REVIEW OF SMALL STATIONARY REFORMERS FOR HYDROGEN PRODUCTION

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Preface

The following report was prepared in support of efforts to develop a new International Energy Agency (IEA) task on the production of hydrogen from carbon-containing materials. The draft report was completed and the results presented during a Task Development Workshop in March 2001. The discussion in this report is based on technology developments that had been reported or were known prior to March 2001. No updates have been made to reflect advancements that have taken place since that time. An update to this report will be a likely outcome of the new IEA Agreement on the Production and Utilization of Hydrogen Task 16, Hydrogen from Carbon-Containing Materials, which officially began in April 2002 and will be active for three years.

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TABLE OF CONTENTS

EXECUTIVE SUMMARY

Approximately 95% of the hydrogen produced today comes from carbonaceous raw material, primarily fossil in origin. Only a fraction of this hydrogen is currently used for energy purposes; the bulk serves as a chemical feedstock for petrochemical, food, electronics and metallurgical processing industries. However, hydrogen's share in the energy market is increasing with the implementation of fuel cell systems and the growing demand for zero-emission fuels. Hydrogen production will need to keep pace with this growing market.

In the near term, increased production will likely be met by conventional technologies, such as natural gas reforming. In these processes, the carbon is converted to CO_2 and released to the atmosphere. However, with the growing concern about global climate change, alternatives to the atmospheric release of CO_2 are being investigated. Sequestration of the CO_2 is an option that could provide a viable near-term solution.

Cost of building sufficient distribution infrastructure and transporting hydrogen over large distances are major economic barriers to the implementation of hydrogen-based technologies, particularly in the transportation sector. Additionally, large-scale central production will depend on market volumes to evolve in order to compensate for the capital expenditures of building up capacity. Thus, distributed production via smaller reformer systems is viewed as an attractive near- to mid-term option for supplying hydrogen, particularly for vehicles and in regions where low-cost natural gas is readily available, and for securing market share for hydrogen technologies.

Reformer technology is commercially available today. However, scale economies in capital cost can be significant. Lower pressure and temperature and lower cost materials are needed to make small-scale, distributed reforming competitive. Minimizing CO_2 emissions must also be addressed, as carbon capture and sequestration will be too costly at the small scale.

Recently, the International Energy Agency's (IEA) Program on the Production and Utilization of Hydrogen launched its new Task 16, Hydrogen from Carbon-Containing Materials, to bring together international experts to investigate some of these near- and mid-term options for producing hydrogen with reduced environmental impacts. In addition to large-scale fossil-based production with carbon sequestration, small-scale reforming for distributed generation and technologies to convert biomass to hydrogen are included in the activity.

This review of current hydrogen production technologies was prepared to facilitate in the planning of collaborative activities to be carried out under the auspices of the IEA and focusing on advancing small-scale reformers for distributed hydrogen production. This report surveys conventional technologies:
- Steam Methane Reforming
- Partial Oxidation
- Auto-Thermal Reforming
- Methanol Reforming
- Catalytic Cracking of Methane
- Ammonia Cracking

Novel reformer technologies, such as sorbent enhanced reforming, ion transport reforming, plasma reforming and microchannel reforming are also discussed. Technologies are reviewed

based on performance characteristics, development status, economics and research issues for small-scale units.

As a result of this survey, the following have been concluded:
- Industry, government and academic researchers from fuel cell, hydrogen and energy producing communities need to identify and prioritize specific issues facing small-scale reformers for producing hydrogen for given applications and resources.
- Market assessment and system studies should be conducted to evaluate reformer technologies for both distributed and centralized hydrogen production, and for refueling station design.

Through the IEA, international experts will be brought together to further discuss these and other issues facing widespread implementation of small-scale reformer technology, particularly for transportation markets.

I. INTRODUCTION

This report to the International Energy Agency (IEA) reviews technical options for small-scale production of hydrogen via reforming of natural gas or liquid fuels. The focus is on small stationary systems that produce pure hydrogen at refueling stations for hydrogen-fueled vehicles. Small reformer-based hydrogen production systems are commercially available from several vendors. In addition, a variety of small-scale reformer technologies are currently being developed as components of fuel cell systems (for example, natural gas reformers coupled to phosphoric acid or proton exchange membrane fuel cell (PAFC or PEMFC) cogeneration systems, and onboard fuel processors for methanol and gasoline fuel cell vehicles). Although fuel cell reformers are typically designed to produce a "reformate" gas containing 40%-70% hydrogen, rather than pure hydrogen, in many cases they could be readily adapted to pure hydrogen production with the addition of purification stages.

As background, we first discuss hydrogen supply options for the transportation sector; both "centralized" (e.g. hydrogen production at a large central plant with distribution to refueling stations via truck or pipeline) and "distributed" (hydrogen production via small-scale reforming or electrolysis at the refueling site). Several recent studies have suggested that distributed hydrogen production via small-scale reforming at refueling stations could be an attractive near- to mid-term option for supplying hydrogen to vehicles, especially in regions with low natural gas prices.

A variety of reforming technologies that might be used in distributed hydrogen production at refueling stations are reviewed. These include steam methane reforming (SMR), partial oxidation (POX), autothermal reforming (ATR), methanol reforming, ammonia cracking and catalytic cracking of methane. Novel reformer technologies such as sorbent enhanced reforming, ion transport membranes, and plasma reformers are discussed. The performance characteristics, development status, economics and research issues are discussed for each hydrogen production technology.

Current commercial projects to develop and commercialize small-scale reformers are described. Finally, we suggest possibilities for future collaborative projects that might be undertaken by the IEA in this area.

II. HYDROGEN SUPPLY OPTIONS FOR THE TRANSPORTATION SECTOR

A. Motivation for Hydrogen as a Transportation Fuel: Environmental and Energy Supply Challenges Facing the Transportation Sector

Globally, the number of vehicles, vehicle miles traveled and transportation energy demand are projected to grow rapidly in the next decades. Continued reliance on current fuels and vehicle technologies poses significant challenges with respect to air pollution, greenhouse gas emissions and energy supply security.

- Combustion of fuels for transportation and heating contributes about two-thirds of all greenhouse gas emissions. Even with efficiency gains, it is likely that low- or zero-carbon fuels will be needed to meet future carbon emission reduction goals.

- The transportation sector accounts for a large fraction of air pollutant emissions. Health and environmental effects of air pollutants (NO_x, CO, VOCs, particulates) are leading to stricter tailpipe emissions regulations worldwide.

- Virtually all transportation fuels today are derived from oil. Oil production is projected to peak worldwide within a decade or so.

A number of alternative fuels and advanced vehicle power plants have been proposed to address these challenges. These include improved internal combustion engine (ICE) vehicles and ICE hybrid electric vehicles (fueled with reformulated gasoline, diesel, CNG, LPG, methanol, ethanol, DME, Fischer-Tropsch liquids or hydrogen), and fuel cell vehicles (fueled with gasoline, methanol or hydrogen).

Hydrogen emerges as a particularly attractive option for the long term based on the following desirable characteristics:

- Hydrogen vehicles have zero or near zero tailpipe emissions.
- Hydrogen can be made from widely available primary energy sources, including natural gas, coal, biomass, wastes, solar, wind, and nuclear power. If hydrogen is made from fossil fuels, it would be possible to capture and sequester CO_2.
- Greatly reduced full fuel cycle emissions of air pollutants and greenhouse gases are possible, if hydrogen is made from natural gas and used in hydrogen fuel cell or ICE vehicles. With hydrogen from renewable or decarbonized fossil sources, full fuel cycle emissions could approach zero.
- Hydrogen fuel cell vehicles are undergoing rapid development worldwide, and are projected to offer good performance and low costs in mass production. Hydrogen fuel cell vehicles are projected to reach lifecycle economic competitiveness with other advanced vehicle/fuel options at mass-produced costs, if external costs are taken into account.

Several recent studies (Ogden et al. 1998, Thomas et al. 1998) have shown that hydrogen is the preferred fuel for fuel cell vehicles. The design of the fuel cell vehicle is simpler with onboard hydrogen storage, and the vehicle is likely to be less costly and more energy efficient than one using liquid fuels (such as gasoline or methanol) with an onboard fuel processor. But developing a refueling infrastructure is seen as more costly and challenging for hydrogen than for liquid fuels.

B. Review of Past Studies of Hydrogen Refueling Infrastructure

Hydrogen offers perhaps the largest potential benefits in terms of reduced emissions of pollutants and greenhouse gases and diversified primary energy supply, but the development of a hydrogen energy infrastructure is often seen as a formidable technical and economic barrier to the use of hydrogen as an energy carrier. A widespread hydrogen distribution infrastructure does not currently exist, although the technologies to produce, store and distribute hydrogen to vehicles are commercially available today.

A key question is how to supply hydrogen to vehicles. A number of near-term hydrogen supply options exist including (see Figure 1):

- Hydrogen produced from natural gas in a large, centralized steam reforming plant, and truck delivered as a liquid to refueling stations

- Hydrogen produced in a large, centralized steam reforming plant, and delivered via small scale hydrogen gas pipeline to refueling stations

- Hydrogen from chemical industry sources (e.g. excess capacity in ammonia plants, refineries which have recently upgraded their hydrogen production capacity, etc.)

- Hydrogen produced at the refueling station via small scale steam reforming of natural gas, or by reforming of a more readily available liquid "hydrogen carrier" such as methanol or ammonia

- Hydrogen produced via small-scale water electrolysis at the refueling station.

In the longer term (Figure 2), hydrogen might be produced via

- Gasification of coal, biomass or wastes

- Electrolysis powered by wind or solar electricity

- Thermochemical production from fossil fuels with CO_2 capture and sequestration.

Recently, several studies have assessed the cost and feasibility of building a hydrogen-refueling infrastructure for vehicles (Ogden et al. 1995; Ogden et al. 1996; Ogden et al. 1998; Ogden 1999a. Ogden 1999b, Directed Technologies, Inc. (DTI) et al. 1997; Thomas et al. 1998a; Moore 1996; Raman 1996; Halvorson et al. 1996, Ferrell et al. 1996, Fairlie 1996, Thomas et al. 1998b, Mark 1997). We summarize the results from two groups that have carried out comprehensive studies of hydrogen infrastructure: Princeton University's Center for Energy and Environmental Studies (this work was directed by the author of this report) and Directed Technologies, Inc., an engineering consulting company that worked with Ford Motor Company to develop estimates of hydrogen infrastructure costs.

The cost of supplying hydrogen to vehicles depends on a host of factors including the local energy prices, and the size of the hydrogen demand.

For refueling stations designed to dispense 0.1 to 1.0 million scf H_2/day (serving a fleet of 14-280 PEMFC buses or 900-9000 PEMFC cars), studies by researchers at Princeton University's Center for Energy and Environmental Studies (Ogden et al. 1995, Ogden 1999a, Ogden 1999b), suggest that small-scale steam reforming of natural gas at the refueling station might offer the lowest delivered hydrogen cost, for energy prices typical of the United States. Delivered costs for hydrogen from onsite small-scale steam reforming are found to be $12-$25/GJ, depending on the size of the refueling station (see Figure 3). For typical U.S. energy prices, distributed hydrogen production via steam reforming gives the lowest delivered hydrogen cost until a large, geographically concentrated demand for hydrogen has built up (say about 3000 cars/sq. mile, an amount equal to about 20% of the cars in Los Angeles). In the early stages of a hydrogen economy distributed production of hydrogen would be preferred. This is also shown in Figure 4, where the infrastructure capital cost per car is illustrated.

Similar results were found in recent studies conducted by Directed Technologies, Inc. (DTI et al. 1997, Thomas et al. 1998). These studies were supported by Ford Motor Company and the United States Department of Energy (USDOE) and were coordinated by Directed Technologies, Inc., as part of the Partnership for a New Generation of Vehicles (PNGV) program. In this study, four major industrial hydrogen gas companies (Air Products and Chemicals, Inc., BOC Gases, Praxair and Electrolyser Corporation) carried out conceptual designs for hydrogen refueling infrastructure. The results of DTI's studies are consistent with Princeton's results.   For example, in recent paper (Thomas et al. 1998) summarizing earlier studies, DTI researchers

cited long term infrastructure capital costs of $230-$380 per vehicle for hydrogen (as compared to Princeton's estimate of $310-$620/car), and $630-$1350 per vehicle for methanol (as compared to Princeton's estimate of ($550-$1400/car). Moreover, the delivered hydrogen costs DTI estimated for gaseous hydrogen refueling stations, based on small-scale onsite reformation of natural gas, are within 5%-10% of Princeton's estimates.

C. Hydrogen Infrastructure Demonstrations

Increasingly, hydrogen refueling infrastructure demonstrations are conducted as part of hydrogen vehicle demonstrations. A list of ongoing hydrogen refueling station projects is given in Appendix A. Over the next several years, small-scale reformers of various types will be demonstrated for hydrogen production.

As part of the California Fuel Cell Partnership, Hydrogen Burner Technologies, Inc. is building a hydrogen refueling station in Thousand Palms, California, to convert methane to hydrogen using a partial oxidation reformer.

The Clean Urban Transport in Europe (CUTE) program is planning demonstrations of 27 hydrogen fuel cell buses in 9 European cities, including hydrogen infrastructure demonstrations.

The Global Environment Facility is planning demonstrations of 30 fuel cell buses in developing countries.

D. Distributed Versus Centralized Hydrogen Production

Distributed hydrogen production via small scale reforming is less costly than centralized production until a large geographically concentrated hydrogen demand has built up. Distributed hydrogen production would be attractive especially in the early stages of a hydrogen economy. Hydrogen could be provided where it was needed, allowing supply to match demand, as more hydrogen vehicles were added to the fleet.

Once a large enough hydrogen energy demand developed (on the order of 10%-20% of the cars in an urban area like Los Angeles using hydrogen), central hydrogen production would become cost competitive with distributed production. Many analysts see eventual production of hydrogen in large centralized plants, with local hydrogen pipeline distribution similar to that for natural gas. At this time, decarbonized fossil hydrogen or other low carbon sources of hydrogen could be phased in (hydrogen from renewables).

If hydrogen is produced at a large centralized energy complex, the added costs for CO_2 capture and disposal are quite small. In contrast, with distributed small-scale hydrogen production from fossil fuels, capture, collection and sequestration of CO_2 from many dispersed small reformers is prohibitively expensive (Ogden 1997). Thus, implementing the fossil hydrogen/CO_2 sequestration scenario for hydrogen supply supposes that hydrogen is produced in large plants. The cost of hydrogen from biomass or wastes is also lower at large scale.

E. Roles for Small Reformers in Development of a Hydrogen Energy System

Small-scale reformers are a key technology for the early stages of a hydrogen economy. Figures 5a and 5b show the possible evolution for a hydrogen energy system. In the early stages, hydrogen is produced onsite for fleet vehicles. Eventually, when demand builds up, a

switch might be made to centralized hydrogen production. This would enable use of low carbon primary sources or decarbonized fossil sources with CO_2 sequestration (Figure 5b).

Below we describe a variety of small-scale reformers that could be used in hydrogen refueling stations.

III. DESCRIPTION OF SMALL-SCALE REFORMER TECHNOLOGIES

In this paper, reforming is defined as the thermochemical processing of a hydrocarbon feedstock in high temperature chemical reactors to produce a hydrogen-rich gas.

The hydrogen production process takes place in several steps. First, a hydrocarbon feedstock (such as natural gas or a liquid fuel) is reformed at high temperature in the presence of a catalyst. Depending on the type of reformer, the feedstock reacts with steam or oxygen at high temperature to produce a synthetic gas or "syngas" composed of H_2, CO, CO_2, CH_4 and H_2O. The syngas is further processed to increase the hydrogen content (CO in the syngas is converted to hydrogen via the water gas shift reaction--see Eq. 2 below). Finally, hydrogen is separated out of the mixture at the desired purity, up to 99.999% for fuel cell applications. Typical materials flows for hydrogen production based on steam methane reforming and partial oxidation are shown in Figure 6.

In this section, we describe various types of reforming processes. We also discuss the commercialization status for various types of small-scale reformer technology. A number of commercial ventures are underway to develop small-scale reformers for stand-alone hydrogen production, and as components in fuel cell systems. These are described below and summarized in Table 1.

A. Steam Methane Reforming

1. Process Description

Catalytic steam reforming of methane is a well-known, commercially available process for hydrogen production (Rostrup-Nielsen 1984, Twigg 1989). In the United States, most hydrogen today (over 90%) is manufactured via steam reforming of natural gas (Heydorn 1995). Hydrogen production is accomplished in several steps: steam reforming, water gas shift reaction, and hydrogen purification. (Figure 6 shows material flows for a typical hydrogen production plant based on steam reforming of natural gas.)

The steam reforming reaction

$$CH_4 + H_2O \leftrightarrow CO + 3\,H_2 \qquad \Delta h = +206.16 \text{ kJ/mol } CH_4 \quad (1)$$

is endothermic and requires external heat input. Economics favor reactor operation at pressures of 3-25 atmospheres and temperatures of 700°C to 850°C. The external heat needed to drive the reaction is often provided by the combustion of a fraction of the incoming natural gas feedstock (up to 25%) or from burning waste gases, such as purge gas from the hydrogen purification system. Heat transfer to the reactants is accomplished indirectly through a heat exchanger. Methane and steam react in catalyst filled tubes. Typically, the mass ratio of steam-to-carbon is about 3 or more to avoid "coking" or carbon build-up on the catalysts.   (At lower steam-to-carbon ratios, solid carbon can be produced via side reactions.)

After reforming, the resulting syngas is sent to one or more shift reactors, where the hydrogen output is increased via the water-gas shift reaction

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta h = -41.15 \text{ kJ/mol CO} \quad (2)$$

which "converts" CO to H_2. This reaction is favored at temperatures of less than about $600^{\circ}C$, and can take place as low as 200°C, with sufficiently active catalysts. The gas exiting the shift reactor contains mostly H_2 (70%-80%) plus CO_2, CH_4, H_2O and small quantities of CO. For hydrogen production, the shift reaction is often accomplished in two stages. A high temperature shift reactor operating at about 350-475°C accomplishes much of the conversion, followed by a lower temperature (200-250°C) shift reactor, which brings the CO concentration down to a few percent by volume or less.

Hydrogen is then purified. The degree of purification depends on the application. For industrial hydrogen, pressure swing absorption (PSA) systems or palladium membranes are used to produce hydrogen at up to 99.999% purity. For PEM or phosphoric acid fuel cells closely coupled to reformers, diluents such as CO_2 and CH_4 are tolerable. However, CO must be reduced to less than about 10 ppm for PEM fuel cells, so a CO removal system such as preferential oxidation must be used.

In a preferential oxidation system, the gas is passed over a catalyst bed, with added air. At certain temperature and stoichiometry conditions, the reaction

$$CO + 1/2\ O_2 \rightarrow CO_2 \qquad\qquad (3)$$

is strongly favored over hydrogen oxidation, so that CO is removed to the level of several ppm. Preferential oxidation technology is being developed for use with reformers in fuel cell cogeneration systems or onboard fuel cell vehicles.

The energy conversion efficiency [= hydrogen out (higher heating value (HHV))/energy input (HHV)] of large-scale steam methane reformers is perhaps 75%-80%, although 85% efficiencies might be achieved with good waste heat recovery and utilization (Katofsky 1993).

2. *Development/Commercialization Status of Various Types of Steam Methane Reformers*

a. Conventional Steam Methane Reformers

Steam methane reformers have been built over a wide range of sizes. For large-scale chemical processes such as oil refining, steam reformers produce 25 to 100 million standard cubic feet of hydrogen per day. (In energy terms, this is enough hydrogen to power a fleet of about 225,000 to 900,000 hydrogen fuel cell cars, each driven 11,000 miles per year.) These systems consist of long (12 meter) catalyst filled tubes, and operate at temperatures of $850^{\circ}C$ and pressures of 15-25 atm, which necessitates the use of expensive alloy steels. Capital costs for a 20 million scf H_2/day steam reformer plant (including the reformer, shift reactor and PSA) are about $200/kW H_2 output; for a 200 million scf/day plant capital costs are estimated to be about $80/kW H_2 (DTI et al. 1997).

Refinery-type (high pressure, high temperature) long tube reformers (see Figure 7a) can be scaled down to as small as 0.1-1.0 million scf/day (the scale needed for producing hydrogen

at refueling stations), but scale economies in the capital cost are significant. The capital cost is about \$750/kW H_2 at 1 million scf/day and \$4000/kW H_2 at 0.1 million scf/day.

Small-scale conventional (long tube, high temperature) steam methane reformers are commercially available from a number of companies, which normally produce large steam methane reformers for chemical and oil industries. The main design constraints for these systems are high throughput, high reliability and high purity (depending on the application. Companies supplying this type of reformer include Haldor-Topsoe, Howe-Baker, Hydrochem, KTI, and Foster Wheeler.

The disadvantages of conventional long tube steam reformers for hydrogen refueling station applications are their large size (12-meter long catalyst-filled tubes are is commonly used), and high cost (which is due to costly materials requirements for high temperature, high pressure operation, and to engineering/installation costs for these one of kind units). For these reasons, it is generally believed in the hydrogen and fuel cell R&D communities that a more compact, lower cost reformer will be needed for stand-alone hydrogen production at refueling stations (Ogden et al. 1996; Thomas et al. 1997).

b. Compact "Fuel Cell Type" Steam Methane Reformers with Concentric Annular Catalyst Beds

At small sizes, a more cost effective approach is to use a lower pressure and temperature reformer, with lower cost materials. Steam methane reformers in the range 2000 to 120,000 scf H_2/day have been developed for use with fuel cells, and have recently been adapted for stand-alone hydrogen production (Halvorson et. al 1997). In these systems, the heat transfer path is curved (see Figure 7b), to make the device more compact, and the reformer operates at a lower temperature and pressure (3 atm, 700°C), which relaxes materials requirements. Estimates of mass produced costs for small "fuel cell type" steam methane reformers indicates that the capital cost for hydrogen production plants in the 0.1 to 1.0 million scf/day range would be \$150-\$180/kW H_2 assuming that 1000 units were produced (DTI et al. 1997). (Costs are given on a higher heating value basis, and for the purpose of comparison, do not include hydrogen compression, storage or dispensing to vehicles.) The capital costs per unit of hydrogen production (\$/kW H_2) are similar for fuel cell type small reformers and conventional, one-of-a-kind large reformers, assuming that many small units are built. Energy conversion efficiencies of 70%-80% are possible for these units.

A number of companies have developed compact steam methane reformers to reform natural gas for closely coupled fuel cells. These include Haldor-Topsoe, International Fuel Cells (IFC), Ballard Power Systems, Sanyo Electric, and Osaka Gas Company.

- Praxair, in a joint venture with IFC, has recently commercialized a small stand-alone hydrogen production system based on this type of reformer (Halvorson et al. 1997).

- Researchers at the Fraunhofer Institute for Solar Energy Systems are designing a more compact multi-tube steam methane reformer with a catalytic heater rather than a burner (Vogel et al. 1998).

- Energy Partners is building residential PEMFC power system (Barbir et al. 2000). Franhofer Institute (Vogel et al. 1998) built methane reformers to make H_2 for use with Energy Partners vehicle.

- Dais-Analytic Corporation is building a residential PEMFC power system with its own reformer (Dais-Analytic Corporation website).

- Sanyo Electric Co. is building a residential PEMFC power system with a multi-tube steam reformer.

- IdaTech is building a residential PEMFC power system with its own multi-fuel reformer that makes 99.9% pure hydrogen. (Edlund et al. 2000)

- IFC is in a joint venture with Toshiba to develop stationary PEMFCs.

Although this technology is newly commercialized, it shows the promise of reduced capital costs as compared to conventional small-scale reformers, as well as compactness.

c. Plate-type Steam Methane Reformers

Another innovation in the design of steam methane reformers for fuel cell systems is the "plate-type" reformer. Plate-type reformers are more compact than conventional reformers with long, catalyst-filled tubes or annular-type reformers with catalyst beds. The reformer plates are arranged in a stack. One side of each plate is coated with a steam reforming catalyst and supplied with reactants (methane and steam). On the other side of the plate, anode exhaust gas from the fuel cell undergoes by catalytic combustion, providing heat to drive the endothermic steam reforming reaction. The potential advantages of a plate reformer are more a compact, standardized design (and lower cost), better heat transfer (and therefore better conversion efficiency), and faster start-up (because each plate has a lower thermal inertia than a packed catalyst bed).

Several companies are involved in developing this technology.

- Researchers at GASTEC have designed a plate-type steam methane reformer, consisting of metal plates coated with ceramic supporting a catalyst. They investigated performance for various reformer and combustion catalyst types, coatings, and substrate materials, and built a 20 kW prototype (van Driel and Meijer 1998). Corrosion-resistant materials were identified for the substrate. Further work is needed to improve the resistance of the catalysts to carbon deposition and sulfur poisoning. Plug Power has entered an agreement with GASTEC in its development of residential size fuel cell systems.

- Researchers at Osaka Gas Company (Shinke et al. 2000) have recently developed a plate-type steam methane reformer system for use with PEM fuel cells, based on earlier work with phosphoric acid fuel cell systems. The various reactors in the steam methane reformer system (e.g. desulfurizer, steam reformer, water gas shift reactor, and CO clean-up stage) are made up of plates of a standard size, greatly reducing the capital cost. Heat transfer and heat integration between reactors is facilitated. A 1 kW reformer was built and tested. Before commercialization, goals are increasing the energy conversion efficiency from present value of about 70% to 77% by reducing heat losses, and increasing the lifetime from 5 to 10 years.

- Air Products patented a plate-type reformer in 1994 (Allam et al. 1994).

- Researchers at Ishikawajima-Harima Heavy Industries (Tokyo, Japan) have patented a plate-type steam methane reformer (Hamada et al. 1997).

- International Fuel Cells holds a patent on a plate-type reformer (LeSieur 1998).

- Researchers at Ztek Corporation (Hsu et al. 2001) have patented a plate-type reformer that can be operated as a steam reformer or a partial oxidation system.

Plate-type steam methane reformers have not yet been commercialized for fuel cell systems, but may allow for future capital cost reductions by simplifying system design.

d. Membrane Reactors for Steam Reforming

Another promising technology is the "membrane reactor", where the steam reforming, water gas shift and hydrogen purification steps all take place in a single reactor. Methane and steam are fed into a catalyst-filled reactor under pressure. On one side of the reactor is a high selectivity palladium membrane that is selectively permeable to hydrogen. As the steam reforming reaction proceeds, the hydrogen is driven across the membrane by the pressure difference. Depending on the temperature, pressure and the reactor length, methane can be completely converted, and very pure hydrogen is produced. Very pure hydrogen is removed as the reaction proceeds. This allows lower temperature operation, and lower cost materials. A potential advantage of this system is simplification of the process design and capital cost reduction, because fewer process vessels will be needed.

There is a large amount of industrial R&D activity on membrane technologies for syngas and hydrogen production. Interest by major energy companies in applying membrane technology to large-scale syngas and hydrogen production may have significant "spin-offs" for small-scale hydrogen production as well. Recently patents have been issued on membrane reactor reforming to a number of companies involved in fuel processor design for fuel cells and on related ion transport membrane technology to oil companies, Exxon, BP Amoco, Standard Oil, and industrial gas companies, Air Products and Praxair (see Appendix B).

- Recently Praxair and Argonne National Laboratory (Shah, M., R.F. Drnevich and U. Balachandran 2000) launched a program to develop a compact, low-cost hydrogen generator based on ceramic membrane technologies. Steam, natural gas and oxygen are combined in a catalyzed autothermal reforming reaction. Oxygen is derived from air, using an oxygen transport ceramic membrane (OTM) that operates at about 800-1000°C. High purity hydrogen is removed using a high selective hydrogen transport membrane, also operating at 800-1000°C. The OTM has been developed by Praxair and others in the Oxygen Transport Membrane Syngas Alliance (BP Amoco, Statoil, Sasol), beginning in 1997, and is now undergoing Phase II pilot demonstration. The hydrogen transport membrane is being developed at Argonne National Laboratory, and is in an earlier stage of development.

- Tokyo Gas company has built and tested a small membrane reactor for production of pure hydrogen from natural gas (Seki et al. 2000) at a rate of 15 Nm^3/h (about 12,000 scf/d), as well as steam reforming and partial oxidation systems.

- Johnson Matthey is working on development of hydrogen separation membranes suitable for use in membrane reactors (Booth et al. 1996).

- The European Commission funded the COCLUP/HYSEP project to develop a hydrogen separation system based on ceramic composite Ag/Pd membranes (Dams et al. 2000). This work is still in the design stage.

- Under a contract from the USDOE CARAT Program, Aspen Systems demonstrated a membrane reactor for steam reforming methane, ethanol and gasoline (Aspen Systems 1999).

- Membrane reactor steam reformers are still undergoing laboratory R&D as well (Kikuchi 2000, Lin and Rei 2000, Aasberg-Petersen et al. 1998, Oklany et al. 1998, Alibrando et al. 1997). This is a potentially interesting area for basic research.

B. Partial Oxidation

1. Process Description

Another commercially available method for deriving hydrogen from hydrocarbons is partial oxidation (POX). Here, methane (or some other hydrocarbon feedstock such as oil) is oxidized to produce carbon monoxide and hydrogen according to

$$CH_4 + 1/2\ O_2\ ->\ CO + 2\ H_2 \qquad \Delta h^\circ = -36\ MJ/kmol\ CH_4$$
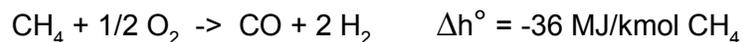
The reaction is exothermic and no indirect heat exchanger is needed. Catalysts are not required because of the high temperature. However, the hydrogen yield per mole of methane input (and the system efficiency) can be significantly enhanced by use of catalysts (Loftus 1994). A hydrogen plant based on partial oxidation includes a partial oxidation reactor, followed by a shift reactor and hydrogen purification equipment (Figure 5b). Large-scale partial oxidation systems have been used commercially to produce hydrogen from hydrocarbons such as residual oil, for applications such as refineries. Large systems generally incorporate an oxygen plant, because operation with pure oxygen, rather than air, reduces the size and cost of the reactors.

Small-scale partial oxidation systems have recently become commercially available, but are still undergoing intensive R&D (Moard 1995, Loftus 1994, Mitchell et al. 1995, Cross et al. 2000). Small-scale partial oxidation systems have a fast response time, making them attractive for following rapidly varying loads, and can handle a variety of fuels, including methane, ethanol, methanol, and gasoline.

The POX reactor is more compact than a steam reformer, in which heat must be added indirectly via a heat exchanger. The efficiency of the partial oxidation unit is relatively high (70%-80%). However, partial oxidation systems are typically less energy efficient than steam reforming because of the higher temperatures involved (which exacerbates heat losses) and the problem of heat recovery. (In a steam methane reforming plant, heat can be recovered from the flue gas to raise steam for the reaction, and the PSA purge gas can be used as a reformer burner fuel to help provide heat for the endothermic steam reforming reaction. In a POX reactor, in which the reaction is exothermic, the energy in the PSA purge gas cannot be as fully recovered.)

Because they are more compact, and do not require indirect heat exchange (as in steam reforming), it has been suggested that partial oxidation systems could cost less than steam reformers. Although the partial oxidation reactor is likely to be less expensive than a steam reformer vessel, the downstream shift and purification stages are likely to be more expensive (Ogden et al. 1996).

Developing low cost purification technologies is key if POX systems are to be used for stationary hydrogen production. Another approach is using pure oxygen feed to the POX, which incurs high capital costs for small-scale oxygen production, but eliminates the need to deal with nitrogen downstream. Oxygen enrichment of incoming air is another way of reducing, but not eliminating, the amount of nitrogen. Innovative membrane technologies such as the ion transport membrane (ITM) may allow lower cost oxygen for POX reactors (Dyer 1999). This is being investigated by Air Products in its research on ion transport membranes (ITMs) (Dyer et al. 2000), and by Praxair and partners in its oxygen transport membrane program (Shah, Drnevich et al. 2000).

2. *Development/Commercialization Status of Partial Oxidation Systems*

A number of companies are involved in developing small-scale partial oxidation systems.

- Small partial oxidation systems have been developed, for use with fuel cell systems, by Arthur D. Little and its spin-off companies Epyx and Nuvera (ADL 1994, Loftus 1994, Mitchell et al. 1995). Epyx is supplying the onboard gasoline reformer for the USDOE's gasoline fuel cell vehicle project (Cross 1999, Chalk 2000). Epyx recently formed a joint company with DeNora called Nuvera, to commercialize POX reformer/PEM fuel cell systems (Cross et al. 2000). Nuvera has reportedly shipped gasoline reformers to automotive companies for testing (Hydrogen and Fuel Cell Letter, October 2000).

- Hydrogen Burner Technology (HBT), Inc. has developed a range of hydrogen production systems based on partial oxidation (Moard 1995, Mauzey et al. 2000). This includes a reformer that produces very pure H_2 for cogeneration in buildings. HBT, with funding from the California Air Resources Board, is installing a natural gas reformer filling station for Sunline Transit at Thousand Palms, CA, to supply H_2 to fuel cell buses and Hythane[®] buses. HBT has a joint venture with Gaz de France to distribute HBT's products in Europe. Phoenix Gas Systems (a HBT sub group) develops systems for industrial hydrogen gas generation.

- Argonne National Laboratory has developed a partial oxidation reformer suitable for use in vehicles (Ahmed et al. 1998).

The USDOE supports work on partial oxidation systems for onboard fuel processors for fuel cell vehicles through the Office of Transportation Technologies Fuel Cell Program (Chalk 2000). Several companies are involved in developing multi-fuel fuel processors for 50 kW fuel cell vehicle power plants. These include:

- As part of the Arthur D. Little/Epyx/Nuvera partnership, a gasoline fuel processor built by Epyx was demonstrated with a PEM fuel cell in 1998. Plug Power is building an integrated 50 kW gasoline/PEMFC system, based on the Epyx reformer.

- McDermott Technology, Inc. and Catalytica are developing a multi-fuel fuel processor for a 50 kW fuel cell.

- Hydrogen Burner Technologies, Inc. is developing a multi-fuel fuel processor for a 50 kW fuel cell.

In addition, a number of automotive companies are in joint ventures to develop gasoline fuel processors based on POX technology. These include:

- General Motors has joined with Exxon Mobil to develop an onboard gasoline fuel processor.

- International Fuel Cells has partnered with Shell Hydrogen to develop and market a variety of fuel processors.

Projects to use partial oxidation systems in stationary fuel cells include:

- Tokyo Gas Company has demonstrated a partial oxidation system for 1 kW fuel cell cogeneration system (Seki et al. 2000).

- McDermott Technology, Inc. (MTI) and Catalytica are working together to develop compact fuel processors for use with PEMFCs and solid oxide fuel cells (SOFCs). This system is designed to reform gasoline and Naval Distillate for PEMFCs.

C. Autothermal Reforming

1. Process Description

Autothermal reformers (ATRs) combine some of the best features of steam reforming and partial oxidation systems. Several companies are developing small autothermal reformers for converting liquid hydrocarbon fuels to hydrogen in fuel cell systems.

In autothermal reforming, a hydrocarbon feed (methane or a liquid fuel) is reacted with both steam and air to produce a hydrogen-rich gas. Both the steam reforming and partial oxidation reactions take place. For example, with methane

$$CH_4 + H_2O \leftrightarrow CO + 3\,H_2 \qquad \Delta h = +206.16 \text{ kJ/mol } CH_4 \quad (1)$$

$$CH_4 + 1/2\,O_2 \rightarrow CO + 2\,H_2 \qquad \Delta h^\circ = -36 \text{ MJ/kmol } CH_4$$

With the right mixture of input fuel, air and steam, the partial oxidation reaction supplies all the heat needed to drive the catalytic steam reforming reaction.

Unlike the steam methane reformer, the autothermal reformer requires no external heat source and no indirect heat exchangers. This makes autothermal reformers simpler and more compact than steam reformers, and it is likely that autothermal reformers will have a lower capital cost. In an autothermal reformer all the heat generated by the partial oxidation reaction is fully utilized to drive the steam reforming reaction. Thus, autothermal reformers typically offer higher system efficiency than partial oxidation systems, where excess heat is not easily recovered.

As with a steam reformer or partial oxidation system, water gas shift reactors and a hydrogen purification stage are needed.

2. Development/Commercialization Status of Autothermal Reformers

Autothermal reformers are being developed by a number of groups, mostly for fuel processors of gasoline, diesel and logistics fuels and for natural gas fueled PEMFC cogeneration systems. These include:

- Argonne National Laboratory is testing ATR systems and catalysts (C. Pereira et al. 1999, C. Pereira et al. 2000, M. Krumpelt et al. 2000, Kopasz et al. 2000).

- International Fuel Cells designed an ATR that runs on logistics fuels (Scoles and Perna, 2000). BWX and McDermott Technology, Inc. Using the IFC ATR, a system was designed to reform Naval distillate for shipboard fuel cells (Scoles and Perna, 2000).

- Fraunhofer Solar Energy Institute is designing ATRs for LPG and diesel fuel. (Heinzel et al. 2000).

- Degussa Metals Catalyst Cerdec is developing catalysts for ATRs used with gasoline (Weiland et al. 2000).

- Johnson-Matthey developed a "Hot-Spot" autothermal reformer (Reinkingh 1998), capable of reforming methanol and methane.

- Honeywell and Energy Partners are developing a 50 kW PEMFC system for buildings cogeneration. Both SMR and ATR are being tried (Ferrall et al. 2000).

- Daimler-Chrysler is developing an ATR for gasoline reforming (Docter et al. 2000).

- McDermott Technologies, Inc. (MTI) and Catalytica are developing a small autothermal reformer for use with diesel and logistics fuels on ships, based on an IFC design. A regenerable desulfurization stage is important for Navy diesel fuel with 1% sulfur. Partners in this are McDermott Technology, Inc., Catalytica Advanced Technologies, Ballard, BWX Technologies, Gibbs and Cox.

- The Idaho National Energy and Environment Laboratory (INEEL), with MTI and Pacific Gas and Electric, have recently begun work on developing a 10 kW ATR system for hydrogen refueling station applications (Anderson 2001).

- Analytic Power has assessed multi-fuel reformer technology, including ATR.

- IdaTech has developed a multi-fuel reformer, which produces very pure hydrogen from methane. It is likely that the reformer is either a POX or ATR type.

- Recently, Hydrogen Burner Technologies, Inc. began development of an autothermal reforming system for use with fuel cells and for hydrogen production.
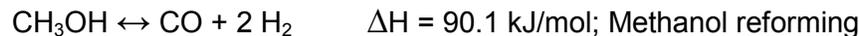
D. Methanol Steam Reforming

1. Process Description

Methanol is a liquid fuel that can be more easily stored and transported than hydrogen. Because it can be readily steam reformed at moderate temperatures (250-350°C), methanol has been proposed as a fuel for fuel cell vehicles. Experimental fuel cell vehicles with onboard methanol reformers have been demonstrated by DaimlerChrysler, Toyota and Nissan. In addition, small hydrogen production systems, based on methanol reforming, are in commercial use.

Here we review technologies for methanol steam reforming. Although these technologies are being developed for fuel processors onboard fuel cell vehicles, it has also been suggested that hydrogen might be produced by steam reforming methanol at refueling stations (Ledjeff-Hey et al. 1998). We discuss the application of methanol steam reformer technologies to hydrogen production.

The reactions for production of hydrogen via methanol steam reforming are as follows:

$$CH_3OH \leftrightarrow CO + 2\,H_2 \qquad \Delta H = 90.1 \text{ kJ/mol; Methanol reforming}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H = -41.2 \text{ kJ/mol; Water gas shift reaction}$$

Or combining these:

$$CH_3OH + H_2O \leftrightarrow CO_2 + 3H_2$$

The reaction takes place in the presence of copper/zinc catalysts in the temperature range 200-350°C. Overall the reaction is endothermic, requiring the application of heat, through an indirect heat exchanger, to a catalyst filled tube or catalyzed plate. Good thermodynamic conversion is found for steam-to-carbon ratios of 1.5 and temperatures of 250-350°C.

Various types of methanol steam reformers have been designed. Earlier designs use catalyst filled tubes that are indirectly heated via combustion of some of the incoming methanol fuel. More recently, there has been an effort to develop "plate type" reformers for methanol reforming. These have a number of potential advantages including compactness, better heat transfer, faster start-up and potentially lower cost. Membrane reactors have also been built for steam reforming methanol.

For refueling station applications, a hydrogen purification stage would be needed, either a pressure swing adsorption unit or a membrane separation stage. The cost of the hydrogen production system might be lower for a methanol steam reformer because it would operate at much lower temperatures than a methane steam reformer. The cost of hydrogen produced from methanol might be higher than hydrogen from small-scale steam reforming, because methanol is generally, although not always, a more expensive feedstock than natural gas. (In the United States, costs for methanol are estimated to be about $11/GJ versus perhaps $4-$5/GJ for methane at the refueling station.) Assuming an energy conversion efficiency (feedstock to hydrogen) of 75% for each system, feedstock costs alone would be about ($11/GJ-$5/GJ)/0.75 = $8/GJ higher for the methanol steam reformer.

2. *Development/Commercialization Status of Methanol Steam Reformers*

- Haldor Topsoe has used small methanol reformers for stand-alone hydrogen production.

- Researchers at Los Alamos National Laboratory have conducted research on methanol steam reforming for PEM fuel cells. Researchers at Argonne National Laboratory have also simulated and built methanol steam reformers.

- Several automakers demonstrating fuel cell vehicles have developed onboard steam reformers for methanol. These include Excellis Fuel Cell Engines (DaimlerChrysler), Toyota and Nissan.

- The European Commission funded two projects to develop onboard fuel processors for fuel cell vehicles as part of the JOULE II project. The MERCATOX project had the goal of producing a prototype integrated methanol reformer and selective oxidation system. Wellman CJB Ltd., a British company that has produced units for steam reforming alcohols, hydrocarbons, ethers and military fuels, coordinated the MERCATOX project. The reformer consists of a series of catalytic plates, with combustion of anode off-gas on one side and reforming on the other side. Loughborough University designed the gas clean-up system. Wellmann built and tested a plate type steam methanol reformer and integrated the system, Rover Cars Company addressed manufacturing and vehicle design issues, and Instituto Superior Technico undertook modeling work (Dams et al. 2000).

- Northwest Power Systems (now called IdaTech) has developed a multi-fuel processor. They have demonstrated pure hydrogen production via steam reforming of methanol, using a palladium membrane for the final purification step (McDermott et al. 2000, Edlund et al. 2000).

- Researchers at InnovaTek, Inc. have demonstrated microreactor technology to create a portable hydrogen source for fuel cells by reforming methanol (Irving et al. 2000).

- Researchers at Mitsubishi Electric Corporation are developing a compact, plate-type steam methanol reformer (Okada et al. 2000).

- Researchers at the Royal Military College, Ontario, Canada, are studying the effects of catalyst properties on methanol reforming (Amphlett et al. 2000).

- Researchers at Honeywell are developing a compact plate-type steam methanol reformer for automotive applications (Tourbier et al. 2000).

- Researchers at NTT Telecommunications Laboratory, and Tokyo University are developing a compact plate-type steam methanol reformer for automotive applications (Take et al. 2000).

- Researchers at Gerhard-Mercator-Universitat are developing compact membrane reactors for methanol steam reforming (Ledjeff-Hey et al. 1998).

E. Ammonia Cracking

Ammonia is widely distributed to consumers today, is low cost and is relatively easy to transport and store, compared to hydrogen. This makes it a potential candidate for use as a hydrogen carrier for fuel cell applications (Kordesch et al. 1998).
Ammonia, NH_3, can be dissociated (or cracked) into nitrogen and hydrogen via the reaction:

$$2 NH_3 \rightarrow N_2 + 3 H_2$$

The reaction is endothermic, and ammonia cracking takes place in indirectly heated catalyst-filled tubes. The dissociation rate depends on the temperature, pressure and catalyst type. The reaction rate is much increased by operation at temperatures of $700^{o}C$ or above (Faleschini et al. 2000), although dissociation can occur at temperatures as low as $350^{o}C$ (Kordesch et al. 1998). The main impurities are traces of unreacted ammonia and nitrogen oxides. The concentration of unreacted ammonia must be reduced to the ppm level for use in PEM fuel cells, although alkaline fuel cells not as sensitive to this. For PEMFC applications where low levels of ammonia impurity are required, a recent study recommends reaction temperatures of $900^{o}C$ (Faleschini et al. 2000).

The overall efficiency of fuel processor systems based on ammonia cracking has been reported to be up to 85% (Krodesch et al. 1998). Maximum values of about 60% were reported by another recent study, by Analytic Power, of small ammonia crackers for PEM fuel cell applications (Yang and Bloomfield 1998), where up to 40% of the product hydrogen was combusted to supply heat to drive the dissociation reaction and to compensate for heat losses.

A potential advantage of ammonia cracking for hydrogen generation in a fuel cell system is simplicity. Unlike a steam reformer system, water is not required as a co-feed with the fuel, and no water gas shift reactors are needed. When an ammonia cracker is closely coupled to a fuel cell no final hydrogen purification stage is needed (Yang and Bloomfield 1998, Kordesch, Gsellmann and Cifrain 1998). Because nitrogen is inert in the fuel cell, it is simply passed through as a diluent.

For pure hydrogen production based on ammonia cracking, however, a costly separation of H_2 and N_2 would be required, for example by using a PSA unit or a hydrogen selective membrane. The cost of pure hydrogen production from ammonia cracking has not been estimated.

F. Thermocatalytic Cracking of Methane

In this approach, methane is broken down into carbon and hydrogen in the presence of a catalyst at high temperature ($850\text{-}1200^{o}C$), according to the reaction

$$CH_4 \rightarrow C + 2 H_2 \qquad \Delta h^{\circ} = 17.8 \text{ kcal/mole } CH_4$$
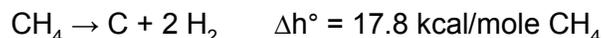
This reaction is endothermic, requiring energy input of about 10% of the natural gas feedstock. Researchers at the Florida Solar Energy Center have studied thermocatalytic methane cracking (Muradov 2000). This technology is still far from commercial application for hydrogen production. The primary issues are low efficiency of conversion and coking (carbon fouling of the catalyst).

Catalytic cracking of other hydrocarbons has been investigated by researchers at Gerhard-Mercator-Universitat at Duisburg, Germany (Ledjeff-Hey et al. 1998, Kalk et al. 2000). Frequent regeneration of the catalyst is required to remove accumulated carbon, but relatively low capital costs are projected because of the system's simplicity.

G. Novel Reformer Technologies

1. Sorbent Enhanced Reforming

Recently several authors have investigated the possibility of sorbent enhanced steam methane reforming (Lyon 1996, Sircar 1996, Han and Harrison 1994, Hufton et al. 2000). Here, an absorbent (such as calcium oxide) is mixed with the steam reforming catalyst, removing the CO and CO_2 as the steam reforming reaction progresses. The resulting syngas has a substantially higher fraction of hydrogen than that produced in a catalytic steam-reforming reactor. A syngas composition was recently reported of 90% H_2, 10% CH_4, 0.5% CO_2 and <50 ppm CO. This reduces the need for downstream processing and purification, which can be expensive in a small-scale steam reformer. Moreover, when CO_2 is removed by the sorbent, the reaction can take place at lower temperature (400-500°C vs. 800-1000°C) and pressure, reducing heat losses and material costs. Sorbent-enhanced systems are still at the demonstration stage, and show promise for low cost. Issues include catalyst and sorbent lifetime and system design.

2. Ion Transport Membrane (ITM) Reforming

Air Products, in collaboration with the USDOE and other members of the ITM syngas team (Cerametec, Chevron, Eltron Research, McDermott Technology, Norsk Hydro, Pacific Northwest Laboratory, Pennsylvania State University, University of Alaska, University of Pennsylvania), is developing ceramic membrane technology for generation of H_2 and syngas. This eight-year $86 million program began in 1997. The membranes are non-porous, multi-component metallic oxides that operate at high temperature (>700°C) and have high oxygen flux and selectivity. These are known as ion transport membranes (ITM). Conceptual designs were carried out for a hydrogen-refueling station dispensing 0.5 million scf/day of 5000 psi hydrogen, following work by Directed Technologies, Inc. Initial estimates show the potential for a significant reduction in the cost of high pressure H_2 produced via this route at the 0.1 to 1.0 million scf/day size. For example, compared to trucked-in liquid hydrogen, the ITM route offers a 27% cost savings.

Oxygen can be separated from air fed to one side of the membrane at ambient pressure or moderate pressure (1-5 psig) and reacted on the other surface with methane and steam at higher pressure (100-500 psig) to form a mixture of H_2 and CO. This can then be processed to make hydrogen or liquid fuels.

Various configurations for the ITM reactor were examined, and a flat-plate system was chosen because it reduced the number of ceramic-metal seals needed.

An independent effort to develop oxygen transport membranes is ongoing at Praxair in conjunction with the Oxygen Transport Membrane Syngas Alliance (BP Amoco, Statoil, Sasol) (see membrane reactor steam reforming section above).

3. Plasma Reformers

Thermal plasma technology can be used in the production of hydrogen and hydrogen-rich gases from methane and a variety of liquid fuels. Thermal plasma is characterized by temperatures of 3000-10,000°C, and can be used to accelerate the kinetics reforming reactions even without a catalyst. The plasma is created by an electric arc. Reactant mixtures (for example, methane plus steam or diesel fuel plus air and water) are introduced into the reactor and H_2 plus other hydrocarbon products are formed (Lynum et al. 1998, Czernichowski et al. 1996, Bromberg et al. 1999).

Researchers at MIT (Bromberg et al. 1999) have developed plasma-reforming systems. The plasma is created by an electric arc in a plasmatron. One set of experiments involved partial oxidation of diesel fuel. Steam reforming of methane was also investigated. The best steam reforming results to date showed 95% conversion of methane and specific energy use (for electricity for the plasmatron) of 14 MJ/kg H_2 (an amount equal to about 10% of the higher heating value of hydrogen). It is projected that the power required for the plasmatron can be reduced by about half. With the National Renewable Energy Laboratory (NREL) and BOC Gases, MIT researchers are evaluating the potential of this technology for small-scale hydrogen production.

Researchers at Idaho National Energy and Environment Laboratory (INEEL) and DCH are also working on plasma reforming (DOE Hydrogen R&D Program Annual Operating Plan, March 2000).

4. Microchannel Reformer

Researchers at Pacific Northwest National Laboratory have developed a novel gasoline steam reformer with micro-channels. The aim of this work is to reduce the size of automotive reformers (Wegeng 1999.)

IV. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE COOPERATIVE PROJECTS

A. Summary of Recent Trends In The Design Of Small-Scale Reformers for Fuel Cells Applications, Syngas and Hydrogen Production

Over the past ten years, a rapidly growing interest in fuel cell and hydrogen technologies has led to a variety of efforts to develop low cost small-scale fuel processors and hydrogen production systems. The trend has been to develop more compact, simpler and, therefore, lower cost reformers. From the conventional "long tube" refinery-type steam methane reformer, fuel cell developers moved toward more compact "heat exchange"-type steam reformers (which are now commercial as fuel cell components and for stand-alone hydrogen production). Plate-type reformers are now undergoing development and testing for fuel cell applications and may be the next step in compactness and simpler design. In plate reformers, each plate has a double function (on one side, the reforming reaction take place, on the other, catalytic heating drives the reaction.) Partial oxidation systems and autothermal reformers offer simpler first stages than steam reformers, but involve more complex purification systems. Advanced purification systems are being devised for these reformers. Sorbent enhanced reforming is another approach that combines several steps in one reactor, with the potential capital cost reductions. An area of intense interest in the fuel cell and hydrogen R&D communities is development of membrane reactors for reforming. Membrane reactors offer further

simplification, because the reforming, water gas shift and purification step take place in a single reactor. Very pure hydrogen is removed via hydrogen-selective permeable membranes. Membrane reactor systems are being tested at small scale.

In parallel with fuel cell developments, there has been a growing interest in innovative technologies for syngas production among large chemical and energy producing companies. For example, ion transport and oxygen transport membranes are under development for syngas applications. These are now being applied to hydrogen production as well. Application of membrane technology to syngas and hydrogen systems is an active area of research in both the fuel cell R&D community and among large-scale producers of syngas such as oil companies. In addition, oil companies such as BP Amoco, Shell, and Exxon/Mobil are involved in joint ventures to develop fuel processors and hydrogen infrastructure demonstrations, such as hydrogen refueling stations based on methane reformers. The oil companies are positioning themselves to become suppliers of hydrogen transportation fuel in the future.

B. Suggestions for Future Collaborative Projects

There are already extensive industry and government programs addressing particular technical issues for small-scale reformers, and for syngas production. We have not attempted to list research priorities for each type of reformer, or select a particular technical area for basic research. Instead, we suggest that the IEA develop collaborative projects aimed at enhancing interactions between researchers engaged in small-scale hydrogen production (fuel cell and hydrogen researchers) and those engaged in large energy production (oil and chemical companies). The purpose of the proposed projects would be to examine the potential impact of recent technical progress for small- and large-scale hydrogen energy production.

- One project could be to identify areas where ongoing research on large-scale syngas technologies could improve small-scale hydrogen production systems for vehicles, and vice versa. To identify such areas, the IEA could convene a group of industry, government and academic researchers from fuel cell, hydrogen and energy producing communities to discuss issues for small-scale reformers for hydrogen production. This group might have particular interest in technologies that could have applications in small- and large-scale hydrogen production and could ultimately facilitate capture of CO_2 during hydrogen fuel production. Membrane technology would appear to be a good candidate for such an information exchange meeting, but other areas might be identified. If gaps in technical knowledge were identified, this could help focus future reformer development efforts.

- Examine the systems implications of new reformer technologies for distributed and centralized hydrogen production. System studies of small-scale hydrogen production at refueling stations, which include recent technology developments such as plate-type reformers and membrane reactor reformers, could be carried out. The reformer could be modeled using ASPEN or a similar process modeling software, and refueling station designs could be evaluated on a consistent basis. This would help identify reformer technologies that are particularly attractive from the system point of view. This study would update and extend earlier studies such as those carried out by DTI or Princeton.

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TABLE 1. SMALL-SCALE REFORMERS FOR HYDROGEN PRODUCTION			
Reformer Type	Companies, Organizations	Development Status	Issues For Use In Hydrogen Refueling Station Applications
Steam Methane Reforming			
Long-tube (12 m), high pressure, high temperature "refinery type" steam methane reformer, high purity H_2 produced via PSA purification (Figure 7a)	Haldor-Topsoe Howe-Baker KTI Foster Wheeler	Commercial	High cost, large physical size, for refueling station applications, long start-up time. Requires continuous operation.
"Heat Transfer Reformer," originally developed for reforming natural gas for fuel cell power systems, concentric annular catalyst beds, lower temperature and pressure, enhanced heat transfer between beds. (Figure 7b)	Haldor-Topsoe (w/ PAFC) IFC (w/ PAFC) Ballard Power Systems (w/PEMFC) Sanyo Electric (w/ PAFC, PEMFC) Osaka Gas Co,(w/ PAFC) Fraunhofer Institute for Solar Energy Studies/Energy Partners (w/ PEMFC) Praxair/IFC for H_2 production	Near commercial as part of FC systems, Praxair/IFC system commercial for stand-alone industrial H_2 production	Much more compact and lower capital cost than refinery type SMRs. Promising as hydrogen supply for vehicles. Better load-following capabilities and turn down.
Plate-type steam methane reformer	GASTEC Osaka Gas Company Air Products IFC Ishikawajima-Harima Heavy Industries Ztek	**R&D** 20 kW prototype built 1 kW system tested Patents in this area " " "	Potentially more compact and lower cost than shell and tube type heat exchangers. Also, start-up time should be much faster, which would be desirable for refueling station applications. Issues are catalyst lifetime and seals.

Reformer Type	Companies, Organizations	Development Status	Issues For Use In Hydrogen Refueling Station Applications
Steam Methane Reforming (continued)			
Membrane reactor steam methane reformer for high purity hydrogen production (Fig. 7d)	Tokyo Gas Company	Built and tested membrane reactor steam reformer producing 15 Nm^3 pure H$_2$/h from natural gas	When steam reforming is done in membrane reactors, the functions of the reformer, shift reactor, and purification stages could be accomplished in one reactor. This should lead to cost savings, and to lower temperature operation. Issues are membrane cost and lifetime. This is an area of intense R&D.
	Johnson Matthey	R&D on H$_2$ separation membranes for membrane reactors	
	Aspen Systems	R&D on membrane reactor for steam reforming of methane, ethanol, and gasoline to produce H$_2$	
	European Commission COCLUP/HYSEP project	Develop membranes for H$_2$ separation	
	McDermott Technology Inc.	Patent on membrane reactor for steam reforming or partial oxidation with high purity hydrogen production	
	Northwest Power Systems (now IDATech)	Patent on membrane steam reformer	
	Natural Resources Canada	"	
	Institute of Gas Technology	"	
	Dais-Analytic	"	

Reformer Type	Companies, Organizations	Development Status	Issues For Use In Hydrogen Refueling Station Applications
Partial Oxidation	Arthur D. Little/Epyx/Nuvera	Development of partial oxidation reformer for fuel cell applications. R&D on multi-fuel and gasoline fuel processors for FCVs.	Partial oxidation systems offer lower cost for reformer stage, and faster start-up. Issue is cost of purification stage.
	Hydrogen Burner Technology, Inc.	Commercially available POX reformer for fuel cells and stand-alone H2 production. Installing NG->H_2 refueling station at Thousand Palms	Hydrogen Burner Technology is demonstrating a refueling station for hydrogen vehicles based on its POX system.
	Argonne National Laboratory	R&D on POX reformer for FCVs	
	USDOE Office of Transportation Technologies is supporting development of 50 kW fuel processor/FCV systems by: Hydrogen Burner Technology Epyx/Nuvera McDermott Technology, Inc. and Catalytica	RD&D of fuel processors for 50 kW vehicle fuel cell power plant	

Partial Oxidation (continued)			

	Other partnerships developing Gasoline Fuel Processors for FCVs
	   GM with Exxon/Mobil
	   IFC with Delphi
	   IFC with Shell Hydrogen
	   DaimlerChrysler
		RD&D	

	Tokyo Gas (POX for FC stationary power)	1 kW demonstration	
	UOP LLC	Patent on POX system for FC	

Reformer Type	Companies, Organizations	Development Status	Issues For Use In Hydrogen Refueling Station Applications
Authothermal Reforming			
	Argonne National Laboratory	R&D on ATR systems and catalysts	Combines desirable features of steam reforming and partial oxidation.
	International Fuel Cells	Designed ATR run on logistics fuels	
	Fraunhofer Solar Energy Institute	Designing ATR for LPG and diesel fuel	
	Degussa Metals Catalyst Cerdec	R&D on ATR catalysts	
	Johnson-Matthey	Demonstrated "hot spot" ATR on methanol and methane	
	Hydrogen Burner Technologies, Inc.	Testing ATR for methane and liquid fuel reforming	
	Honeywell and Energy Partners are developing ATR for FC cogeneration Systems	R&D	
	McDermott Technology, Inc. (MTI) and Catalytica	R&D on ATR Fuel processor for shipboard fuel cells	
	INEEL, MTI, PG&E	R&D on ATR for H_2 refueling station	

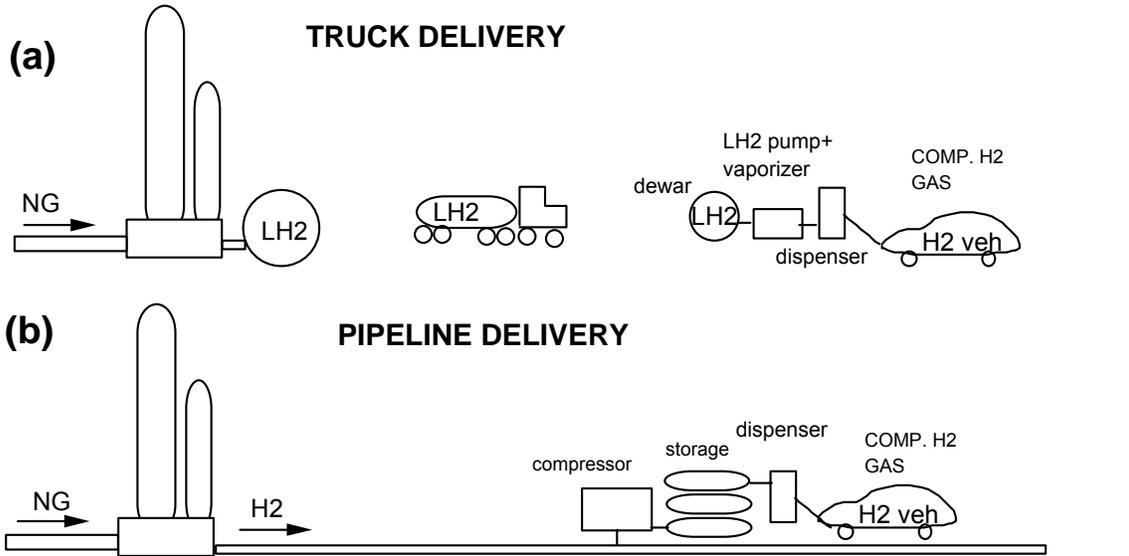| Reformer Type	Companies, Organizations	Development Status	Issues For Use In Hydrogen Refueling Station Applications
Methanol Steam Reforming			
	Haldor Topsoe	Commercial small H_2 production system	
	Xcellsis Fuel Cell Engines	Demonstrated methanol reformer FCV	Fuel processor is still in R&D stage. Methanol is easier to reform than methane or gasoline. For hydrogen refueling station applications, the high cost of methanol vs. methane feedstock is an issue.
	Toyota	"	
	Nissan	"	
	MERCATOX project (part of EC's Joule II project) Wellmann CJB Ltd. Loughborough University Rover Cars Insitituto Superior Technico	R&D to develop compact, plate type methanol steam reformer	
	Northwest Power systems	Demonstrated pure H_2 production from methanol	
	Mitsubishi Electric	R&D on compact plate type methanol reformer for FCVs	
	Honeywell	"	
	NTT Telecommunications/Tokyo University	"	
	Gerhard-Mercator-Universitat	"	

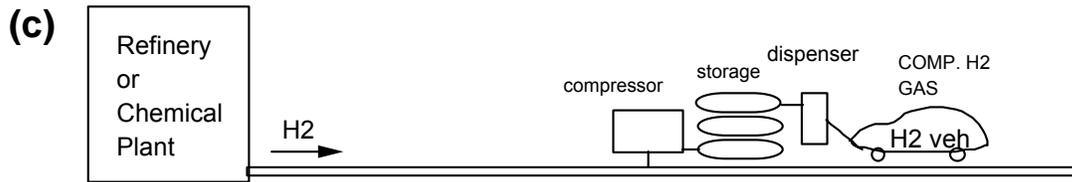| Reformer Type	Companies, Organizations	Development Status	Issues For Use In Hydrogen Refueling Station Applications
Ammonia Cracking			
	Analytic Power	Built small ammonia cracker to produce pure H_2	
	Kordesch, et al., ZEVCO	R&D on ammonia cracker for FCVs	
Sorbent Enhanced Reforming			
	Air Products and Chemical, Inc.	Demonstration of pilot plant	Promises lower capital costs than conventional steam methane reformer.
Ion Transport Membranes			
	Air Products, with the USDOE and Cerametec, Chevron, Eltron Research, McDermott Technology, Norsk Hydro, Pacific Northwest Laboratory, Pennsylvania State University, University of Alaska, and University of Pennsylvania, is developing ceramic membrane technology for generation of H_2 and syngas. This eight year, $86 million program began in 1997	R&D	Promises improved methods for hydrogen production from syngas by providing low-cost oxygen from air at small scale.
	Praxair with Argonne National Lab	R&D to develop H_2 generator based on Oxygen and Hydrogen Transport Membranes	

Reformer Type	Companies, Organizations	Development Status	Issues For Use In Hydrogen Refueling Station Applications
Catalytic Cracking of Methane			
	Florida Solar Energy Center	Basic science	Catalyst must be regenerated frequently to remove carbon
	Gerhard-Mercator-Universitat	"	
Plasma Reformer			
	MIT	R&D	
	INEEL	"	

NEAR TERM GASEOUS H2 SUPPLY OPTIONS
CENTRALIZED REFORMING

(a)   **TRUCK DELIVERY**

NG

LH2

LH2

dewar

LH2 pump+ vaporizer

LH2

dispenser

COMP. H2 GAS

H2 veh

(b)   **PIPELINE DELIVERY**

NG

H2

compressor

storage

dispenser

COMP. H2 GAS

H2 veh

CHEMICAL BY-PRODUCT HYDROGEN

(c)

Refinery or Chemical Plant

H2

compressor

storage

dispenser

COMP. H2 GAS

H2 veh

ONSITE REFORMING

(d)

reformer

compressor

storage

dispenser

COMP. H2 GAS

H2 veh

NG

ONSITE ELECTROLYSIS

(e)

ELECTRICITY

electrolyzer

compressor

storage

dispenser

COMP. H2 GAS

H2 veh
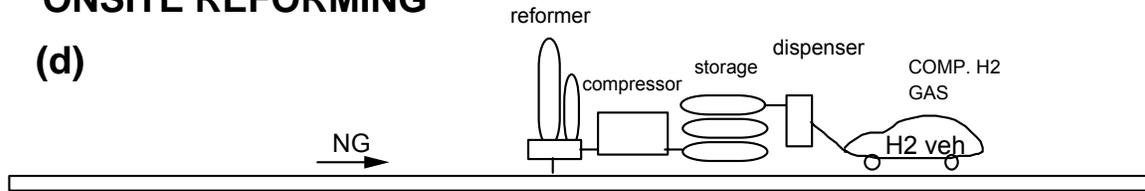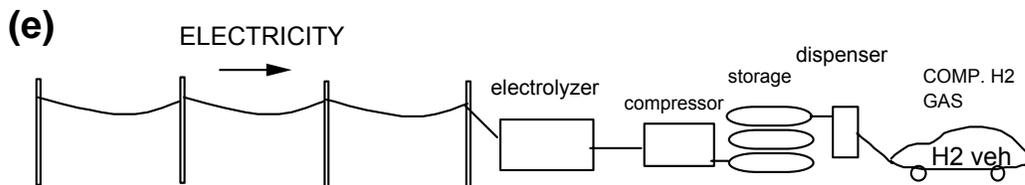
Figure 1.

LONG TERM HYDROGEN SUPPLY OPTIONS

H2 via BIOMASS, COAL or MSW GASIFICATION

BIOMASS,
COAL or
MSW

compressor

storage

H2

H2 veh
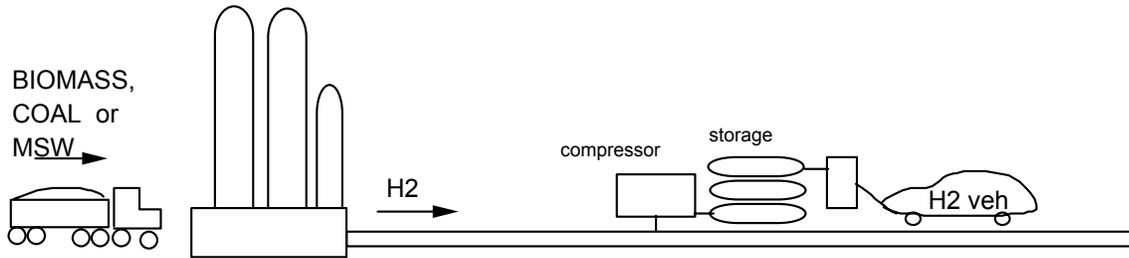
SOLAR or WIND ELECTROLYTIC HYDROGEN

PV
Array

electrolyzer

compressor

storage

COMP. H2
GAS

H2 veh

Wind
Turbine

electrolyzer

storage

H2

compressor

storage

H2 veh
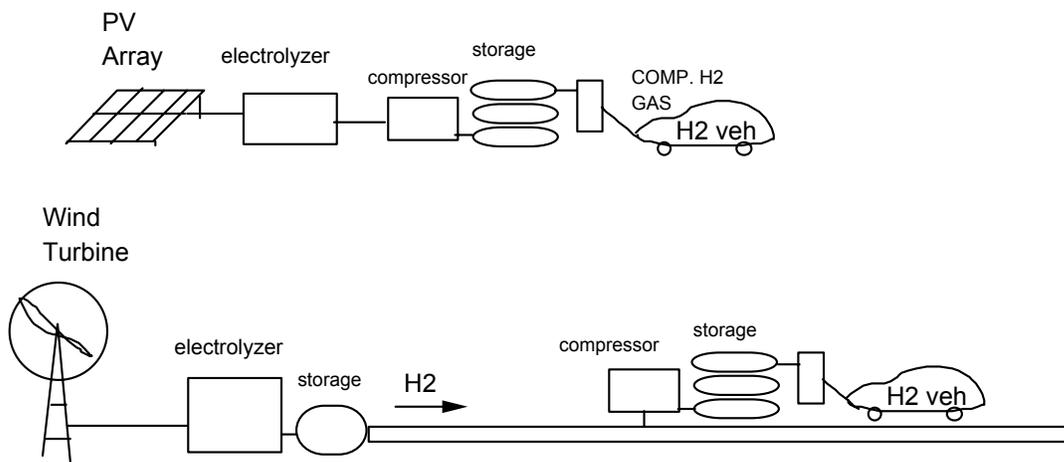
H2 FROM HYDROCARBONS w/CO2 SEQUESTRATION

NG,
BIOMASS
or COAL

H2

compressor

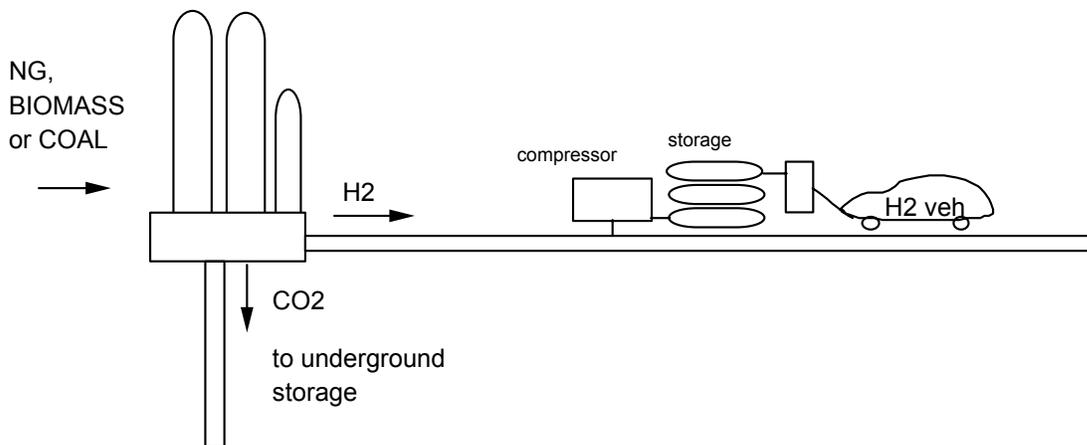storage

H2 veh

CO2

to underground
storage

Figure 2.

Delivered Cost of Hydrogen Transportation Fuel ($/GJ)
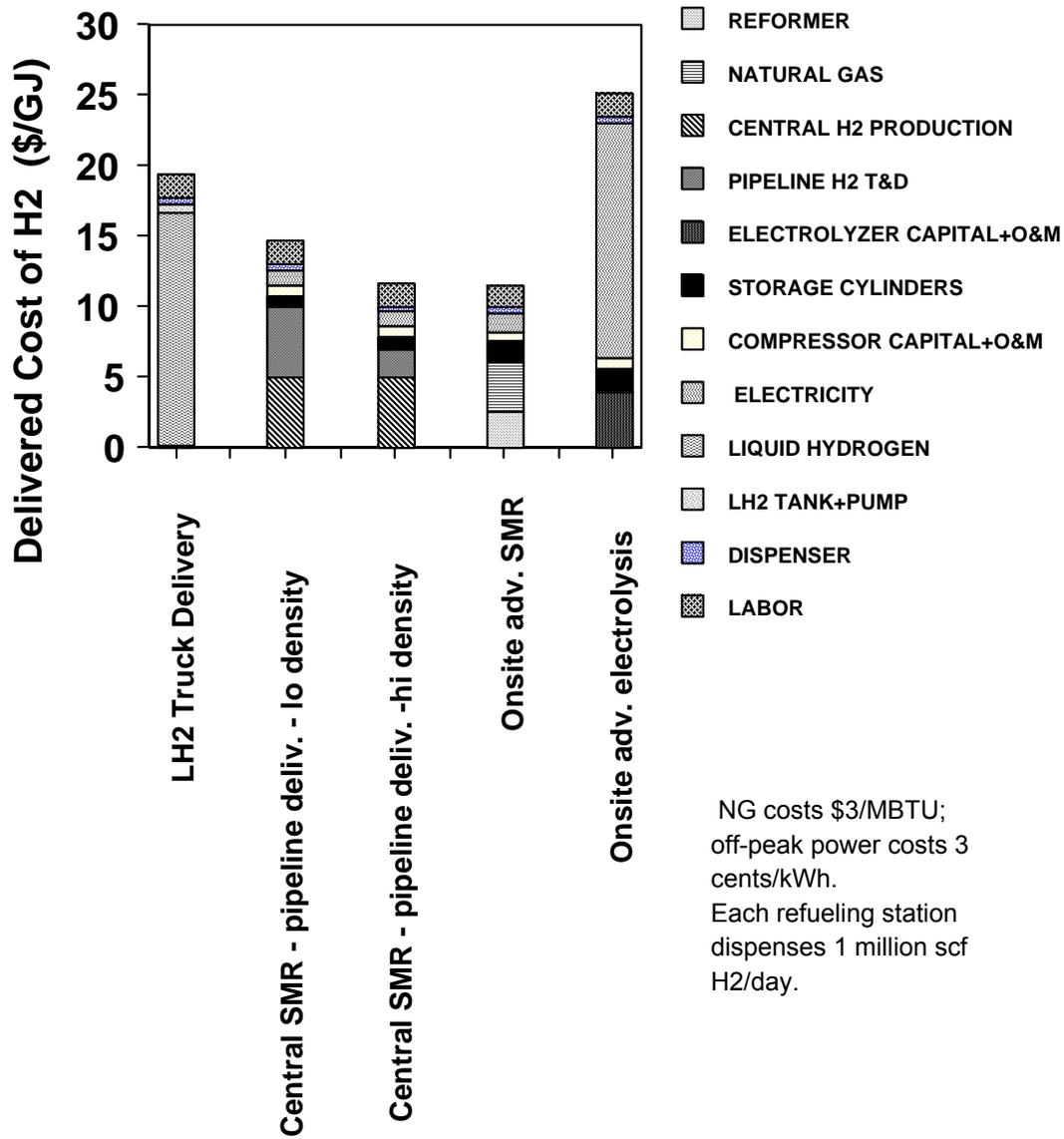
Figure 3.

Capital Cost of H2 Infrastructure ($/car)

Figure 4.

EARLY INFRASTRUCTURE

Central H2
Production Plant

Decentralized
Production
from NG

and/or

NG,
Wastes
or Coal

H2 to other
users

Bus or Car
Fleets

NG

CITY SCALE INFRASTRUCTURE

Central H2
Production from
NG, Coal, Biomass
or Wastes, w/ H2
Distrib to Many
Refuel Stations

If NG
available
Decentralized
Production of
H2 from NG at
Refueling
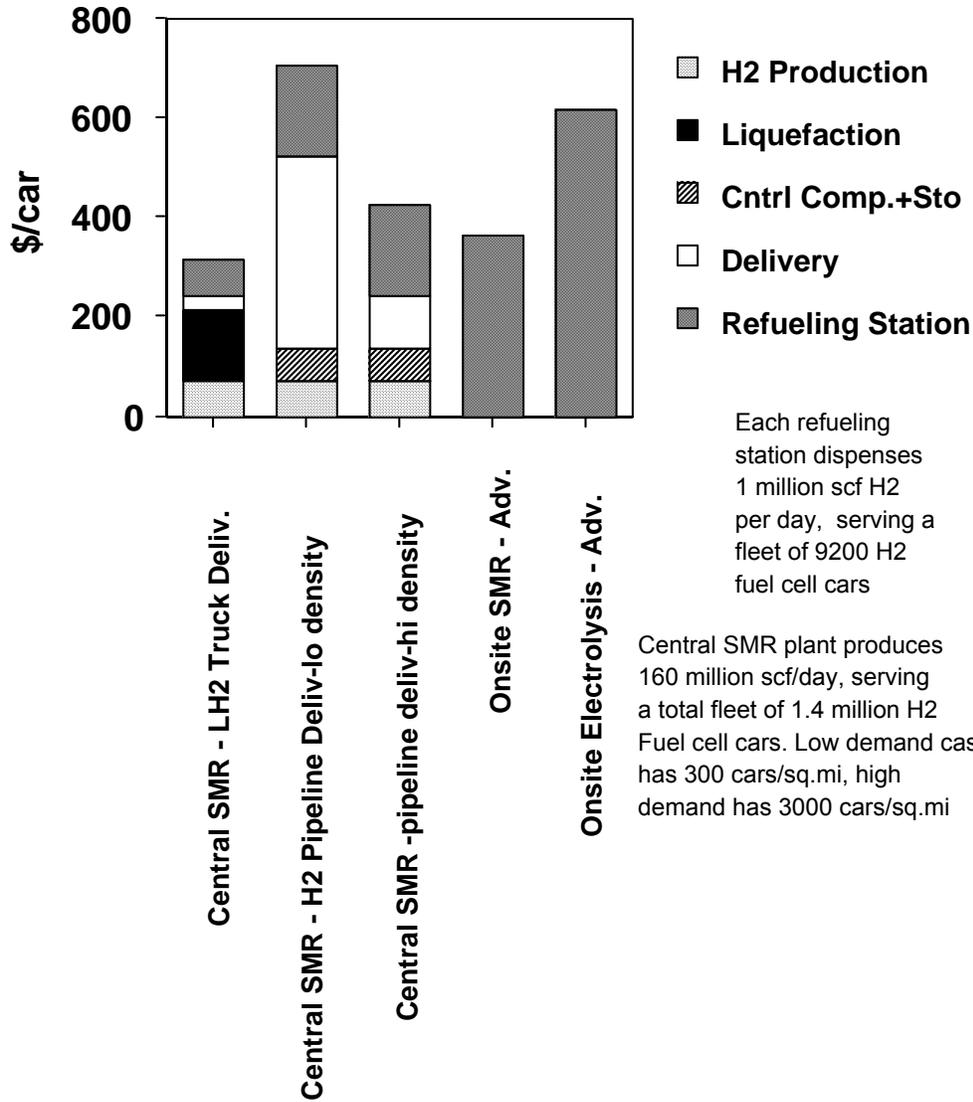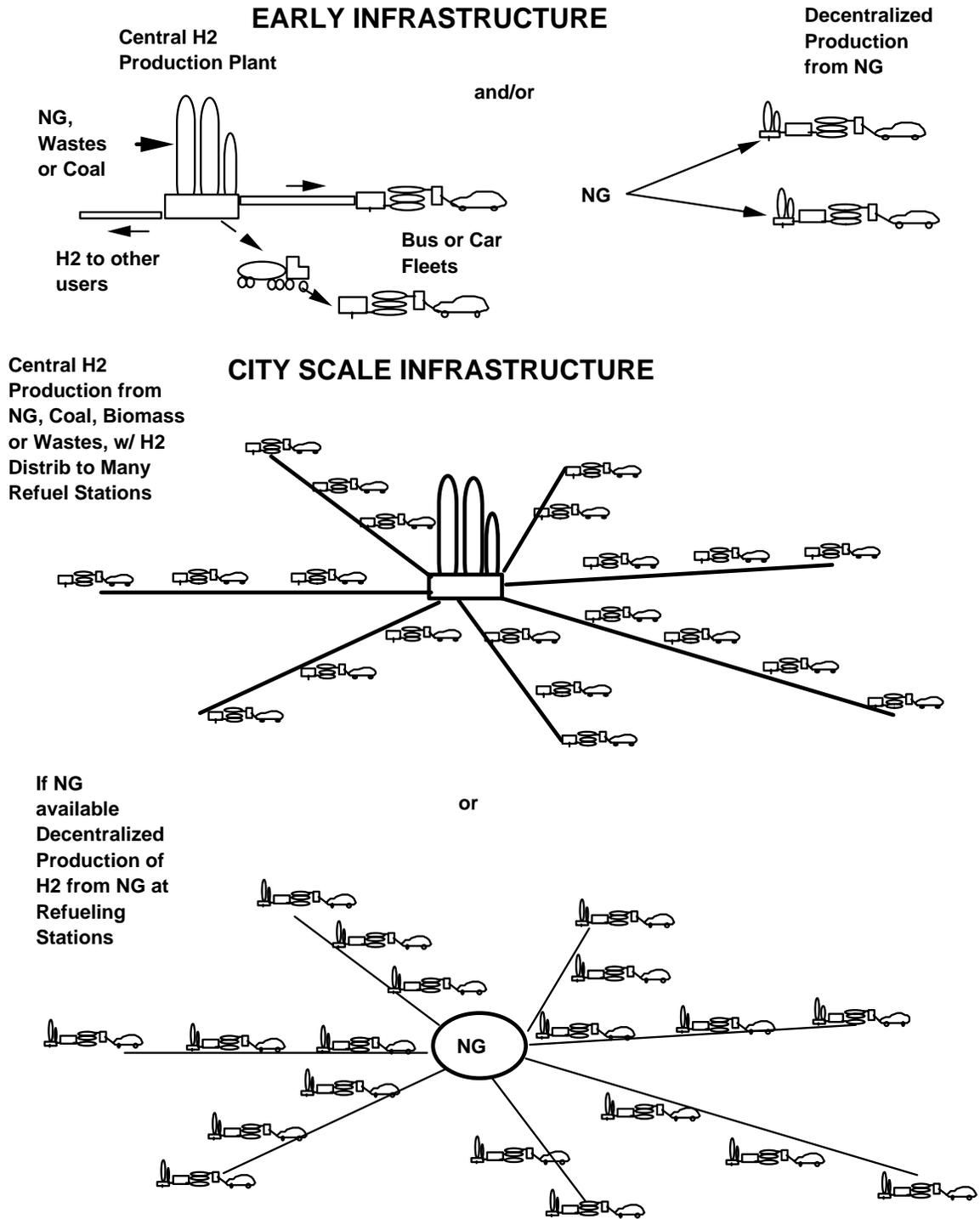Stations

or

NG

Figure 5a.

HYDROGEN ENERGY ECONOMY W/CO2 SEQUESTRATION

**Central H2
Production from
NG, Coal, Biomass
or Wastes, w/ H2
Distrib to Many
Refuel Stations**

CITY 1

**CO2 to
Sequestration
Site**

CITY 2

CITY 3

**CO2
Sequestration
Site**

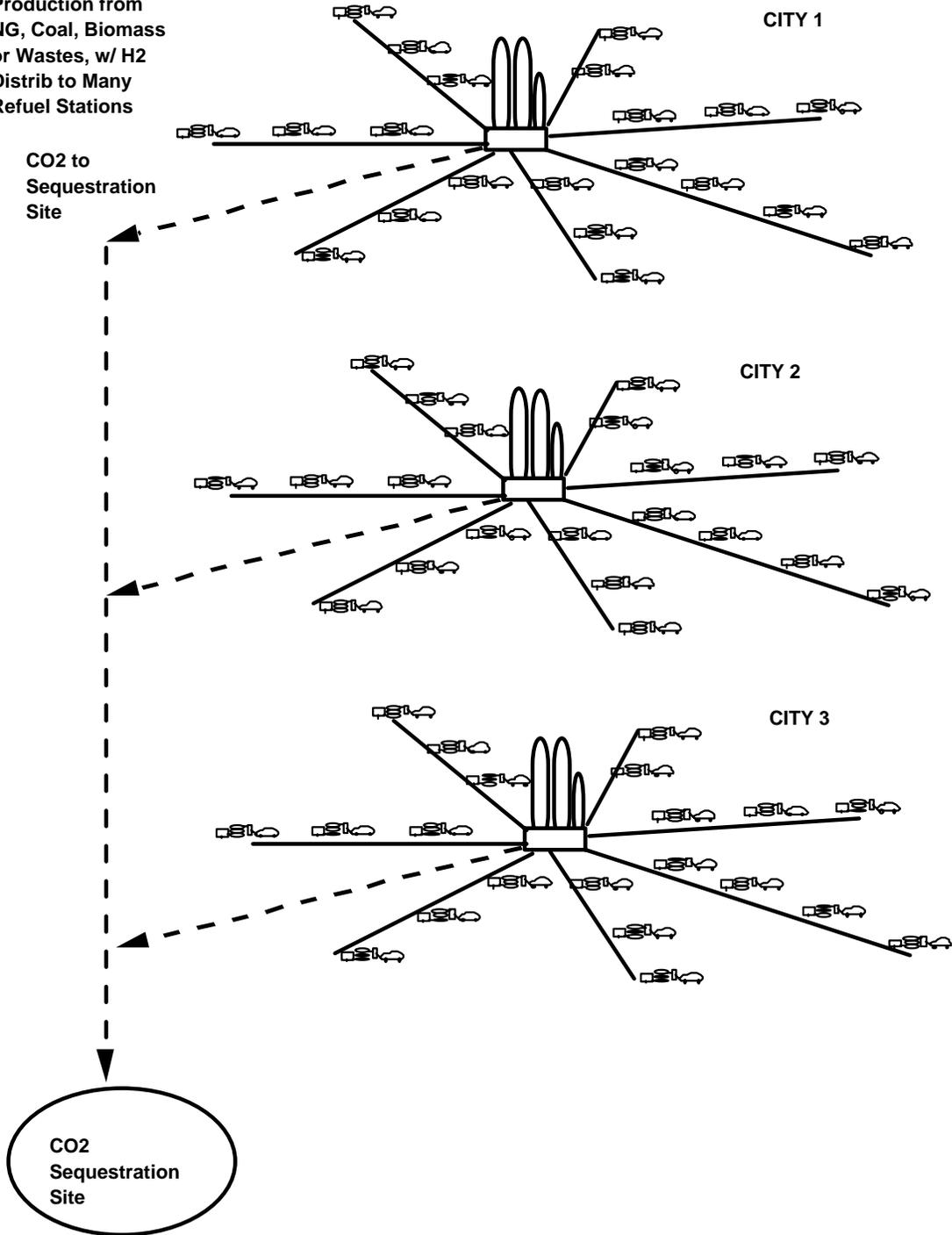**Figure 5b.**

THERMOCHEMICAL HYDROGEN PRODUCTION METHODS

STEAM REFORMING

Natural Gas or
Light Hydrocarbon

Steam →

Heat → **Steam Reformer**

Syngas
H2, CO, CO2,
CH4. H20

Steam → **Shift Reactor
CO+H20->CO2+H2**

Waste
gases ← **Hydrogen Purification**

Pure H2

H2 Storage ← **Compressor**

to H2 Users

PARTIAL OXIDATION

Natural Gas or
Liquid Fuel

Oxygen
or air →

Partial Oxidation

Syngas
H2, CO, CO2,
CH4. H20

Steam → **Shift Reactor
CO+H20->CO2+H2**

Waste
gases ← **Hydrogen Purification**

Pure H2

H2 Storage ← **Compressor**

to H2 Users

Figure 6.

CONVENTIONAL SMALL SCALE STEAM
METHANE REFORMER DESIGN

AIR

REFORMER
BURNER
FUEL GAS

FEED
CH4, STEAM

FLAME

TOP VIEW

CATALYST-
FILLED
TUBES

12 m

REFORMER BURNER FLUE GASES
(TO HEAT RECOVERY BOILER)

SYNGAS
H2, CO, CO2, CH4, H20
TO SHIFT REACTOR
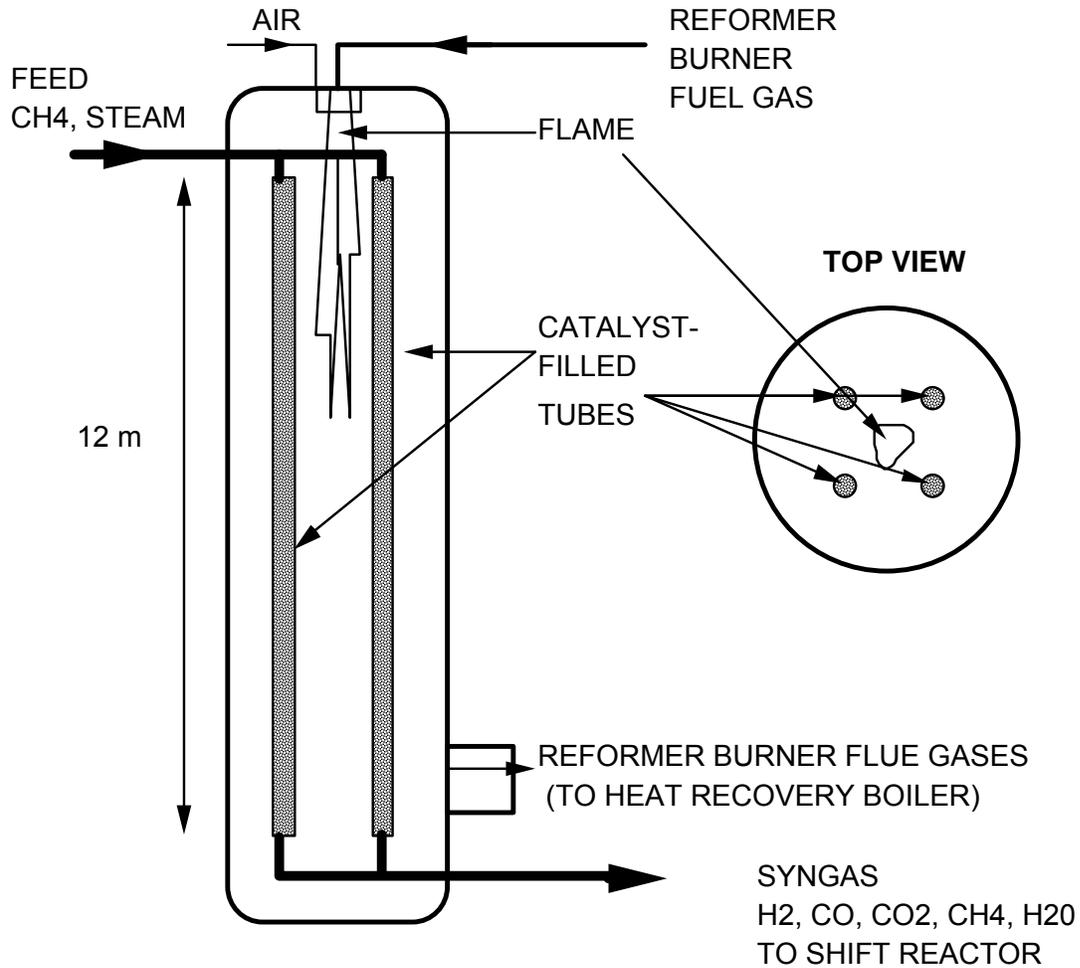
SINGLE REFORMER TUBE

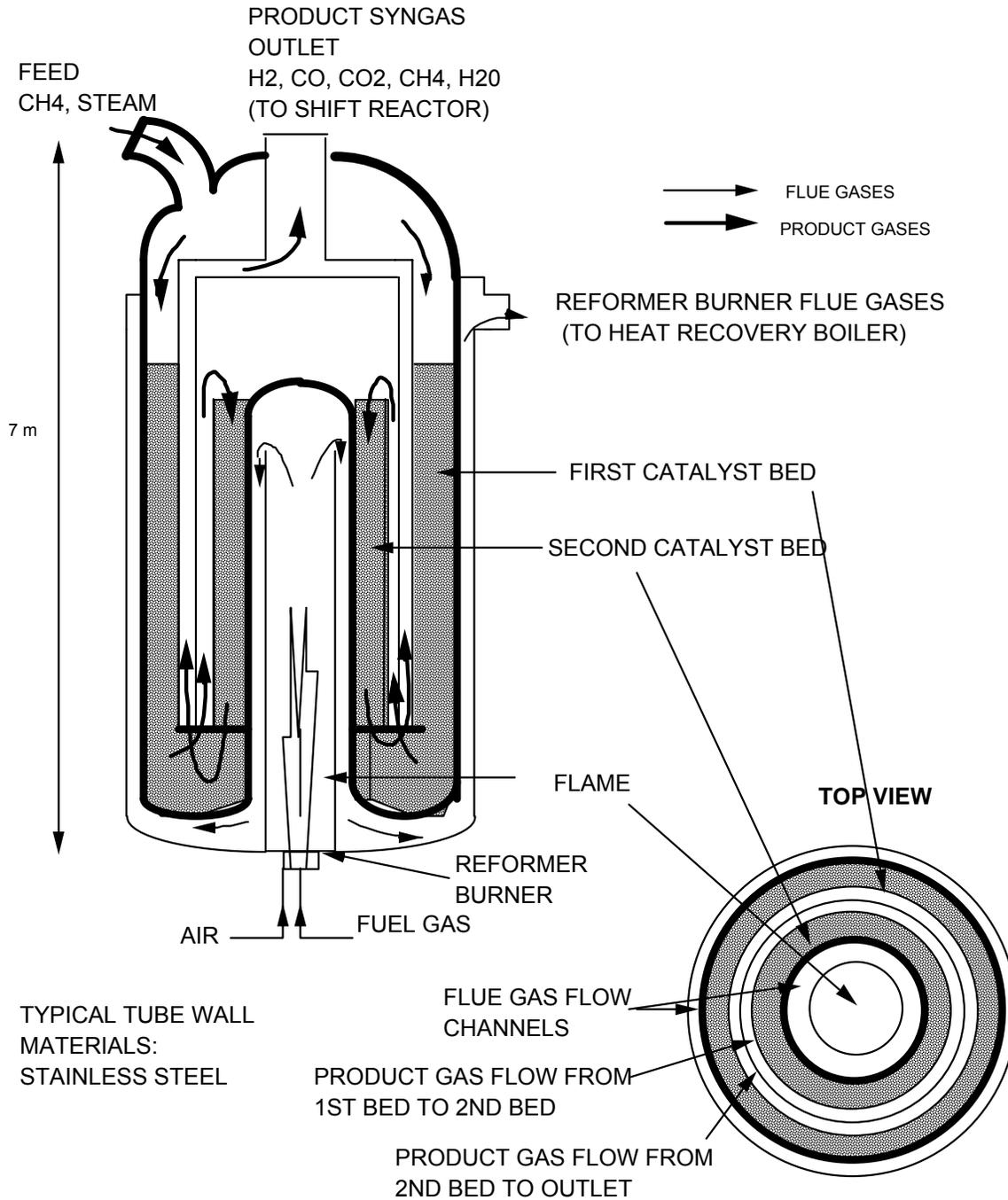TYPICAL
CATALYST
MATERIALS:
NICKEL ON
ALUMINA
SUPPORT
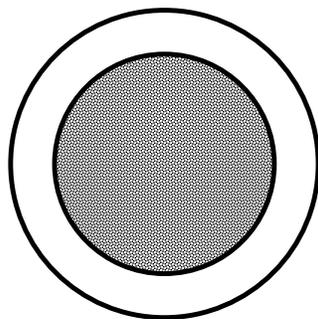
TYPICAL TUBE WALL
MATERIALS:
HIGH ALLOY STEELS:
HK-40, IN 519

TYPICAL DIMENSIONS:
WALL THICKNESS: 10-20 mm
TUBE DIAMETER: 70-160 mm
TUBE LENGTH: 12 m

Figure 7a

COMPACT, TUBULAR, SMALL SCALE STEAM METHANE REFORMER DESIGNED FOR FUEL CELL APPLICATIONS, WITH CONVECTIVE HEAT TRANSFER
(Based on Haldor-Topsoe "Heat Exchange Reformer")

PRODUCT SYNGAS
OUTLET
H2, CO, CO2, CH4, H20
(TO SHIFT REACTOR)

FEED
CH4, STEAM

FLUE GASES

PRODUCT GASES

REFORMER BURNER FLUE GASES
(TO HEAT RECOVERY BOILER)

7 m

FIRST CATALYST BED

SECOND CATALYST BED

FLAME

TOP VIEW

REFORMER
BURNER

AIR

FUEL GAS

FLUE GAS FLOW
CHANNELS

TYPICAL TUBE WALL
MATERIALS:
STAINLESS STEEL

PRODUCT GAS FLOW FROM
1ST BED TO 2ND BED

PRODUCT GAS FLOW FROM
2ND BED TO OUTLET

Figure 7b

APPENDIX A. Hydrogen Refueling Station Projects

Increasingly, hydrogen refueling infrastructure demonstrations are conducted as part of hydrogen vehicle demonstrations. A list of ongoing hydrogen refueling station projects is given in Table A.1. Over the next several years, small-scale reformers of various types will be tried.

Table A.1: Hydrogen Vehicle Refueling Station Demonstrations Worldwide

Site/participants	Year	Type of Refueling System
Univ. of California Riverside, CA	1995	PV Electrolysis supplying hydrogen for IC engine pick-up truck
Xerox Park, Canoga, CA Clean Air Now, Xerox	1995	PV Electrolysis supplying hydrogen for IC engine cars
Humboldt State University, Schatz Energy Center Palm Desert, CA	1997-	PV Electrolysis supplying hydrogen for IC engine cars
Ford Motor Company, Dearborn, Michigan	1998-	Trucked in liquid H_2, vaporized to provide high pressure gas
Chicago Transit Authority, Chicago, IL Ballard Power Systems, Air Products	1998-2000	Trucked in liquid H_2 vaporized to provide high pressure gas to three fuel cell buses
City of Las Vegas, NV Air Products, Plug Power	2000-2004	Plans include: Truck delivered H_2 and small-scale reforming of natural gas producing H_2 and CNG/H_2 blends for ICE vehicles
BC Transit Vancouver, British Columbia Ballard Power Systems, Stuart Energy	1998-2000	H_2 is produced via electrolysis using off-peak power for three fuel cell buses
BC Hydro	2001	H_2 refueling station based on electrolysis under construction
Sunline Transit, Thousand Palms, CA Hydrogen Burner Technology, California Air Resources Board	1999-	Production of H_2 via small scale partial oxidation of natural gas for H_2 buses
California Fuel Cell Partnership	2001-	Planned demonstration of refueling systems for up to 20 H_2 fuel cell vehicles; Sacramento H_2 station has trucked in LH_2 to supply high pressure H_2 gas to vehicles
AC Transit, California	Late 2001	H_2 refueling station planned for fuel cell buses

Table A.1: Hydrogen Vehicle Refueling Station Demonstrations Worldwide
(continued)

Clean Urban Transport for Europe (CUTE) Project 10 cities in Europe plus Perth, Western Australia	Planned 2002-	Planned demonstration of 30 fuel cell buses in 10 European cities. Various types of H_2 supply will be implemented including small-scale reformers
Global Environment Facility/UNDP	2002-	Planned demonstration of 30 fuel cell buses in developing country cities
MAN/Siemens		Planned demonstration of fuel cell buses
Munich Airport	1999	Liquid hydrogen refueling station for airport buses and BMW cars
Daimler Chrysler	2001-	Planned H_2 fuel cell bus demonstrations
Reykavik, Iceland Shell Hydrogen	2001	H_2 refueling station based on electrolysis using low cost geothermal power
WE-NET Project, Japan	2001	2 H_2 refueling stations: Electrolysis (Takamata) Steam Reforming (Osaka)

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