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**REPORT TO THE INTERNATIONAL ENERGY AGENCY**

**REVIEW OF SMALL STATIONARY REFORMERS  
FOR HYDROGEN PRODUCTION**

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# **REVIEW OF SMALL STATIONARY REFORMERS FOR HYDROGEN PRODUCTION**

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# REVIEW OF SMALL STATIONARY REFORMERS FOR HYDROGEN PRODUCTION

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## I. INTRODUCTION

This report to the International Energy Agency 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 cogeneration systems, and onboard fuel processors for methanol and gasoline fuel cell vehicles). Although fuel cell reformers are typically designed to produce a “reformat” 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 are reviewed that might be used in distributed hydrogen production at refueling stations. These include steam methane reforming, partial oxidation, autothermal reforming, 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 fluid 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<sub>x</sub>, 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, that would have 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<sub>2</sub>.
- 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 reach lifecycle economic competitiveness with other advanced vehicle/fuel options at mass produced costs, if external costs are accounted for.

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 lower cost 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<sub>2</sub> 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, 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<sub>2</sub>/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 US 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 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 and was coordinated by Directed Technologies Inc. (DTI), 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 plans demonstrations of 30 hydrogen fuel cell buses in 10 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 used 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<sub>2</sub> capture and disposal are quite small. In contrast, with distributed small-scale hydrogen production from fossil fuels is capture, collection and sequestration of CO<sub>2</sub> from many dispersed small reformers is prohibitively expensive (Ogden 1997). Thus, implementing the fossil hydrogen/CO<sub>2</sub> 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 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 central hydrogen production. This would enable use of low carbon primary sources or decarbonized fossil sources with CO<sub>2</sub> 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 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<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O. 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



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:



which "converts" CO to H<sub>2</sub>. This reaction is favored at temperatures of less than about 600°C, and can take place as low as 200°C, with sufficiently active catalysts. The gas exiting the shift reactor contains mostly H<sub>2</sub> (70-80%) plus CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O and small quantities of and 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<sub>2</sub> and CH<sub>4</sub> 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



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 (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 degrees°C and pressures of 15-25 atm, which necessitates

use of expensive alloy steels. Capital costs for a 20 million scf H<sub>2</sub>/day steam reformer plant (including the reformer, shift reactor and PSA) are about \$200/kW H<sub>2</sub> output; for a 200 million scf/day plant capital costs are estimated to be about \$80/kW H<sub>2</sub> (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<sub>2</sub> at 1 million scf/day and \$4000/kW H<sub>2</sub> at 0.1 million scf/day.

Small-scale conventional (long tube, high temperature) steam methane reformers are commercially available from a number of companies that 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, Foster Wheeler.

The disadvantages of conventional long tube steam reformers for hydrogen refueling station applications are their large size (12 meter length is commonly used for catalyst-filled tubes), 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<sub>2</sub>/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<sub>2</sub> 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<sub>2</sub>) 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). Fraunhofer Institute, (Vogel et.al 1998) built methane reformers to make H<sub>2</sub> for use with Energy Partners vehicle.
- Dais-Analytic Corporation is building residential PEMFC power system with its own reformer (Dais-Analytic Corporation website).
- Sanyo Electric Co. is building residential PEMFC power system with multi-tube steam reformer.
- IdaTech is building 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 (Figure 7c). 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 (Figure 7d). Methane and steam are fed into a catalyst filled reactor under pressure. On one side of the reactor is a palladium membrane that is selectively permeable to hydrogen, with high selectivity. 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.

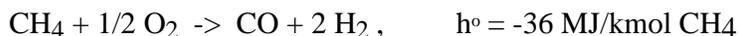
There is a large amount of industrial R&D activity on membrane technologies for syngas and hydrogen production. Interest by major energy companies in applying membrane technology to large scale syngas and hydrogen production may have significant "spin-offs" for small scale hydrogen production as well. 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<sup>3</sup>/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



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, since 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, where 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 where 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 be lower cost 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 by Arthur D. Little and its spin-off companies Epyx and Nuvera for use with fuel cell systems (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 for cogeneration in buildings, that produces very pure H<sub>2</sub>. HBT is installing a natural gas reformer filling station for Sunline Transit at Thousand Palms, CA, with funding from the California Air Resources Board to supply H<sub>2</sub> 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 US Department of Energy 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:

- Arthur D. Little/Epyx/Nuvera. 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 with Exxon Mobil to develop an onboard gasoline fuel processor.
- International Fuel Cells with Shell Hydrogen to develop and market a variety of fuel processors

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

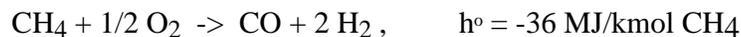
- Tokyo Gas Company has demonstrated a partial oxidation system for 1 kW fuel cell cogeneration system (Seki et.al 2000).
- McDermott technology, Inc. (MTI) and Catalytica are working together to develop compact fuel processors for use with PEMFCs and SOFCs. This system is designed to reform gasoline and Naval Distillate for PEMFCs.

### **C. Auto-thermal reforming**

#### **1. Process Description**

Autothermal reformers 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



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 (ATR) 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 cogen. 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. 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 producing 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 on an autothermal reforming system for use with fuel cells and for hydrogen production.

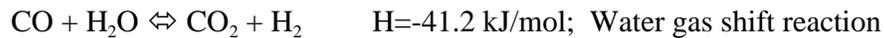
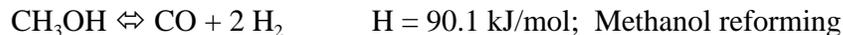
## D. Methanol steam reforming

### 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 application of methanol steam reformer technologies to hydrogen production.

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



Or combining these:



The reaction takes place in the presence of copper/zinc catalysts in the temper 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 US, 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  $(\$11/\text{GJ}-\$5/\text{GJ})/0.75 = \$8/\text{GJ}$  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. 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 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 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<sub>3</sub> can be dissociated (or cracked) into nitrogen and hydrogen via the reaction:



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°C or above (Faleschini et.al 2000) although dissociation can occur at temperatures as low as 350°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°C (Faleschini et. al 2000).

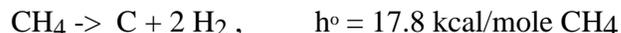
The overall efficiency of fuel processor systems based on ammonia cracking has been reported to be up to 85% (Kordesch et.al 1998). Maximum values of about 60% per reported by another recent study by Analytic Power of small ammonia crackers for PEM fuel cell applications (Yang and Bloomfield 1998), where up to 40% of the product hydrogen was combusted to supply heat to drive the dissociation reaction and 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 (Yang and Bloomfield 1998, Kordesch, Gsellmann and Cifrain 1998) no final hydrogen purification stage is needed. Since 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<sub>2</sub> and N<sub>2</sub> would be required, for example 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 (850-1200°C), according to the reaction.



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-Universität 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**

### **▪ 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<sub>2</sub> 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<sub>2</sub>, 10%CH<sub>4</sub>, 0.5% CO<sub>2</sub> 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<sub>2</sub> is removed by the sorbent, the reaction can take place at lower temperature and pressure (400-500°C vs. 800-1000°C), 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.

### **▪ 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<sub>2</sub> 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 potential for significant reduction in the cost of high pressure H<sub>2</sub> 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<sub>2</sub> 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 with the Oxygen Transport Membrane Syngas Alliance (BP Amoco, Statoil, Sasol) (see membrane reactor steam reforming section above).

#### ▪ **Plasma reformers**

Thermal plasma technology can be used to in the production of hydrogen and hydrogen-rich gases from methane and a variety of liquid fuels. A thermal plasma is characterized by temperatures of 3000-10,000°C, which 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<sub>2</sub> 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<sub>2</sub> (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 NREL and BOC, 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).

- **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 to drive 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 is both 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, and 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<sub>2</sub> 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 central hydrogen production. System studies of small-scale hydrogen production at refueling stations could be carried out including recent technology developments such as plate-type reformers and membrane reactor reformers. The reformer could be modeled using ASPEN or a similar process modeling software, and refueling station designs could be carried out 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.

## REFERENCES

Aasbeeg-Petersen, C.S. Nielsen, and S. Laegsgaard Jorgensen, "Membrane Reforming for Hydrogen," *Catalysis Today*, 46, pp. 193-201, 1998.

Ahmed, S., M. Krumpelt, R. Kumar, S. Lee, J. Carter, R. Wilkenhoener, and C. Marshall, "Catalytic Partial Oxidation Reforming of Hydrocarbon Fuels," 1998 Fuel Cell Seminar Abstracts, November 16-19, 1998, Palm Springs, CA, p. 242-245.

Alibrando, M., H.S. Hahm and E.E. Wolf, "Partial oxidation of methane to synthesis gas on a Rh/TiO<sub>2</sub> Catalyst in a Fast Flow Porous Membrane Reactor," J.C. Baltzer A.G., Science Publishers, 1997.

Amphlett, J., R. Mann, B. Peppley, and C. Thurgood, "PEM Fuel Cell Hydrogen Production by Methanol-Steam reforming: the Effect of Catalyst Activation," 2000 Fuel Cell Seminar Abstracts, October 30-November 2, 2000, Portland, OR, p. 276-279.

Anderson, R.P., "Hydrogen Research, Development and Demonstration Activities at the Idaho National Engineering and Environment Laboratory (INEEL)," presented at the 12<sup>th</sup> National Hydrogen Association Meeting, March 6-8, 2001.

Appleby, A.J. August 1996. "Fuel Cell Technology: Status and Future Prospects," *Energy: The International Journal*, v. 21, No. 78, pp.521-653.

Arthur D. Little. May 1994. "Multi-Fuel Reformers for Fuel Cells Used in Transportation, Assessment of Hydrogen Storage Technologies, Phase I Final Report," USDOE Office of Transportation Technologies, Contract No. DE-AC02-92-CE50343.

Aspen Systems, "Compact Single Stage Fuel Reformer for PEM Fuel Cells," Proceedings of the USDOE CARAT Program Review, Troy, Michigan, September 23, 1999.

Booth, J., M. Doyle, S. Gee, J. Miller, L-A Scholtz, P. Walker, "Advanced Separation via Thin Supported Pd Membranes," Proceedings of the 11<sup>th</sup> World Hydrogen Energy Conference, Stuttgart, Germany, June 23-28, 1996.

Bromberg, L., A. Rabinovitch, N. Alexeev and D,R, Cohn, "Plasma Catalytic Reforming of Natural Gas," Proceedings of the 1999 Hydrogen Program Review, NREL/CP-570-26938, 1999.

Bromberg, L., A. Rabinovitch, N. Alexeev and D,R, Cohn, "Plasma Reforming of Diesel Fuel," Proceedings of the 1999 Hydrogen Program Review, NREL/CP-570-26938, 1999.

Buswell, R. July 4, 1978. "Multi-tube Catalytic Reaction Apparatus," US Patent No. 4,098,588.

Buswell, R. et.al. November 1, 1994. "Hydrocarbon Fueled Solid Polymer Fuel Cell Electric Power Generation System," US Patent No. 5,360,679.

Buswell, R. et.al. January 16, 1996. "Catalytic Hydrocarbon Reformer with Enhanced Heat Transfer Mechanism," US Patent No. 5,484,577.

Chalk, S., "FY2000 Progress Report for Fuel Cell Power Systems," US DOE, Energy Efficiency and Renewable Energy, Office of Advanced Automotive Technologies, October 2000.

Cross, J., W.L. Mitchell, P. Chintawar, M. Hagan, C. Thompson, D. Swavely, "PEM Fuel Cell Power Technology", 2000 Fuel Cell Seminar Abstracts, October 30-November 2, 2000, Portland, OR, p. 260-263.

Cross, J., "Gasoline Fuel Processing: A System Perspective," presented at the IQPC Fuel Cells Infrastructure Conference, Chicago, IL, December 6, 1999.

Czernichowski, A., P. Czernichowski, and A. Ranaivosoloarimanana, "Plasma Pyrolysis of Natural Gas in a Gliding Arc Reactor," Proceedings of the 11<sup>th</sup> World Hydrogen Energy Conference, Stuttgart, Germany, June 23-28, 1996, p. 637-645, 1996.

J. Cuzens, J. Mauzey, and R. Woods, "Fuel-Flexible Fuel Processor," 1998 Fuel Cell Seminar Abstracts, November 16-19, 1998, Palm Springs, CA, p. 234-237.

Dams, R.A.J., S.C. Moore, and P.R. Hayter, "Compact, Fast-Response Methanol Fuel Processing Systems for PEMFC Electric Vehicles," 2000 Fuel Cell Seminar Abstracts, October 30-November 2, 2000, Portland, OR, p. 526-529.

Dennis, E.B. May 1994. "Design and Feasibility of a Gaseous Hydrogen Refueling Station Based on Small Scale Steam Reforming of Natural Gas," Princeton University senior thesis, Department of Chemical Engineering.

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

Docter, A., G. Konrad, and A. Lamm, "Reformer for Gasoline and Gasoline-Like Fuels," 2000 Fuel Cell Seminar Abstracts, October 30-November 2, 2000, Portland, OR, p. 538-541.

G.J. Doell, D.P. Bloomfield, and T.N. Tangredi, "Status of residential Power Generator program at Dais-Analytic Power Corporation," 2000 Fuel Cell Seminar Abstracts, October 30-November 2, 2000, Portland, OR, p. 487-490.

P. Dyer, Air Products and Chemicals, Inc., Ion Transport Membranes, presentation at the United States Department of Energy Hydrogen Program 1999 Annual Peer Review Meeting, Lakewood, CO, May 4-6, 1999.

P.N. Dyer and C. M. Chen, "ITM Syngas and ITM H<sub>2</sub>," Proceedings of the 2000 Hydrogen Program Review, NREL/CP-570-28890, 2000.

Ecker, Ernst, UOP Division of Praxair, private communications 1996.

Edlund, D., W.A. Pledger, and A. Dickman, "Field Testing Residential Fuel Cell Systems," 2000 Fuel Cell Seminar Abstracts, October 30-November 2, 2000, Portland, OR, p. 496-499.

Fairlie, M., FCV Fuel Supply Infrastructure: The Electrolysis Option, Electrolyzer, Ltd., Toronto, Canada, December 1996.

Faleschini, G., V. Hacker, M. Muhr, K. Kordesch, R. Aronsson, "Ammonia for High Density Hydrogen Storage," 2000 Fuel Cell Seminar Abstracts, October 30-November 2, 2000, Portland, OR, p. 336-339.

Farris, P. International Fuel Cells, private communications 1996.

Ferrall, J., T. Rehg, S. Simpson, O. Savin and P. Sokolov, "System Design of a Combined Heat and Power PEM plant for Buildings Applications," 2000 Fuel Cell Seminar Abstracts, October 30-November 2, 2000, Portland, OR, p. 401-404.

Ferrell, J., A Kotar and S. Stern, Direct hydrogen fueled proton exchange membrane fuel cell system for transportation applications, Final Report, BOC Gases, Murray Hill, NJ, September 1996.

George, Ranji, South Coast Air Quality Management District, private communications, 1995, 1996.

Haldor-Topsoe. 1988. "Endurance Testing of a High-Efficiency Steam Reformer for Fuel Cell Power Plants", EPRI Report No. AP-6071.

Haldor-Topsoe. 1993. "Heat Exchange Reformer", company brochure.

Halvorson, T.G., C.E. Terbot and M.W. Wisz, Hydrogen production and fueling system infrastructure for PEM fuel cell powered vehicles: Final Report, Praxair, Inc., Tonawanda, New York, April 1996.

Halvorson, T. and P. Farris, Onsite hydrogen generator for vehicle refueling application, *Proceedings of the '97 World Car Conference*, 19-22 January, 1997, Riverside, CA, pp. 331-338.

- Hamada, K., M. Mizusawa, and M. Koga, "Plate Reformer," US Patent No. 5,609,834, March 11, 1997.
- Han C. and D. Harrison. 1994. "Simultaneous Shift Reaction and Carbon Dioxide Separation for the Direct Production of Hydrogen," *Chemical Engineering Science*, v. 49, No. 24B, pp. 5875-5883.
- Henizel, A., B. Vogel, T. Rampe, A. Haist, and P. Hubner, "Reforming of Fossil Fuels: R&D at the Fraunhofer Institute for Solar Energy Systems," 2000 Fuel Cell Seminar Abstracts, October 30- November 2, 2000, Portland, OR, p. 256-259.
- Heydorn, B. "By Product Hydrogen Sources and Markets," Proceedings of the 5th National Hydrogen Association Meeting, March 23-25, 1994, Washington, DC, pp. 6-59 to 6-80.
- Hsu, M. and E.D. Hoag, "Thermally enhanced compact reformer," US Patent No. 6,183,703, Feb.6, 2001.
- J. Hufton, S. Mayorga, T. Gaffney, S. Naturaj, M. Roa, S. Sircar, "Sorption Enhanced Reaction Process for Production of Hydrogen," Proceedings of 1998 USDOE Hydrogen Program Review Meeting, April 28-30, 1998, Arlington, VA, NREL/CP-570-25315, pp. 693-706.
- J. Hufton, W. Waldron, S. Weigel, M. Rao, S. Nataraj, S. Sircar, "Sorbent Enhanced Reaction Process for the Production of Hydrogen," Proceedings of the 2000 Hydrogen Program Review, NREL/CP-570-28890, 2000.
- Irving, P., W. Allen, T. Healey, W. Thomson, "Novel Catalytic Reforming Using Microtechnology with Advanced Separations Technology," Proceedings of the 2000 Hydrogen Program Review, NREL/CP-570-28890, 2000.
- Kalk, T., F. Mahlendorf, and J. Roes, "Cracking of Hydrocarbons to Produce Hydrogen for PEM Fuel Cells," 2000 Fuel Cell Seminar Abstracts, October 30- November 2, 2000, Portland, OR, p. 317-320.
- Kikuchi, E., "Membrane Reactor Application to Hydrogen Production," *Catalysis Today*, 56, pp. 97-101, 2000.
- King, D., Howe-Baker Engineering, private communications, 1993.
- Kordesch, K., J. Gsellmann, and M. Cifrain, "Revival of Alkaline Fuel Cell Hybrid Systems for Electric Vehicles," 1998 Fuel Cell Seminar Abstracts, November 16-19, 1998, Palm Springs, CA, p. 387-390.

Krumpelt, M., J.D. Carter, R. Wilkenhoener, H.D. Lee, and J-M Bae, and S. Ahmed, "Catalytic Autothermal Reforming for Fuel Cell Systems," 2000 Fuel Cell Seminar Abstracts, October 30-November 2, 2000, Portland, OR, p. 542-545.

Larson, E.D., R.H. Williams, R.E. Katofsky and J. Chen. July 1995. "Methanol and Hydrogen from Biomass for Transportation with Comparisons to Methanol and Hydrogen from Natural Gas and Coal," Princeton University Center for Energy and Environmental Studies Report No. 292.

Larson, E.D., E. Worrell and J. Chen. January 1996. Princeton University Center for Energy and Environmental Studies Report No. 293.

Ledjeff-Hey, K., V. Formanski and J. Roes, "Compact Hydrogen Production for PEM Fuel Cells in a Membrane Reactor, 1998 Fuel Cell Seminar Abstracts, November 16-19, 1998, Palm Springs, CA, p. 345-348.

Ledjeff-Hey, K., T. Kalk and J. Roes, "Catalytic Cracking of Propane for Hydrogen Production for PEM Fuel Cells," 1998 Fuel Cell Seminar Abstracts, November 16-19, 1998, Palm Springs, CA, p. 349-352.

Lin, Y. and Rei, M., "Process Development for Generating High Purity Hydrogen by Using Supported Palladium Membrane Reactor as Steam Reformer," International Journal of Hydrogen Energy," 25, pp. 211-219, 2000.

Lynum, S., R. Hildrum, K. Hox and J. Hugdahl, "Kvaerner based Technologies for Environmentally Friendly Energy and Hydrogen Production," Proceedings of the 12<sup>th</sup> World Hydrogen Energy Conference, Buenos Aires, Argentina, June 21-26, 1998, p. 637-645.

Lyon, R., Energy and Environmental Research Corp., private communications 1996.

Mark, J., Fuel Choices for fuel cell vehicles, *Proceedings of the '97 World Car Conference*, 19-22 January, 1997, Riverside, CA, pp. 393-406.

Mauzey, J., R. Woods, and S. Barge, "Automotive Fuel Processor," 2000 Fuel Cell Seminar Abstracts, October 30-November 2, 2000, Portland, OR, p. 534-537.

McDermott, S., D. Edlund, W.A. Pledger, K. Pearson, and D. Kelly, "Results of Fuel Processor Lifetime Testing," 2000 Fuel Cell Seminar Abstracts, October 30-November 2, 2000, Portland, OR, p. 296-299.

Mitchell, W., J. Thijssen, J.M. Bentley 1995. "Development of a Catalytic Partial Oxidation Ethanol Reformer for Fuel Cell Applications," Society of Automotive Engineers, Paper No. 9527611.

Mitchell, W. April 2, 1996. "Development of a Partial Oxidation Reformer for Liquid Fuels," Society of Automotive Engineers, Proceedings, Fuel Cells for Transportation TOPTEC, Arlington, VA.

Minet, Ronald G. and T. Tsotsis, "Catalytic ceramic membrane steam/hydrocarbon reformer," US Patent No. 4,981,676, Jan. 1, 1991.

Moore, R.B. Ford Hydrogen Infrastructure Study, Summary Report Subcontract No. 47-2-R31155, Air Products and Chemicals, Inc., Allentown, PA, March 1996.

Muradov, N. " Thermocatalytic CO<sub>2</sub>-Free Production of Hydrogen from Hydrocarbon Fuels," Proceedings of the 2000 Hydrogen Program Review, NREL/CP-570-28890, 2000.

Ogden, J., T Kreutz, S. Kartha and L. Iwan, Assessment of technologies for producing hydrogen from natural gas at small scale, Princeton University Center for Energy and Environmental Studies Draft Report, November 26, 1996.

J. Ogden, "Hydrogen Systems and CO<sub>2</sub> Sequestration, " Proceedings of the 9th National Hydrogen Association Meeting, Arlington, VA, March 3-5, 1998.

Ogden, J. and T. Kreutz, M. Steinbugler, "Fuels for fuel cell vehicles: vehicle design and infrastructure issues," Society of Automotive Engineers Technical paper No. 982500 , presented at the SAE Fall Fuels and Lubricants Meeting and Exposition, San Francisco, CA, October 19-22, 1998.

J. Ogden, "Prospects for Building a Hydrogen Energy Infrastructure," chapter in Annual Review of Energy and the Environment, vol. 24, pp. 227-79, 1999.

J. Ogden, "Developing a Refueling Infrastructure for Hydrogen Vehicles: A Southern California Case Study," International Journal of Hydrogen Energy, vol. 24, pp. 709-730, 1999.

J. Ogden, M. Steinbugler and T. Kreutz, "A Comparison of Hydrogen, Methanol and Gasoline as Fuels for Fuel Cell Vehicles," Journal of Power Sources, vol. 79, pp. 143-168, 1999.

Ohsaki, K. et.al. April 6, 1993. "Apparatus for Catalytic Reaction," US Patent No. 5,199,961.

Okada, T., Y. Gonyo, M. Matsumura, and K. Mitsuda, "Development of Methanol Reformer for PEFC at Mitsubishi Electric," 2000 Fuel Cell Seminar Abstracts, October 30-November 2, 2000, Portland, OR, p. 248-251, 2000.

- Oklany, J. S., K. Hou and R. Hughes, "A Simulative Comparison of Dense and Microporous Membrane Reactors for the Steam Reforming of Methane," *Applied Catalysis A: General*, 170, p. 13-22, 1998.
- Pereira, C., R. Wilkenhoener, S. Ahmed and M. Krumpelt, "Liquid Fuel Reformer Development," *Proceedings of the 1999 Hydrogen Program Review*, NREL/CP-570-26938, 1999.
- Pereira, C., and J-M. Bae, S. Ahmed and M. Krumpelt, "Liquid Fuel Reformer Development: Autothermal reforming of Diesel Fuel," *Proceedings of the 2000 Hydrogen Program Review*, NREL/CP-570-28890, 2000.
- Raman, V., "H<sub>2</sub> Reformer, Fuel Cell Power Plant, and Vehicle Refueling System," *Proceedings of the 2000 Hydrogen Program Review*, NREL/CP-570-28890.
- Raman, V., *Commercial Pathways to Hydrogen Fuel Infrastructure, Proceedings of the '97 World Car Conference*, 19-22 January, 1997, Riverside, CA, pp. 307-314.
- Reinkingh, J. , "Hot Spot Fuel Processor," *Society of Automotive Engineers, Fuel Cells for Transportation TOPTEC*, Cambridge, Mass, March 18-19, 1998.
- Rostrup-Nielsen, J.R. 1984. *Catalytic Steam Reforming*, Springer-Verlag, New York, NY.
- Sederquist, R.A. Jan. 31, 1978. "Steam Reforming Process and Apparatus Therefor," US Patent No. 4,1071,330.
- Sederquist, Nov. 28, 1995. "Fuel Cell Power Plant Reformer Burner Gas Flow Control System," US Patent No. 5,470,360.
- Seki, T., J. Komiya, H. Fujiki, Y. Shirasaki, K. Inoue, T. Miura and I. Yasuda, "Development of Fuel Processing Systems for PEFC Residential Stationary Application," *2000 Fuel Cell Seminar Abstracts*, October 30- November 2, 2000, Portland, OR, p. 376-379.
- Scoles, S. and M.A. Perna, "Naval Distillate Reforming for Navy Ship Service Applications," *2000 Fuel Cell Seminar Abstracts*, October 30- November 2, 2000, Portland, OR, p. 252-255.
- Shah, M., R.F. Drnevich and U. Balachandran, "Integrated Ceramic Membrane System for Hydrogen Production," *Proceedings of the 2000 Hydrogen Program Review*, NREL/CP-570-28890, 2000.
- Shinke, N., S. Higashiguchi and K. Hirai, *2000 Fuel Cell Seminar Abstracts*, October 30- November 2, 2000, Portland, OR, p. 292-295.

- Sircar, S. , M. Anand, B. Carvill, J. Hufton, S. Mayorga, and B. Miller. 1996. "Sorption Enhanced Reaction Process (SERP) for Production of Hydrogen," presented at the USDOE Hydrogen R&D Program Review Meeting.
- Stahl, H. et.al. May 16, 1989. "Reactor for the Catalytic Reforming of Hydrocarbons," US Patent No. 4,830,843.
- Take, T., M. Tomura, T. Yaki, C. Kiyohara, T. Ishino, H. Kameyama, "Cu-Zn/Al<sub>2</sub>O<sub>3</sub>/Al Plate Catalyst for a Methanol Reformer," 2000 Fuel Cell Seminar Abstracts, October 30-November 2, 2000, Portland, OR, p. 413-416.
- Thomas, C.E., Overview of onboard liquid fuel storage and reforming systems, *Proceedings Fuel Cells for Transportation TOPTEC*, April 1-2, 1996, Arlington, VA, Society of Automotive Engineers.
- Thomas, C.E., I.F. Kuhn, B.D. James, F.D. Lomax, and G.N. Baum, Affordable hydrogen supply pathways for fuel cell vehicles, *International Journal of Hydrogen Energy*, v. 23, No. 6, 1998.
- Thomas, C.E., B.D. James, F.D. Lomax, and I.F. Kuhn, Societal impacts of fuel options for fuel cell vehicles, Society of Automotive Engineers paper No. 98FL-602.
- Tourbier, D. J. Ferrall, and T. Rehg, "Automotive PEM Fuel Cell System Development," 2000 Fuel Cell Seminar Abstracts, October 30-November 2, 2000, Portland, OR, p. 405-408.
- Twigg, M.V.,ed. 1989. *Catalyst Handbook*, Wolfe Publishing, Ltd., Frome, England.
- Van Driel, M. and M. Meijer, "A Novel Compact Steam Reformer with Heat Generation by Catalytic Combustion Augmented by Induction Heating," 1998 Fuel Cell Seminar Abstracts, November 16-19, 1998, Palm Springs, CA, p. 218-221.
- Vogel, B., G. Schaumberg, A. Schuler, A. Henizel, "Hydrogen Generation Technologies for PEM Fuel Cells," 1998 Fuel Cell Seminar Abstracts, November 16-19, 1998, Palm Springs, CA, p. 364-367.
- Weiland, S., F. Baumann and K-A Starz, "New Catalysts for Autothermal Reforming of Gasoline and Water Gas Shift Reactors," 2000 Fuel Cell Seminar Abstracts, October 30-November 2, 2000, Portland, OR, p. 309-312.
- Wegeng, R.S., "Reducing the Size of Automotive Fuel Reformers," presented at the IQPC Fuel Cells Infrastructure Conference, Chicago, IL, December 6, 1999.
- Williams, R.H. January 1996. "Fuel Decarbonization for Fuel Cell Applications and Srquestering of the Separated CO<sub>2</sub>," Princeton University Center for Energy and Environmental Studies Report No. 296.

Yang, L. and D.P. Bloomfield, "Ammonia Cracker for Fuel Cells," 1998 Fuel Cell Seminar Abstracts, November 16-19, 1998, Palm Springs, CA, p. 294-297.

**TABLE 1. SMALL SCALE REFORMERS FOR HYDROGEN PRODUCTION**

<b>Reformer Type</b>	<b>Companies, Organizations</b>	<b>Development Status</b>	<b>Issues For Use In Hydrogen Refueling Station Applications</b>
<b>Steam Methane Reforming</b>			
Long-tube (12 m), high pressure, high temperature “refinery type” steam methane reformer, high purity H <sub>2</sub> 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 <sub>2</sub> production	Near commercial as part of FC systems,  Praxair/IFC system commercial for stand-alone industrial H <sub>2</sub> 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 (Figure 7c)	GASTEC Osaka Gas Company Air Products IFC Ishikawajima-Harima Heavy Industries Ztek	<b>R&amp;D</b> 20 kW prototype built 1 kW system tested holds 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.
<b>Reformer Type</b>	<b>Companies, Organizations</b>	<b>Development Status</b>	<b>Issues For Use In Hydrogen Refueling Station Applications</b>
<b>Steam Methane Reforming</b>			

<b>(continued)</b>			
<p>Membrane reactor steam methane reformer for high purity hydrogen production (Fig. 7d)</p>	<p>Tokyo Gas Company</p> <p>Johnson Matthey</p> <p>Aspen Systems</p> <p>European Commission COCLUP/HYSEP project</p> <p>McDermott Technology Inc.</p> <p>Northwest Power Systems (now IDATech) Natural Resources Canada Institute of Gas Technology Dais-Analytic</p>	<p>Built and tested membrane reactor steam reformer producing 15 Nm<sup>3</sup> pure H<sub>2</sub>/h from natural Gas</p> <p>R&amp;D on H<sub>2</sub> separation membranes for membrane reactors</p> <p>R&amp;D on membrane reactor for steam reforming of methane, ethanol, gasoline to produce H<sub>2</sub></p> <p>Develop membranes for H<sub>2</sub> separation</p> <p>Patent on membrane reactor for steam reforming or partial oxidation with high purity hydrogen production</p> <p>Patent on membrane steam reformer</p> <p>“</p> <p>“</p> <p>“</p>	<p>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&amp;D.</p>



<b>(continued)</b>	<p>Gasoline Fuel Processors for FCVs</p> <p>GM with Exxon/Mobil IFC with Delphi IFC with Shell Hydrogen DaimlerChrysler</p> <p>Tokyo Gas (POX for FC stationary power)</p> <p>UOP LLC</p>	<p>RD&amp;D</p> <p>1 kW demonstration</p> <p>Patent on POX system for FC</p>	
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<b>Reformer Type</b>	<b>Companies, Organizations</b>	<b>Development Status</b>	<b>Issues For Use In Hydrogen Refueling Station Applications</b>
<b>Autothermal Reforming</b>			
	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 cogen 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 H2 refueling station	

<b>Reformer Type</b>	<b>Companies, Organizations</b>	<b>Development Status</b>	<b>Issues For Use In Hydrogen Refueling Station Applications</b>
<b>Methanol Steam Reforming</b>			
	<p>Haldor Topsoe</p> <p>Xcellsis Fuel Cell Engines</p> <p>Toyota</p> <p>Nissan</p> <p>MERCATOX project (part of EC's Joule II project) Wellmann CJB Ltd. Loughborough University Rover Cars Insitituto Superior Technico</p> <p>Northwest Power systems</p> <p>Mitsubishi Electric</p> <p>Honeywell</p> <p>NTT Telecommunications/Tokyo University Gerhard-Mercator-Universitat</p>	<p>Commercial small H<sub>2</sub> production system</p> <p>Demonstrated methanol reformer FCV</p> <p>“</p> <p>“</p> <p>R&amp;D to develop compact, plate type methanol steam reformer</p> <p>Demonstrated pure H<sub>2</sub> production from methanol</p> <p>R&amp;D on compact plate type methanol reformer for FCVs</p> <p>“</p> <p>“</p> <p>“</p>	<p>Fuel processor is still in R&amp;D stage.</p> <p>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.</p>
<b>Reformer Type</b>	<b>Companies, Organizations</b>	<b>Development Status</b>	<b>Issues For Use In Hydrogen Refueling Station Applications</b>

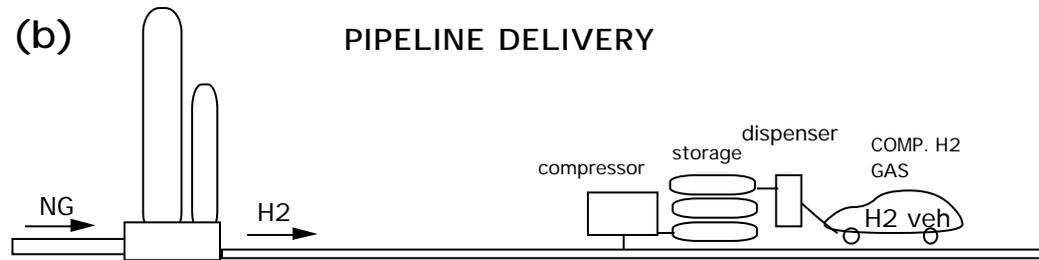
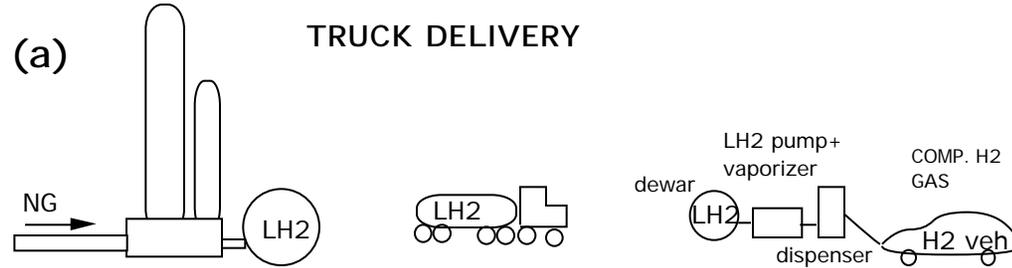
<b>Ammonia Cracking</b>			
	Analytic Power  Kordesch et.al ZEVCO	Built small ammonia cracker to produce pure H <sub>2</sub>  R&D on ammonia cracker for FCVs	
<b>Sorbent Enhanced Reforming</b>			
	Air Products and Chemical, Inc.	Demonstration of pilot plant	Promises lower capital costs than conventional steam methane reformer.
<b>Ion Transport Membranes</b>			
	Air Products with the USDOE and Ceramtec, 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 <sub>2</sub> and syngas. This eight year, \$86 million program began in 1997  Praxair with Argonne National Lab	R&D  R&D to develop H <sub>2</sub> generator based on Oxygen and Hydrogen Transport Membranes	Promises improved methods for hydrogen production from syngas by providing low cost oxygen from air at small scale.

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

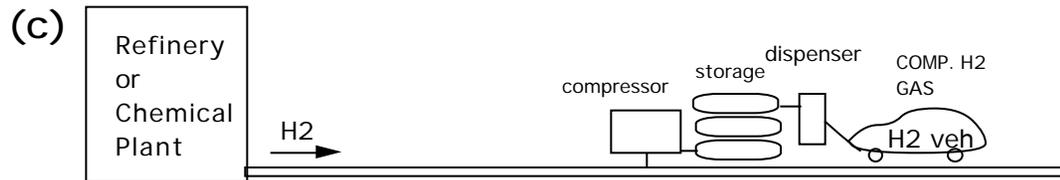


# NEAR TERM GASEOUS H2 SUPPLY OPTIONS

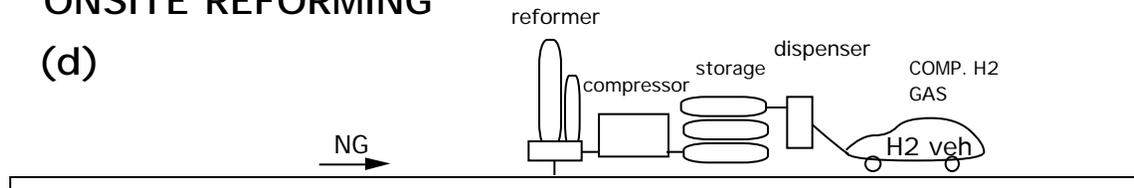
## CENTRALIZED REFORMING



## CHEMICAL BY-PRODUCT HYDROGEN



## ONSITE REFORMING



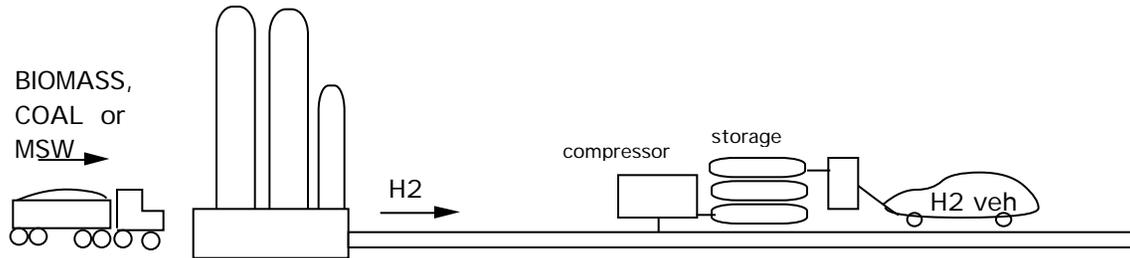
## ONSITE ELECTROLYSIS

(e) -----

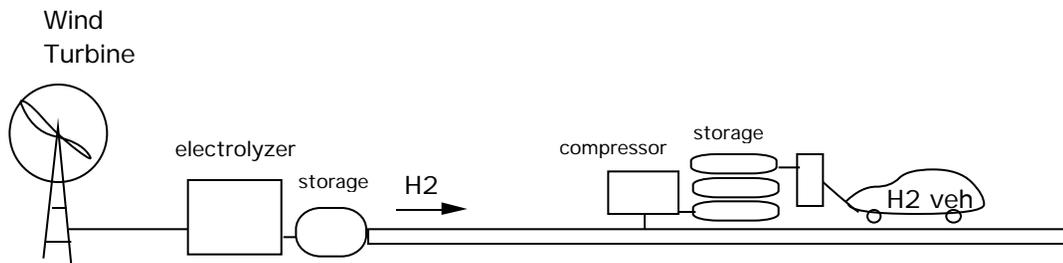
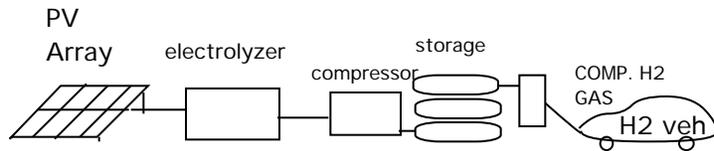
Figure 1.

# LONG TERM HYDROGEN SUPPLY OPTIONS

## H2 via BIOMASS, COAL or MSW GASIFICATION



## SOLAR or WIND ELECTROLYTIC HYDROGEN



## H2 FROM HYDROCARBONS w/CO2 SEQUESTRATION

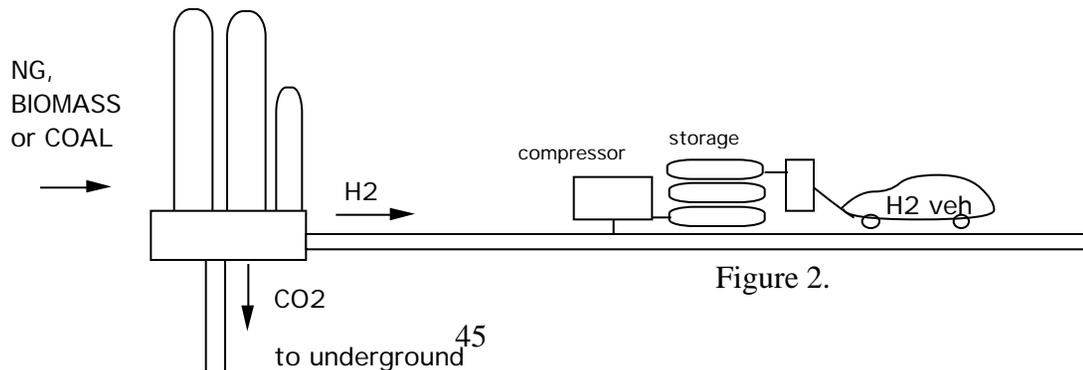


Figure 2.



# Delivered Cost of Hydrogen Transportation Fuel (\$/GJ)

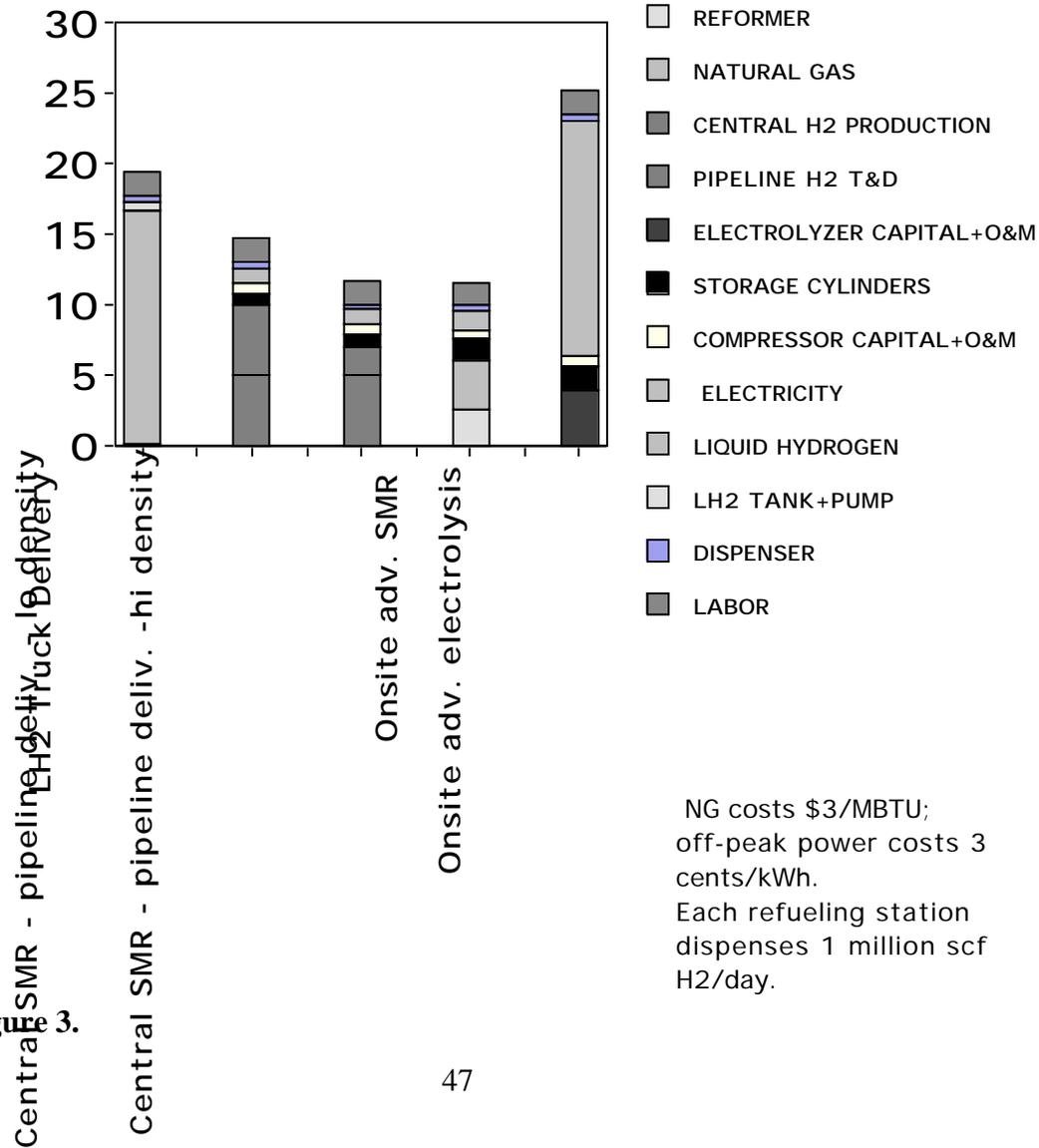


Figure 3. Delivered Cost of Hydrogen Transportation Fuel (\$/GJ)

# Capital Cost of H2 Infrastructure (\$/car)

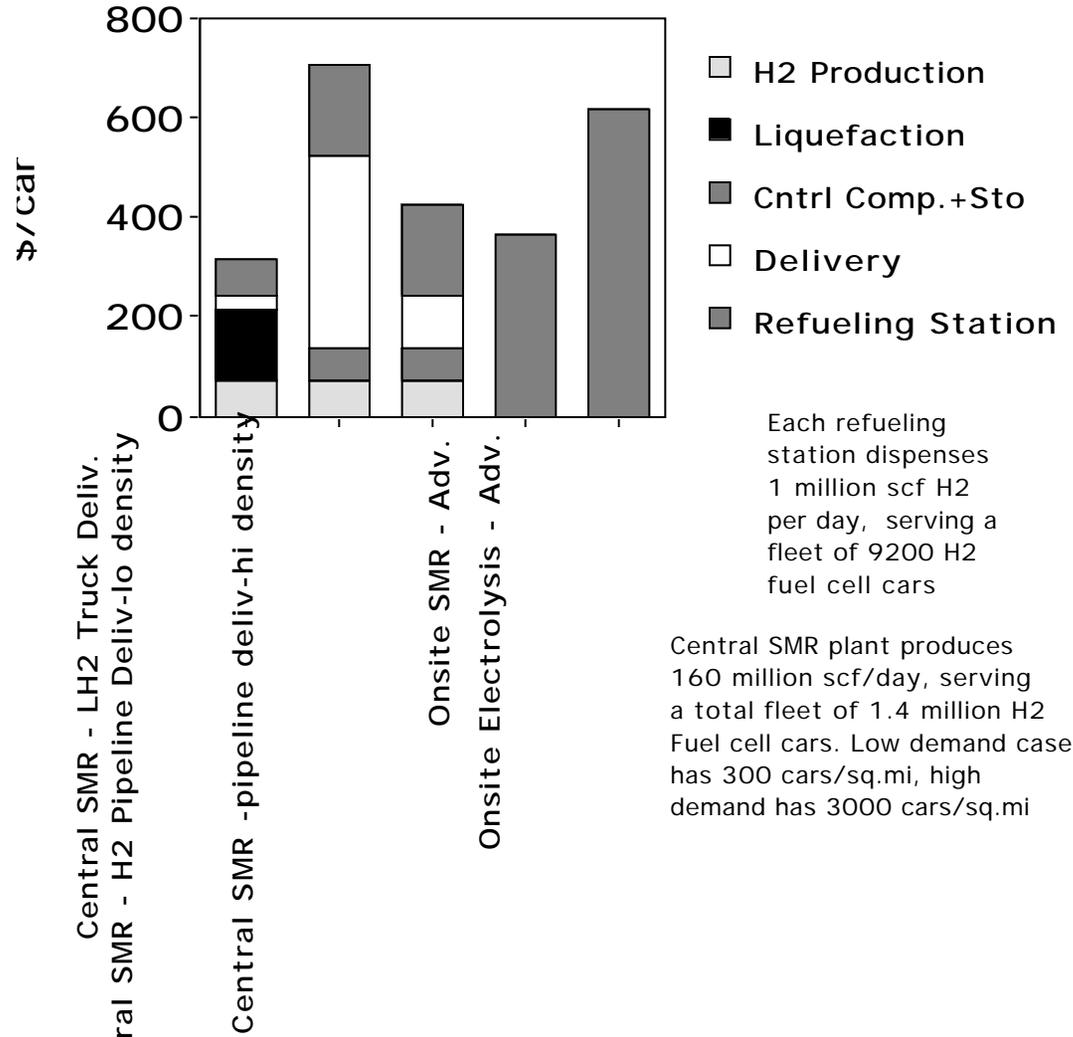
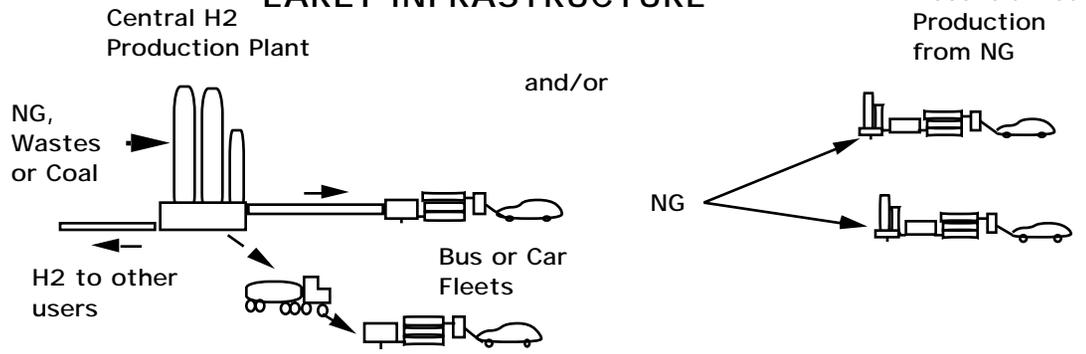


Figure 7



## EARLY INFRASTRUCTURE



## CITY SCALE INFRASTRUCTURE

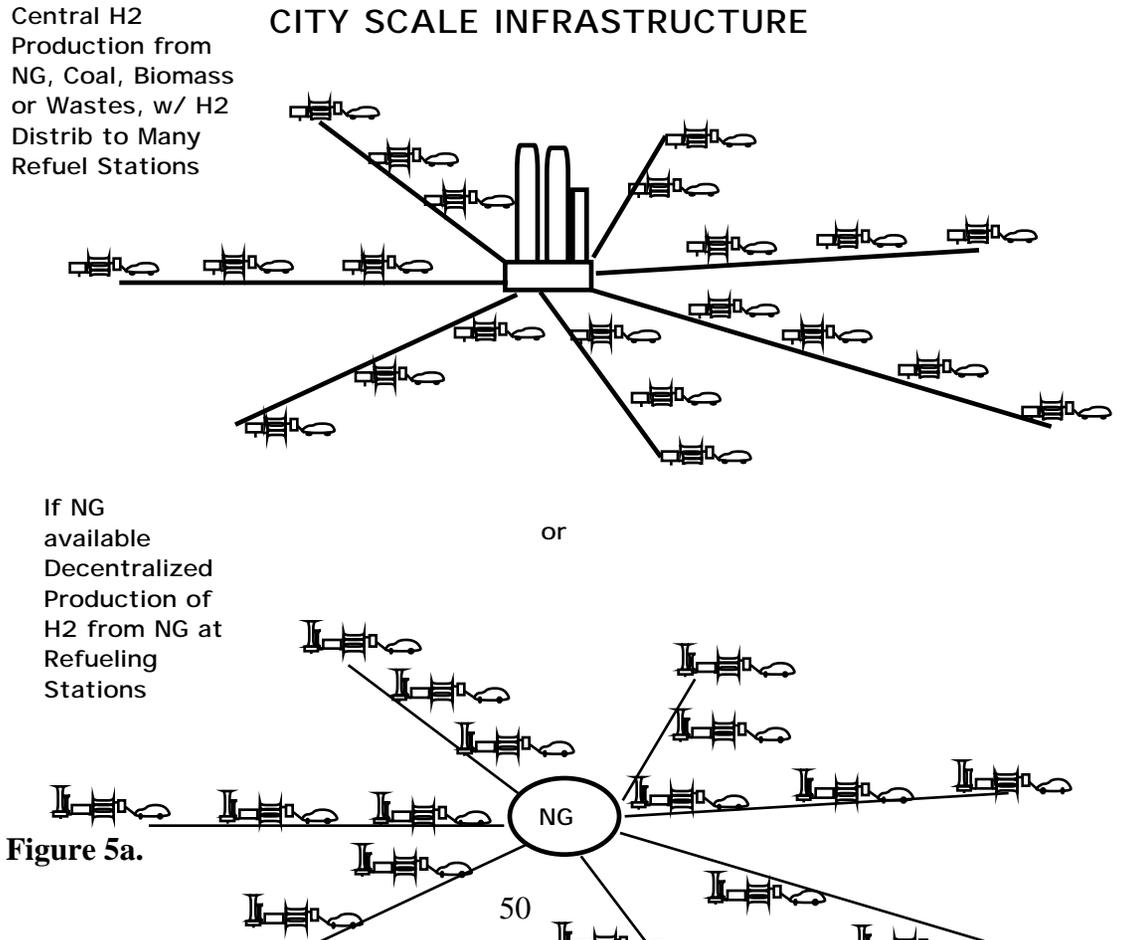


Figure 5a.

# HYDROGEN ENERGY ECONOMY W/CO2 SEQUESTRATION

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

CO2 to  
Sequestration  
Site

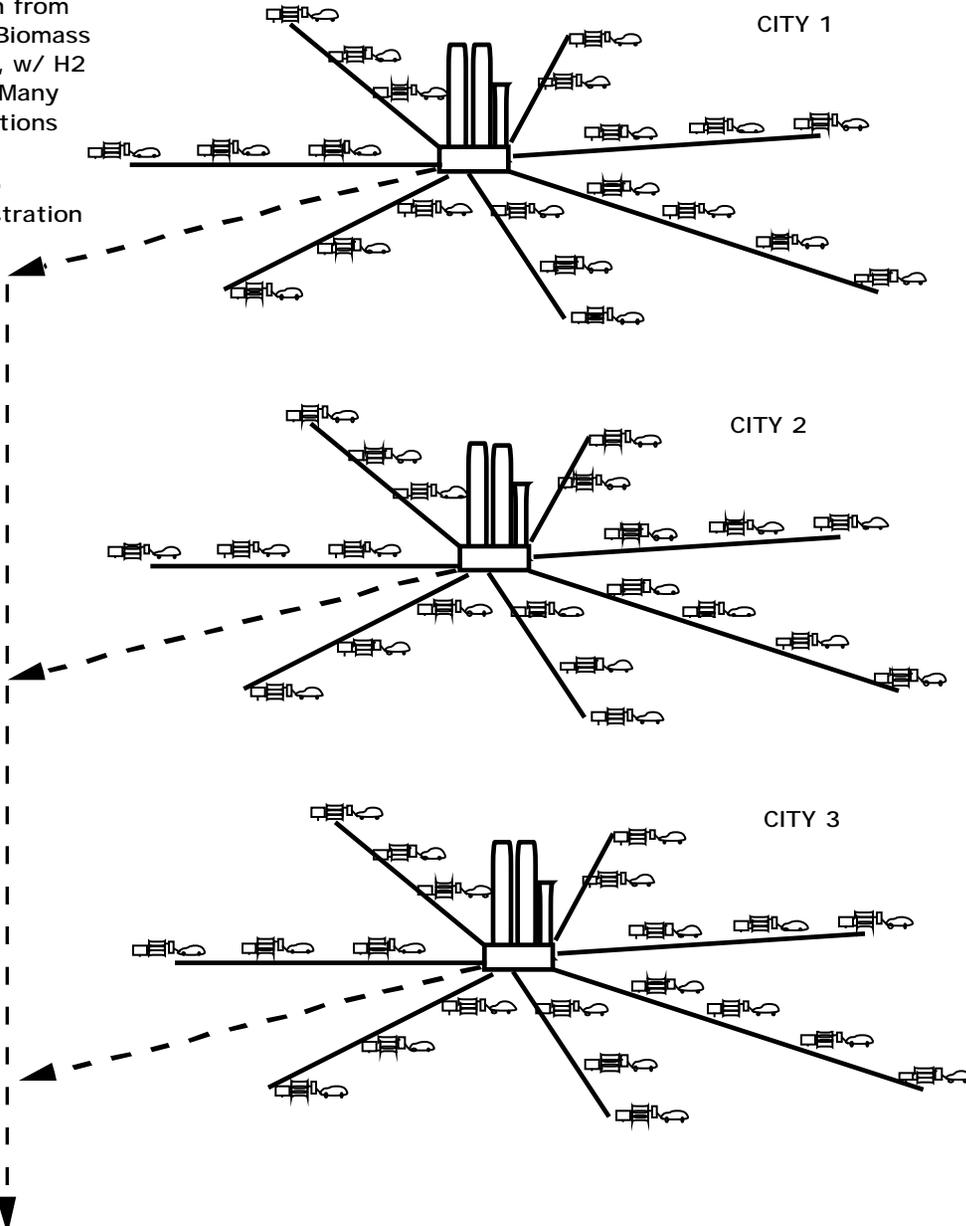
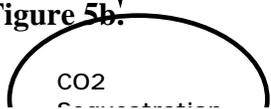
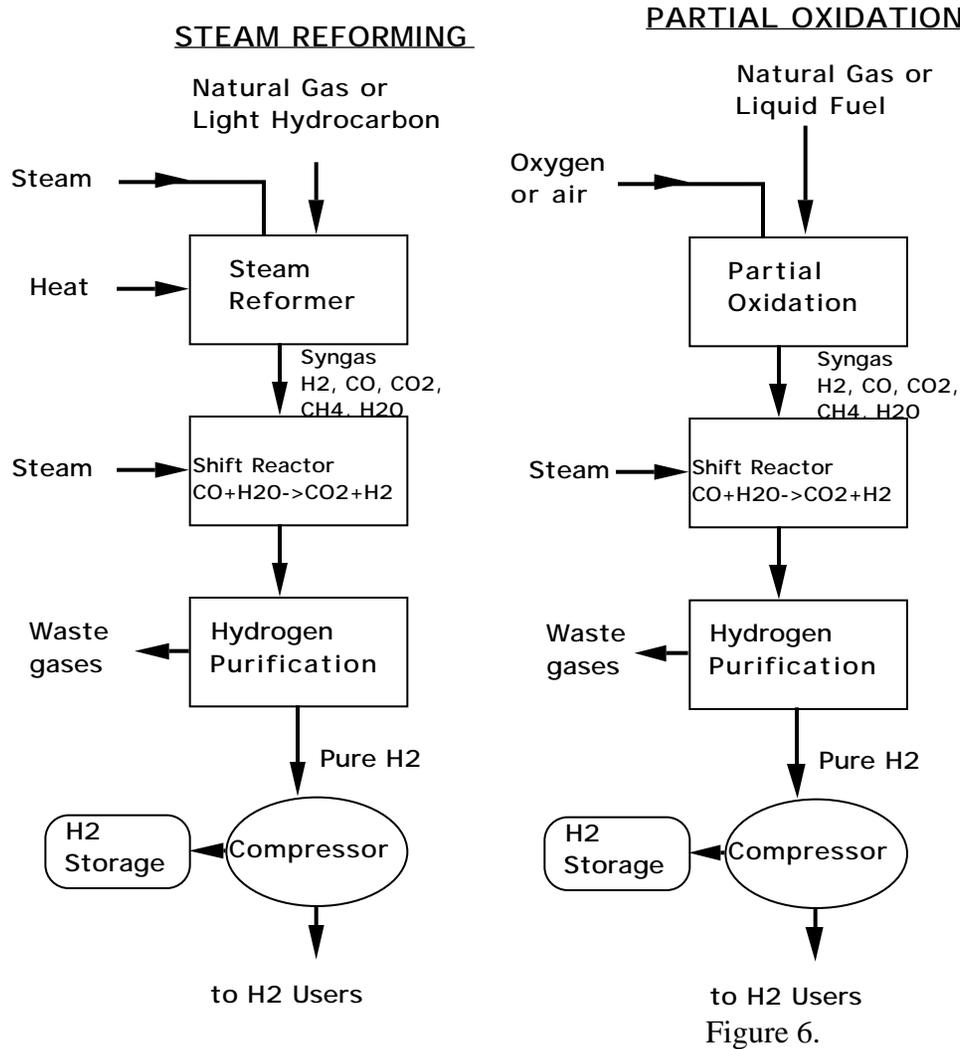


Figure 5b.

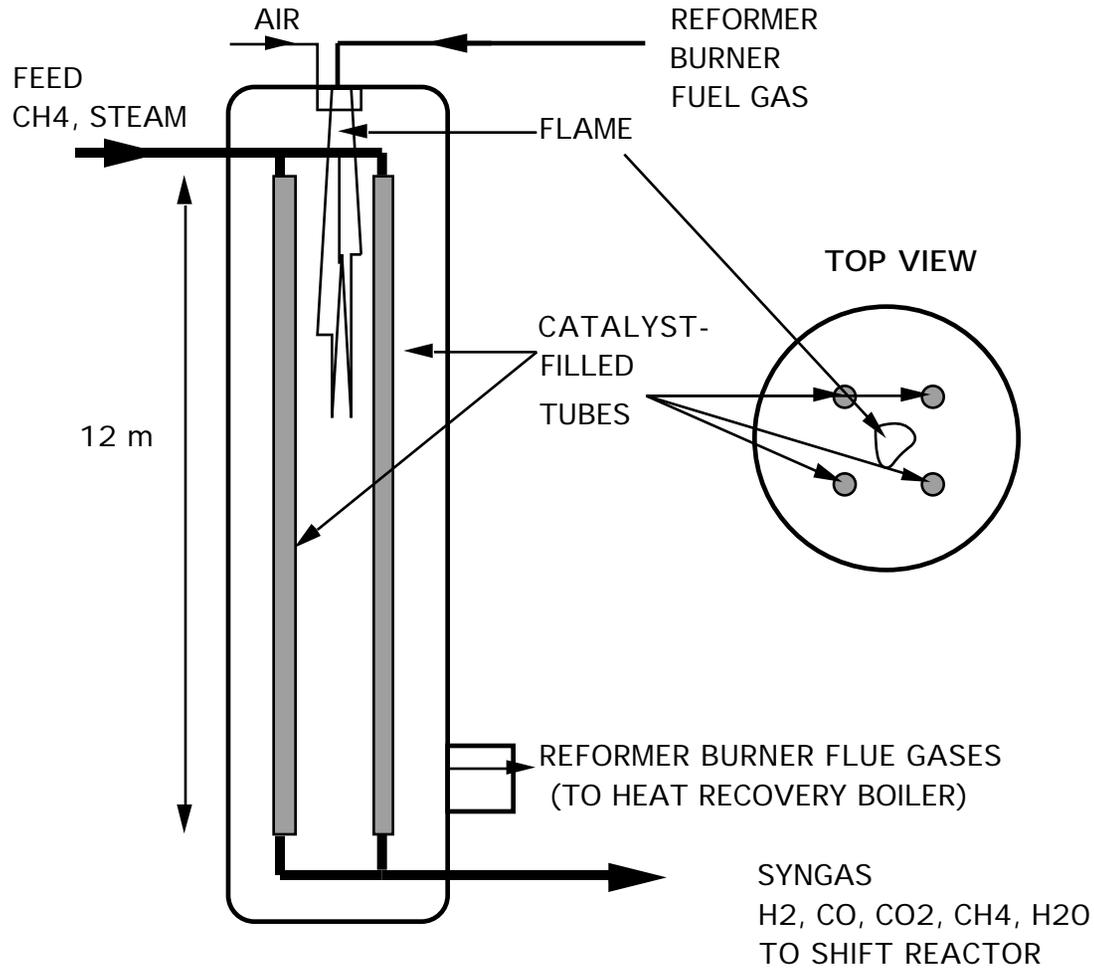




# THERMOCHEMICAL HYDROGEN PRODUCTION METHODS

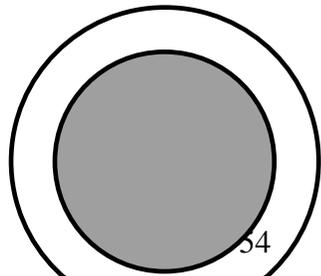


METHANE REFORMER DESIGN



SINGLE REFORMER TUBE

TYPICAL CATALYST MATERIALS:  
NICKEL ON ALUMINA SUPPORT



TYPICAL TUBE WALL MATERIALS:  
HIGH ALLOY STEELS:  
HK-40, IN 519

Figure 7a

TYPICAL DIMENSIONS:

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

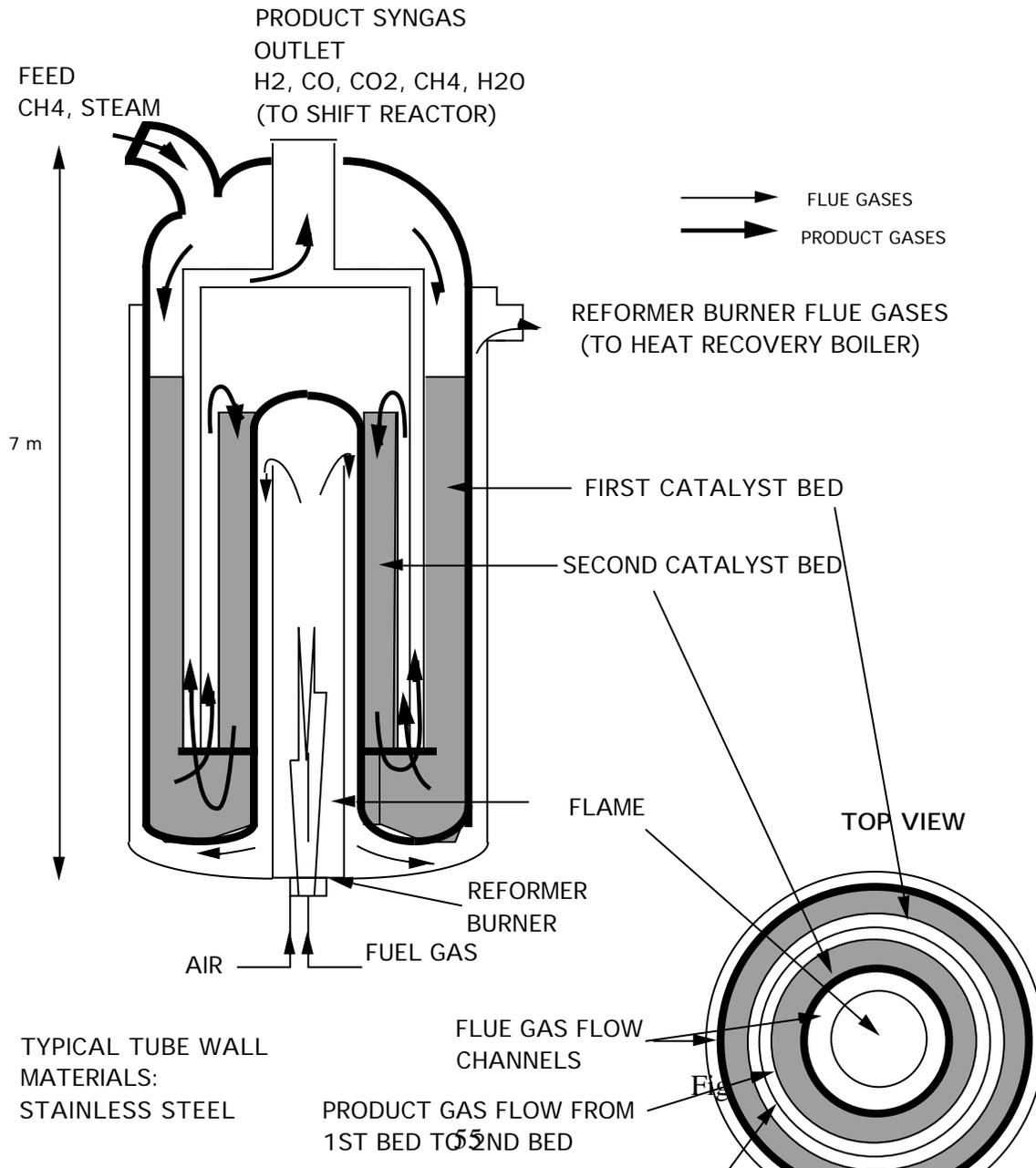


Figure 7c. Plate Type Reformer

TO BE ADDED

Figure 7d. Membrane Reactor for Steam Reforming

TO BE ADDED

## **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 <sub>2</sub> vaporized to provide high pressure gas
Chicago Transit Authority, Chicago, IL Ballard Power Systems, Air Products	1998-2000	Trucked in liquid H <sub>2</sub> 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 <sub>2</sub> and small scale reforming of natural gas producing H <sub>2</sub> and CNG/H <sub>2</sub> blends for ICE vehicles
BC Transit Vancouver, British Columbia Ballard Power Systems, Stuart Energy	1998-2000	H <sub>2</sub> is produced via electrolysis using off-peak power for three fuel cell buses
BC Hydro	2001	H <sub>2</sub> refueling station based on electrolysis under construction
Sunline Transit, Thousand Palms, CA Hydrogen Burner Technology, California Air Resources Board	1999-	Production of H <sub>2</sub> via small scale partial oxidation of natural gas for H <sub>2</sub> buses
California Fuel Cell Partnership	2001-	Planned demonstration of

		refueling systems for up to 20 H <sub>2</sub> fuel cell vehicles; Sacramento H <sub>2</sub> station has trucked in LH <sub>2</sub> to supply high pressure H <sub>2</sub> gas to vehicles
AC Transit, California	Late 2001	H <sub>2</sub> 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 <sub>2</sub> 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 <sub>2</sub> fuel cell bus demonstrations
Reykavik, Iceland Shell Hydrogen	2001	H <sub>2</sub> refueling station based on electrolysis using low cost geothermal power
WE-NET Project, Japan	2001	2 H <sub>2</sub> refueling stations: Electrolysis (Takamata) Steam Reforming (Osaka)

## **APPENDIX B.**

### **LIST OF RECENT PATENTS RELEVANT TO SMALL SCALE HYDROGEN PRODUCTION VIA REFORMING**

#### **Plate-type Reformers**

Allam, R.J., Bassett, J.D., Abradro, J., and P.L. DaPrato, “Integrated plate-fin heat exchange reformation,” US Patent No. 5,324,452, June 28, 1994. (Air Products and Chemicals)

Hamada, K., M. Mizusawa, and M. Koga, “Plate Reformer,” US Patent No. 5,609,834, March 11, 1997. (

Hsu, M. and E.D. Hoag, “Thermally enhanced compact reformer,” US Patent No. 6,183,703, Feb.6, 2001. (Ztek)

LeSieur, R., “Compact Fuel Gas Assemblage,” US Patent No. 5,733,347, March 31, 1998. (International Fuel Cells)

#### **Membrane reactor reformers**

Minet, Ronald G. and T. Tsotsis, “Catalytic ceramic membrane steam/hydrocarbon reformer,” US Patent No. 4,981,676, Jan. 1, 1991. (No corporate affiliation given)

Verrill, C.I., L.J. Chaney, K.E. Kneidel, R.A. McIlroy, and R.M. Privette, “Compact Multi-Fuel Steam Reformer,” US Patent No. 5,938,800, August 17, 1999. (McDermott Technology, Inc.) steam reforming

Shirasaki, Y., M. Gondaira, Y. Ohta, et.al, “Hydrogen producing Apparatus,” US Patent No. 5,639,431, June 17, 1997. (Tokyo Gas Company, Mitsubishi Heavy Industry) steam reforming

J.Z. Galuszka, “Process for producing syngas and hydrogen from natural gas using a membrane reactor,” US patent No. 5,637,259, June 10, 1997. (Natural Resources Canada). – partial oxidation reforming

D. Edlund and W.A. Pledger, “Steam reformer with Internal Hydrogen Purification,” US Patent No. 5,997,594, Dec. 7, 1999. (Northwest Power Systems LLC)

L.G. Marionowski and D.K. Fleming, "Hydrogen forming reaction process," US Patent No. 4,810,485, March 7, 1989. (IGT) steam reforming with membrane separation of H<sub>2</sub>

D.P. Bloomfield and A.N. Rabe, "Electrochemical autothermal reformer," US Patent No. 6,143,159, Nov. 7, 2000. (Analytic Power).

### **Partial Oxidation Reformers**

R. Woods, L. Greiner, and D. Moard, "Integrated Power Module," US Patent No. 6,033,793, March 7, 2000. (describes Hydrogen Burner Technology's POX plus PSA system).

L.G. Clawson, W.L. Mitchell, J.M. Bentley, and J.H.J. Thijssen, "Method and apparatus for converting hydrocarbon fuel into hydrogen gas and carbon dioxide," US Patent No. 6,126,908, October 3, 2000. (Arthur D. Little, Inc.)

R.J. Sanger, et.al "Apparatus for Providing a Pure Hydrogen Stream for Use with Fuel Cells," US Patent No. 6,190,623, Feb. 20, 2001. (UOP)

### **Ion Transport Membranes**

S. Nataraj and S.L. Russek, "Synthesis gas Production by Ion Transport Membranes," US patent No. 6,077,323, June 20, 2000. (Air Products and Chemicals, Inc.)

Gottzmann, C.F., R. Prasad, J.M. Schwartz, V.E. Bergsten et.al "Tube and shell reactor with oxygen selective ion transport ceramic reaction tubes," US Patent No. 6,139,810, Oct. 31, 2000. (Praxair, Standard Oil).

Kleefisch, M.S., C.A. Udovich, J.G. Masin, T.P. Kobylinski, "Membrane reactor hollow tube module with ceramic/metal interfacial zone," US Patent No. 5,935,533, August 10, 1999. (BP Amoco)

Abeles, B., R.B. Hall, M. Zhou, "Multi-layer membrane composites and their use in hydrocarbon partial oxidation," US Patent No. 5,846,641, Dec. 8, 1998. (Exxon)

B.M. Sheikh-Ali and G.E. Wnek, "Ion conducting membrane for fuel cell," US patent No. 6,110,616, August 29, 2000. (Dais-Analytic)

## **Methanol Reformers**

J. Meusinger, L. Haart, and U. Stimming, "Membrane reactor for producing CO and CO<sub>2</sub> free hydrogen," US Patent No. 6,129,861, Oct. 10, 2000. (Forschungszentrum Julich GmbH)

R. Autenrieth et.al "Process for methanol reforming apparatus," US Patent No. 6,074,770, June 13, 2000. (DBB Fuel Cell Engines)

R. Kumar et.al "Fuel cell system for transportation applications," Argonne National Laboratory, US Patent No. 5,248,566, Sept 28, 1993. (ANL)

G. Bohm, et. al, "Process for obtaining a high hydrogen low carbon monoxide gas," US Patent No. 5,904,913, May 18, 1999.