ON-SITE SMALL METHANE STEAM REFORMER IN A HYDROGEN REFUELING STATION FOR FUEL CELL BUSES IN MADRID

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1. INTRODUCTION

Hydrogen is seen in Europe as an alternative fuel for transportation capable to reduce the dependability of crude oil supplies and to reduce the greenhouse effect. European Commission's (EC) targets for hydrogen shares in the energy consumption in transportation sector in Europe are 2% in the year 2015 and 5% in 2020.

Bio fuels and natural gas are considered, together with hydrogen, as the only alternative fuels that can really be on the market with a significant share at the horizon of year 2020. The market penetration foreseen and targeted by the EC for each of these fuels is shown in table 1.

year	bio fuels	natural gas	hydrogen	total
2005	2 %			2 %
2010	6 %	2 %		8 %
2015	7 %	5 %	2 %	14 %
2020	8 %	10 %	5 %	23 %

Table 1: targeted market shares for alternative fuels in the European Union

To start the way towards this targets, the EC is supporting several projects related to fuel cell technologies and hydrogen production and logistics with the aim to provide a prompt market penetration further to a period of demonstrations.

Two EC supported projects to demonstrate fuel cell powered buses are ongoing: CUTE (Clean Urban Transport for Europe) and CITYCELL.

CUTE, and its parallel project ECTOS to be developed in Iceland, are promoted by Daimler-Chrysler and will demonstrate the operation of 30 fuel cell Citaro model buses in ten (10) European cities (Amsterdam, Barcelona, Stockholm, Hamburg, London, Luxembourg, Madrid, Porto, Reykjavik and Stuttgart) as well as their different options to provide hydrogen to the vehicles.

CITYCELL is promoted by Iveco and Rénault and will demonstrate 4 hybrid fuel cell buses with several models of bodies and power train. Participant cities are Berlin, Madrid, Paris and Torino with one bus on each.

The public bus fleet operator in Madrid, Empresa Municipal de Transportes (EMT), decided to participate in both projects, following its endeavour for a better environment in the city, already made a reality through its 110 natural gas buses running on the streets today.

The presence of 4 fuel cell buses in Madrid running for some years on regular lines, starting early May 2003, with a regular demand of hydrogen, suggested that it would be a great opportunity to test and demonstrate an innovative and feasible new technology to provide it.

2. THE HYDROGEN REFUELLING PLANT CONCEPT IN MADRID.

The hydrogen refuelling plant had to fulfil a set of requirements or criteria useful to the purposes of demonstration at a reasonable cost and limited risk. Thus the plant had to be

- innovative but reliable
- of a technology able to produce enough hydrogen to allow the FC vehicles to take off in a next future
- able to produce hydrogen with the quality required by PEM fuel cells
- of reduced footprint
- of friendly operation by the user (EMT)

- able to produce hydrogen at competitive cost
- able to progress quickly to low initial investment costs
- able to produce hydrogen with a perfectly controlled quality

Gas Natural and its partner in this project, the oil company Repsol YPF, proposed to EMT the option to produce the hydrogen from natural gas locally at the bus depot. EMT is confident on the natural gas supply because of its experience with its large fleet of natural gas buses, thus the idea to produce hydrogen from the same source was easily accepted.

The participation of an expert on hydrogen compression, storage and dispensing was of great importance in the plant engineering. Air Liquide, a company active in the business of industrial gases, plays the roles related to the hydrogen logistics in the plant.

A team of technicians from these three companies, Air Liquide, Gas Natural and Repsol YPF, manages the project in very close co-operation. Air Liquide is responsible for the global project and specifically for hydrogen handling ; Gas Natural and Repsol YPF are responsible for the on-site hydrogen production.

On-site hydrogen production technology was chosen to be reliable at the refuelling station opening time, thus steam reforming, a well-known process largely used in big plants, was considered to be the best option.

Since Air Liquide can provide supplementary road transported hydrogen to the plant, reformer capacity can be below the maximum demand of all four FC buses when operating simultaneously.

Steady hydrogen production to respond to the demand from all four buses is around 75 Nm^3/h. Selected capacity for the on-site steam reformer was 50 Nm^3/h, a figure below the maximum demand; the decision obeys to the following criteria:

- more time running at full capacity
- enough capacity to provide valuable results from the demonstration
- frequent “start-and-stops” avoided when not all the buses are on service
- lower cost

Figure 1 displays an artist view of the station according with the project lay out (still on erection at the time this paper was prepared). From left to right there is an area to park road transported platforms with cylinders for compressed hydrogen, the cabinet for a high pressure compressor and a container with the reforming group inside; at the rear of the bus, beside it, there is the dispenser with meter.

figure 1

Hydrogen leaving from the reformer group in the container is supplied at 200 bar, to allow a connection in parallel with cylinders on the platforms that transport hydrogen at this pressure.

One set of cylinders on a platform, with a capacity of 4000 Nm^3 of hydrogen, remains stationary as a buffer, upstream of the high pressure compressor inlet. This compressor supplies hydrogen at 400 bar to the dispenser to allow filling the tanks on the buses at 350 bar.

Piping is designed to allow the cylinders on platforms to be filled with hydrogen coming from the reformer. Thus, in the circumstances where there is no hydrogen demand from the buses (i.e. because of major maintenance), the reformer can continue its production for hydrogen retail market.

3 METHANE STEAM REFORMER

Even though methane steam reforming is a worlwide known technology to produce hydrogen at low cost, it has been used only in big production plants. Experience in low capacities, with hydrogen quality suitable for PEM fuel cells, is only at the level of prototypes and in demonstration projects.

Gas Natural and Repsol YPF ordered the small reformer engineering, assembling and supply to a german manufacturer, Carbotech Anlagenbau GmbH. This company, owned by the chemical group Rütgers and with experience on gases purification, started a new development of very small methane steam reformers, named generically HCG (for Hydrogen Compact Generator), in the range between 5 and 200 Nm^3/h of capacity. The ordered reformer is HCG-50. (Figure 2 displays the HCG-5)

figure 2

The development of HCG concept is not a downscale from reformer designs for big plants but a complete new one. On the grounds of the essential technology for methane steam reforming, there is a sound analysis of volumes and processes allocated in each step of the reforming process to compact the plant. Overall size reduction is a must for this small hydrogen generators if their suitability for future hydrogen service stations is targeted.

The HCG-50 is designed for automatic operation. Start, stop, normal operation, emergency shut down and adjustment to changing operating conditions are automatically carried out and guarded by the control system.

Personnel supervision is reduced to regular visual inspections and maintenance work within defined intervals. Remote control can be established via Profibus or an optional telephone line.

The complete system is containerised. Cooling chilled water is supplied from closed loop system with a tube and fins air heat exchanger placed on the container roof. Hence, integration of the system is very simple as only process gas connections as well as a single power cable have to be supplied.

The complete plant will be workshop assembled and tested before delivery. Thus, installation on site is reduced to placing the container on prepared foundations, mounting the interconnecting piping and supplying the required natural gas, water and electrical interfaces.

Containerisation and lag of needs for a further on-site assembling provides easier access to official certification on safety issues. The European marking CE for safety is accepted by all the State Members in the European Union what removes border-crossing barriers.

3. Reformer plant description

The HCG 50 mainly consists of the following parts:

- Natural gas and water conditioning,
- Steam- methane- reforming,
- Hydrogen purification and
- Hydrogen compression.

Natural gas is compressed by a two stage compressor to approx. 16 bar. Prior to the steam reforming sulphur components in the natural gas are removed by an activated carbon twin filter.

Reforming pressure up to 16 bar reduces the geometric volume (water volume) in pressure vessels (reformer, filters, etc.) and is ideal for a downstream treatment by means of PSA or membrane. Previous compression of natural gas requires cheaper compressors than hydrogen compressors.

Before being injected in the reformer tube, the fresh water is softened and demineralised by a ion-exchanger multi-stage water conditioning system. The demineralised water is then injected via a metering pump directly into the reformer tube.

Main part of the steam reformer is a heated reformer tube which carries the nickel catalyst for the reforming process. Different from traditional steam reformers, the steam is generated inside the reformer tube and not by an external steam boiler. This is achieved by an integrated evaporator that utilises the heat of the hot reformate, hydrogen rich syngas, leaving the reformer tube. Due to the water evaporation inside the reformer tube, the temperature at the tube head is very low (approx. 300 °C) which avoids sealing problems. Also the reformate is abruptly cooled which avoids formation of soot. (see figure 3)

Inlet and outlet of the reformer tubes are located on the tube head. The tubes are internally designed as U-type gas duct. Tubes can be held only by their upper part ; this allows a free thermal expansion without causing additional mechanical stresses. There are 3 tubes in a furnace.

Heating of the reformer tubes in the furnace is carried out by a recuperative burner for direct heating. High efficiency is achieved due to an integrated counter flow heat exchanger that provides also low NO_x emissions.

Burning technology is a proprietary development of WS Wärmeprozesstechnik GmbH on the concept of flameless oxidation (FLOX®). The dramatic reduction of heat transfer by radiation allows a steady operation even if the Wobbe index of the fuel gas has variations. This is of relevant importance during the transient initial steps when the fuel gas shifts from natural gas to tail gas.

The reformate leaving the steam reformer is cooled by a water cooled tubular heat exchanger. During cooling excess water is removed from the reformate. This condensate can be recycled to reduce the water load of the water conditioning system.

Hydrogen purification is achieved by means of pressure swing adsorption (PSA). The PSA unit consists of four adsorber vessels and a number of process valves that control the PSA cycle. Pure hydrogen from the PSA unit is sent to the hydrogen booster

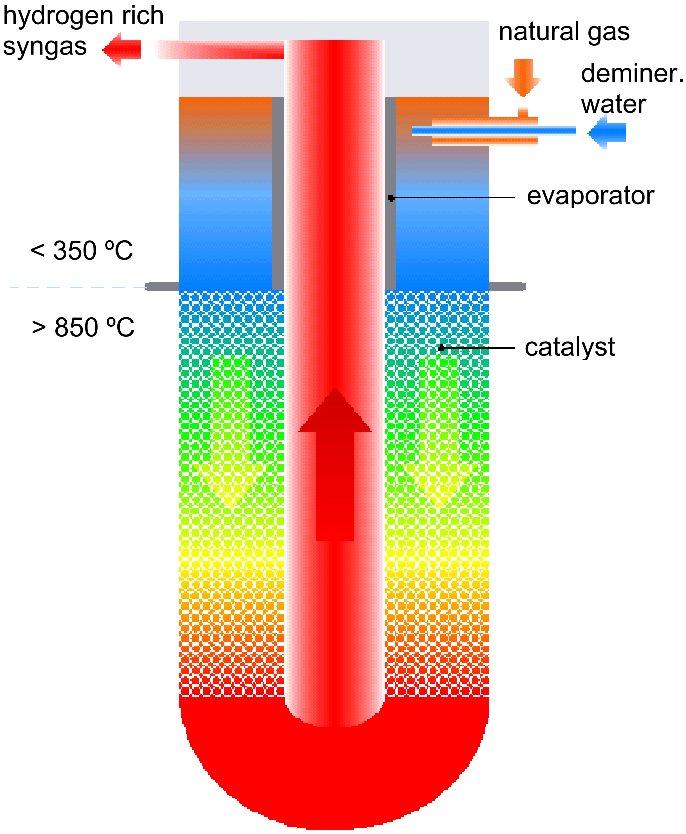

figure 3

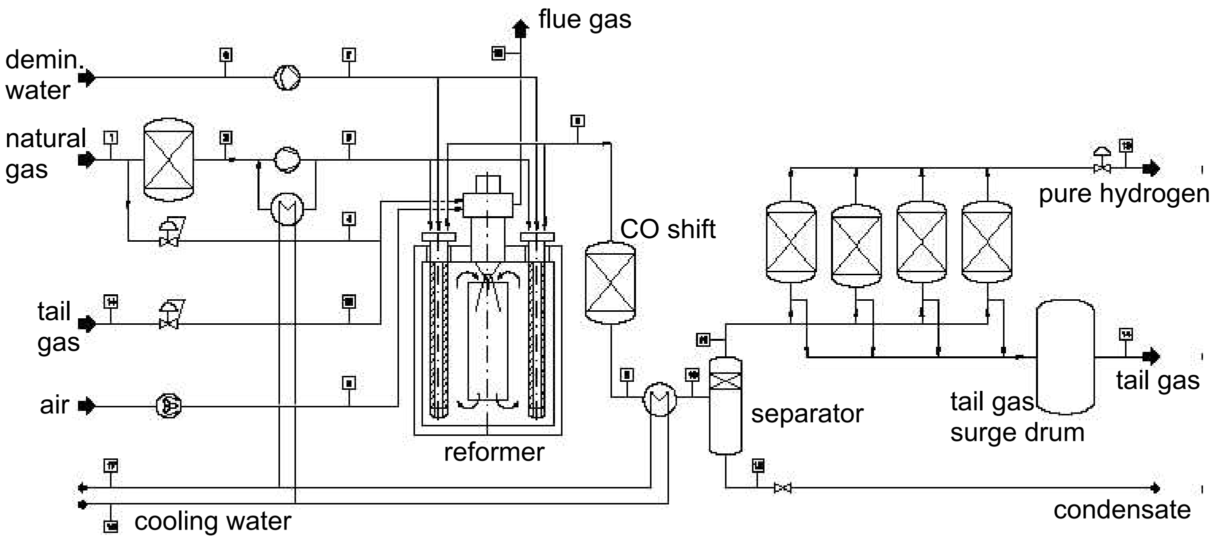

figure 4

compressor via a product gas surge tank, while the PSA off-gas, called tailgas, is sent to the reformer burner. During normal operation the burner can be operated solely on the tailgas stream. Figure 4 shows the schematic for the process.

Further compression of the hydrogen product gas is carried out by a two stage diaphragm compressor that supplies a hydrogen pressure of 200 bar.

3.2. Process description

The hydrogen generation process is divided into the generation of a hydrogen rich reformate stream by means of steam-methane-reforming (SMR) and the following hydrogen purification by means of pressure swing adsorption (PSA).

3.2.1. Steam- methane reforming

Methane and steam are converted at approx. 900 °C in the presence of a nickel catalyst to a hydrogen rich reformate stream according to the following reactions:

(1) $CH_4 + H_2O \rightarrow CO + 3\,H_2$

(2) $CO + H_2O \rightarrow CO_2 + H_2$

Thus, the reformate consists of hydrogen, carbon monoxide and carbon dioxide. Depending on the actual pressure, temperature and steam-to-carbon ratio, different equilibrium conditions are achieved that determine the exact composition of the gas. In addition the reformate stream contains unconverted methane and water as the steam-to-carbon ratio is always higher than the reaction stoichiometry requires. Also inert components of the natural gas stream can be found in the reformate.

3.2.2. Hydrogen purification

The CarboTech patented hydrogen purification process is based on a physical adsorption phenomena, whereas highly volatile compounds with low polarity, as represented by hydrogen, are practically non-adsorbable compared to molecules such as CO_2, CO, and CH_4. Hence most impurities in the feedgas stream can be selectively adsorbed and high-purity hydrogen product is obtainable.

The pressure swing adsorption (PSA) process is working between two pressure levels:

- Adsorption of impurities is carried out at high pressure to increase the partial pressure and, therefore, the loading of the impurities on the adsorbent material.
- Desorption and regeneration of the adsorbent takes place at low pressure to reduce the residual loading of the impurities as much as possible, in order to achieve a high product purity, high delta loading adsorption/desorption and subsequently a high hydrogen recovery.

The hydrogen purification unit consists of 4 adsorber vessels filled with an adsorbent material, basically molecular sieve. During normal operation each adsorber vessel operates in an alternating cycle of adsorption, regeneration and pressure build-up.

3.2.3. Adsorption

During the adsorption phase reformate enters from the bottom into one of the adsorber vessels. When passing the adsorber vessel all feedgas components except hydrogen are kept on the internal surface of the adsorbent material so that pure hydrogen leaves the adsorber vessel at the vessel top.

Before the adsorbent material is completely saturated with the adsorbed reformate components the adsorption phase is stopped and another adsorber vessel that has been regenerated before is automatically switched into adsorption mode thus, guaranteeing a continuous hydrogen supply.

3.2.4. Regeneration

Regeneration of the saturated adsorbent material is achieved by a stepwise depressurisation of the adsorber vessel to nearly atmospheric pressure. Most of the gas that leaves the adsorber vessel during this phase is used to purge and build-up pressure in other adsorber vessels since it still contains certain amounts of hydrogen. Thus, guaranteeing a maximum hydrogen yield.

At low pressure the adsorber vessel is purged with depressurisation gas from another adsorber vessel and small amounts of product gas to enhance the regeneration of the adsorbent.

3.2.5. Pressure build-up

Before the adsorption phase starts again, the adsorber vessel is re-pressurised stepwise to the final adsorption pressure.

After a pressure balance with an adsorber that has been in adsorption mode before, the final pressure build-up is achieved with product gas.

3.3. Design bases

3.3.1. Performance Data

- Product gas

Temperature		ambient	
Pressure,	outlet HCG 50	4.0	bar(g)
	after compression	200.0	bar(g)
Flow		50.0	Nm^3/h
Composition [volumetric basis]			
$CO + CO_2$		< 2.0	ppm
C_{1+}		< 1.0	ppm
O_2		< 500.0	ppm
H_2O (only vapour)		< 40.0	ppm
$He + Ar + N_2$		< 1.0	%
ΣS		< 1.0	ppm
NH_3		< 0.01	ppm
H_2		balance	
Inorganic content, max. (conductivity)		< 5.0	µS
Inorganic content, max.		< 0.01	% ash

- Flue- gas

Temperature, approx.	< 300	°C
Pressure	athmospheric	
Flow	130.0	Nm^3/h
Composition [volumetric basis], estimated		
$CO + CH_4$	< 0.01	%
CO_2	< 25.0	%
N_2	< 80.0	%
O_2	< 4.0	%
H_2S	< 5.0	mg/m^3
NO_x	< 50.0	mg/m^3

- Condensate

Flow, approx.	30.0	l/h
Pressure	> 8.0	bar(g)

This condensate is fed again to the process to reduce the amount of demineralised tap water.

3.3.2. Utilities

The following utilities are provided to the reformer plant to achieve the above mentioned performance data. A general tolerance of 5% is allowed to these utilities.

- Natural gas

Impurities :	THT	< 25.0	mg/m^3
	O_2	< 0.5	Vol.-%
Consumption		22.0	Nm^3/h
Pressure, min.		1.0	bar (g)
Pressure, max		4.0	bar(g)
Temperature:		ambient	

- Town water

Consumption, approx.:	100.0	l/h
Connected capacity, max.:	200.0	l/h
Pressure, min.:	2.0	bar (g)
Pressure, max.:	6.0	bar (g)
Temperature:	ambient	

- Electricity

Installed power,	HCG 50:	34.0	kW
	incl. booster:	45.0	kW
Power demand,	HCG 50:	19.0	kW
	incl. booster:	30.0	kW

Voltage: 380/50 V/Hz

- Nitrogen

  Nitrogen is required during initial start- up and extensive shut- down of the plant.
  Consumption: 50.0 m^3
  Pressure: 16.0 bar (g)
  Temperature: ambient
  Oxygen content < 0.5 %

3.3.3. Site conditions

Installation: outdoor
Ambient temperature, max.: 40.0 °C
Ambient temperature, min.: -5.0 °C
Design temperature for basic and detail engineering: 25.0 °C
Hazardous area classification outside battery limit: none
It has been assumed that the atmosphere at plant site is not particularly corrosive.

3.3.4. Equipment noise level

Noise level as an 8-hour time-weighted average is less or equal 75 dB(A) at 3m distance from the container enclosures.

3.3.4. Overall dimensions

The footprint of the container module is of 12m x 3.0m, with 3.5m height, excluded the water-to-air heat exchanger.

3.4. Container lay-out

Container size is big enough to contain all the necessary components and equipment for the reforming process plus natural gas and hydrogen compressors. In separate compartments in the same container there is allocation for water softening and electric power and electronic control. Cylinders with pattern gases for on-line CO analysers periodic calibration are permenently inside the container.

Lay out could have been more compact thus requiring lower overall dimensions, however, for this project, for demonstration purposes, more room to allow easy movements inside the container, the presence of more people than strictly necessary for maintenance but for visits, etc. was preferred.

Figure 5 provides general information about main components lay-out.

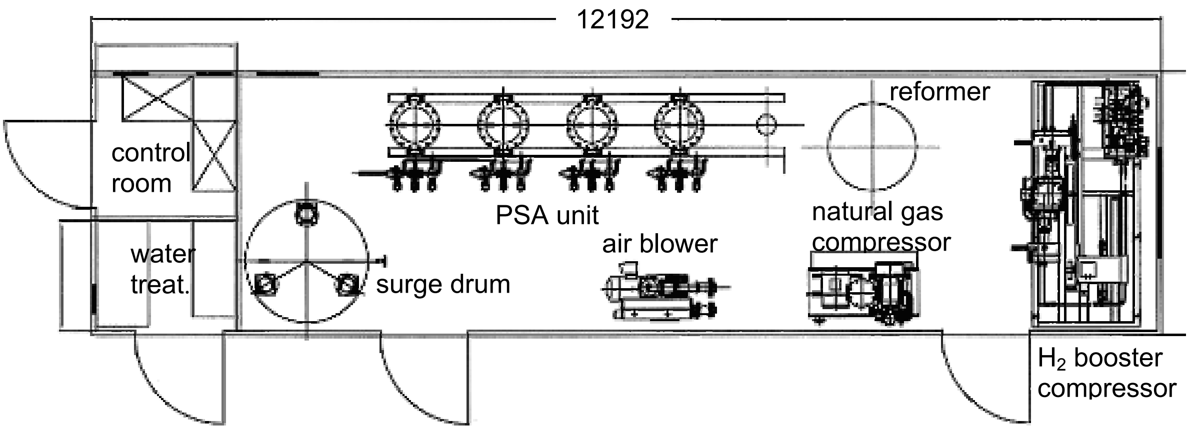

Figure 5

3.5. Reformer monitoring

Reformer operation is permanently monitored through data logger system that acquire process data and frequent sampling analysis from gas chromatography. Chromatograph is placed inside the control room in the container.

The experience gained with this demonstration will allow to define the requirements for the coming on-site reformers that could provide hydrogen to demo and pre-commercial activities in the field of fuel cell powered vehicles.

Since the buses that operate in Madrid are servicing regular urban lines, their filling logistics will provide a valuable experience to define the needs for capacity modularity, ability to respond to cold and warm starts, buffer sizes, etc.

A more sound knowledge on the reforming process will provide the grounds to analyse the ability of this reforming technology to be fed with other fuels.

4. A FORESIGHT TO THE FUTURE

This is not yet time for a massive take off of fuel cell powered vehicles but for some significant demonstration operations. These will provide a minimum mass production that will permit significant improvements and cost reductions on small on-site methane steam reformers. Identification of needs from bus fleet operators and agents in the field of service stations that will participate in such projects will help to provide standardisation.

In short to medium term, cost reductions can be foreseen to be in the range of 20 to 30%. In long term, sound improvements and standardised mass production can reduce the cost down to 50%.

Size can be easily reduced by 25 to 40% with improved designs in the PSA by means of shorter cycling modes and smaller adsorber beds.

The present use of natural gas on small reforming plants helps to open doors to a future use of biogas, still on the test fase. Use of biogas to produce hydrogen through reforming technology is a significant step towards a conservative and CO_2-neutral energy use.