



IEA - HIA Task 16
Hydrogen from Carbon Containing
Materials

Subtask C

**Small-scale Reformers for Stationary
Hydrogen Production with Minimum
CO₂- emissions**

Preface

Task 16 to the IEA Hydrogen Implementing Agreement concerns Hydrogen production from Carbon-Containing Materials. This Task started in March 2002 and will be finalized in 2005. The overall objective is to promote the development of efficient and economic processes for hydrogen production from fossil and biomass resources, while keeping CO₂ emissions at a minimum.

The activities are organised in three Subtasks:

A: Large-scale integrated hydrogen production

B: Hydrogen from biomass

C: Small stationary reformers for distributed hydrogen production

Subtask C has been a task-shared activity with nine industrial companies, six academic institutes and R&D companies. The goal was to provide recommendations on small-scale reforming based on current commercial and R&D activities of the members.

There are a large number of international networks and projects on hydrogen technologies but very few of them address in depth issues related to small-scale reforming. We are convinced that by working together on technical and market barriers facing small-scale reforming, we can contribute to the future hydrogen economy by advancing this transition pathway to hydrogen.

During the three years of the Subtask C program, the group members have demonstrated strong commitment to the program with continuous and significant contributions. Several presentations, reports and memos have been submitted and thoroughly discussed. The result is a comprehensive technology assessment and an analysis of market requirements for a future small-scale reforming business.

I would like to express my gratitude to the Subtask C members for their commitment, contribution and presence in all the meetings.

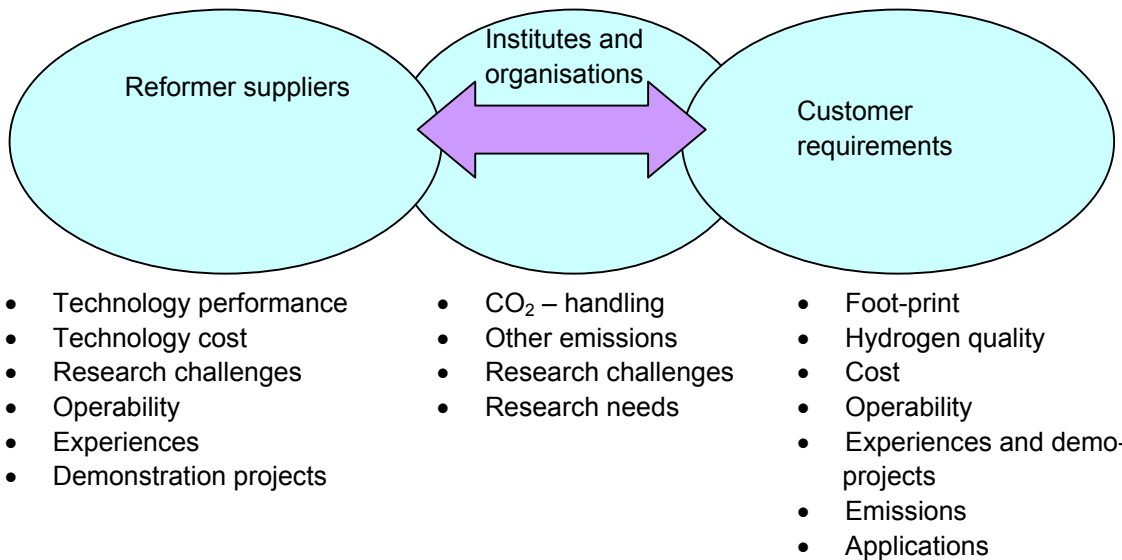
I would also like to acknowledge the contribution of the Hydro Oil & Energy Research Center in developing this final report.

July 2005, Anne Marit Hansen, Subtask C leader

The work program and activities in Subtask C

Subtask C activities 2002 - 2004

The objective of Subtask C has been to define system solutions for early markets by evaluating the reformer technology from two angles, the market requirements and the technology performance.



The methodology was based on present commercial and research activities of the members. A work-plan with detailed activities and deliverables was developed in 2003 and maintained during the entire program. Moreover, a communication tool was established, i.e., a password protected web room for the members, managed by the Subtask C leader. This web-site has been used to upload and download all reports, presentations and other input that have been provided in the work program.

The members are from 16 organisations and 11 countries.

Subtask C members 2002 – 2005

Member	Company	Country
John Bøgild Hansen	Haldor Topsøe	Denmark
Takayuki Azuma	Osaka Gas	Japan
Akira Obuchi	Mitsubishi Kakoki Kaisha, Ltd.	Japan
Erik Polman	Gastec	The Netherlands
David Cepla	Hyradix	USA
Thomas Muller	Gaz de France	France
Elodie Dejean	Gaz de France	France
Ulrich Hofmann	IGS Mahler	Germany
Jacques Saint-Just	H2 Plus Ltd	France
Bjørg Andresen	IFE	Norway
Corfitz Nelsson	SGC	Sweden
Henrik Solgaard Andersen	Hydro	Norway
David Tliang	IESE	Singapore
Yuji Ieiri	ENAA	Japan
Antoni Julia	Gas Natural	Spain
Mike Jones	BP	UK
Steve Lelewer	Intelligent Energy	USA
Anne Marit Hansen	Hydro	Norway

In the work-program the following deliverables has been submitted

Title	Responsible	Time	Type
Review of Small Stationary Reformers for Hydrogen Production ¹	Joan M. Ogden Princeton University	2002	Report IEA/H2/TR-02/002
Hydrogen Quality Requirements for Fuel Cells	Hydro	2002	Presentation and report
Progress reports	BP, Gas Natural, Gaz de France, Hydro	2002 - 2005	Presentations at meetings
Small-scale reforming and fuel processors: technology status and experience from demo-projects	Osaka Gas, Hyradix, IGS Mahler, Mitsubishi Kakoki Kaisha, Gas Natural	2002 - 2005	Progress reports and presentations at each meeting
Hydrogen Quality Requirements for Fuel Cells	Intelligent Energy	June 2003	Memo
Experiences from operating the Madrid hydrogen filling station	Gas Natural	June 2003	Memo
Fuels and fuel processing options for fuel cells	Haldor Topsøe	March 2005	Presentation
Small-scale reforming: technology status and market requirements	Kiwa (formerly Gastec)	December 2004	Report
CO ₂ -emissions from small stationary reformers	IFE	January 2005	Report
Small scale reformers and fuel processors for combined heat and power applications	Gaz de France	June 2005	Report

¹ This report was developed on a contract basis for the IEA HIA and was used as a starting point for the Subtask C Program

Subtask C had 8 meetings with 4 technical visits, and one concluding seminar

Time	Location	Organizer	Participants
June 5, 2002	Brussels	Hosted by Hydro, kick-off meeting	10
November 21, 2002	Brussels	Hosted by Hydro	10
June 5, 2003	London	Hosted by Hydro	10
September 11, 2003	Paris	Hosted by Gaz de France with technical visit to Gaz de France CHP – fuel cell laboratory	12
February 11, 2004	Madrid	Hosted by Gas Natural with technical visit to the Madrid hydrogen refueling station	15
June 29 – July 3, 2004	Yokohama and Osaka	Hosted by ENAA and Osaka Gas with technical visit to 5 hydrogen refueling stations in Japan	13
November 2-3, 2004	Stuttgart	Hosted by Mahler, technical visit to the Stuttgart hydrogen refueling station	11
March 2 –3, 2005	London	Hosted by BP	10
June 15 –17, 2005	Oslo	Hosted by Hydro and IFE, visit to IFE laboratory and Utsira wind-hydrogen plant	40*

*) Concluding seminar with invited participants

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1 Introduction

At early stages of a hydrogen economy, the demand for hydrogen will be for small volumes and geographically decentralised. Small production units can be modular, scalable and can provide hydrogen where needed, allowing the supply to match the demand as the number of hydrogen vehicles increases.

Small-scale reformers are commercially available from several vendors who are targeting the conventional industrial gas market. Few of them are presently aiming at the hydrogen refuelling station market. Newcomers are developing small-scale reformers for integration with fuel cells. The aim is for electricity production and distributed Combined Heat and Power (CHP) markets. Most of these fuel cells are based on the Proton Exchange Membrane (PEMFC).

In this report we will focus on commercial and pre-commercial small-scale reforming technology (time frame of 5-10 years), rather than on future technologies that are presently basic research and might become commercial in the long term (beyond 20 years). The report is the result of the activities undertaken within the IEA HIA Task16, Subtask C: Small Stationary Reformers for Hydrogen Production. The Subtask objective is to make recommendations for the design of small reformers by analysing the technology status and market requirements. The Subtask members (15 members from 11 countries) represent a wide spectrum of players including technology providers, academic researchers, and technology users.

2 Markets for small-scale reformers

The main markets for small-scale reformers in the early phase of a hydrogen economy are considered to be hydrogen filling stations and distributed energy production, essentially through fuel cells for electricity and combined heat and power production.

As an example of the potential market size, the current market of gasoline and diesel in EU-25² is 15 EJ/yr, which corresponds to about 1400 Bcm H₂/yr on an equivalent energy basis. The European Commission's² potential for the market share of hydrogen in the transportation sector is 5 % by 2020³. This corresponds to about 8000 filling stations with a capacity of 1000 Nm³ H₂/hr. There are currently 135,000 service stations in EU-25.

The European Hydrogen and Fuel Cell Technology Platform (HFP) submitted a Strategic Research Agenda (SRA) in August 2005. The purpose of this agenda is to make recommendations for research for the seventh Framework program and subsequent programmes. The SRA recommends a budget share of 22% for hydrogen production, of which 8% for chemical conversion technologies, including reforming.

In 2050 hydrogen is expected to be widely available in industrial nations at competitive cost. According to the SRA, the market share for transport fuel for vehicles is expected to be 50% in 2050. In the medium term (2030), a significant fraction of hydrogen is expected to be produced by on-site reforming of natural gas and other hydrocarbons. In the long-term it is expected that large-scale hydrogen production with CO₂ capture and pipeline distribution will be the option of choice in centralised areas.

Hydrogen from hydrocarbon fuels is a bridging technology that is important for the entry of hydrogen to the market, and it has the potential to remain important in the long-term in certain applications when linked with carbon capture and sequestration. Reforming technologies for fossil fuels thus pave the way for future renewable fuels and biomass resources. This effort should be balanced with parallel research on hydrogen production from renewable and carbon free energy sources.

The HFP "Snapshot" for 2020 indicates that the mass roll-out of hydrogen fuelled road transport is expected to be around 2015/2020⁴.

Key Assumptions on Hydrogen & Fuel Cell Applications for a 2020 Scenario^{3 4}

	Portable Fuel Cells For handheld electronic devices	Portable Generators & Early Markets	Stationary Fuel Cells Combined Heat and Power (CHP)	Road Transport
EU H ₂ /FC Units Sold per Year projection 2020	~ 250 million	~ 100,000 (~ 1 GW _e)	100,000 to 200,000 (2-4 GW _e)	0.4 million to 1.8 million
EU Cumulative Sales projections until 2020	n.a.	~ 600,000 (~ 6 GW _e)	400,000 to 800,000 (8-16 GW _e)	1- 5 million
EU Expected 2020 Market Status	Established	Established	Growth	Mass market roll-out
Average Power Fuel Cell System	15 W	10 kW	<100 kW (Micro CHP) >100 kW (Industrial CHP)	80 kW
Fuel Cell System Cost Target ¹	1-2 €/kW	500 €/kW	2,000 €/kW (Micro CHP) 1,000-1,500 €/kW (Industrial CHP)	< 100 €/kW (for 150,000 units per year)

² PRIMES European energy and transport scenarios and key drivers, September 2004

³ EU Directive 2003/30/CE

⁴ The European Hydrogen and Fuel Cell Technology Platform, Strategic Overview

The SRA foresees that by 2030, 25% of presently centralised power generation in Europe will be replaced by distributed energy systems, operating essentially on natural gas. The Deployment Strategy snapshot assumed that by 2020 the cumulated number of units sold could be between 400 000 and 800 000 representing 8 and 16 GW_e of installed capacity. Subtask C members see these numbers as optimistic. Nevertheless they are an indication that the size of the small-scale reformers/fuel processors market will be substantial if stationary fuel cells develop as predicted.

The typical size of small-scale reformers for hydrogen filling stations is considered to be between 100 and 300 Nm³ H₂/hr. This size is considered suitable for early stages of the hydrogen economy (i.e. 2015) in line with the forecasted numbers for the first hydrogen vehicles. Currently this market comprises a number of demonstration projects worldwide, in Japan, Europe and the US.

In a few sectors where trucked in hydrogen is expensive, on-site reforming can be an attractive alternative in 2005.

The market for reformers used in distributed energy applications comprises small clients including households, buildings and small communities, with a power range from 1 to 30 kW_e. Depending on the system efficiency, 1 kWh_e would require 0.5 to 1.0 Nm³ H₂ (66 to 33% efficiency). Several such demonstration plants exist worldwide.

Available feeds for small-scale reformers are natural gas and liquid hydrocarbons including LPG, naphtha and diesel. Natural gas is considered to be the most competitive feedstock during the introduction phase of the hydrogen economy. In regions without access to natural-gas grid other hydrocarbons and biofuels can be alternatives. Other energy carriers such as methanol, dimethylether (DME) and ammonia can be imported from areas where natural gas is available at low cost.

In this section we analyse the customer requirements for the reforming technology. We focus on hydrogen filling stations and combined heat and power markets. Technology status and challenges for small-scale reformers are assessed. The feedstock of interest is natural gas since it is expected to become the fuel of choice for introducing fossil carbon based hydrogen into the energy market.

2.1 The hydrogen filling station market

About 100 hydrogen-filling stations are built for demonstration purposes (see. www.hyweb.de) with 13 of them based on reforming, and 18 based on electrolysis. In demonstration projects customer requirements such as cost and footprint are not critical issues. However, future commercial products should comply with customer requirements in order to be competitive. Customer demand will evolve over time, from the short to the long term. Regulations and safety aspects could be a challenge in the near term, but are expected to be common practice in the long term.

As a part of the Subgroups effort, Gastec⁵ has performed a technical study on small-scale reformers for hydrogen filling stations with the following objectives:

- Identify the customer (filling station owner) requirements for the short term (5 years) and the long term (20 years). This has been done via a questionnaire to the Subtask members and other relevant stakeholders.
- Compare the economics of small-scale reforming with alternative technologies, on-site electrolysis, trucked-in hydrogen and CNG. This has been done by a technology benchmarking for the short and long terms.

The result of the work is summarised below.

⁵ Gastec – currently Kiwa group

2.1.1 Hydrogen production cost

In Europe, hydrogen produced by commercially available technologies for on-site reforming of natural gas costs between 0.20 and 0.40 €/Nm³, depending on natural gas cost, investment cost and depreciation period

Hydrogen from on-site electrolysis is more expensive with prices from 0.35 to more than 1 €/Nm³, depending on electricity cost.

Table 1 Current commercial cost⁶ and efficiency benchmark figures for small-scale natural gas reforming including gas clean up and electrolysis

On-site technology	Efficiency (LHV basis)	Non-Energy cost (€/Nm ³)	Energy cost (€/Nm ³)	CO ₂ -intensity (kg CO ₂ /kg H ₂)
On-site steam reforming	65-75%	0.10 – 0.27	0.12	9.5
Electrolysis	65-70%	0.09 -1.80	0.27 – 0.45	0 - 27

In Europe, large –scale hydrogen produced from natural gas costs 0.06 to 0.10 €/Nm³. This is about three times natural gas feedstock cost on an energy basis, but close to the price of untaxed gasoline at the refinery gate. Transportation over 160 km of compressed hydrogen gas adds another 0.20 €/Nm³ compared to 0.01 to 0.02 €/Nm³ for liquid hydrogen.

Data concerning the US, as reported by the DOE, are about the same⁷. Hydrogen from small on-site reformers below 700 Nm³/hour are reported to be around 0.45 €/Nm³ of hydrogen. For the year 2020 the target cost is 0.10 €/Nm³.

Table 2 Cost data for on-site small-scale steam reforming in US⁸

	(LHV Basis)	Non-Energy cost €/Nm ³	Energy cost €/Nm ³
USD = 0.76 EUR			
On-site reforming US-DOE, July 2003	62-75%	0.30	0.04

In Japan, the cost of hydrogen is high since natural gas is imported in the form of LNG. The current cost level is 0.5 to 0.7 €/Nm³ for industrial use. The target cost for the year 2020 is 0.3 €/Nm³, and is significantly higher than for Europe and the US.

From these prices we see that on-site reforming could become economically competitive to centralized production. This competitiveness depends partly on distance from production facilities.

The following figure summarizes the previous discussion on present and target costs for hydrogen production.

⁶ The cost of natural gas is 4 €/GJ, the cost of electricity is 0,05 – 0,07 €/kWh. The capacity range for electrolysis is from 470 Nm³/hour to 9 Nm³/hour for the non –energy cost. (source SRA, European Hydrogen and Fuel Cell Technology Platform, August 2005)

⁷ DOE solicitation DE-PS36-03GO93007, July 2003

⁸ DOE, 2003

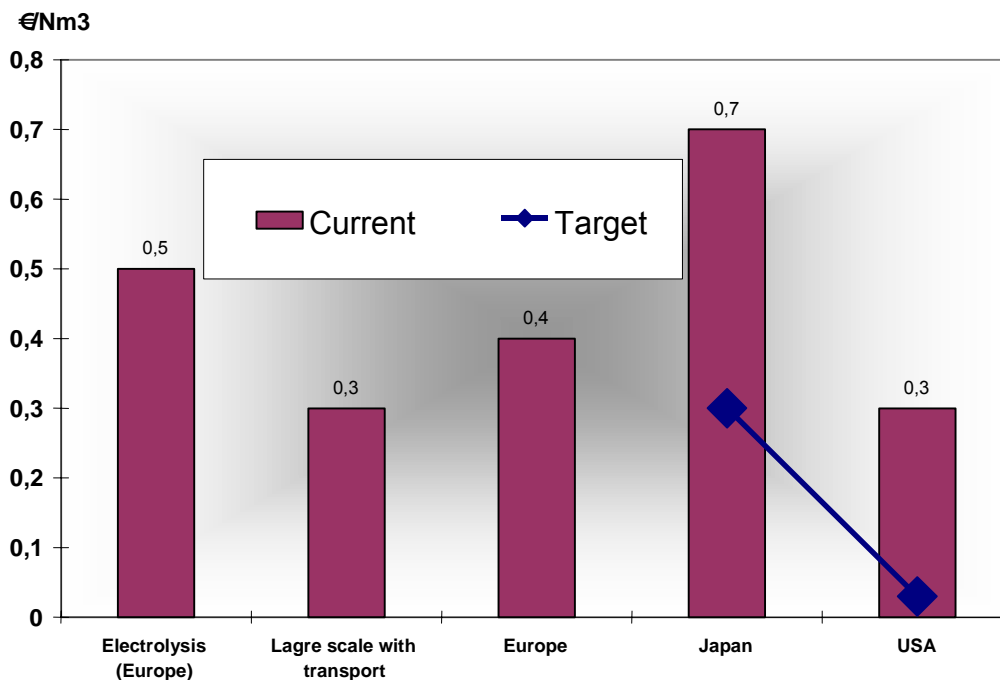


Figure 1 Hydrogen production cost compared to target

2.1.2 Stakeholder requirements

Customer requirements have been collected and discussed with the Subtask members and other relevant stakeholders. The following is a list of customer requirements for filling-station reformers in a 20 years perspective. The Subtask C members agreed on all these requirements except for the requirement for CO₂ –capture and handling.

- Reliability and durability
- Production capacity
- Foot print and height
- Automatic and remote monitoring
- Variable-load that follows the demand pattern
- Decrease of the start-up and shut-down times
- Service, training and maintenance
- Standards, certifications and safety
- Efficiency > 80 %
- Hydrogen purity 99,95% and CO < 1 ppmv
- Costs
- CO₂ capture

2.1.2.1 Cost requirement

For the long term the hydrogen cost mentioned in the DOE⁹ research program seems a good guideline. The DOE objective of 0.03 \$/Nm³ hydrogen for the reformer and purification capital costs is very ambitious.

⁹ DOE solicitation DE-PS36-03GO93007Hydrogen production and delivery research, July 2003

2.1.2.2 Hydrogen Production Capacity

The Subtask C members agreed that a production range from 100 – 300 Nm³/h would fit the needs in the short and medium term, i.e. 2020.

In the DOE program, a capacity of 690 kg/day (7500 Nm³/day) is considered to be suitable for a hydrogen filling station that will satisfy the needs of 140 fuel cell vehicles per day. In this program a utilization factor of 90% is assumed. This means that a reformer size of 350 Nm³/h combined with a storage capacity of about 2000 Nm³ would be appropriate.

An alternative scenario that avoids the use of large hydrogen storage at the station should use a larger production capacity. The reformer will have a capacity of 700 Nm³/h and a low turndown ratio of 0.4 in order to be in line with the off-peak hydrogen demand.

It is difficult to predict the ideal reformer size for a filling station in 2020. The capacity is defined within the following limits:

- A continuous running reformer (>90% load)
- A reformer operated within a minimum storage and a high load flexibility

A scenario of a 700 Nm³/h reformer was discussed. Several suppliers, including the Subtask members claim that the 700 Nm³/h capacity is technically feasible. Nevertheless, the market demand, up to 2020, could be satisfied with production capacities of 100-300 Nm³/h since there will be very few vehicles to refuel.

2.1.2.3 Hydrogen fuel quality

As a part of the Subtask C effort, Intelligent Energy distributed a questionnaire on hydrogen purity requirements for fuel cells to the major fuel cell developers as well as the major fuel cell vehicle developers. The number of responses was very low. It may be that the existing specifications are sufficient or that the information is considered to be confidential. Intelligent Energy's survey is shown in Table 3.

An ISO-standard exists for hydrogen product quality, ISO 14687 "Hydrogen Fuel - Product Specification". However, this standard has not been found suitable for fuel cell applications and a work group, ISO/TC 197 WG 12, has been set to review the standard. The group suggested to rename the current standard ISO 14687-1 "Hydrogen fuel – Product specification – Part 1: All applications except fuel cell applications", and to prepare a new standard ISO 14687-2 "Hydrogen fuel – Product specification - Part 2: Fuel cell applications". The work is in progress, and there is currently no agreed international standard for fuel cell applications.

Table 3 Intelligent Energy survey on hydrogen quality requirements

Characteristics	ISO-Standard (micromoles/mole)			Ballard		Daimler		Avista		Gore (g)	
	Grade A	Grade B	Grade C	Nominal	Maximum	Nominal	Maximum	Nominal	Maximum	Nominal	Maximum
Hydrogen purity (mole fraction %)	98 %	99.9%	99.99%	99.99%		99.9%	99.9%	~98%	~40%	Lower hydrogen content in the fuel stream will result in voltage loss in the stack (predicted by Nerst Eq.)	
Total gases			50								
Water	NC (a)	NC	(b)		0.50 %	< 5vpm	<50 ppm (l) <0.1% (v)	No known issues other than H2 dilution		Water is beneficial up to saturation - beyond saturation- effect will depend on stack ability to liquid water	
Total hydrocarbon	100	NC	(b)		1 ppm	<1vpm	<1 ppm	see above		Hydrocarbons such as alkanes act only as diluents. However, others such as benzene(alkenes), alcohols maybe poisons.	
O2	(a)	100	(c)		500 ppm	<1vpm	<500 ppm	0.80 %	~5%	At low levels (1%) will have little effect	Explosive limit
Argon	(a)		(c)		1 %	<200 vpm	<200 ppm inerts	No known issues other than H2 dilution		Act as diluents only and therefore will only provide voltage losses as determined by Nernst Eq.	
Nitrogen	(a)	400	(b)		1 %		see above	see above		see above	
Helium			39		1 %		see above	see above		see above	
CO2			(d)		2 ppm combined (CO+CO2)	<2vpm	<2 ppm combined (CO+CO2)	see above		On Pt catalyst undergoes reverse water gas shift to CO	Effect is mitigated using Pt/Ru catalyst as anode
CO	1		(d)					~10 ppm	~100 ppm with air bleed	Strong poison at ppm levels	
Sulfur	2	10			1ppm	<1vpm	<1 ppm	~ 5 ppm	unknown	Strong poison at ppm levels and lower	
Mercury		0						unknown	unknown	No information	
Ammonia					0.010 ppm	<0.01vpm		~5 ppm	unknown	Strong poison at ppm levels	
Permanent particulates	(f)	(e)	(e)		Max inorganic content - 0.01% ash	<10 ppm max particle size	< 10mm	unknown	unknown	Would predict particles blocking gas access to catalyst	

(a) combined water, oxygen, nitrogen and argon: max 1,900 micromole/mole

(b) combined, water, and hydrocarbon: max. 9 micromole/mole

(c) combined oxygen and argon: max. 1 micromole/mole

(d) Total CO2 and CO: max 1 micromole/mole

(e) to be agreed between supplier and customer

(f) The hydrogen shall not contain dust, sand, dirt, gums, oils or other substances in an amount sufficient to damage the fueling station equipment or the vehicle (engine) being fuelled.

(g) Intelligent Energy stated that at present they would utilize Gore's recommendations

The survey suggests that the concentration of impurities such as ammonia, carbon monoxide and sulphur compounds should be very low. The content of inert gases, that are diluents, affects the efficiency of the fuel cell, and the vehicle manufacturers tend to set stricter specifications on inert gases than stationary fuel cell developers.

The specifications used by the Japanese Hydrogen Fuel Cell (JHFC) program is given in Table 4 together with the range of impurities obtained from the reformers tested in the program. The program comprises reformers fed with naphtha, LPG, gasoline and methanol. As can be seen from the table, the hydrogen produced by reforming meets the specifications set by the project which are stricter than the specifications listed in Table 3.

Table 4 Hydrogen quality achieved within the JHFC program.

	ISO/TC197 FCV Specifications	JHFC Specifications	H ₂ Stations results
H ₂ purity	> 99.99 %	> 99.99 %	99.996 - 99.998 %
CO	< 0.2 ppm	< 1. ppm	0.02 – 0.06 ppm
CO ₂		< 1. ppm	0.01 – 0.97 ppm
N ₂		< 50. ppm	3.03 – 22.1 ppm
O ₂		< 2. ppm	< 0.01 ppm
Hydrocarbons		< 1. ppm	0.1 – 0.11 ppm
Sulfur	ND		< 0.0001 ppm
	Provisional < 0.02 ppm		
	Recommended < 0.0002 ppm		
HCHO	ND		< 0.01 ppm
	Provisional < 0.05 ppm		
	Recommended < 0.01 ppm		
HCOOH	ND		< 0.01 ppm
	Provisional < 0.5 ppm		
	Recommended < 0.04 ppm		

The above specifications reflect the sensitivity of the PEM fuel cells today that operate at about 80°C. It is expected that PEM fuel cells will develop towards operation at higher temperature (120-200°C), which will achieve better robustness and tolerance for impurities like CO and sulphur. Other type of fuel cells like Molten Carbonate (650°C) and Solid Oxide (800-1000°C), thanks to their high operating temperatures, can run directly on several hydrocarbons via internal reforming, and their tolerance for impurities is high enough for most available feedstocks¹⁰.

Table 5 Fuel quality requirements for fuel cells¹¹

Gas	Proton Exchange Membrane	Alkali	Phosphoric Acid	Molten Carbonate	Solid Oxide
H ₂	Fuel	Fuel	Fuel	Fuel	Fuel
CO	10. ppm ^a	50 ppm	0.5 – 1% ^d	Fuel ^b	Fuel ^b
CH ₄	Diluent	Diluent	Diluent	Diluent/ Fuel ^c	Diluent/ Fuel ^c
CO ₂	Diluent	50. ppm	Diluent	Diluent	Diluent
S (as H ₂ S)	Poison	Unkown	50. ppm	0.5 ppm	1. ppm

¹⁰ Fuel cell handbook, 5th edition, 2000, <http://www.fuelcells.org/info/library/fchandbook.pdf>

¹¹ A. Siddle, K. D. Pointon, R. W. Judd and S.L. Jones, Fuel Processing For Fuel Cells - A Status Review and Assessment of Prospects, DTI/Pub URN 03/1644, <http://www.dti.gov.uk/energy/renewables/publications/pdfs/f0300252.pdf>

- a) Up to 100 ppm can be acceptable if small quantities of air (2.%) are blend into the fuel stream due to oxidation of adsorbed CO
- b) Most CO utilisation is via water-gas-shift reaction on the anode or internal reforming
- c) CH₄ utilisation is generally by internal reforming
- d) Tolerance increases with operating temperature

The IEA Annex on Advanced Fuel Cell was consulted on hydrogen gas quality for fuel cell and participated at two Subtask C meetings in 2005.

2.1.2.4 Foot print and height

In the short term, compact and containerized plants are the appropriate solution since customers do not want to see an obtrusive chemical plant on their premises. In the long term, underground plants comparable to present petrol stations are a likely solution. In Figure 2, the achievements in compactness 2002 – 2005 is illustrated.

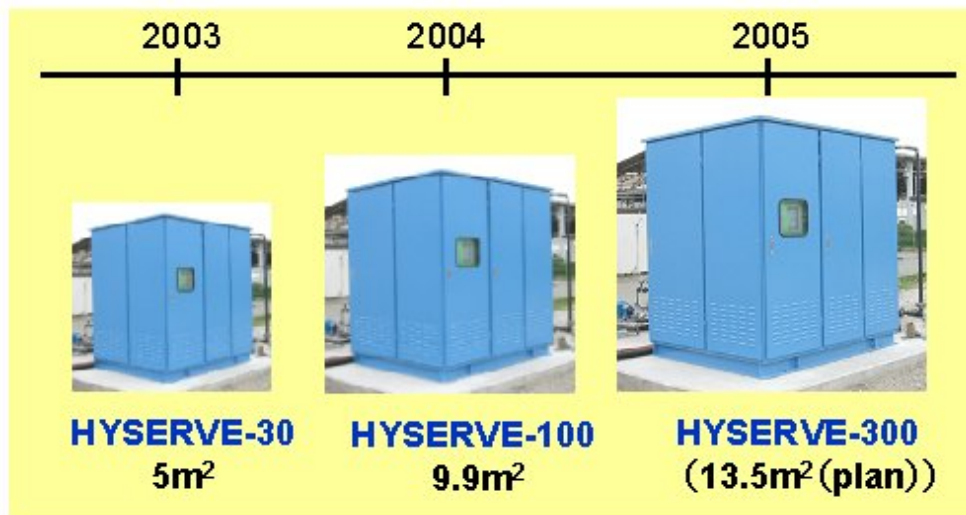


Figure 2 Development of compact reformers¹²

2.1.2.5 Load variation and start-up behaviour

A turndown ratio of 0.4 (possible to operate on 40% load) and a hot start-up time of 1 hour should provide the necessary operational flexibility. A small storage with a capacity of few hours of hydrogen demand, combined with short start-up and shutdown times will allow for the follow-up of the demand pattern. During maintenance a tube trailer can be used.

2.1.3 CO₂ capture and storage

On-site CO₂ capture is considered to be costly and will add complexity to the design and operation of a reformer. If CO₂ emissions are taxed, the on-site reforming option versus other hydrogen production and distribution alternatives will become less attractive. Therefore, hydrogen filling stations based on on-site reforming may be regarded as an intermediate solution that would facilitate the build-up of a hydrogen infrastructure and the use of hydrogen powered vehicles. A sustainable solution for the long term may involve central reforming with CO₂ capture and a hydrogen pipeline network to filling stations. Development of cost effective technologies for CO₂ handling in small-scale reforming may be regarded as a necessity that will allow the technology to maintain a strong market

¹² Osaka Gas data

position in the long term. In the short and medium term the requirement for CO₂ handling is not expected for on-site reforming. The CO₂ intensity of on-site reforming is competitive to electrolysis (see Table 6). The reformer technology can be used for renewable feedstock from biomass sources, thus eliminating the need for CO₂ handling locally.

Table 6 CO₂ emissions in different hydrogen production pathways¹³

Production pathway	g CO ₂ /MJ
Electrolysis on-site	
Traditional European electric grid mix	206
Renewable resources	~ 0
Natural gas from the European gas mix	
CGH ₂ * from a central plant	88
CGH ₂ * from on-site production	101

*) CGH₂ – compressed gaseous hydrogen

2.1.4 Benchmarking

For the short term, Compressed Natural Gas (CNG), trucked-in hydrogen, and on-site electrolysis are possible benchmarking technologies in terms of costs. These technologies are competitive technologies whose cost can be evaluated fairly precisely.

For the long term, conventional fuels such as gasoline and diesel will be the benchmark as it is expected that by then, hydrogen will be able to compete with these fuels on a cost basis.

2.1.4.1 Benchmark technology for small-scale reforming

Before defining the targets for new reformers a comparison is made with state of the art reformers. A questionnaire was prepared and filled out by three of the Subtask C developers of compact small-scale reformers. A reformer showing good performance on footprint and cost is the Osaka Gas Hyserve-100 system. Systems from other manufacturers show about the same performance. In the year 2005, one can order this reformer that has the following specifications:

– Hydrogen Capacity	100 Nm ³ /h
– NG consumption	40 Nm ³ /h
– Footprint	3.8 x 2.6 m ²
– Volume	28 m ³
– Efficiency (HHV)	70%
– Operating range	40 to 100%
– Electricity consumption	20 kW
– Cold start-up time	4 hours
– Start-up from standby	1 hour
– Operating pressure	0.8 MPa
– Catalyst replacement	40,000 hours
– Reformer tube replacement	100,000 hours
– PSA valves replacement	every 2 years
– Inspection	every year
– Capital cost	450,000 €

¹³ L-B-Systemtechnik GmbH (2002), GM Well-to-wheel analysis of energy use and greenhouse gas emissions of advanced fuel/vehicle systems – a European study, <http://www.lbst.de/gm-wtm>

Assuming a depreciation schedule of 15 years, an interest rate of 10% and a total availability of 50%, the capital cost for the reformer and purification unit is 0.13 €/Nm³.

2.1.4.2 Benchmark technology for electrolysis

Currently the alternative hydrogen production method for filling stations is electrolysis. The following information was obtained from a manufacturer of commercial electrolyzers:

– Capacity	200 Nm ³ /h
– Footprint	9 x 9 m ²
– Volume	245 m ³
– Efficiency	73 %
– Operating range	20 to 100%
– Electricity consumption	4.8 kWh per Nm ³ of H ₂
– Cold start up time	2 minutes
– Start up from standby	No stand-by mode
– Operating pressure	3 MPa
– Inspection/maintenance	low
– Lifetime	Very long (few moving parts)
– Capital costs	790,000 €

Assuming a depreciation schedule of 15 years, an interest of 10% and a total occupancy of 50%, the capital cost is 0.12 €/ Nm³ for pure hydrogen gas (99.9%) supplied at 30 bars. Electrolyzers show the advantage of rapid start up and large turn down ratio of 0.2. The technology is more mature than small-scale reforming. A scenario for the year 2020 with a cost decrease of 50% is described in section 2.1.4.4.

2.1.4.3 Benchmark technology for CNG

CNG fuel may be a short-term alternative for conventional fuels. Comparison between hydrogen refuelling and natural gas refuelling is not straightforward. For example the vehicle cost and the well-to-wheel fuel efficiency should be taken into account. In the present work we focus on the cost for the owner of the filling station. The following is basic information on CNG¹⁴ refuelling:

– Capital costs	340.000 €
– Natural gas costs	0.17 €/Nm ³
– Maintenance	13,000 €/year
– On site costs	10,000 €/year
– Compression up to	250 bars
– Capital cost	0,02 €/Nm ³

2.1.4.4 Cost comparison of small-scale reforming, electrolysis and CNG refuelling

The following costs are evaluated:

- Capital costs (for hydrogen production and purification units)
- Energy costs (mainly natural gas for reformers and electricity for electrolyzers)
- Maintenance costs
- Catalyst replacement costs
- Hydrogen storage costs
- Hydrogen compression costs (up to 300 or 700 bars)

¹⁴ Gastec – the Netherlands

- Dispenser costs
- On-site costs, e.g. civil engineering

The last four cost categories are not taken into account in the following comparative analysis. Six scenarios are considered:

1. "A" The state of the art electrolyser described in paragraph 2.1.4.2
2. "B" An electrolyser of year 2020 with 50% lower capital costs than "A"
3. "C" The state of the art reformer described in paragraph 2.1.4.1 of 100 Nm³/h
4. "D" The state of the art reformer scaled up to 700 Nm³/h assuming industrial scale-up factors for investment costs (a 2 fold capacity increase results in a 1.4 higher capital cost)
5. "E" 700 Nm³/h reformer of the year 2020 with 50 % lower capital cost and an improved overall efficiency target value of 75 %
6. "F" Natural gas refuelling (250 barg)

The reformer of year 2020 would meet the targets defined by the DOE of 0.11 \$/Nm³ for capital costs and 0.02 €/Nm³ for purification.

The following assumptions were made for the cost analysis:

- 10% interest rate, 15 year lifetime
- Natural gas cost: 0.17 €/m³
- Electricity cost: 5 €/kWh
- No credit for the oxygen generated by the electrolyser
- All costs refer to the calorific content of 1 Nm³ of hydrogen.

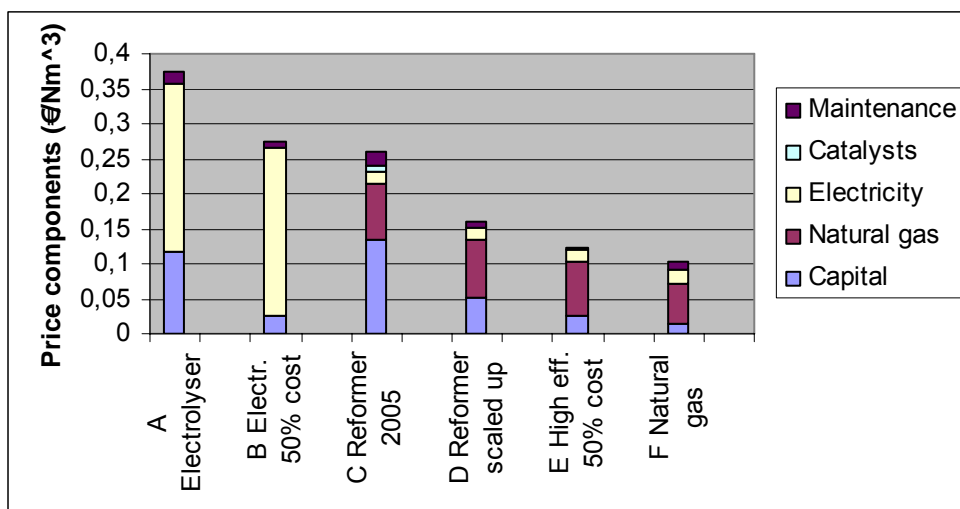


Figure 3 Six scenarios for capital and energy costs for on-site reforming, on-site electrolysis, and natural gas refuelling

The analysis shows the following:

- Capital costs for reforming are already lower than for electrolysis (C vs. A & B).
- Natural gas refuelling is cheap due to low capital costs (F)
- For electrolyzers a reduction in capital costs will help, but the total costs for hydrogen production are dominated by electricity costs (B vs. A).

- After scaling-up (e.g. 10 000 units) the present technology of small-scale reformers, the hydrogen produced by means of reforming will be significantly cheaper than electrolysis (D vs. C).
- Further technology improvements leading to 50% lower investment costs for reformers and an overall efficiency of 75 %, will result in a further decrease in hydrogen production cost by 4 €/Nm³ (E vs. D).

2.1.5 Challenges for small-scale reformer developments

In this section, we underline the challenges and developments for small-scale reformers, and recommendations for future research and demonstration programs are made. Projections on the technical feasibility and needed research efforts were made by a team of experts specialized in basic reformer concepts, market introduction of novel reformers and industrial reformer development.

2.1.5.1 Feasibility of targets on system cost and size

For 2020, the group forecasts that the standard for the production capacity should be in the range of 100 – 300 Nm³/hour. Capacities above 300 could be met by combining available standard systems. Many experts claim that, by continuous product development, a 700 Nm³/h reformer with its purification unit could fit in a 12m³ container by the year 2020. However, the Subtask C members agree that a capacity of 500 Nm³/h is a foreseeable maximum-size for on-site reformers that can ensure the customer requirements on compactness. A one-skid design and mass production of at least 10,000 reformers are regarded as necessary conditions to reach the cost target. However, it is unlikely that by the year 2020 a production volume of 10,000 is reached. The feasibility of this target is therefore questionable unless political and global developments accelerate the production of on-site hydrogen filling stations.

2.1.5.2 Need for novel technologies

The most common technology used for conversion of natural gas to hydrogen is steam reforming. Industrial experience shows that this technology is reliable and mature. CPO (catalytic partial oxidation), ATR (auto-thermal reforming) and sorbent-enhanced reforming are alternative techniques that may lead to either more compact and cheaper reformers or reformers with more rapid start-up times. All these options are likely, and the choice will follow from the total design of an integrated reformer-purification system.

Many experts agree that the efforts should concentrate on the development of an integrated design for the reformer, the purification unit and the compression equipment. The gas separation system is, at present, one of the most voluminous parts of the system and can be sized down at increased pressure. The design should lead to an overall optimization and should also consider how the system can be mass-produced. Natural gas reforming at increased pressure may lead to a more compact design. However, national regulations may limit the pressure level in the reformer system.

In the long terms, development of cost effective methods for small-scale CO₂-capture, storage and transportation may be required for small-scale reformers to maintain a high market share in the hydrogen energy market.

2.1.6 Need for accompanying actions

Long-term commitment of national governments and international bodies to the hydrogen economy remains a concern. Manufacturers are willing to progress with product development but they are not sure whether the market will materialize fast enough to justify investments. It is clear that the

industry driven - domestic development of the market is too slow to drive the manufacturing of reformer systems with the targeted volume and price.

2.2 Decentralised combined heat and power market

The European strategic research agenda, HFP, foresees that by 2030, 25% of the actual centralised power generation in Europe will be replaced by decentralised energy sources. Integrated reformer/fuel-cell systems are currently developed for the micro CHP market. These micro-systems are designed to meet residential heat and power demand, from a single household up to small apartment buildings.

According to Frost & Sullivan study¹⁵ the incentives for micro-generation are:

- Environmental policies
- Regulations on electricity-selling possibility and interconnection
- Electricity and gas prices
- Public acceptance
- Market pull from energy utilities

According to these criteria, Germany appears as the country with the most favourable context, and UK as the early market leader¹⁵ (Figure 4).

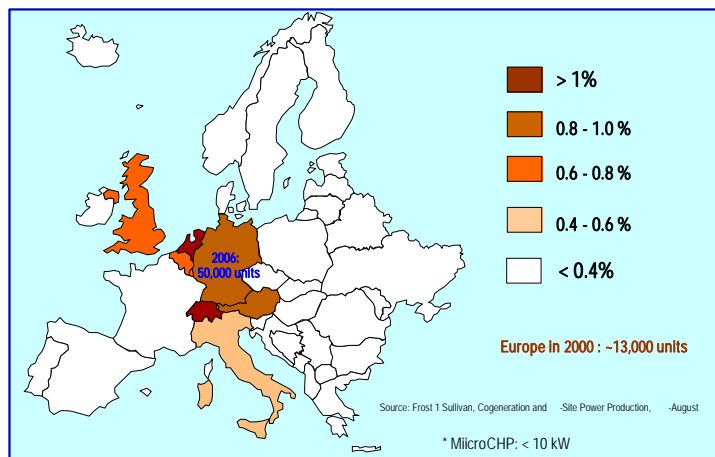


Figure 4 Projected share of micro CHP in total installed power capacity in Europe by 2010

The micro-cogeneration market can be divided into three segments:

- Residential (1 - 30 kW_e): most of the present systems are based on low temperature PEMFC that are more suitable with respect to cost and reliability, cycling and load following.
- Commercial (few hundred kW_e): this segment is shared between PEMFCs and high temperature fuel cells, Solid Oxide and Molten Carbonate (SOFCs, MCFCs). Technical requirements may be less severe in this segment although excellent heat recovery for both heating and processes is mandatory.
- Industrial (> 1 MW): a less developed segment where SOFCs and MCFCs are more suitable. Important criteria in industrial environments are fuel flexibility and large heat needs. In recent years, there have been many R&D activities on hybrid systems where the fuel cell is integrated with a microturbine. Such a system can achieve high

¹⁵ Frost and Sullivan, Cogeneration and On-site Power Production, July-August 2001.

efficiencies (70%). However, in this segment, the fuel cell has to compete with more conventional technologies including micro-turbines, internal combustion engines and the Stirling engine.

In the residential segment the fuel cell will replace the traditional boiler. Therefore, its primary function is to satisfy thermal needs (heating and hot water), and the electricity is a by-product that can be sold to the grid, thus providing an acceptable payback time for the installation. Accordingly, the sizing and the control strategy of the fuel cell are mostly based on thermal needs. This requirement puts a severe constraint on fuel cells that have a high electric efficiency, such as PEMFCs that are fit primarily for power generation. Current prototypes comprise a complementary boiler to satisfy peak thermal needs (10-25 kW_{th}) while keeping the fuel cell power to 1-5 kW_e. Another design is based on a larger fuel cell that can satisfy all the thermal needs, coupled with a water tank in order to level the peak thermal demand and produce domestic hot water.

PEMFC prototypes delivered for small-scale CHP run mostly on reformat fuels (mixture of H₂, CO₂, CH₄, N₂ and traces of CO). Present purification techniques are not suitable for integration with small CHP systems due to added complexity and cost. Metallic membranes, based on Pd alloys, are promising, although a compressor is needed upstream to create enough gradient to drive the hydrogen through the membrane.

Feedback from current CHP demonstration projects shows the following:

- Long cold start-up time of 1 hour, due to the reformer that is incompatible with the heat-demand profile. This is another justification for the use of a complementary boiler, unless the reformer is kept in a stand-by mode (with additional energy consumption).
- Extensive cycling (start-stops) reduces fuel cell and reformer durability. One reason is the degradation of hydrogen quality due to the reformer behaviour. Impurities in hydrogen affect the PEM fuel cell catalysts and membrane. Technical breakthroughs providing new materials and design are the ultimate solution to reach acceptable values of 3000 cycles during the lifetime of the product.
- Too many maintenance operations that are needed with today's systems (ex. sulphur cartridge replacement) are not acceptable for residential customers.

2.2.1 Household micro CHP system

Gaz de France has analysed the economic feasibility of micro-CHP for a typical 4 member family house in France. The cost structure is based on French utility costs. The following assumptions are made:

- Annual thermal need of the house: 20,000 kW_{th}
- Natural gas cost: 2.71 €/kWh HHV
- Electricity cost: 7.54 €/kWh HHV
- Boiler (23 kW_{th}): 1800 €, thermal efficiency 85% LHV
- Scenarios analysed:
 - S1: 1 kW_{th} FC + Boiler
 - S2: 3 kW_{th} FC + Boiler
 - S3: 5 kW_{th} FC + Boiler
 - S4: 9 kW_{th} FC + Water storage tank
- For each scenario, realistic S_{real} and optimistic S_{opt} foreseen performances and cost data are considered
- The excess electricity is sold back to the grid, at buying cost, without any obligation to guarantee a minimal power value

The results of the simulations (

Table 7) show that none of the scenarios give an acceptable payback time shorter than 5 years. A higher electric rate, from 7.54 to 10 €/kWh, lowers substantially the payback period, from 11.5 years down to 6.8 years (scenario S4_{opt}), but this payback time is not yet acceptable.

Table 7 Cost estimates for a residential small CHP system

	S1 real	S1 opt	S2 real	S2 opt	S3 real	S3 opt	S4 real	S4 opt
FC thermal power (kW _{th})	1	1	3	3	5	5	9	9
El. Efficiency ¹⁶	0.35	0.4	0.35	0.4	0.35	0.4	0.35	0.4
Th. Efficiency	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Unit cost (incl. boiler or water tank) in €	6000	4000	9000	6000	11000	8000	15000	10000
Maintenance: annual cost surplus over boiler maintenance cost (€)	300	150	300	150	300	150	150	0
FC operating hours	5000	5000	4000	4000	3000	3000	2222	2222
Results for an electric rate of 7.54 €/kWh								
Annual savings (€)	-146	28	70	277	162	383	467	711
Return period (years)	infinite	79.3	103.0	15.2	56.7	16.2	28.2	11,5
Results for an electric rate of 10 €/kWh								
Annual savings (€)	-38	151	328	572	485	752	897	1203
Payback period (years)	infinite	14.6	21.9	7.35	19.0	8.2	14.7	6.8

2.2.2 Semi-centralised residential CHP system

An alternative concept is based on an isolated reformer (capacity of 100-300 Nm³/hr) that provides pure hydrogen to several residential PEMFC (Figure 5). The fuel cells are fed via a hydrogen storage tank in order to de-couple instantaneous hydrogen-demand from hydrogen-production. Moreover, it allows for the start of the fuel cells while the reformer is warming-up during the start-up of the entire installation. This design has the merit of reducing the investment-cost for the customer at the detriment of the utility. The utility should build adequate infrastructure for the distribution of hydrogen within a residential area and overcome many regulation barriers.

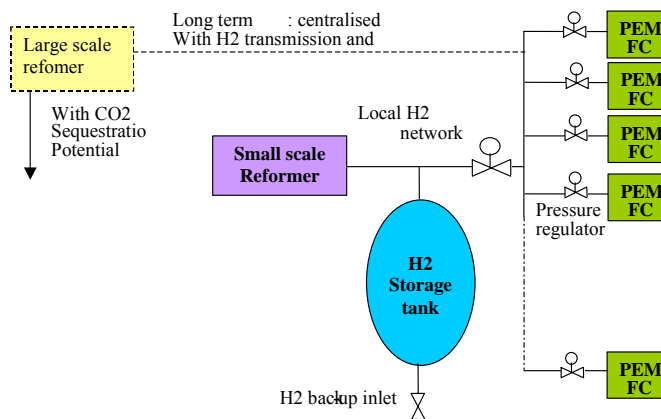


Figure 5 Centralised and semi-decentralised reformers providing pure hydrogen to several residential PEMFCs.

In order to make a cost estimate of the semi-centralised design and compare it with the centralised large-scale design, the following assumptions were made:

¹⁶ All efficiencies are calculated on a LHV base.

- All houses are equipped with 9 kW_{th} PEMFC, regulating thermal needs via hot water storage tanks. Excess electricity is sold back to the grid.
- Gas and electricity rates are the same as before
- The cost of the fuel cell is reduced by 30%
- The overall efficiency of the CHP unit is increased by 10 points, equally spread over thermal and electric contributions
- Hydrogen distribution costs are 20% higher than those of NG: 2.7 and 2.1 €/Nm³ from centralized and semi-centralised sources respectively
- Land cost for the reformers are not included

The results of the cost estimates are presented in Table 8. Similar to the household design, the semi-centralised design gives payback periods longer than 12 years. A higher electric rate of 10 €/kWh lowers the payback period to an optimistic value of 5.6 years.

In conclusion, with the present cost and without taking into account any technological issue, no PEMFC based CHP system can payback for itself in less than five years. For the market to develop, technological advances are needed in order to reach higher energy efficiencies and lower costs. Favourable utility rates, mass manufacturing and fiscal incentives will also play a major role for creating the market.

Table 8 Cost analysis of small and large scale reforming that provide hydrogen to residential PEMFCs

Hydrogen delivery scenario	Semi decentralised 100 Nm ³ /h H ₂ + H ₂ distribution	Semi decentralised 300 Nm ³ /h H ₂ + H ₂ distribution	Centralised large scale + transmission + distribution
FC thermal power	9	9	9
El. Efficiency ¹⁷	0.45	0.45	0.45
Th. Efficiency	0.45	0.45	0.45
Unit cost (incl. boiler or water tank), €	6700	6700	6700
Maintenance: annual cost surplus over boiler maintenance cost €	0	0	0
FC operating hours	2222	2222	2222
H ₂ cost at the FC inlet, (€/kWh LHV)	0.162	0.141	0.111
Results with an electric rate of 7.54 €/kWh HHV			
Annual saving (€)	-450	-104	389
Payback period (years)	Infinite	Infinite	12.6
Results with an electric rate of 10 €/kWh HHV			
Annual saving (€)	41,83	387,51	881,34
Payback period (years)	117,14	12,64	5,56

2.3 HCNG fuel: hydrogen / natural gas blends

Blending hydrogen obtained from renewable sources with natural gas would be a path to lower CO₂ emissions. Also hydrogen/natural gas blends can reduce the emissions of NO_x, hydrocarbons and CO from NG-vehicles. During the last 15 years a number of field tests on using HCNG as a vehicle fuel have been conducted around the world, and mostly in North America. The results show up to 50 % reduction of NO_x, CO and hydrocarbons (other than methane).

A typical CNG bus is filled with 200-250Nm³ of CNG. A 20% hydrogen supplementation leads to 40-50 Nm³ of hydrogen for each bus. For a fleet of 25 buses this is equal to approximately 1000-1250 Nm³ of hydrogen per day or 1.7 Nm³/h per bus.

A disadvantage of using small reformers for introducing hydrogen into the CNG system is that the overall CO₂ emissions will increase compared to today's CNG only scenario.

Besides transportation, HCNG can be used in various markets including gas turbines, gas engines, boilers and cooking appliances. The use of small amounts of hydrogen (< 3 vol.%) would not involve substantial costs apart from hydrogen production. Higher hydrogen content requires significant upgrades of the gas distribution network and end-user appliances. For these markets, large scale SMR with CO₂ capture would be a better solution rather than small-scale reforming. Nevertheless, the cost effectiveness of HCNG use for greenhouse gas emissions reduction (including CO₂) is rather low compared to conventional options.

¹⁷ All efficiencies are calculated on a LHV basis.

3 Demonstration projects: hydrogen filling stations

Currently, spring 2005, there are about 90 hydrogen-refuelling stations in operation around the world. Most of these stations are linked to research and demonstration projects. While the first stations were limited with respect to capacity, performance and design, the new stations opened in Singapore, Berlin and Washington in 2004 points the way to the future. These stations are public and multi-fuels with the same service and supply as a modern petrol station. Most of the current stations in Europe and the US are based on trucked-in compressed, liquefied hydrogen and on-site electrolysis. In Japan, most of the stations are based on reforming of hydrocarbon fuels, including natural gas, LPG, petrol and naphtha. Japan seems to be in the forefront of development of small-scale compact reformers for on-site hydrogen production.

The Subtask C members are involved in various demonstration projects:

- Gas Natural is the owner of the reformer plant of the refuelling station for the CUTE buses in Madrid. The reformer is supplied by Carbotech.
- IGS Mahler supplier and partner in the hydrogen station for three buses in Stuttgart (the European CUTE project)
- Osaka Gas develops small-scale reformers for decentralised hydrogen production. Osaka Gas operates a hydrogen refuelling station with hydrogen production based on natural gas in Osaka.
- Mitsubishi Kakoki Kaisha, a developer of small-scale reformers, has supplied units to four of the hydrogen refuelling stations in Japan (Toho Gas, Tokyo Gas, Nippon Oil and Idemitsu Oil stations).
- HyRadix, a supplier of small-scale reformers, has supplied a reformer to the hydrogen refuelling station in Palm Springs, California.

3.1 Activities in Japan 2002 - 2005

Two hydrogen filling stations have been built last year for the Aichi 2005 Expo. Presently, the number of stations with on-site reforming in Japan is 9, including 4 stations based on NG reforming (Table 9). These filling stations have accumulated a total of 3500 filling operations, and a delivery of 6780 kg of hydrogen (during the 2002-2004 period). The quality of hydrogen supplied is suitable for fuel cell vehicles (Table 11).



Figure 6 Osaka city hydrogen filling station using Osaka Gas reformer (a) Osaka Gas Compact reformer HYSERVE – 100 (100 Nm³).



Figure 7 Mitsubishi Kakoki Kaisha naphtha reformers (a small 50 Nm³/h type is installed in Yokohama Asahi hydrogen station)



New Model H₂ Generator Under Development



Comparison

	Existing	New Model
Feedstock consumption	100	80
Site area	100	45

Table 9 List of hydrogen filling stations in Japan (2005)

Production	Location	Feedstock	Capacity (Nm ³ /hr)	Contractor and (reformer supplier)	Dispensing Pressure (MPa)
On-site	Osaka	Town gas	30	Iwatani, Osaka Gas	25-35
	Torishima			(Fuji Electr.)	
On-site	Shikoku	Electrolysis (PEM)	30	Nippon Sanso	25-35
	akamatu			(Electri: Mitsubishi)	
Off-site	Yokohama	H2 from NaCl	30	Iwatani, Tsurumi Soda	25-35
	Tsurumi	Electrolysis			
On-site	Yokohama	Desulfurized	30	Cosmo Oil Co.	25-35
	Daikoku-cho	Gasoline			
On-site	Yokohama	Naphtha	50	Nippon Oil Corp.	25-35
	Asahi-ku			(Mitsubishi KK)	
Off-site	Tokyo	Liquid hydrogen	-	Iwatani, Showa-Shell	25-35
	Ariake				plus LH2
On-site	Tokyo	LPG/Town gas	50	TokyoGas,NipponSanso	25-35
	Senju			(Mitsubishi KK)	
On-site	Kanagawa	Methanol	30	Japan Air Gases	25-35
	Kawasaki				
Mobile	Tokyo (METI)	H2 cylinders	-	Nippon Sanso	25-35
On-site	Aichi (Tokai)	Town gas	40	Toho Gas	25-35
On-site	Kanagawa	Kerosene	50	Idemitsu Oil	25-35
	Hadano			(Mitsubishi KK)	
On-site	Kanagawa	Electrolysis (Alkali)	30	Kurita-Shinane-Cl	25-35
	Sagamihara				
	Tokyo				
Mobile	Oume	Town gas	30	Babcock-Hitachi	25-35
On-site	Aichi Expo 1	Town gas	100	Osaka Gas	35
Off-site	Aichi Expo 2	Coke oven gas	100		35

Reported incidents are related to hydrogen production as well as hydrogen dispensing units:

- A crack was found at the outlet of one of the reactor tubes of a reformer, probably due to thermal stress under repeated start-up/shutdown operations.
- Hydrogen leakage from breakaway devices (emergency couplers) was reported from few stations. It is due to cracks caused by excess stress.
- During filling operations, discrepancies were found between the hydrogen amount delivered to the vehicle and the amount displayed by the dispenser. This is due to the calibration and accuracy of the flow meter.
- Another filling issue is related to the ambient temperature. When ambient temperature is high, as it is in summer, hydrogen temperature inside the vehicle tank can be higher than usual. Consequently, the filling operation will stop at a lower pressure than the usual target pressure.

Table 10 Total amount of hydrogen delivered to fuel cell vehicles in Japan in 2002, 2003 and 2004 from on-site reforming

H ₂ Station	Start date	2002	2003	2004
Mobile	02/12	235	758	670
YHM Daikoku	03/3	65	354	452
YHM Asahi	03/4		171	143
Senjuu	03/5		279	279
Ariake	03/5		1670	1407
Kawasaki	03/8		50	59
YHM Tsurumi	03/12		14	10
Hadano	04/4			127
Sagamihara	04/4			18
Ohme	04/6			19
Total H ₂ in kg		301	3294	3182

Table 11 Emissions from Japanese filling stations with on-site reforming

Impurity (vol. ppm)	Kawaski	Ariake	Sagamihara	Senjuu	Detection limit
	Methanol	LH ₂	Electrolysis	LPG	
CO	0.05	0.02	0.02	0.02	0.01
CO ₂	0.29	<0.01	<0.01	<0.01	0.01
Hydrocarbons	< 0.05	<0.05	< 0.05	< 0.05	0.05
Benzene	< 0.005	<0.005	< 0.005	< 0.005	0.005
Sulphur	< 0.0001	<0.0001	< 0.0001	< 0.0001	0.0001
Methanol	< 0.01	<0.01	< 0.01	< 0.01	0.01
HCOOH	< 0.01	< 0.01	< 0.01	< 0.01	0.01
Formaldehyde	< 0.01	< 0.01	< 0.01	< 0.01	0.01
Acetone	< 0.01	< 0.01	< 0.01	< 0.01	0.01
NH ₃	< 0.001	< 0.001	< 0.001	< 0.001	0.001
H ₂ O	< 0.5	< 0.5	< 0.5	0.9	0.5
O ₂	< 0.01	< 0.01	< 0.01	< 0.01	0.01
Ar	< 0.03	< 0.03	0.36	0.11	0.03
N ₂	1.70	0.03	84.6	0.12	0.03
He	< 3.	< 3.	< 3.	< 3.	3.

3.2 Activities in Europe

Development and demonstration of on-site reformers is being done in projects for stationary combined heat and power systems and for providing hydrogen fuel.

The two hydrogen filling stations in Stuttgart and Madrid have high public profile. Both stations are part of the EC funded CUTE project. The CUTE project is a large European project with nine hydrogen stations in nine cities in Europe. In 2006 the project will be extended to more European cities, including Reykjavik, Berlin. The Berlin station will use on-site reforming of LPG (with a capacity of 100 Nm³/h). Moreover, the new project has a global prospective as after Beijing and Perth joined the project.

3.2.1 Stuttgart filling station

The station is owned by the local bus company SSB and operated by the energy utility EnBW. Besides on-site reforming, trucked-in hydrogen ensures the back-up supply. The reformer plant, supplied by Mahler IGS (Figure 8), started on September 2003 and services three Citaro fuel cell buses, with a filling time of 20 minutes at a pressure of 15 bar. The capacity-range of the plant is 50-100 Nm³/hr. Start-up times are 1 and 18 hours for hot and cold starts respectively. As of December 2004, the plant has produced 250,000 Nm³ of hydrogen with expected quality (CO < 1 ppm). A total of 18 incidents (shut-downs) were reported: 12 caused by malfunction of one flow meter, 2 for repair of the furnace, and 4 caused by control-software. At the station, hydrogen is stored in two tanks, a middle-pressure tank of 200-350 bar (10 m³), and a high-pressure tank of 400 bar (2 m³).

The performance of the buses is satisfactory, with a consumption rate of 23 kg-H₂/100 km, and a driving range of 18,000 km/year



Figure 8 Stuttgart filling station layout

3.2.2 Madrid filling station

The refuelling station in Madrid is established and operated by Air Liquide. The purpose of the station is the refuelling of 4 fuel cell buses (75 Nm³/h) from on-site reforming and trucked-in hydrogen.

The reformer, supplied by CarboTech (Figure 9), started on May 2003. Gas Natural is the reformer's owner and operator. During 2004, the plant produced a total of 49,000 Nm³. The hydrogen quality is sufficient to meet DaimlerChrysler specifications and the off-spec hydrogen produced during the warm-up is vented. The operation pressure of the refuelling station is 16 bar, and the current set price for hydrogen is 0.30 €/Nm³. Various tests were conducted including shutdown / start-up operations, safety and remote control. The start-up time of the plant is 8 hours for a cold start (4 h for the reformer and 4 h to stabilize the PSA unit), and 4 hours for a hot start. These times vary slightly, depending on the initial conditions. Hydrogen purity and plant efficiency are as expected.

Frequent start-ups and shutdowns lead to energy losses during transients and to equipment damages. Two cracks and two leaks were reported. The refuelling station will run until May 2006 according to the CUTE contract. The CUTE partnership has applied for a renewal of the project with additional partners. If this is accepted the operation of the station will be extended until May 2007.

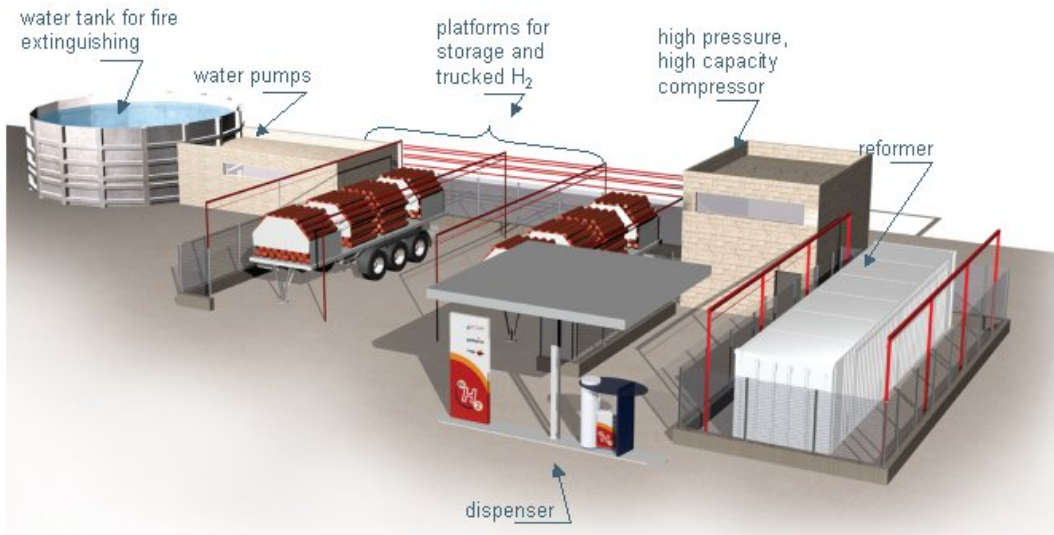


Figure 9 Madrid filling station layout

3.3 Activities in USA and Canada

Table 12 North American hydrogen filling stations based on natural gas reforming¹⁸

Location	Project Partners	Opening date	Technology	Comment
Thousand Palms, California	SunLine Transit Agency, HyRadix, DOE	2004	Catalytic ATR	See 3.3.1 (below)
Auburn, California	California Fuel Cell Partnership	2004	Ztek High Performance Steam Methane Reformer (HPSR)	HPSR converts natural gas supplied by PG&E to hydrogen at a rate of 600 scfh.
Oakland, California	Alameda-Contra Costa Transit, ChevronTexaco	August 2005	SMR	Will fuel AC Transit's fleet of 3 fuel cell buses
Chino, California	Kia-Hyundai America Technical Center, UTC Fuel Cells, ChevronTexaco Technology Ventures	February 2005	Natural gas reforming	Part of 5-year DOE cost-sharing program
Las Vegas, Nevada	Nevada Test Site Development Corp., DOE, Corporation for Solar Technologies and Renewable Resources, APCI and city of Las Vegas	November 2002	SMR	First multi-purpose station, uses 50kW PEMFC for electricity sale, and produces H2 and H2/CNG blends
University Park (Penn State University) ¹⁹	DOE, APCI, Penn State	2004	SMR + PSA	Commercial station project. Will feature H2 filling up to 7000 psi, uses Pdc Machines compressor
Toronto, Ontario	Hydrogenics, City of Toronto, Canadian Transportation Fuel Cell Alliance	2003	SMR	70 kg/day of hydrogen; and a 50kW PEMFC for peak-shaving.

¹⁸ <http://www.fuelcells.org/info/charts/h2fuelingstations.pdf>

¹⁹ D A Guro, Development of a turn key hydrogen fueling station, DOE hydrogen program, FY 2004

3.3.1 Thousand Palms, California

HyRadix has supplied a reformer plant to the SunLine Transit Agency (Figure 10). The technology is based on Auto Thermal Reforming (ATR) at 650°C, 10 bar gas-input and 7.5 bar gas-output²⁰. The filling station, which opened on April 2004, can provide pure hydrogen to fuel cell vehicles, as well as 20%-80% hydrogen-natural gas blends (HCNG) to service NG-vehicles. Presently, the station services a fleet of different buses: 5 HCNG, one fuel cell, and one internal combustion engine bus. The plant footprint is 2.4m x 6.m, and the capacity range is 50-100 Nm³/hr. The hydrogen purity is 99.999%, where the removal of inert gases by PSA has been a challenge. Cold start-up takes 3 hours while the hot start-up takes 2 hours. The plant has been operational for 2300 hours, and can be operated unattended with daily start-stops.

The following emissions were reported: NO_x <20 ppm, CO < 5 ppm, SO_x < 1 ppm, and hydrocarbons < 200 ppm.

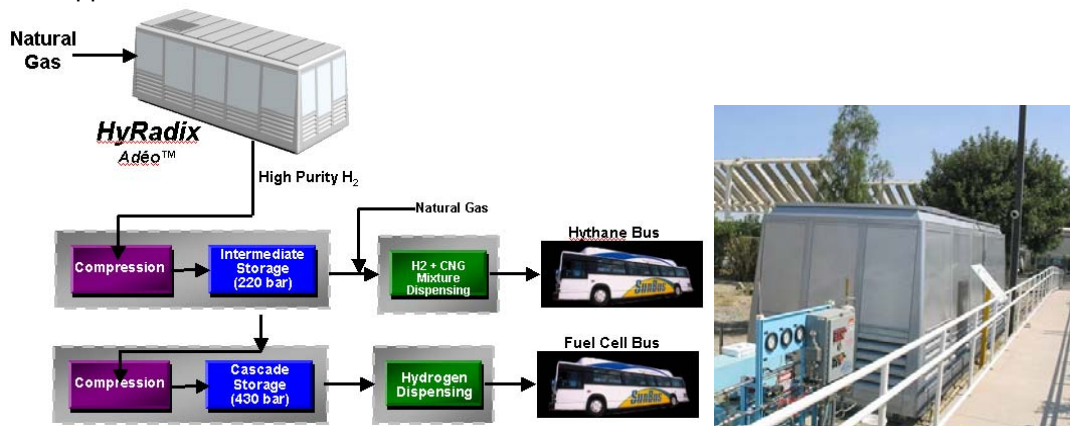


Figure 10 SunLine Transit Agency filling station in California

²⁰ M Davies et al., Hydrogen filling technology, DOE hydrogen program, FY 2004

4 Technology status of small scale reforming

Reforming is the process of transforming hydrocarbons into hydrogen. The process takes place in three main stages (Figure 11): (i) reforming, (ii) water-gas shift, and (iii) purification.

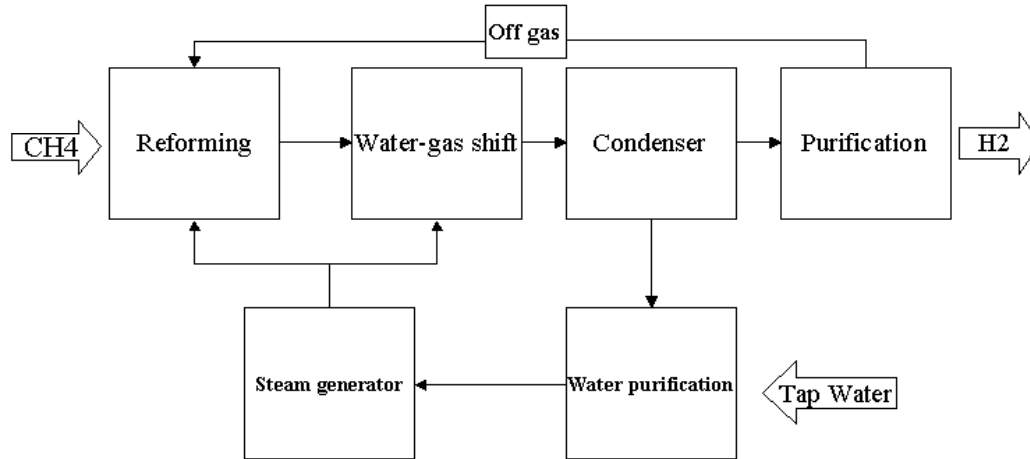
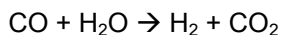


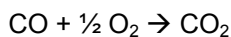
Figure 11 Schematic of natural gas reforming process for hydrogen production

In the first stage (reforming), and depending on the type of reactor, natural gas feedstock reacts with steam (in a steam reforming reactor, SMR) or oxygen (in a partial oxidation reactor, POX) to produce a synthesis gas (syngas) that is composed mostly of H₂ and CO. In the second stage (water gas shift), the syngas reacts with steam and produces more hydrogen according to the reaction:



The produced gas is 50-60% hydrogen rich, the rest is composed of CO₂, CH₄, H₂O and a fraction of CO (0.5-1%). Surplus water from the gas exiting the shift reactor is condensed and recycled. Very often, removal of organic compounds and dissolved CO₂ is necessary prior to sending water back to the steam generator unit.

In the last step (purification), dry reformat is either sent to a purification unit or to a preferential-oxidation reactor, depending on the intended use for hydrogen. For industrial hydrogen, that requires a purity of 99.999%, Pressure-Swing Absorption (PSA) is the technology of choice for hydrogen production capacities of 50-1,000 Nm³/hour. Palladium membrane is another alternative but has been considered uneconomic for production capacities above 10 Nm³/h. For fuel cell applications, a preferential oxidation process is usually preferred to methanation to reduce the CO content to a few ppm's.



The reforming process is somewhat flexible with respect to feedstock. Fossil fuels like LPG and naphtha have been used commercially as feed for steam reformers. POX reformers have been operated with heavy fraction of fossil fuels like diesel and heating oils as feed. Reforming processes have been developed for partially oxidised compounds like dimethylether and methanol. These compounds are easier to reform than hydrocarbons and less heat transfer is involved. The process design is simpler and the associated technologies are in some locations competitive despite high feed costs. Gas-To-Liquid (GTL) fuels produced from natural gas via the Fischer-Tropsch process are excellent reformer feeds thanks to the absence of sulphur, olefins and aromatics. Large GTL plants are already operating and several are under construction. The production of GTL fuels is

predicted to become significant within a decade²¹. Ethanol from agricultural products is already produced for transportation purposes and has enjoyed extensive R&D funding. However, it is difficult to reform because of its tendency to form ethylene, a strong coke precursor²². Ammonia has received much less interest, probably due to concerns about toxicity, explosion risks, and poisoning of the PEMFC membrane. Ammonia is, however, handled on a major scale worldwide with an excellent safety record. It is the only hydrogen carrier produced on large scale at relatively low cost, which do not emit CO₂ when used locally.

Steam-reforming processes are sensitive to impurities in the feeds. Purification of the feed is important for the performance of the reformer and downstream units. Water needs to be treated to avoid fouling of steam generator facilities as well as catalysts. Catalytic ATR and POx units will in some locations require purification of incoming air to avoid poisoning of the catalytic systems.

Many concepts have been proposed for CO₂ capture from large-scale reformers. The same principles can be applied for small-scale reformers. However, little attention has been paid on cost effective scale down of these processes because of its lack of interest for small-scale reformers. However, new reformer concepts have been launched to reduce the CO₂ avoidance cost like thermocatalytic cracking, sorbent enhanced reforming and cyclic autothermal reforming. The technology status for CO₂ capture technologies is reviewed in paragraph 4, while the new reformer initiatives are reviewed in paragraph 4.1.4.

In the following a detailed review of the technologies for reforming of hydrocarbon is given. Focus has been on commercial and semi-commercial process developed for the hydrogen filling station market.

4.1 Hydrogen production from hydrocarbons

4.1.1 Steam reforming

Steam reforming is the most widely applied technology for the production of hydrogen from fossil fuels. The reaction is endothermic and requires external heat supply:



The external heat can be achieved by the combustion of a fraction of incoming natural gas (up to 25%), eventually supplemented by the combustion of the purge gas from the hydrogen purification step. The reaction takes place at high temperatures of 700-900°C and pressures of 15-45 bar, in the presence of catalysts (Ni supported on Al₂O₃). A steam-to-carbon mass ratio of 3 is needed to avoid the formation of carbon on the surface of the catalyst and its deactivation. The reaction is equilibrium constrained, and conversion is favoured by high temperature, low pressure and high steam-to-carbon ratio.

²¹ T.H. Fleisch, R.A. Sills; Third Topical Conf. Natural Gas Utilization, p. 375. AICHE Spring Natl. Meeting New Orleans 2003

²² F. Joensen, J. R. Rostrup-Nielsen; J. Power Sources **105** (2002) p. 195-201

It is essential that the reforming process avoids the formation of carbon. The following table presents the three basic mechanisms that lead to coking:

Table 13 Basic mechanisms leading to the formation of carbon on the catalyst surface²³

Type of carbon	Mechanism	Enhanced by
Encapsulating carbon (polymeric carbon)	Formed from heavy hydrocarbons at low temperature, < 500°C	Low H ₂ O/C Low H ₂ /C Aromatic/olefinic feed
Filamentous carbon (whisker-like carbon, catalytic coke)	Formed at high temperature, > 450°C by a catalytic mechanism	Low H ₂ O/C Low activity Aromatic/olefinic feed
Pyrolytic carbon (soot)	Formed by radical mechanism in the gas phase at high temperature, > 600°C	Low H ₂ O/C High pressure High pressure Acidic surfaces Low reactivity High skin temperature

An important disadvantage of heavier hydrocarbons, compared with natural gas, is their tendency to poison the reforming catalyst by depositing elemental carbon on its surface. Indeed, the conversion of heavy hydrocarbons, above 650°C, always starts with their decomposition into lighter hydrocarbons such as olefins that are strong coke precursors²². Steam reforming is not commercially applied for feedstocks heavier than naphtha.

After reforming, the produced syngas that contains 5-10% CO goes through water gas shift reactors for further hydrogen production according to the reaction:



The process takes place at lower temperatures than reforming and uses cheaper catalysts (Fe, Cu supported on Al₂O₃). Very often, the shift process is accomplished in two steps. First, a high temperature shift-reactor (350-500°C) with Fe/Al₂O₃ catalyst, where CO content is reduced to 3%. Next, a low temperature shift-reactor (200-300°C) with Cu/Al₂O₃ catalyst, where CO content is reduced to 0.5-1%. However, small-scale reforming often uses only a medium temperature shift-reactor (300-400 °C), with a precious metal catalyst.

4.1.1.1 Conventional steam reformers

Large-scale steam reformers of a wide range of sizes have been built for the chemical industry and oil refining. They can produce 0.7 to 3 million Nm³ of hydrogen per hour. The reactor, that operates at 850°C and pressures of 15-45 bar, consists of a 12-15 meter tubes, filled with catalyst, located inside a gas-fired furnace (Figure 12). Capital cost for a 5.7 million Nm³/h plant (including the reformer, the shift reactor, and PSA) is about \$80/kW H₂²⁴. These reactors can be scaled-down to 1000 Nm³/h with increased capital costs.

Disadvantages of conventional steam reformers are their large size (12-15m long tubes) and high cost (due to operations at high temperature and pressure that require expensive materials).

²³ Catalytic steam reforming, J.R.Rostrup-Nielsen, Springer-Verlag Berlin, 1984

²⁴ Directed Technologies, Inc., Air Products and Chemicals, BOC Gases, The Electrolyser Corp., and Praxair, Inc., July 1997, "Hydrogen Infrastructure Report", prepared for Ford Motor Company Under USDOE Contract No. DE-AC02-94CE50389, Purchase Order No. 47-2-R31148

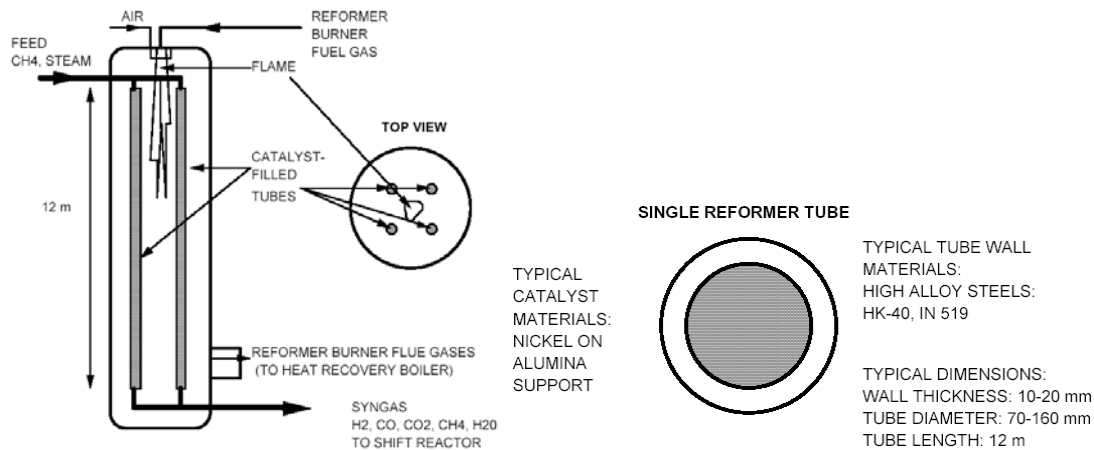


Figure 12 Conventional large-scale steam reformers²⁵

4.1.1.2 Conventional tube reformers for small scale operation

Conventional tube reformers have been built for a wide capacity range from 100 to 100,000 Nm³/hr. Various vendors (Haldor Topsoe, Caloric, KTI, Mahler, Hydro-Chem, Mitsubishi Kakoki Kaisha and Pan American Enterprises) offer reformers with capacities smaller than 1,000 Nm³/hr.

The reformer consists of 8-12 m long tubes containing the catalyst, and operated at about 850°C and pressures of 15-25 bar. These operating conditions require the use of expensive alloy steel. Typically, about 50% of the fired duty is consumed by the reaction and the rest is used for preheating and steam generation. The overall furnace efficiency is above 90%.

The reformer tubes are located in the radiation zone of the furnace. Hence the common use of radiation reformers or high-temperature reformers as names. They are the most efficient reformers and are the choice for high production capacities.

4.1.1.3 Gas heated reformers

In these systems the heat transfer is accomplished by convection instead of radiation as in tubular reformers. About 80% of the fired duty is used for the reforming reaction, compared to only 50% in a tubular reformer. Designs with the catalyst placed in bayonet tubes are typical for large plants. Reformers with the catalyst placed in concentric annular catalyst beds have been developed for small-scale plants. In these systems the heat transfer path is curved (see Figure 13) in order to make the reformer more compact. Some of the reformers operate at lower pressure and temperature (3 bar, 700°C) than tubular reformers, which relaxes the constraints on material requirements.

²⁵ J Ogden, Review of small stationary reformers for hydrogen production, report to the International Energy Agency, 2001

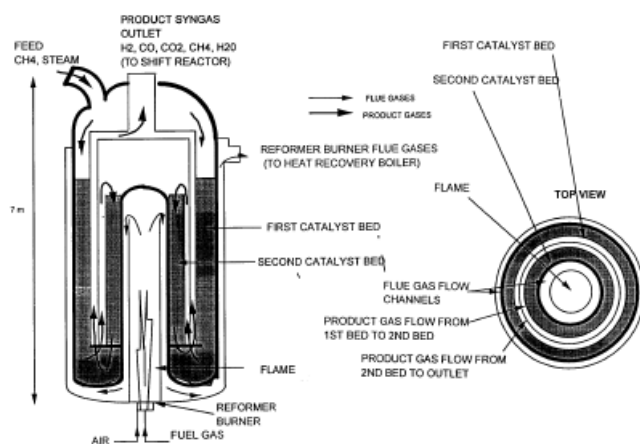


Figure 13 Flow-path in a compact reformer with convective heat transfer (Haldor Topsoe design)

- Haldor-Topsoe has delivered 10 industrial plants since 1992 in the range of 500–10,000 Nm³/hr. The system efficiency is about 71.5% (LHV: Low Heating Value). The hydrogen is supplied at 20 bar. The cold start-up time is 18-24 hours and hot start-up takes 10-60 minutes.
- Kinetics Technology International (KTI) provides heat-exchanged reformers (HER®) for the production range of 100–1,720 Nm³/hr. The reactor consists of conventional reformer tubes located in the flue gas convection zone. The reactor height is 7-12 m. The calculated efficiency is 71.8%. A total of 5 units are in operation.
- Mahler has developed a compact reformer, Hydroform-Compact, with concentric annular catalyst beds. A prototype is installed in the hydrogen filling station in Stuttgart (see section 3.2).
- CarboTech has developed a compact reformer for hydrogen filling stations based on WS-Reformer-GmbH reformer technology (Flox®) and their own PSA technology. CarboTech has delivered one unit to Repsol as a part of the EU-CUTE project for the H₂-filling station in Madrid (section 3.2). Moreover, the company has also delivered a 100 Nm³/hr unit to Linde AG for the Munich Airport station.
- Mitsubishi Kakoki Kaisha Ltd. (MKK) has developed a compact reformer that uses feedstock and PSA off-gas as fuels for the burner. The unit is skid mounted and can be remotely monitored. The reactor can reform various fuels including town gas, LPG (propane and butane), naphtha and kerosene. A hydrogen purity of 99.999% was reached. Reported emissions are: CO (1 ppm), CO₂ (1 ppm), CH₄ (1 ppm), NO_x (20 ppm), SO_x (1 ppm) and soot (1 mg/Nm³). MKK has delivered several units with a capacity of 50 Nm³/h to hydrogen filling stations in Japan: Nagoya (town gas), Tokyo (LPG), Yokohama (naphtha) and Hadano (kerosene).
- Osaka Gas is developing natural gas reformers for residential cogeneration systems and hydrogen filling stations. Their HYSERVE system is a compact steam reformer with PSA for hydrogen purification. The reformer is a cylindrical type in which the burner creates a circular flow of combustion gas and operates at 0.8-0.9 MPa and 750°C. The efficiency is 70% (HHV: High Heating Value). High Performance DeSulfurization technology (HPDS) that removes sulphur to a level of 1-2 ppb is utilised. Osaka Gas has developed catalysts for steam reforming (ruthenium based) and water gas shift reactions. The shift reactor is integrated with the HPDS unit. The product purity is reported to be 99.999%. The standard unit does not include water purification. Both the reformer and the PSA are delivered in one container. HYSERVE

technology is commercial, with HYSERVE-30 in operation at hydrogen filling stations since January 2002. A durability of 90,000 hours was demonstrated that includes 1200 shut-down/start-up cycles, and 25,000 load-change operations.

- Harvest has supplied steam reformers to several hydrogen refuelling stations in US operated by Air Products²⁶.
- Hexion has developed a 50 Nm³/hr steam reformer with PSA purification, HPU-L-5.0. The company is in cooperation with Ballast Nedam for the development of hydrogen refuelling stations²⁷.

Apparently, all these companies, except Osaka Gas, are using conventional steam reforming catalysts (except Osaka Gas that uses a Ru catalyst) in their design. These catalysts are sulphur sensitive and require effective sulphur removal units for the clean-up of natural gas prior to the entry to the reformer. Moreover, the catalysts are pyrophoric (may ignite in contact with air) and nitrogen or other inert gases are required for purging during shutdown.

- The company H₂Gen is developing a compact reformer using sulphur resistant catalysts. Therefore, no prior desulphurisation is required. The commercialization is planned for 2007. Hydrogen can be produced at a pressure of 15 bar and a purity of 99.999%. Reported impurities are: O₂ (1 ppm), H₂O (1 ppm), CO (1 ppm), CO₂ (1 ppm), CH₄ (1 ppm), and N₂ (20 ppm). The unit has a size of 2.13 m x 2.90 m x 2.16 m, and a weight of 3175 kg. The entire system can be remotely monitored²⁷.

4.1.1.4 Plate-type and microchannel reformers

Another potential innovation in the design of steam reformers is the plate-based reformer. The reformer uses several plates. For each plate, one side is coated with steam reforming catalysts and is supplied with methane and steam, and on the other side of the plate the methane undergoes catalytic combustion, providing the necessary heat for the endothermic steam reforming (Figure 14). Promising systems appear to be those using thin catalyst layers coated on compact heat exchangers. They have demonstrated heat transfer rates higher than 20 – 200 kW/m² in laboratory tests and up to 50kW/cm³ reactor volume. The residence time is in order of millisecond compared to about 1 second for conventional reformers. Advantages of the plate design are compactness, better heat transfer, fast start-up, and integration with PEM fuel cells when running at 600°C.

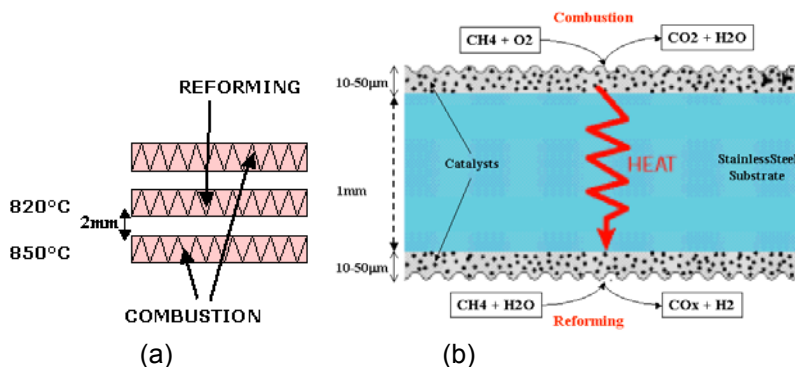


Figure 14 (a) Drawing of a plate reformer, (b) Principle of operation of the Advantica reformer²⁸

²⁶ http://www.afvi.org/palmsprings/event_conf_cd/may4/800-930/C1/McCarthy.pdf

²⁷ Fuel cell Today, May 2005, <http://www.fuelcelltoday.com>

²⁸ A. Siddle, K. D. Pointon, R. W. Judd and S.L. Jones, Fuel Processing For Fuel Cells - A Status Review and Assessment of Prospects, DTI/Pub URN 03/1644, <http://www.dti.gov.uk/energy/renewables/publications/pdfs/f0300252.pdf>

The plate reformer was developed for the integration with fuel cells. The following companies are actively working in this area:

- Accentus has demonstrated a plate reformer for offshore GTL process²⁹.
- Ztek is using a special type of plate reformer where the plates are used as heat transfer medium. They have built an 18 Nm³/hr prototype that produces hydrogen with a purity of 99.99%, and operated it for 8000 hrs³⁰.
- Velocys has developed a micro-channel reformer concept that has been applied for syngas production. This concept can also with small modifications be used for small-scale hydrogen production³¹.

A variant of the plate-type reformer is the honeycomb reformer where reforming and combustion occur in alternating channels. This design has a potential for further compactness (Figure 15).

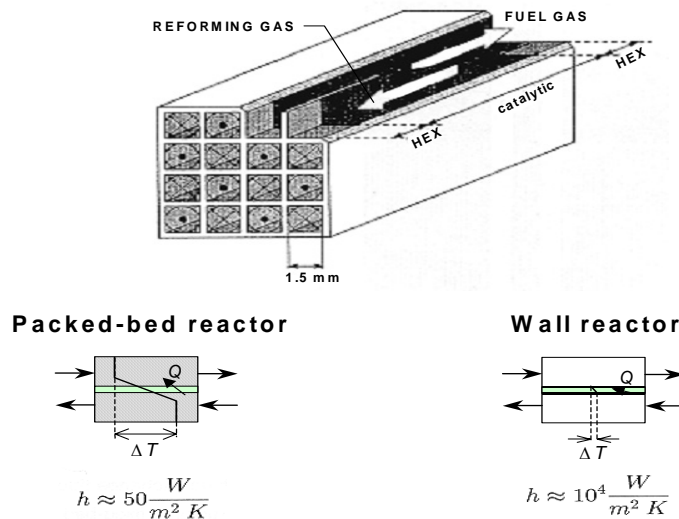


Figure 15 Drawing of a honeycomb reformer

4.1.2 Partial oxidation process

In Partial Oxidation (POX), methane is oxidized to produce carbon monoxide and hydrogen according to the following reaction:



The reaction is exothermic and therefore does not require an indirect heat exchanger. Although catalysts are not needed in the process, thanks to the high operating temperature, but their presence significantly increases the hydrogen yield per mole of methane. Durability is a challenge for catalytic combustion catalysts since they may be submitted to very high temperatures and runaway reactions. Similar to a steam reforming plant, a partial oxidation plant includes a POX reactor, a shift reactor and a hydrogen-purification unit. Large-scale units normally incorporate an oxygen plant, since operation with pure oxygen rather than air reduces the size and cost of the process. The energy efficiency of POX can reach relatively high values, 65%. However, its high operating temperature and low heat recovery makes it less energy efficient than SMR. Indeed, unlike SMR systems, POX systems cannot take advantage of heat recovery by combusting fuel from

²⁹ http://www.accentus.co.uk/hydrogen_economy_applications.htm

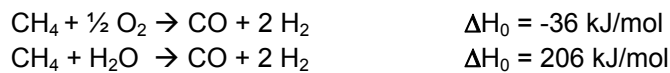
³⁰ <http://www.ztecorp.com/PDF/600HCutSheet.pdf>

³¹ <http://www.velocys.com>

the PSA off-gas. Small-scale POX systems have not, to the authors knowledge, been commercialised, and are still undergoing intensive R&D for further improvements. Their ability to bypass an indirect heat exchanger is a clear advantage for size and cost reductions. Furthermore, POX reformers have fast response-time that makes them attractive for fuel cell applications. At high temperature, POX systems can reform a variety of fuels including methane, LPG, gasoline, diesel, methanol and ethanol. This fuel flexibility makes POX technology attractive for various applications such as onboard reforming, portable and stationary reforming systems. However, these advantages do not compensate for the low energy efficiency of POX technology that limits its use in hydrogen filling stations.

4.1.3 Autothermal reforming

Autothermal reforming (ATR) combines partial oxidation and steam reforming reactions in a single reactor where natural gas is mixed with both steam and oxygen (or air):



In the first step of ATR, natural gas reacts with oxygen and undergoes an exothermic partial oxidation reaction. Next, the generated heat is used to drive the endothermic steam reforming reaction when steam enters the reactor. With the right mixture of input fuel, air and steam, the POX reaction supplies the heat required by the SMR reaction. Similar to a POX reformer, the ATR reformer does not require an external heat supply, and therefore is likely to be less costly and more compact than an SMR reformer. However, the steam reforming reaction is substantially slower than the partial oxidation reaction, and this makes the ATR reactor larger than the POX reactor. In an ATR reactor the heat generated by the partial oxidation reaction is fully utilised in driving the steam reforming reaction. Therefore, the ATR reactor has a higher efficiency than the POX reactor where excess heat is not easily recovered. Similar to SMR and POX reformers, an ATR reformer also needs water-gas shift and hydrogen purification units. As with POX reforming, the utilisation of the energy available from the PSA off-gas remains a big challenge. Moreover, when applying air as the oxygen source, the ATR reformer has to handle nitrogen that will affect the design of the PSA, as well as the specific energy content of the PSA off-gas.

ATR with an open flame POX followed by a catalytic SMR is a traditional concept widely used in industry. ATR reactors can operate at significantly lower steam-to-carbon ratio than steam reformers. Therefore, the technology has been applied for large-scale units producing syngas with low H₂/CO ratio for methanol and Fischer-Tropsch synthesis. Many companies have worked on the development of small-scale ATR systems, particularly for multi-feed on-board reforming. However, for H₂-fuelling stations the two companies that are known to be close to commercialisation are HyRadix and ChevronTexaco.

- HyRadix's technology uses high-pressure (7 barg) air catalytic ATR reactor with a down stream high temperature shift reactor. Dedicated PSA units supplied by Questair, are used to separate hydrogen from nitrogen. HyRadix has delivered a demonstration unit to the SunLine Transit Agency in Palm Springs California.
- ChevronTexaco has developed an ATR based hydrogen process that was put in operation in February 2005 at the Hyundai-Kia America Center, in Chino, California. The unit produces hydrogen from natural gas, using ChevronTexaco Technology Ventures proprietary autothermal reforming technology. The unit is claimed to be capable of producing hydrogen from corn-based ethanol.
- Membrane Reactor Technology (MRT) has started the development of a fluidised-bed ATR reactor with in-situ separation of hydrogen by a planar Pd-membrane. A 50 Nm³/hr (2 m x 4.6 m

x 2.1 m) prototype has been built that produces hydrogen at 7 bar with a purity of 99.99%. The unit converts grid NG (20 Nm³/h) with an efficiency of 82% (HHV).

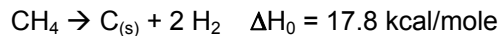
- Plug-Power Inc., offers GenSite-H₂ units with a production capacity of 8 Nm³/hr at a pressure of 10 bar. The unit provides Hydrogen with a purity of 99.95% and CO-CO₂ impurities of 10 ppm.

4.1.4 Novel reforming technologies

Interest in small-scale hydrogen production from hydrocarbons has resulted in the development of several new concepts but none of them is close to commercialisation.

4.1.4.1 Thermocatalytic cracking of methane

In this process, methane is broken down to hydrogen and carbon, sometimes in the presence of a catalyst at 800-1200°C, according to the reaction:



The reaction is endothermic and requires energy input. Several concepts have been suggested on how to supply the energy and handle the solid coke formed, but none of them, to the best of the author's knowledge, is near commercialisation.

The Florida Solar Energy Centre is working on such catalytic reformers for the cracking of liquid and gaseous hydrocarbons³².

4.1.4.2 Sorbent-enhanced reforming

The basic idea is to capture the CO₂ as it is produced in the reaction zone. Consequently the reaction equilibrium is shifted towards hydrogen production. CO₂ removal can be achieved by solid sorbents such as calcium oxide or Mg-Al hydrotalcite³³. The system can operate periodically in two modes: CO₂-absorption mode, followed by CO₂-desorption mode where the released CO₂ could be sent to a sequestration unit. Potential advantages of this concept are simple design (no shift reactor and less constraint on or no PSA), low reaction temperatures (below 500°C), reduced clean-up cost, and CO₂ capture. Sorbent materials should satisfy the following conditions: high CO₂ uptake, rapid kinetics, stability at high steam concentration, regenerability and low cost.

Reported results are promising but further work is needed to make the technology competitive with conventional reforming (Table 14). Present technical issues include sorbent kinetics and lifetime, the need for less steam in sorbent regeneration, and new system design for increased fuel conversion and heat integration.

³² N Muradov, JOURNAL OF POWER SOURCES, 2003, Volume: 118, Number: 1-2 (MAY 25), Page: 320-324; N Muradov et al., INTERNATIONAL JOURNAL OF HYDROGEN ENERGY, 2005, Volume: 30, Number: 3 (MAR), Page: 225-237

³³ H. T. J Reijers, D. F. Roskam-Bakker, J. W. Dijkstra, R. P. de Shmidt, A. de Groot, R. W. van den Brink, Hydrogen production, through sorption enhanced reforming, ECN, the Netherlands http://www.ecn.nl/_files/sf/klimaat/ehc2003sorption.pdf

Table 14 Comparison of conventional steam reforming (SR) and sorption-enhanced reforming (SER)³³

	Small-scale SR	Sorbent-enhanced reforming
T (°C)	800	500
P (bar)	10	1.7
CH ₄ conversion (%)	84	66
Efficiency (LHV)	70	39
steam/CH ₄ ratio	3	6
steam/H ₂ ratio	1.1	2.3
H ₂ purity (%)	99.999	89
Fraction CO ₂ adsorbed	0	50

- Dutch ECN³³ is working on new sorbent materials based on hydrotalcites.
- ChervronTexaco is developing a single bed based CaO-sorbent for CO₂. The reforming process is SMR followed by water-gas-shift. In addition, the system will contain a desulphurisation unit, a methanation unit and a tail gas oxidizer³⁴.

4.1.4.3 Autothermal Cyclic Reformer (ACR)

General Electric Global Research is developing an Autothermal Cyclic Reformer (ACR) for hydrogen filling stations. ACR is based on catalytic steam reforming operating in a 3-steps cycle: (step 1 - Reforming) steam reforming of the fuel in a Ni catalyst bed, (step 2 - Air Regeneration) heating the catalyst bed through oxidation of the Ni catalyst, and (step 3 - Fuel Regeneration) reducing the catalyst to the metallic state. The heat required for the endothermic reforming step is provided during the exothermic air regeneration step. The ACR process consists of two reactors cycling between the reforming and regeneration (air and fuel) steps. The product stream is 70% hydrogen rich. CO concentrations at inlet and outlet of the shift reactor are 13-20% and 1.25% respectively. Praxair has developed a 3-bed PSA for integration with the ACR reactor. Preliminary tests show a hydrogen purity of 99.996% and 75% recovery at 120 psig³⁵.

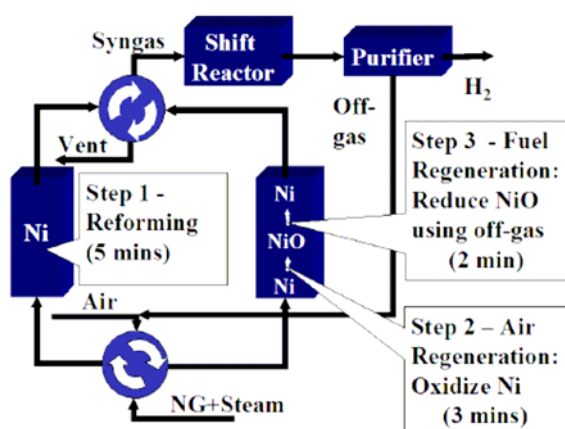


Figure 16 Autothermal Cyclic Reforming (ACR) from General Electric

³⁴ J Stevens, Development of a 50-kW Fuel Processor for Stationary Fuel Cell Applications Using Revolutionary Materials for Absorption-Enhanced Natural Gas Reforming, DOE hydrogen program, FY 2003, http://www.eere.energy.gov/hydrogenandfuelcells/pdfs/ivd18_stevens.pdf

³⁵ R. Kumar et al., Autothermal cyclic reforming based hydrogen generating and dispensing systems, DOE hydrogen program, FY 2004, http://www.eere.energy.gov/hydrogenandfuelcells/annual_report04.html

4.1.4.4 Ion transport membrane reforming (ITM)

ITM technologies may involve either oxygen transport (as O^{2-} ions) or hydrogen transport (as H^- or H^+)³⁶. Two consortiums headed by Praxair and Air Product respectively, have headed the development of oxygen transporting membranes for syngas production.

A Praxair led consortium (BP Amoco, Statoil, Sasol) is developing a system that combines an ATR based oxygen membrane with a water-gas shift reactor incorporating a hydrogen membrane. Praxair is developing a Pd-Ag hydrogen membrane supported on a ceramic material. Control of the pore size and porosity of the ceramic substrate is critical to ensuring that the Pd-Ag coating is leak-free. To reach significant hydrogen fluxes porous ceramic substrate and thin film membranes are needed. Hydrogen flux also increases with increased partial pressure and operating temperature. Several designs were tested with substrate pore sizes between 50 and 5 mm, and membrane film thicknesses of 15-8 microns³⁷.

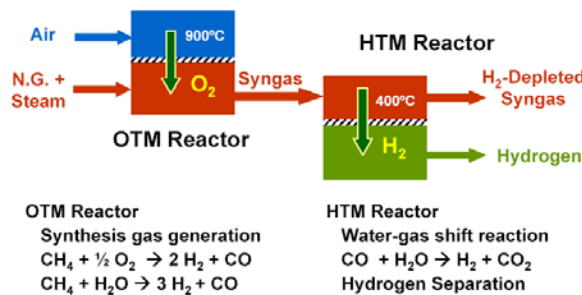


Figure 17 Praxair ITM concept combining oxygen (OTM) and hydrogen (HTM) ion transporting membranes

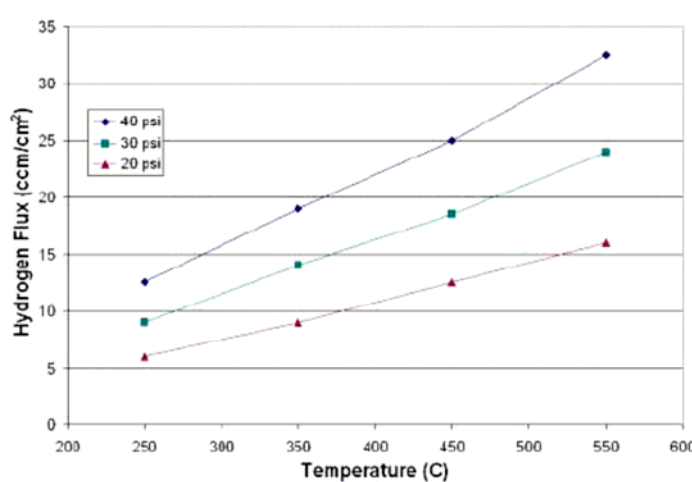


Figure 18 Hydrogen flux through a Pd-Ag membrane of 5µ thickness

An Air Products led consortium (DOE, Hydro, Ceramtec, Chevron, Eltron Research, McDermott, Penn State University, University of Pennsylvania, University of Alaska) is developing an ATR based oxygen membrane for the production of syngas. A microchannel planar membrane design was found to achieve high rates of heat and mass transfer (Figure 19). The membrane is made of $(La_{1-x}Ca_x)O_{3-\delta}$.

³⁶ M. Sjardin, Techno-economic prospect of small-scale membrane reactors in a future hydrogen fuelled transportation sector, Utrecht University, 2004, ISBN 90-393-3812-4

³⁷ J Schwartz et al., Integrated Ceramic Membrane System for Hydrogen production, DOE hydrogen program, FY 2004

$\text{Ca}_x\text{FeO}_{3-\delta}$ perovskite, where $0 < x < 0.5$, $y > 1.0$ and δ makes the compound charge neutral³⁸. A pilot-scale membrane with a capacity of 28,320 Nm³/h was demonstrated. Tests were conducted under synthesis gas conditions, between 800 and 900°C, and at pressures of 15 – 30 bar.

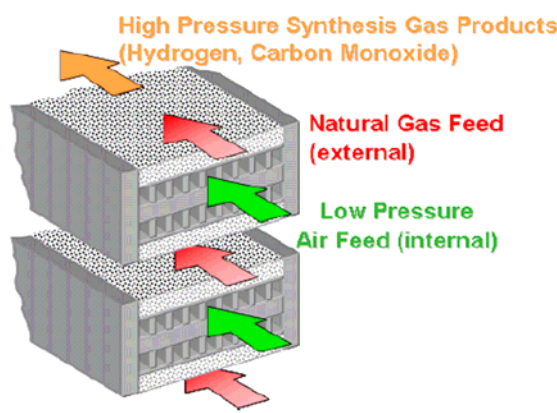


Figure 19 ITM syngas ceramic membrane module

ITM technology faces many challenges including membrane stability and lifetime under numerous start-ups and shutdowns, increase of gas permeability, the need for inexpensive membrane manufacturing with the potential for mass production, and system design and integration. Several groups are developing ITM reactors but the technology is still in the R&D stage with some demonstration projects at the pilot scale. Most developments are targeting large-scale hydrogen and syngas production rather than small-scale applications. However, some studies^{24,36} suggest that the technology has a potential for use in small-scale reforming.

4.1.4.5 Palladium membranes

Mitsubishi Heavy Industries has developed a steam reformer of natural gas equipped with palladium membranes for hydrogen separation (Figure 20). The natural gas, mixed with steam and preheated by the exhaust gas from the burner, is converted to mainly hydrogen and CO₂ in the catalyst bed. The hydrogen is separated inside the membrane and withdrawn from the reformer at atmospheric pressure.

³⁸ C M Chen et al., Ceramic Membrane Reactor Systems for Converting Natural Gas to Hydrogen and Synthesis Gas (ITM Syngas), DOE hydrogen program, FY 2004

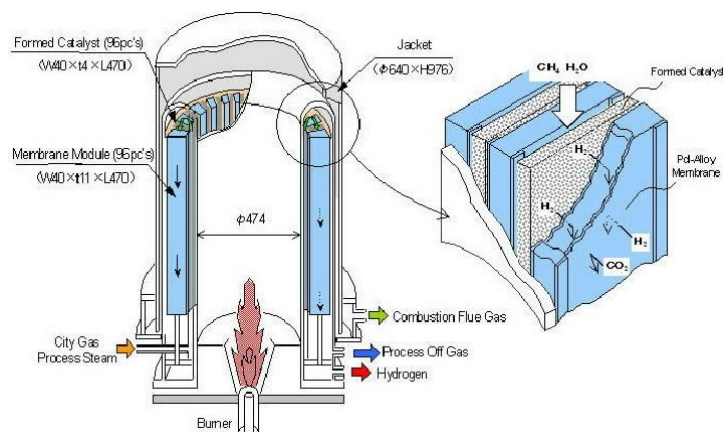


Figure 20 Mitsubishi Heavy Industries membrane reformer³⁹

The US National Energy Technology Laboratory⁴⁰ is developing a water-gas-shift reactor integrated with Pd and Pd-Cu membranes that operates without a catalyst at temperatures of 300-900°C. Preliminary results show that CO conversion surpassed the equilibrium conversion when the argon gas sweep-rate for hydrogen removal is high enough. Moreover, CO and H₂O do not significantly affect hydrogen transport by their interactions with the membrane surface.

Innovatek has developed a steam reforming microchannel reactor (InnovaGenTM) integrated with a Pd-alloy based membrane⁴¹. The reactor is a multifuel reformer, for 1-2.5 kW PEM fuel cells, and was tested with NG and diesel. Hydrogen permeation depends on hydrogen-partial pressure and membrane thickness; a purity of 99.995% was achieved.

4.1.4.6 Plasma reformers

Plasma reactors can produce hydrogen from methane and a variety of liquid fuels. A thermal plasma is characterised by temperatures of 3,000-10,000°C, at which temperatures, fossil fuels are decomposed. The plasma is generated by an electric arc or by induction. Several plasma concepts are under development for small-scale hydrogen production. MIT has tested several designs including partial oxidation of diesel⁴² (Figure 21), biofuels and ethanol⁴³. A stream of 40% hydrogen can be obtained after the shift reaction. Power conversion efficiencies of 70-80% and start-up times of 90 seconds are claimed. Disadvantages of plasma reforming include the degradation of the anode that needs to be replaced every 1000 hours⁴⁴ and electrical power consumption. The French company Etudes Chimiques et Physiques⁴⁵ has claimed electrical power consumption as low as 2% of the output syngas energy content, and 99% conversion of natural gas with 60% energy efficiency.

³⁹ <http://www.mhi.co.jp/mcec/product/membrane.htm>

⁴⁰ R. Killmeyer et al., Water gas shift membrane reactors studies, DOE hydrogen energy program, FY 2004, http://www.eere.energy.gov/hydrogenandfuelcells/annual_report04.html

⁴¹ P. Irving et al., Novel catalytic fuel reforming, DOE hydrogen energy program, FY 2004, http://www.eere.energy.gov/hydrogenandfuelcells/annual_report04.html

⁴² L. Bromberg, D.R. Cohn, A. Rabinovich, and J. Heywood, EMISSIONS REDUCTIONS USING HYDROGEN FROM PLASMATRON FUEL CONVERTERS, <http://www.osti.gov/energycitations/servlets/purl/827860-8awUTb/native/827860.pdf>

⁴³ K. Hadidi, L. Bromberg, D.R. Cohn, A. Rabinovich, N. Alexeev and A. Samokhin, PLASMA CATALYTIC REFORMING OF BIOFUELS, 2003

http://psfcwww2.psfc.mit.edu/library/03JA/03JA028/03JA028_full.pdf

⁴⁴ L Bromberg, DR Cohn, A Rabinovich, N Alexeev, Plasma Catalytic Reforming of Methane, IJHE, 24(1999) 1131-37

⁴⁵ GlidArc-assisted production of synthesis gas from natural gas, proceedings of the 1st European hydrogen energy conference, Grenoble, France 2003

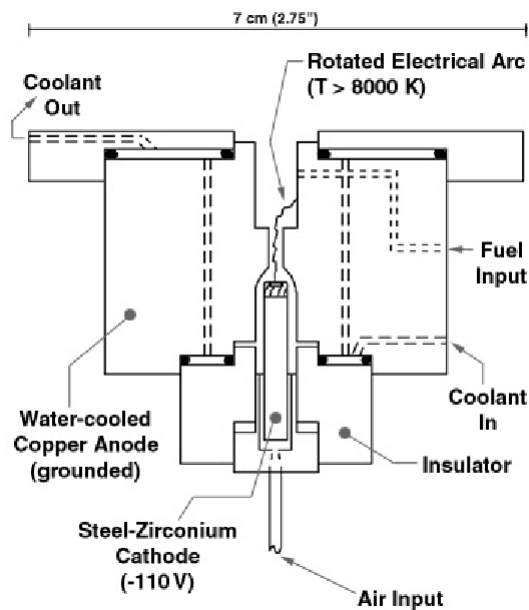


Figure 21 MIT Plasma Reformer²⁸

Plasma reactors have been used for decades in the commercial production of acetylene from natural gas with co-production of hydrogen. The technology is licensed by Hüls (presently Degussa-Hüls).

4.2 Feed Purification Technologies

Purification of incoming feeds to a reformer is essential to avoid catalyst deterioration, corrosion and fouling of the reformer. Feed impurities may also affect life time of down stream fuel cells which is very sensitive to impurities like sulphur and chlorine.

4.2.1 Sulphur removal technologies

Natural gas may contain sulphur compounds at the ppm level. In addition, sulphur compounds are nearly always added as odorant in pipeline-distributed gas for leakage detection. The sulphur level in European natural gas varies between 1 and 30 ppm. Although some reforming steps may use materials that are sulphur tolerant, sulphur is an extreme poison for water gas shift catalysts, membrane reactors and fuel cells. Therefore, fuel desulphurisation should be performed either before or after the reformer. Several methods for sulphur removal have been developed (Table 15). They can be classified into four groups:

- Physical solvents (liquid amines followed by the Claus process)
- Catalytic processes (Clinsulf from Linde AG, COS from Engelhard)
- Chemical sorbents (PUREASPEC from ICI Syntex)
- Solid absorbents (membranes, molecular sieves, activated carbon)

Table 15 Methods of Sulphur removal²⁸

Agent	Removes	Regenerative Step
Amine counter-current wash (e.g. monoethanolamine, diethanolamine)	H ₂ S	Heat treatment of amine
N-methyl-2-pyrrolidone (Purisol process)	CS ₂ , H ₂ S, COS	Boiling at low pressures
Refrigerated methanol (Rectisol process)	All S species	Flashed and vapour stripped
Polyethoxyether (Selexol process)	H ₂ S, RHS, CO ₂ , COS	Pressure letdown of rich solvent
Alkaline solution, typically caustic soda, followed by oxidation (Merox process)	Mercaptans	Caustic Soda recovered in oxidation
Activated carbon, commonly Cu-promoted	Medium weight S-species	High temperatures
Zeolites, silica gels, sorbents and molecular sieves	H ₂ S, COS, mercaptans	Reversible adsorption (temperature, pressure-swing)
Hydrodesulphurisation catalysts (Co/Mo oxides on alumina support, Ni/Mo oxides if hydrodenitrogenation is also required)	Most sulphur species	Tow-bed system
Heated zinc oxides (400°C) including ZnO (ICI Puraspee)	H ₂ S, mercaptans, disulphides	Non-regenerable (disposal)
Iron oxide sponges (Sulfatreat, Sulfur-Rite)	H ₂ S, mercaptans	Replace
Activated aluminas (Alcoa Selexorb)	H ₂ S, COS	Replace
Low temperature shift catalyst (guard bed containing small crystallite-size zinc oxide)	(as ZnO)	Heat treatment partially successful. Later replace
RVS-1 adsorbent	S from hot gases	Fully regenerable by oxidation
Selective oxidation to SO _x followed by adsorption on sorbents or absorption	H ₂ S, RHS, COS	Non-regenerable adsorbent (disposal)

Conventional hydrodesulphurisation is a hydrogenation process with Co/Mo-oxide catalyst at 250-350°C, and the resulting H₂S is removed by reaction with ZnO at the same temperature. In small-scale units, activated carbon and other solid absorbents are a better choice for sulphur removal via absorption. Usually, the sorbent needs to be replaced every 3-6 months, depending on the sulphur content. However, activated carbon does not remove COS, for which a catalytic hydration into CO₂ and H₂S is necessary.

In the case of POX reforming or other sulphur tolerant primary conversion processes that convert the S-compounds into H₂S, ZnO can be used to remove sulphur down-stream the primary conversion process.

4.2.2 Water purification

Incoming water needs to be purified to avoid scaling in the steam generator and poisoning of various catalysts. The prevailing technologies are reverse osmosis and ion exchange. Both processes give water of acceptable quality. Filters are normally used up-stream the ion-removal units to remove particulates and organics. Reverse osmosis inherently produces a large stream of rejected water. Ion exchange produces less water, but rejected water has a high concentration of ions and has to be treated as a chemical. Typical specifications for purified water are a resistance smaller than 10 Mega-Ohm, and SiO₂ content smaller than 10 ppb.

4.2.3 Purification of incoming air

Incoming air in ATR and POX systems may contain contaminants that deactivate catalysts and sorbents either reversibly or irreversibly. Of particular concern is chlorides often present in the air near the sea and lakes. Chlorides will poison most low temperature catalysts and fuel cells. Purification of the incoming air by sorbents or washing is necessary in many locations.

4.3 Hydrogen product purification

4.3.1 Pressure Swing Adsorption

PSA remains the common method for hydrogen purification. It consists of 4-8 columns with zeolites and active carbon as adsorbents. Hydrogen will elute first due to its low adsorption capacity. Methane will adsorb in the active carbon if properly designed. N₂ will come next followed by CO. O₂ and Argon will come in the same peak and close to nitrogen. CO₂ will not elute.

The cycle time for the adsorption/desorption process is typically 0.5-4 minutes. Reliability of the valves and fluidisation during depressurisation are important mechanical-design issues. Questair has introduced rotary valves that replace widely used solenoid valves. Rotary valves remove the need for optimising the operation of individual valves by complex system control. This simplifies the design and reduces the cost.

For N₂ containing gas, modified zeolites with high capacity for N₂ adsorption are needed to obtain high H₂ recovery. Very often, desiccants (alumina, silica-gel) and active carbon are used for pre-treatment and protection of zeolites. Indeed, desiccants trap species that can adsorb strongly (H₂O, NH₃ and CO₂) or weakly (hydrocarbons) on zeolites and deactivate them. The kinetics of adsorption/desorption reactions depends on the temperature. Therefore, if not properly insulated, the operation of the PSA might be affected by fluctuations of the ambient temperature over the day and along the year.

As its name indicates, the driving force in PSA is the pressure difference between adsorption and desorption steps. The optimum pressure for H₂ recovery is around 20 bar and most industrial PSA units operate at this pressure with H₂-recovery of 75-85%. In small-scale reformers, the reforming reaction is normally conducted at lower pressures to avoid equilibrium limitations. Therefore, the PSA has been designed for 8-10 barg and the rated recoveries are in the range of 70-75%.

In the case of SMR, the heating value of the PSA off-gas corresponding to 75% H₂-recovery covers 90% of the energy required for the steam reforming. Higher H₂ recovery will not affect the energy efficiency of the process. However, to improve the robustness of the process and to reduce investment cost it is important to increase the recovery.

4.3.2 Metallic membranes

Hydrogen molecules adsorb on one side of the membrane, dissociate into hydrogen atoms that diffuse through the metallic film, and reach the other side of the membrane where the atoms recombine and desorb as H₂ molecules. Very high purity of 99.9999% is achievable. Pd-alloy based membranes, operating at about 500°C, have been used commercially for many years for the purification of hydrogen generated in small-scale reforming (< 1 m³/hr). However, the membrane cost is too high for higher capacities. Present challenges in the development of Pd-membranes are:

- Better thermal stability via alloying, and improved ceramic support with high porosity.
- Increased H₂-diffusivity by reducing membrane thickness, and use of alloys to improve diffusivity at low temperatures.
- Prevent H₂ embrittlement at low temperatures
- Increased sulphur and chlorine tolerance.

Power+Energy⁴⁶ offers Pd-alloy based purification units for flows up to 24 Nm³/h.

4.3.3 Polymeric membranes

Hydrogen is absorbed in the membrane and diffuses as molecules. All species that can absorb and diffuse in the polymer will contaminate the H₂ product. Typical H₂ purity is 85 %. The selectivity of polymer membranes is too low to be used for high purity applications.

4.3.4 Ceramic membranes

Hydrogen molecules diffuse through ceramic micro-pores. The membrane selectivity is determined by relative diffusion rates and is controlled by the pore size and affinity vis-à-vis incoming molecules.

A ceramic membrane with selectivity close to that of Pd-membranes has recently been announced by Japan Fine Ceramics Center⁴⁷. The membrane is a composite of dispersed Ni-nanoparticles in amorphous silica. The membrane shows a hydrogen permeance of 1.4x10⁻⁷ mol/(m² sec Pa) at 500°C, which is an order of magnitude lower than for Pd-membranes.

Zeolite based membranes are not commercially available. Several companies are working in this area, but they are mostly aiming for other applications than H₂ separation.

Sandia National Laboratory is developing silica and aluminosilica ZSM-5 membranes with low defects⁴⁸. This implies that the permeation selectivity is governed by size exclusion (molecular sieving) since few molecules permeate through crystalline defects. Preliminary permeation tests performed at 25-120°C and 1 bar, with binary and gas mixtures, show high hydrogen flux and selectivity.

4.3.5 Proton transporting membranes

Proton transporting membranes are based on oxides (perovskites) that conduct protons at high temperatures of 700–1100°C. The transport is a 3-step mechanism similar to that of metallic membranes: (i) hydrogen dissociative adsorption, (ii) proton diffusion, and (iii) hydrogen recombinative desorption. Diffusion rates are lower than for Pd-membranes but the material cost is substantially cheaper.

⁴⁶ http://www.purehydrogen.com/site_2002/products.shtml

⁴⁷ <http://www.rite.or.jp/English/lab/chemical/kokusaise/5.pdf>

⁴⁸ Tina M. Nenoff, Defect free thin film membranes for H₂ separation and isolation, DOE hydrogen program FY 2004, http://www.eere.energy.gov/hydrogenandfuelcells/annual_report04.html

Table 16 Summary of commercial purification techniques⁴⁹

Purification technology	Selling company	H ₂ flow rate (Nm ³ /h)	Dimensions (m)/ Weight (kg)	T (°C)	Feed P (bar)	H ₂ (bar)	H ₂ -recovery (%)	H ₂ -concentration (%)	Cost (\$)
PSA	Quest Air	5-200	1.42*1.10*2.25/ 1700-2900 1.2*1.5*2.3/ up to 1700-3000	4-50	3-21	< 0.5 bars less than feed pressure		~99 <10 ppm CO <10 ppm C3+ <0.1 ppm H ₂ S	90 000 ³
Fast cycle PSA	SeQuel Technologies	1-6	Height=1 ¹ Diameter= 0.4 ¹	-	2.7-5	~ 0.1 bars lower than feed pressure	73 ≥ 60		20 000 ¹
PSA	Donaldson	10	-	-	10	-	70		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		>99.9	88 000 (5 Nm ³ /h) ≥3000 000 (500 Nm ³ /h)
Pd-Ag membrane	Power & Energy	Small ≥ 1 Large≈78-625	-	350-450	≤13	Not fixed	60-80		-
Pd-Cu membrane reactor	ATI Wah Chang	0.8-3.8	21-27 kg	350-400	10	ambient	70	> 99.999	9255-22 922
Pd-Ag membrane	R & B Consulting	0.72	-	430	>25 ³	0.1	70	99.999	-
TSA+Metal Oxides	SAES Pure Gas	5-500	-	20-35 °C	3.5-10	max. 1 bar lower than P _{feed}		Water at ppb-levels H ₂ S and CO at ppb-levels	125 000 (15 Nm ³ /h) 220 000 (150 Nm ³ /h)
PROX	Estimated by CAT	based on 1 Nm ³ /h	< 5 kg	120-180	ambient	ambient	-	~ 70 vol%, < 20 ppm CO	~ 100
Methanisation	Estimated by CAT	based on 1 Nm ³ /h	< 5 kg	200-300	ambient	ambient	-	~ 70 vol%, < 20 ppm CO	~ 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

⁴⁹ A K Jannasch, F Silversand, Upgrading of reformat gas for different applications with focus on small scale hydrogen production, Rapport SGC, ISSN 1102-7371

Table 17 Summary of advantages and disadvantages of various purifications techniques⁴⁹

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 in-mature and expensive technology
Polymer 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 reformat 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 pressure 	<ul style="list-style-type: none"> - complex solvent and recirculation systems are needed
Water-gas shift	<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	<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

5 Review of CO₂ capture technologies

CO₂ is the main emission from small-scale reformers. Exhaust gases show typically CO₂-concentrations between 5 to 20 vol%.

Table 18 Typical exhaust gas content from two different small reformers⁵⁰

Supplier	Model	Total exhaust flow (Nm ³ /h)	NO _x Vol ppm	O ₂ Vol %	CO Vol ppm	CO ₂ Vol%
Osaka Gas	HYSERVE-100, 100 Nm ³ /h H ₂	275	16-21	2.6-3.3	2.0-5.5	15-18
Hyradix	ADEO 100 Nm ³ /h H ₂	650	< 20	11.1	< 5	8.3

5.1 Steam Methane Reforming with CO₂ capture

A possible flow sheet for an SMR fuel processor with CO₂-capture is shown in Figure 22. The CO₂-capture unit can be placed at the exhaust of the burner (after cooling) and will handle all the CO₂ produced: from reforming, water gas shift, and burning of purged gas. Another possibility is to capture CO₂ at high pressure prior to the H₂-purification step. The tail gas of the PSA unit, which contains mainly methane, is recycled and used as feed in the process (Caloric HCE-process⁵¹). However, although this solution is considered to be more economic than CO₂ capture from the exhaust gas, it does not reach 100% CO₂-removal unless part of the produced hydrogen is used as fuel for the reformer.

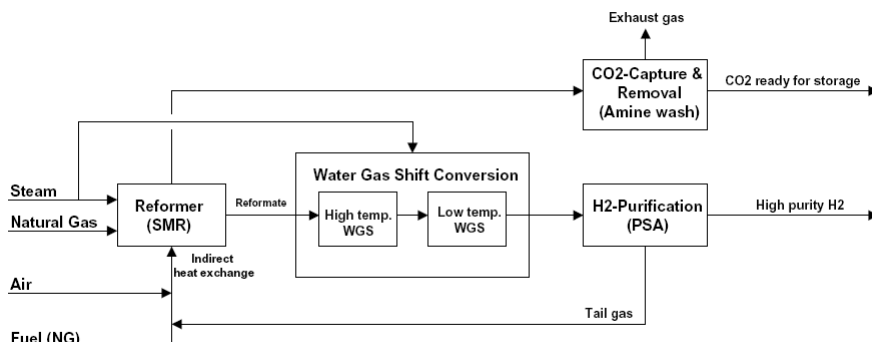


Figure 22 Schematic drawing of an SMR fuel processor with CO₂-capture and removal⁵²

5.1.1 Amine wash process

The CO₂ capture and removal process used for medium and large-scale steam reformers is the amine wash process, which is based on an aqueous absorption/stripping technology (Figure 23). The gas to be treated is sent to the absorber where CO₂ is removed by absorption using an appropriate amine solution. The treated gas exits from the top of the absorber while the rich amine solution from the bottom is sent to the stripper (regenerator) where the CO₂ is desorbed by steam stripping at about 100-120°C. Regenerated amine solution is continually recycled between the absorber and the stripper. Stripped CO₂ is discharged from the top of the regenerator (off-gas). CO₂ concentrations down to ppmv level can be obtained in the lean amine solution⁵³. Hot flue gases can cause solvent degradation and decrease the absorber efficiency. The flue gas must be cooled to a water dew point of 50°C before entering the absorber.

⁵⁰ Private communication Takayuki Azuma (Osaka Gas Co., Ltd) and David Cepla (HyRadix Inc.).

⁵¹ <http://www.caloric.com/main.html>

⁵² Jin, Y. and Canin, J. (2004) Overview of fuel reformation and processing technologies for hydrogen fuel cells, <http://fuelreformer.sirti.org/docs/2A2BABF9-C04F-791A-3CE25F4BC2725C21.pdf>

⁵³ Kirk-Othmer, (1999) Concise Encyclopedia of Chemical Technology, Fourth Edition, March 1999, Wiley NY, Vol. 12, 950-982

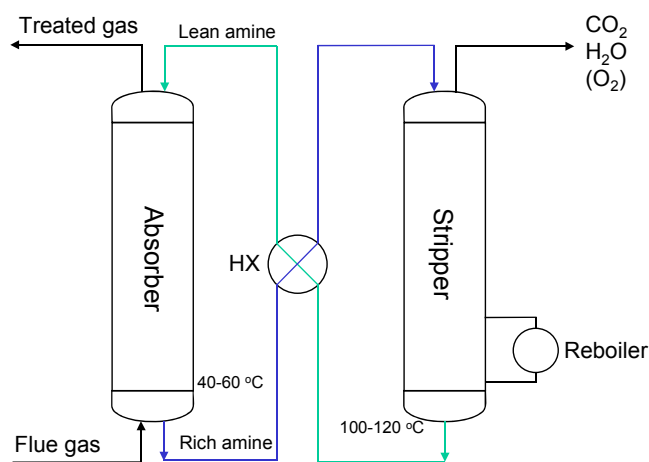


Figure 23 Typical absorber-stripper system⁵⁴

Good absorbents for CO₂ capture from flue gases must be active at low CO₂-partial pressure and tolerate oxygen and NO_x⁵⁵. Many acid gas treatment processes operate at thousands of kPa_g and cannot remove CO₂ to less than about 10 kPa_g partial pressure. These high-pressure processes can be used by compression to normal operating pressure, followed by recovery of a portion of the compression energy in expanders. However, the overall energy consumption results in unattractive economy. The only commercial absorbents enabling recovery of dilute CO₂ from atmospheric pressure gas are Mono-Ethanol-Amines (MEA) and other primary amines including the newly developed hindered amines⁵⁵.

Absorption processes that are effective at low pressure are the most energy demanding with respect to regeneration. A design challenge is to minimize the regeneration energy by selecting a solvent with relatively low reaction energy, and to use low-value heat sources to provide this energy⁵⁵.

Oxygen can cause corrosion and solvent degradation problems. The use of carbon steel is attractive due to low cost, but it can rapidly corrode in the presence of oxygen. Also, uninhibited alkanolamines such as Diethanolamine (DEA) and MEA can be excessively degraded in an oxygen environment. Flue gas streams with at least 1.5vol% oxygen are preferred to maintain inhibitor activity. Alternatives are to use expensive alloys, remove all oxygen or a continuous addition of an oxygen scavenger to the solvent. This is however not commercially demonstrated.

Sulphur oxides (SO_x) in flue gases react irreversibly with MEA to produce non-reclaimable corrosive salts that are very detrimental to plant operation. For small-scale reforming plants, the sulphur concentrations of the feed (mainly H₂S) have to be reduced down to ppb-level to avoid poisoning of the reforming catalyst. Therefore SO_x will not represent a problem for the amine wash system coupled to a small-scale reformer.

Nitrogen oxides have led to corrosion of steel and amine degradation in several plants. The most problematic of the NO_x is NO₂, which reacts to form nitric acid in the amine solvent and ultimately stable salts⁵⁵.

Several companies supply MEA-units of different sizes, like Fluor Daniel Inc. (Econamine FG) and UOP (Amine Gard-II, Figure 24). However, the technology has not yet been scaled down to small-scale applications.

⁵⁴ Rochell, G. (2001) CO₂-Capture by Aqueous Absorption Stripping; Opportunities for better Technology. http://www.netl.doe.gov/publications/proceedings/01/carbon_seq_wksp/Rochell_Sep.pdf

⁵⁵ Chapel, D. G. et al. (2001) Recovery of CO₂ from Flue Gases: Commercial Trends. Proceedings of the First National Conference on Carbon Sequestration, Washington DC, DOE/NETL-2001/1144, http://www.netl.doe.gov/publications/proceedings/01/carbon_seq/2b3.pdf

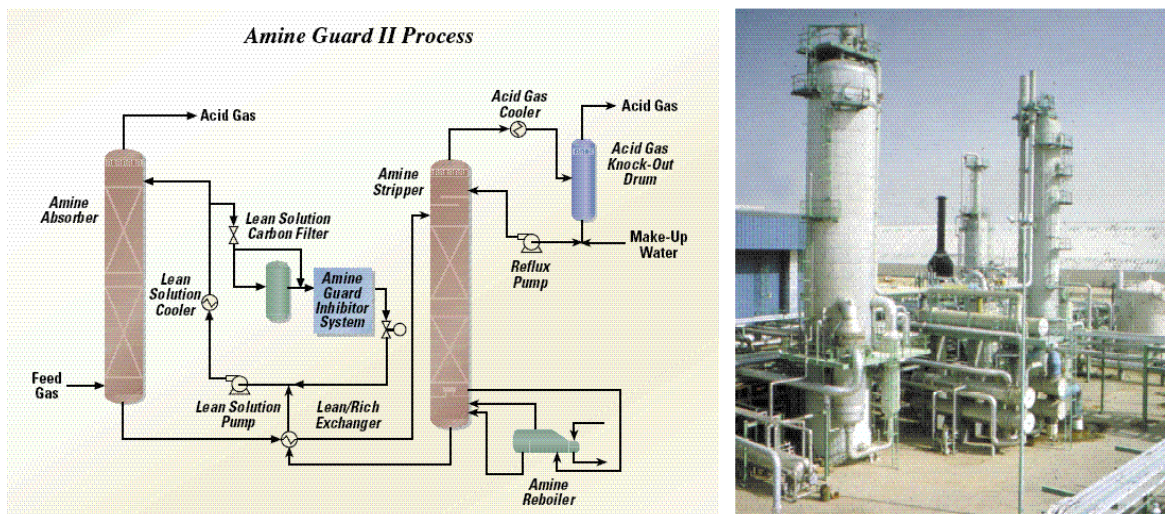


Figure 24 The UOP Amine Guard II process and a picture of one unit⁵⁶

5.1.2 High pressure absorption processes

Several absorption processes or solvents need a higher pressure to be effective. This is the case for the Selexol process (UOP), where CO₂ recovery is directly proportional to the partial pressure of CO₂ in the flue gas. Limitations with respect to the pressure are also the case for the less reactive solvents, including methyldiethanolamine (MDEA), diethanolamine (DEA), di-isopropanolamine (DIPA), triethanolamine (TEA). Other processes that are affected by CO₂ partial pressure include hot potassium carbonate, molecular-sieves membranes and cryogenic separation⁵⁷. For these processes, compression of the flue gas up to operating ranges will be expensive for economical CO₂ recovery⁵⁵.

5.1.3 Hot Potassium Carbonate

Hot potassium carbonate (HPC) or "Hot Pot" is effectively used in ammonia, hydrogen, ethylene oxide and natural gas plants. To improve CO₂ absorption, mass transfer and to inhibit corrosion, activators and inhibitors are added. These systems are known as Activated Hot Potassium Carbonate (AHPC)⁵⁵. The most widely licensed of these is the Benfield process, with over 675 units worldwide licensed by UOP⁵⁸ (Figure 25), and the Catacarb process, with over 100 units licensed as of 1992 by Eickmeyer & Associates⁵⁹. Other commercial processes are the Exxon Flexsorb HP process, which uses a hindered amine activator, and Giammarco-Vetrocoke's new process, which uses an organic activator. The full capacity of the "hot pot" family of processes requires a feed CO₂ partial pressure of about 700 kPa⁶⁰. The Benfield and Catacarb processes are commercially available for applications at a minimum CO₂ partial pressure of 210-345 kPa_g.

⁵⁶ UOP, Gas Processing applications. <http://www.uop.com/objects/94%20AmineGuard2.pdf>

⁵⁷ Holmes, A. S. Recovery of CO₂ from Man-made Sources Using Cryogenic Distillation Techniques, conference paper, U.S.D.O.E. and Argonne National Laboratory, February 1985

⁵⁸ Gas Processes Handbook '98, Hydrocarbon Processing, Vol. 77, No. 4, April 1998

⁵⁹ Gas Process Handbook '92, Hydrocarbon Processing, Vol. 71, No. 4, April 1992

⁶⁰ Kohl, A. L., Nielsen, R.B. (1997) Gas Purification, fifth edition, Gulf Publishing Co, Houston, Texas, 1997, ISBN 0-88415-220-0

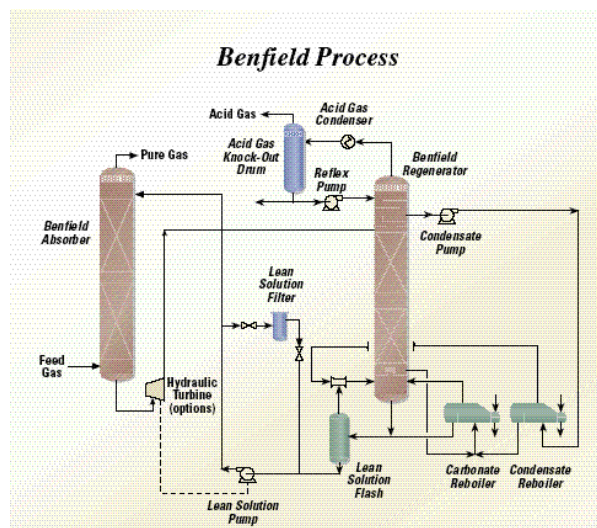


Figure 25 The UOP Benfield process⁶¹

5.1.4 Polymer Membranes

In order to use membranes, costly compression and heat exchange are needed to reach high pressure feed, and the result will be an impure CO₂ product. For instance, SEPAREX membrane systems (Figure 26) are currently offered by UOP for feed pressures starting at 2750 kPa_g⁵⁸. There are currently no commercial applications of membranes for recovery of CO₂ from flue gases, though they have been used in Enhanced Oil Recovery to recycle CO₂ from the associated gas. The most likely applications for membranes are in small skid-mounted plants where an impure CO₂ product is acceptable, and off-shore applications that can take advantage of their compact size and low weight⁵⁵.

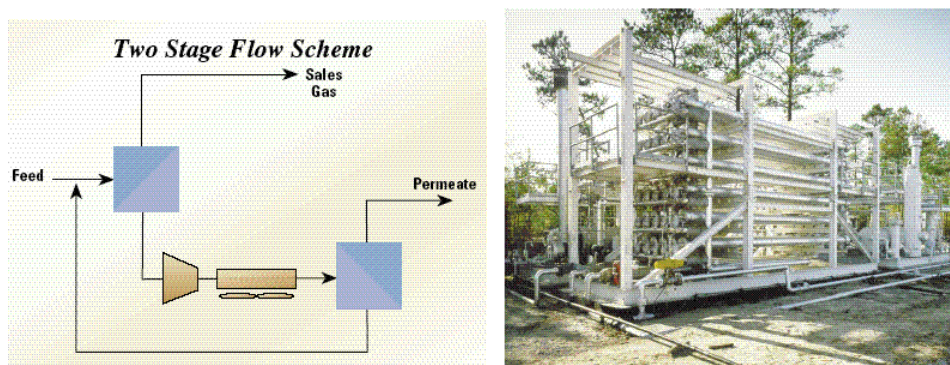


Figure 26 UOP's SEPAREX membrane unit⁶²

5.1.5 Sterically hindered amines

Kansai Electric Power Company (KEPCO) and Mitsubishi Heavy Industries have developed a proprietary process based on a sterically hindered amine, called KS-1 as a replacement for MEA in flue gas treatment (Figure 27). KS-1 has lower circulation rate (due to its high lean to rich CO₂ loading differential), lower regeneration temperature (110°C), and 10-15% lower heat for its reaction with CO₂. It is non-corrosive to carbon steel (less than 25 μm/yr) at 130°C in the presence of

⁶¹ UOP, Gas Processing applications. <http://www.uop.com/objects/99%20Benfield.pdf>

⁶² UOP, Gas Processing applications, <http://www.uop.com/objects/98%20Separex.pdf>

oxygen⁶³⁻⁶⁴. Another sterically hindered amine, AMP (2-amino-1-methyl-1-propanol) may have similar properties as KS-1⁶⁵.

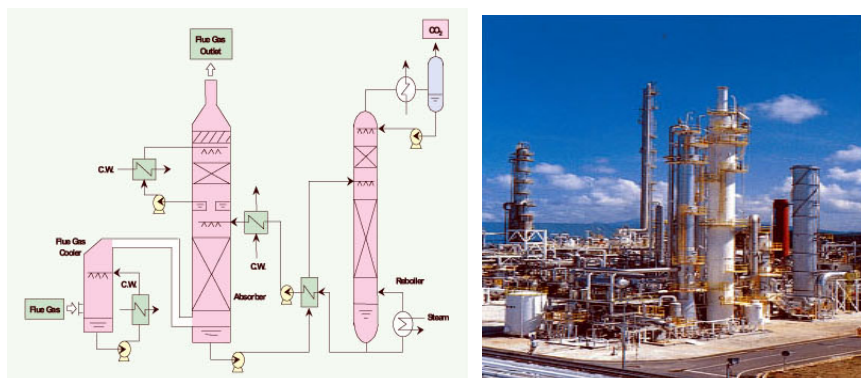
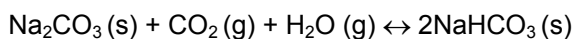


Figure 27 The KEOCO/Mitsubishi KS-1 process and a picture of one unit⁶⁶

5.1.6 Low temperature gas-solid separation

The removal of CO₂ from flue gas using solid Na₂CO₃ is based on the following reversible reaction:



The process is thought to be capable of capturing 25 to 50% of CO₂ without imposing significant energy penalty on the overall process. Increased CO₂-capture is possible but with a small energy penalty on the plant⁶⁷. A schematic diagram of the CO₂ capture process is shown in Figure 28. Flue gas and steam enter the carbonator reactor where CO₂ is captured by the solid sorbent. Next, CO₂ is released by providing recovered heat to the regenerator. The regenerated-sorbent flows continuously from the regenerator to the carbonator while the carbonated-sorbent flows continuously in the opposite direction. Dual circulating fluidised bed or transport reactors can be used to provide steady state operation⁶⁷.

⁶³ Suda, T., Fujii, M., Yoshida, K., Iijima, M., Seto, T., Mitsuoka, S. (1992) Development of Flue Gas Carbon Dioxide Recovery Technology, First International Conference on Carbon Dioxide Removal, Amsterdam, The Netherlands, Pergamon Press, March, 1992, pp. 317-324

⁶⁴ Mimura, T., Shimojo, S., Suda, T., Iijima, M., Mitsuoka, S. (1995) Research and development on energy saving technology for flue gas carbon dioxide recovery and steam system in power plant, Energy Conversion and Management, Vol. 36., No. 6-9, June-September 1995, pp. 397-400

⁶⁵ Gelowitz, D. (1993) Carbon Dioxide Extraction: Optimization of Facility and Solvent Technologies, Chapter 6, pp. 28-33, Regina, Saskatchewan, April, 1993

⁶⁶ Global Environment Center Foundation (GEC) and The Japan Society of Industrial Machinery Manufacturers (JSIM). Flue Gas CO₂-Recovery Unit, Mitsubishi Heavy Industries Ltd. (MHI). http://nett21.gec.jp/JSIM_DATA/AIR/AIR_4/html/Doc_093.html

⁶⁷ Harrison, D.P., Ya, L., Green, D.A., Turk, B.S., Gupta, R.P. (2002) Carbon Dioxide Capture from Flue Gas using Dry Regenerable Sorbents. Proceedings of the Conference on "Future Energy Systems and Technology for CO₂ Abatement". Nov. 2002, Antwerpen, Belgium

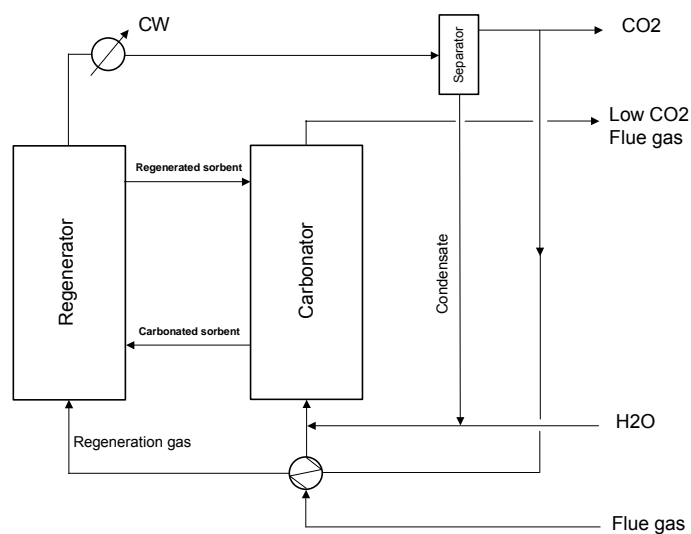


Figure 28 Schematic diagram of the low temperature gas-solid CO₂ capture process⁶⁷

Table 19 Commercial CO₂ scrubbing solvents⁶⁸

	Solvent name	Solvent type	Process conditions
Physical solvents	Rectisol	Methanol	-10/-70°C, > 2 MPa
	Purisol	N-2-methyl-pyrrolidone	-20/+40°C, > 2 MPa
	Selexol	Dimethyl ethers of polyethyleneglycol	-40°C, 2-3 MPa
	Fluor solvent	Propylene carbonate	Below ambiante temperatures, 3.1-6.9 MPa
Chemical solvents	MEA	2,5-N-monoethanolamine and inhibitors	40°C, ambiante-intermediate pressures
	Amine guard	5-N- monoethanolamine and inhibitors	40°C, ambiante-intermediate pressures
	Econamine	6-N-diglycolamine	80-120°C, 6.3 MPa
	ADIP	2,4-N-diisopropanolamine, 2-N-methyldiethanolamine	35-40°C, > 0.1 MPa
	MDEA	2-N-methyldiethanolamine	
	Flexsorb, KS-1, KS-2, KS-3	Hindered amine	
	Benfield and versions	Potassium carbonate & catalysts, Lurgi & Catacarb processes with Arsenic-trioxide	70-120°C, 2.2-7 MPa
Physical/Chemical Solvents	Sulfinol-D, Slufinil-M	Mixture of DIPA or MDEA, water and tetrahydrothiopene (DIPAM) or diethylamine	> 0.5 MPa
	Amisol	Mixture of methanol and MEA, DEA, diisopropanolamine (DIPAM) or diethylamine	5/40°C, > 1 MPa

⁶⁸ Prospects for CO₂ Capture and Storage, International Energy Agency, 2004

5.2 Cost of CO₂ capture from small-scale reforming

At present hydrogen produced by on site reforming of natural gas is more expensive than hydrogen produced from natural gas on a large scale. It is however expected that on site reforming could become economically competitive to central production in the future⁶⁹.

In order to evaluate the costs of including new technologies for reduced CO₂-emissions, transportation and storage costs have to be included. The total costs will depend on the technology and size of the plant, and the volumes of CO₂ being transported as well as the transportation distance. The cost of CO₂ storage depends on the site, the location and the method of injection. CO₂ capture will require additional energy. Then total avoided costs will include the emissions inherent to the additional energy demand from capture systems.

The main cost of introducing CO₂ capture in small-scale reforming is the increased investment costs due to an additional unit or process for CO₂ capture. Depending on the degree of complexity in the additional equipment the operating costs could also increase. Additional costs include the transport of the captured CO₂ to a central intermediate CO₂ storage facility. Comparing on site hydrogen production (small-scale reforming) with hydrogen delivered on site from a large scale plant, the transport costs of hydrogen to the filling station most probably will equal the transport cost of CO₂ from on-site reforming. A storage tank will be needed on the filling station in both cases either for hydrogen or for CO₂. The costs for CO₂ storage, for instance in an aquifer, are assumed to be the same whatever is the CO₂ source.

The recently published IEA report "Prospects for CO₂ capture and storage"⁷⁰ states that the cost of CO₂ capture and storage ranges from a 40 USD benefit to a 100 USD/tonne CO₂ cost, if all capture storage options are considered. At present, for the vast majority of options the total cost of CO₂ capture and storage could be within 50 to 100 USD per tonne of CO₂ emission reduction. The report states that the main costs are on the capture side. If future efficiency gains are taken into account the cost of capture could decline to around 25 – 30 USD/tonne CO₂ for gas-fired plants.

For large-scale power production a comprehensive economic and cost analysis for CO₂ capture has been performed for the different scenarios in the CO₂ Capture Project (CCP)⁷¹. For pre-combustion technology (hydrogen membrane reformer and sorption enhanced reforming) the study shows that CO₂-capture costs in the range 22.5 to 34.1 USD/tonne CO₂ are at reach (avoided costs from 24.4 to 42.7 USD/tonne CO₂). The amount of captured CO₂ in the study is in the range of 1.3 to 1.5 million tonne annually. As a comparison the baseline cost (amine MEA technology) is 49.0 and 61.6 USD/tonne CO₂ for capture and avoided CO₂ respectively.

If data obtained for CO₂ capture from large scale plants future CO₂ capture costs could be in the range of 16 – 20 USD/tonne CO₂ (65% of large scale costs). This could increase the cost of produced hydrogen from a small-scale reforming by 0.015 USD/Nm³ H₂, assuming a production of 700 Nm³/hour and 13 tonne CO₂ per day.

Adding CO₂ capture to existing small-scale reforming technology is not considered as a likely future option, unless it is for some special demonstration purposes. Retrofitting solutions are possible, but will be too expensive. A possible solution with respect to CO₂ capture is to include the option into the unit from the start. Scale-up of production of small-scale reforming units in a standardized form will reduce the overall production costs.

⁶⁹ Polman, E.A.(2005) IEA Task 16C Technology Development Study

⁷⁰ IEA Energy Technology Analysis (2004), ISBN 92-64-10881-5

⁷¹ Melien, T (2005) Economical and cost analysis for CO₂ capture costs in the CO₂ capture project scenarios. In Carbon Dioxide Capture for Storage in Deep Geologic Formations, Volume 1, D.C.Thomas and S.M.Benson (eds) Elsevier 2005, 47-87

5.3 Other emissions and pollutants from reforming

5.3.1 Gas emissions

The heat and steam required for the reforming process are generally provided by burning the tail gas from the hydrogen purification process topped up with the required amount of fuel. The flue gas from the burner is the only significant gas emission from a reformer under normal operation.

Emissions from combustion include NO_x, SO_x, CO, Particulate matter (PM), and hydrocarbons (HC). At present reforming temperatures, NO_x emissions can be kept low, down to 10-20 ppm level. SO_x emissions, typically 1 ppm, originate from sulphur contained in natural gas. Therefore SO_x emissions depend on the quality of NG and desulphurisation equipment in use. Hydrocarbon emissions from NG combustion are mostly methane, which is a greenhouse gas. Emissions of 100-200 ppm were reported. Current combustion technologies can emit CO at low levels of 5 ppm, and PM emissions are similarly insignificant.

Some of the small-scale steam reformer developers, e.g. Carbotech and Osaka Gas, are using regenerative burners to reduce NO_x and CO to low levels. Some of the ATR based processes are utilising catalytic burners for the PSA tail gas and will also emit substantially less NO_x and CO than conventional burner technologies. Many gas-heated reformers operate at a high oxygen surplus which will reduce the emissions of NO_x, SO_x, CO, PM, and HC

5.3.2 Noise

Noise is considered a pollutant in many countries and in most cases there are strict regulations of acceptable noise levels in living areas. The actual levels vary somewhat from country to country but acceptable values are typically 45-55 dB depending on the type of surrounding buildings. The first small scale hydrogen plants that have been put in operation show that it is possible to achieve low noise levels even though the plant is located very close to living areas, such as the Stuttgart filling station for the CUTE project. It is possible to achieve very low noise levels through the use of silencers but at high costs.

5.3.3 Waste water

The reforming process requires deionised water and this results in pollutants as ions from the deionisation system. Depending on the concentration, it might not be allowed to discharge any waste water from the deionisation system into the municipal waste water system.

5.3.4 Conclusions

The only significant source of non-CO₂ emissions, i.e. exhaust emissions from hydrogen plants is the combustion of fuels to supply process heat. As temperature requirements are moderate and the technology for natural gas combustion technologies is very well developed, the emissions of NO_x, SO_x, PM and HC can be kept at the same levels as for other related technologies (i.e. boilers). The only two somewhat significant pollutants are NO_x and HC while the emissions of CO, PM and SO_x are very likely to not be an issue. Noise and waste water are two other pollutants from hydrogen production plants that must be considered when a hydrogen plant should be built.

6 Subtask C Results 2002 – 2005

The technology providers have achieved significant progress in system quality and technology performance. Market survey shows that the gap between customer requirements and technology performance can be overcome. During the three years of the Subtask C program a strong network has been developed. The participation in meetings has been high with more than 10 (75%) members present at each meeting. The concluding event in Oslo with 40 invited participants illustrated the importance of the small-scale reforming technology for the hydrogen roadmap.

The results of our analysis on how the technology can meet the market requirements have been reported. CO₂-handling and emission performance as well as the use of the technology for providing hydrogen to integrated combined heat and power plants are also reported.

The highlights are:

- Small – scale reformers for on-site hydrogen production are presently (2005) competitive with on-site electrolysis, and in some region are even competitive with trucked in hydrogen
- The short – term customer priorities include costs, footprint, reliability, durability and hydrogen gas quality
- CO₂- performance of the small-scale reformer is good, CO₂ – capture is not feasible with current costs and technologies
- Exhaust emissions are marginal and within acceptable urban limits
- System integration and design simplification are needed in order to shorten the gap to commercialisation
- The Subtask C members recommends to continue the work in a new Annex
- Companies involved in reformer development are not in the mass-production phase, and the gap between the current technology and a future commercial product is still large. Mass production of reformers will require substantial reduction in the number of components and system complexity. Identification of strategies to overcome the gaps is of high importance. Proprietary issues have to be addressed in order to secure the commercial interest of the participants.

- In order to meet the long term cost targets (e.g. non taxed gasoline) the plant cost must be reduced by a factor of 2,5 – 3. The potential cost-reduction for the auxiliaries is 70 %, and according to Osaka Gas, the potential for cost-reduction for the complete plant is 20 – 30 %. A comprehensive cost-reduction study could be made by an independent research institute in order to assess these statements, particularly in terms of cost reduction induced by a mass production.

- Hydrogen price, based on the Osaka Gas technology, is close to the taxed Japanese gasoline (with 50% tax). Moreover, competitiveness with trucked-in hydrogen is already achieved, and the number of hydrogen trailers may decrease. Benchmarking with conventional fuels, and with alternative and competing technologies, could be a useful tool to define and update targets for the reformer technology as the hydrogen fuel market develops.

- Monitor data and experiences from demonstration plants. A procedure for learning from demo-projects should be established. A common monitoring program can be built, and collected data can be checked against present and future standards on product quality, safety, defects and incidents.

The reformer technology is a potential on-site production option for the new hydrogen market. The results presented in this report show that the small-scale reformer technology is likely to become competitive on cost, footprint and operability. However, experience data are still limited and few references can be made to modern large-scale plants in operation. The Subtask C members have

concluded that further networking under the IEA system is needed. Therefore, a new IEA - Annex is proposed on the development of reformer technologies and distributed on-site hydrogen supply systems based on reforming. A draft work-program will be developed on the basis of the results and recommendations from the present Task 16 – Subtask C.

7 Recommendation and further work

Subtask C members and the stakeholders at the concluding event in Oslo agreed that there is a strong need to continue the harmonised effort to develop on-site reforming for efficient and clean hydrogen.

The overall objective of a new effort is to provide a basis for harmonisation of the technology for on-site hydrogen production from hydrocarbons and renewable resources.

The challenges for a continued effort are:

- Develop a basis for three fixed capacities for the reformer unit
- Develop input for a type approval system for on-site reformer systems
- Develop a reformer design that takes into account industrial mass production
- Develop a global market guide for the on-site hydrogen reformers

The approach is to use the results in Task 16 – Subtask C as a basis for a new effort. The current network of participants is expected to increase with new members. In June 2005 the concluding event in Oslo gathered 40 experts, and some of them expressed interest. The group will be composed of industrial stakeholders and academic researchers. Other stakeholders can be from public institutions. Industrial representatives will be from the reformer suppliers and energy utilities.

During the past three years, 2002-2005, the reformer technology has been improved significantly to meet the demands of the customers and stakeholders in the transport sector. Major improvements have been achieved on system compactness, efficiency, automated operation and costs. There are, however, still challenges on system integration and optimisation of various components including compressors, gas storage, control units and hydrogen dispensers. Furthermore, the number of installed prototypes and their operating hours are still limited.

The companies active in the reformer business have different origins. The later players are spin-offs of scientific and research organizations attracted, in particular, by the promises attached to fuel cells. They are mainly active in the development of fuel cell processors. Others are in the energy sector, such as Osaka Gas (natural gas business), or they are suppliers of industrial plants, such as Mitsubishi Kakoki Kaisha Ltd, IGS Mahler and Haldor Topsøe.

In the work program, the main focus has been on the small-scale reformers market. This will remain the main focus in the continuation of the program.