxides and water.

- Project proposal for filling station applications

We propose a pre-study to give a detailed prospect for a fuel processor system for filling stations with a capacity of about 10 – 20 nm³/h of hydrogen. The pre-study will focus on the following items:

- Detailed system description for a filling-station application including gas purification
- Process-and instrumentation diagrams
- Process data
- General lay-out of the unit with 3D CAD-drawings
- Interface to existing system and installation
- Cost estimation and administration of a demonstration project
- Financing

The overall aim is to initiate the demonstration project by the autumn off 2005 and to commission the unit at a suitable site by the spring of 2006. Apart from using natural gas as the feed stock it would be equally simple to use biogas and LPG. This fact will probably broaden the application and simplify the financing of the demonstration unit(s). In the demonstration project it shall be possible to build, erect and commission more than one unit.

6. References

1. SGC-report under print "Reliability study of STUR-10 kWh₂", Anna-Karin Jannasch, Fredrik Silversand, Catator AB, 2004
2. Communication with AGA Linde
3. Fuel Cell Handbook, 5th edition, 2000
4. V.S. Bagotzky, N.V. Osetrova, A.M. Skundin, Russian J. Electrochem., Vol. 39, No. 9, p. , 2003.
5. K. K. Bhatia, C-Y. Wang, Electrochim. Acta, Vol. 49, p. 2333, 2004
6. S. Gottesfield, J. Pafford, J. Electrochem. Soc., Vol. 135, p. 2651, 1988
7. J. C. Amphelht, R.F. Mann, B.A. Peppley, Int. J. Hydrogen Energy, Vol. 21, No.8, p. 673, 1996
8. C. Stone, Ballard Power Systems, Abstract in 2004 Fuel Cell Seminar, San Antonio, 2004.
9. Presentation of Dr. Paloma Ferreira, CIEMAT-CSIC (Centre for Energetic, Environmental and Technological Research, Institute for Catalysis and Petrochemistry-Spanish Council for Scientific Research, Madrid, Spain, 2004
10. S. Watanabe, M. Tatsumi, M. Akai, Japan Automobile Research Institute, Tsukuba, Japan, Abstract in 2004 Fuel Cell Seminar, San Antonio, Texas
11. P.J. de Wild, R.G. Nyqvist, F.A. de Bruijn and E.R. Stobbe, Energy Research Center of the Netherlands ECN.
12. C. Sishla, G. Koncar, R. P. Laton, S. Gamburzv, A.J. Appleyby, O.A. Velez, J. Power Sources, Vol. 71, p. 249, 1998
13. D.C. Papegeorgopoulos, F. A. de Bruijn, J. Electrochem. Soc., Vol. 149, p. A140, 2002
14. F.A. de Bruijn, D.C. Papegeorgopoulos, E.F. Sitters, G.J. M Janssen, J. Power Sources, Vol. 110, p. 117, 2002
15. F.A. Uribe, S. Gottesfeld, T.A. Zawodzinski, J. Electrochem. Soc. , Vol. 149, p. A293, 2002
16. Y. Matsuzaki, I. Yasuda, Solid State Ionics, Vol. 132, p. 261, 2000
17. E.E. Petersen and A.T. Bell, "Catalyst Deactivation", Marcel Dekker Inc., New York, p. 152, 1987
18. SGC-report " Fuel Processor for small scale production of hydrogen", no. 139, 2003, Fredrik Silversand
19. Z.F. Zhou, C. Gallo, M.B. Pague, H. Schobert, S.N. Lvov, J. Power Sources, Vol. 133, p. 181, 2004
20. C.G. Bauer, T.W. Forest, Int. J. Hydrogen Energy , Vol. 26, p. 55, 2001
21. P. Tunestål, M. Christensen, P. Einewall, T. Andersson, B. Johansson, O. Jönsson, Manuscript "Hydrogen Addition For Improved Lean Burn Capabilities of Slow and fast Burning Natural Gas Combustion Chambers 2002-01-2686".
22. Report "30 years of PSA Technology for Hydrogen Purification ", J. Stöcker, M. Whysall, UOP, Antwerp, Belgium, G.P. Miller, UOP, Des Plaines, Illinois, 1998
23. Report "PSA Technology Hits the Fast Lane", M. Babicki, A. Hall, 2003
24. Communication with Dr. Sean Mezei, QuestAir
25. Communication with Dr. Scot Appel, SeQuel Technologies
26. Communication with Dr. Don White, Donaldson Filtration Solutions, see also www.donaldsson.com.
27. Communication with Mr Riu Oliver, H₂-product group, Air Liquide Engineering.
28. Communication with Mr Charles T. Page, Air Product and Chemicals, Prism membranes.
29. Communication with Mr Hayashi Manabu, Ube Industries

30. Communication with Dr Limaye Santosh, Vestceramics
31. T.S. Moss, N.M. Peachey, R.C. Snow, and R.C. Dye, *Int. J. Hydrogen Energy*, Vol. 23, No. 2, p. 99, 1998
32. Report "Hydrogen Purification: Efficiency comparisons between Nickel/Titania and Palladium membrane Technologies", D. Alvarez, J. Spiegelman, S. Petani, see also <http://www.aeronex.com>
33. Specification for Johnson-Matthey's Pd-alloy hydrogen purifiers.
34. Communication with Dr Tom Purcell, Johnson & Matthey.
35. Communication with Prof. Robert Buxbaum, REB Research & Consulting.
36. R. Farrauto, S. Hwang, L. Shore, W. Ruettinger, J. Lampert, T. Giroux, Y. Liu, O. Ilinich, *Annu. Rev. Mater. Res.*, 33:1-27, 2003
37. Ghenciu, A.F. *COSSMS* 6, 389, 2002
38. X. Wang, R.J. Gorte, J.P. Wagner, *J. of Catalysis*, Vol. 212, p. 225, 2002
39. A. Gouget, F. Meunier, J.P. Breen, R. Burch, Mi.I. Petch, A.F. Ghenciu, *Journal of Catalysis*, 226, 382-392, 2002
40. J.M. Zalc, V.Sololovskii, D.G. Löffler, *Journal of Catalysis*, 206, 169-171 (2002)
41. J.P. Wagner, A.L. Wagner, L.C. Yeping, US Patent Application, Appl. No. 10/758, 552, 2004
42. US Patent Application Publication, Appl. No: 10/108/814, 2002
43. R.R. Willigan, R. Radhakrishnan, H. Cardator, S.M. Opalka, Z. dardas, T.H. Vanderspurt, *Pre-prints-American Chemical Society, Div. Pet. Chem.*, Vol. 49 (1), p. 42, 2004

Appendix 1. Summary of different available reformat purification units developed and manufactured by different companies.

Purification technology	Selling company	Name of unit	Product flow rate (Nm ³ /h)	Dimensions (m)/ Weight (kg)	Operation T (°C)	Feed P (bar)	Product P (bar)	H ₂ -recovery (%)	H ₂ -concentration of product gas (%)	Estimated Cost (\$)
PSA	Quest Air	H-3200	5-200 5	1.42*1.10*2.25/ 1700-2900 1.2*1.5*2.3/ up to 1700-3000	4-50 50	3-21 4	< 0.5 bars less than feed pressure	73	Depends on operation conditions ~99 <10 ppm CO <10 ppm C3+ <0.1 ppm H2S	90 000 ³
Fast cycle PSA	SeQuel Technologies	prototype	1-6 6	Height=1 ¹ Diameter= 0.4 ¹	-	2.7-5 2.7	~ 0.1 bars lower than feed pressure	≥ 60 60	depends on operation conditions	20 000 ¹
PSA	Donaldson Company	ALG20-60S	10	-	-	10	-	70	Elimination of CO ₂ , HC, SO ₂ and water.	5195 without pneumatic controller ² , 7290 with pneumatic controller ²
Pd-Ag membrane	Idatech	-	0.03	-	350-450	7-15	1-2	-	> 99	For lease only: 2000/month
Pd-Ag membrane	Johnson-Matthey	-	5-500	-	350	21	0-2	depends on operation condition	>99.9	88 000 (5 Nm3/h) ≥3000 000 (500 Nm3/h)
Pd-Ag membrane	Power & Energy	-	Small-scale ≥ 1 Large-scale ≈78- 625	-	350-450	≤13	Not fixed	60-80	Depends on operation condition	-
Pd-Cu membrane	ATI Wah Chang	-	0.8-3.8	Weight=21-27 kg	350-400	10	ambient	70	> 99.999	9255-22 922
Pd-Ag membrane reactor	R & B Consulting	prototype	0.72	-	430	>25 ³	0.1	70	99.999	-
TSA+Metal Oxides (e.g. Ni/NiO)	SAES Pure Gas	-	5-500	-	20-35 (purification) ≈ 200 (regeneration)	3.5-10	max. 1 bar lower than feed gas pressure	depends on operation condition	Water at ppb-levels H ₂ S at ppb-levels CO at ppb-levels	125 000 (15 Nm3/h) 220 000 (150 Nm3/h)

PROX	estimations made by CAT	-	estimation based on 1 Nm3/h	< 5 kg	120-180	ambient	ambient	-	~ 70 < 20 ppm CO	~ 100
Methanisation	estimations made by CAT	-	estimation based on 1 Nm3/h	< 5 kg	200-300	ambient	ambient	-	~ 70 < 20 ppm CO, under the assumption that CO ₂ has been removed.	~ 20

- 1) According to communication with Dr Limaye Santosh, Vestceramics
- 2) The pneumatic controller will allow you to change the cycle time and repressurisation time to attain optimal performance.
- 3) By the company recommended feed gas pressure

Appendix 2. Summary of advantages and disadvantages of different reformate gas purification techniques.

Technology	Advantages	Disadvantages
PSA	<ul style="list-style-type: none"> - conventional PSA = established technology - delivery of product gas at high pressure - relatively long life-time of adsorbent - generates high purity grade of product gas, i.e. > 99.9 % - besides water and condensable hydrocarbons, impurity tolerant - no PROX/methanisation reactor is needed - rapid start-up 	<ul style="list-style-type: none"> - sensitive to liquid components, e.g. water, heavier HC, especially the Fast Cycle PSA - moving parts (valves) - difficult to scale - conventional PSA=large, heavy - smaller, more compact units, e.g. Fast Cycle PSA, still immature and expensive technology
Polymer membrane (Hollow fibre membrane)	<ul style="list-style-type: none"> - operates at relatively low temperature - high tolerance towards impurities - no moving parts 	<ul style="list-style-type: none"> - high pressure required - delivery of product gas at low pressure - relatively non-selective - low purity grade at moderate hydrogen recovery, i.e. ~85 % H₂(g).
Pd-alloy membrane	<ul style="list-style-type: none"> - generates excellent purity grade of product gas, i.e. > 99.99 %. - water tolerant - easy to scale - no PROX/methanisation reactor is needed - no moving parts 	<ul style="list-style-type: none"> - high pressure required - delivery of product gas at low pressure - fragile to rupture - sensitive to poisons such as S, O₂, halogens. - expensive
Ni/NiO-catalyst	<ul style="list-style-type: none"> - generates excellent purity grade of product gas (i.e. > 99.999 % H₂(g)), under the assumption that the feed gas is relatively pure, i.e. approx. > 99 % H₂(g) - operating at ambient temperature and pressure. - no moving parts 	<ul style="list-style-type: none"> - pyrophoric, thus, very sensitive to O₂. - short life time in the case of reformate purification - time consuming regeneration
TSA	<ul style="list-style-type: none"> - operates at ambient pressure - non-expensive - no moving parts 	<ul style="list-style-type: none"> - conventional TSA: time consuming regeneration ¹ - difficult to obtain high product purity grade.
Absorption	<ul style="list-style-type: none"> - in general lower pressure drop needed than for membranes and PSA - product gas delivered at high 	<ul style="list-style-type: none"> - complex solvent and recirculation systems are needed

	pressure	
Water-gas shift reaction (WGS)	<ul style="list-style-type: none"> - increases the hydrogen efficiency - cheap - no pressurisation of reaction gas is needed - no moving parts - easy to scale 	<ul style="list-style-type: none"> - only CO-removal - very or moderately sensitive to S (depending on the catalyst formulation)
Preferential Oxidation Reaction (PROX)	<ul style="list-style-type: none"> - cheap - no pressurisation of reaction gas is needed - no moving parts - easy to scale 	<ul style="list-style-type: none"> - only CO-removal - sensitive to S - dilute fuel stream - critical temperature control of reactor is needed
Methanisation	<ul style="list-style-type: none"> - cheap - no pressurisation of reaction gas is needed - no moving parts - easy to scale 	<ul style="list-style-type: none"> - only CO-removal - methane concentration increases - very or moderately sensitive to S (depending on the catalyst formulation) - for efficient CO-removal, CO₂ has to be upstream removed

¹ CAT suggested regenerative adsorbent wire mesh concept is a so called Fast Cycle TSA, where the regeneration cycle is, compared to conventional TSA, significantly reduced, see section 4.3. in this report.



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