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TECHNOECONOMIC FEASIBILITY ANALYSIS OF HYDROGEN PRODUCTION BY INTEGRATED CERAMIC MEMBRANE SYSTEM

Minish M. Shah and Raymond F. Drnevich
Praxair, Inc.
Tonawanda, NY 14150

U. Balachandran, S. E. Dorris, and T. H. Lee
Argonne National Laboratory
Argonne, IL 60439

Abstract

Praxair, with Argonne National Laboratory as a subcontractor, has initiated a program to develop a small-scale hydrogen production system based on ceramic oxygen transport membrane (OTM) and hydrogen transport membrane (HTM). This system has a potential to significantly reduce the cost of hydrogen for use in the transportation sector for fuel cell vehicle fueling stations and in the industrial sector as a small, on-site hydrogen supply. This paper summarizes the results obtained from a technoeconomic feasibility evaluation, as well as the associated HTM performance.

Based on the preliminary economic evaluation, the projected hydrogen cost from a 5,000 scfh plant will be in the range of \$11 to \$14/MMBtu, depending on the number of plants built each year. A significant membrane development program will be required to achieve this cost. To meet the Department of Energy (DOE) target of \$6 to \$8/MMBtu, an additional development program will also be required to reduce the cost of the balance of the plant equipment.

Introduction

Hydrogen is expected to play a vital role in the transportation sector for fuel cell vehicles (FCVs) and in the distributed power generation market for stationary fuel cells. One of the crucial factors for successful introduction of FCVs on U.S. roadways is a low-cost supply of hydrogen. The demand for hydrogen at fueling stations for FCVs is projected to be less than 10,000 scfh. Currently, liquid is the preferred mode of supply for such low-volume requirements. However, the cost of liquid hydrogen is very high at \$29 - \$45/MMBtu depending on volume, location, and length of contract (Chemical Marketing Reporter 2001). To be competitive with cars running on gasoline, the cost of hydrogen delivered to a vehicle must be below \$20/MMBtu. A small on-site plant can eliminate the costs associated with liquefaction and distribution. A key challenge for the on-site plant is to reduce capital costs. The approach taken in this program is to reduce capital costs by reducing the complexity of the process and thus reduce the equipment needed to generate hydrogen.

Praxair has defined a process concept that integrates various processing steps in a single reactor. A schematic diagram of the integrated-membrane reactor separator is shown in Figure 1. The reactor is divided into three compartments by integrating both OTM and HTM into a single unit.

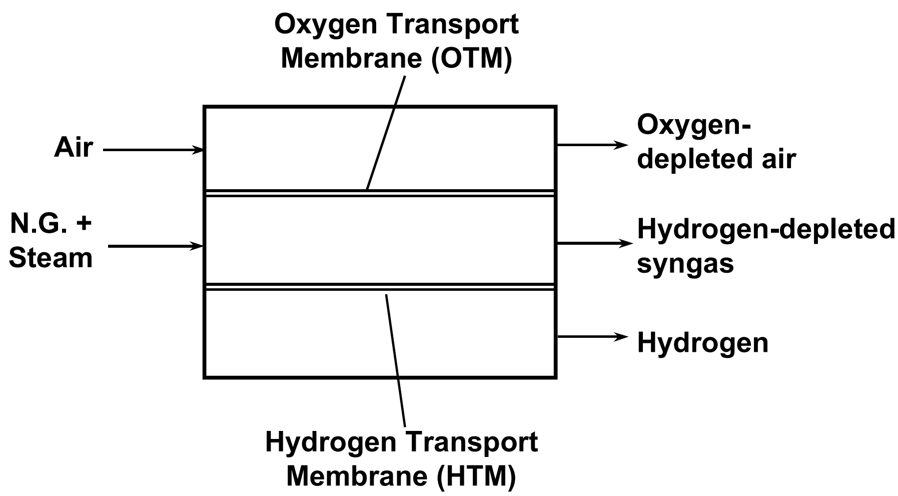

Figure 1. Integrated Membrane Reactor Separator

Air at low pressure (~25 psia) is passed to the retentate side of the OTM and compressed natural gas (200 - 300 psia) and water/steam are passed to the permeate side of the OTM. Oxygen is transported across the OTM to the permeate side, where it reacts with natural gas to form syngas. A portion of natural gas also reacts with steam to form syngas. Additional hydrogen is formed by the water-gas shift reaction:

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2 \qquad \text{(Partial Oxidation)}$$
$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \text{(Reforming)}$$
$$H_2O + CO \rightarrow H_2 + CO_2 \qquad \text{(Shift)}$$

A catalyst is incorporated in the reactor to promote the reactions. The syngas is also exposed to the retentate side of the HTM. Hydrogen is transported to the permeate side of the HTM by the partial pressure difference driving force. Due to removal of hydrogen from the reaction zone, more hydrogen is formed by the reforming and shift reactions.

As much hydrogen as possible is recovered from the reaction zone by transport through the HTM to the permeate side. Eventually, a partial pressure pinch between the reaction zone and the permeate side is reached, limiting the amount of hydrogen that can be recovered.

Technical Feasibility Analysis

Product Slate

A small volume of hydrogen is required by customers in the fats and oils, float glass, utilities, chemicals, electronics, and metals industries. A majority of these customers are supplied with liquid hydrogen. However, most of them need hydrogen in gaseous form. Therefore, significant number of opportunities are available, if a small on-site plant can supply hydrogen to these customers at a cost that is lower than the cost of liquid.

In the transportation sector, fueling facilities for FCVs will require small on-site hydrogen plants. A typical gas station fuels 200 cars per day or supports 1800 cars over a nine-day refilling cycle for a typical passenger car. A small plant producing 1000-5000 scfh of hydrogen will be able to refuel 11-55 cars per day (or support 100-500 cars over a complete refueling cycle). For the average gas station, this range will represent 5-25% of the total automotive traffic.

Most of the industrial customers require a minimum purity of 99.99%. For a hydrogen FCV, CO can be detrimental to the fuel cell. Although other impurities do not poison the fuel cell, overall hydrogen purity must be high so the fuel cell can be operated at a high hydrogen utilization rate. Therefore, an overall purity of about 99%, with less than 10 ppm CO, is acceptable for fuel cell applications.

The pressure requirements for majority of industrial customers is below 200 psia. In the transportation sector, the required pressure will depend on whether hydrogen is stored as high-pressure gas or as a low-pressure alternative such as a metal hydride. For on-board storage of 5,000 psia of hydrogen, a fueling station may have to store hydrogen at ~7,500 psia for quick filling.

The present analysis is limited to hydrogen production at the pressure attained from the membrane reactor, 15 psia. Three production capacities were selected for economic feasibility analysis: 1,000, 2,000, and 5,000 scfh.

Process and System Design

Various process options, based on the integrated OTM-HTM reactor, separate OTM and HTM reactors, and an air POX reactor integrated with a HTM were reviewed. Based on the preliminary assessment, the process with integrated OTM-HTM reactor was selected because of its potential for compact plant design and high efficiency. Based on an initial feasibility assessment, it was determined that there are no technical issues that will prevent the development of the integrated OTM-HTM reactor. A process model was developed for an integrated OTM-HTM reactor. The production capacity of 1,000 scfh of hydrogen was used for performance assessment.

A flowsheet for a process based on the integrated OTM-HTM reactor was developed. The pressure on the reaction side was selected to be 250 psia and the pressure on the permeate side was selected to be 20 psia. Heat and mass balances were established. The following simplifying assumptions were made:

- Plug flow exists in various compartments of the reactor (i.e., no radial concentration gradients)
- There were no heat transfer limitation

A kinetic model from the literature was used for the reforming and shift reactions (Xu 1989). Average oxygen flux was assumed for the OTM, based on the values reported in the literature (Shao 2001). For the HTM, a partial pressure pinch of 5 psi was used, i.e., hydrogen partial pressure in the reaction zone is always 5 psi higher than the pressure on the permeate side. Based on initial flux data, it was determined that the average flux through the HTM under the reactor operating conditions would be 1.5 $cm^3/cm^2/min$.

The overall efficiency of the plant is defined as follows:

$$H_2 \text{ Efficiency} = \frac{\text{Energy Recovered in } H_2 \text{ (HHV) x 100}}{\text{Energy Input in Natural Gas (HHV)}}$$

Based on this definition, the H_2 efficiency of the process is 75.8% (HHV or higher heating value). In comparison, large steam methane reforming (SMR) plants achieve 68% H_2 efficiency (HHV). Including the energy recovered in exported steam, large SMR plants achieve overall thermal efficiency of 80 – 85%, depending on the scale of production. In the case of the OTM-HTM process, there is no steam export. Therefore, the overall thermal efficiency is the same as the H_2 efficiency. The main reason for the lower efficiency of the OTM-HTM process is higher heat losses from the small reactor on a percentage basis. Another reason for the high efficiency of large-scale SMR plants is co-production of steam for export. Table 1 summarizes utility consumption.

Table 1. Consumption of Utilities

Hydrogen capacity, scfh	1,000
N.G., scfh	424
Power, kW	4.6
Water, gpm	1.1
H_2 Efficiency, %(HHV)	75.8 %

Feasibility Assessment

The feasibility assessment was carried out to identify the technical issues and to determine if any technical issues will prevent the integration of OTM and HTM into one reactor. The assessment was based on the current knowledge of OTM and HTM performance characteristics. The progress made to date in Praxair's syngas alliance program indicates that all of the components associated with the OTM reactor will be available before this program is completed. Detailed design of the OTM-HTM reactor was prepared and important design issues were assessed. The issues that require further development to improve economics were defined in this phase and they form the basis for the development needs of the next phase.

The HTM is the critical undeveloped component. Based on discussions with Argonne National Laboratory (ANL) and the work performed by others developing hydrogen membranes, we anticipate that a cost-effective HTM can be developed. The following issues have been assessed in this phase of the program.

Operating Temperature

For the integrated OTM-HTM reactor, the operating temperature should be such that both OTM and HTM can provide high flux. The work done so far indicates that the preferred temperature for the HTM is between 500 and 900^oC and flux is found to increase with temperature up to 900^oC. Based on previous work done at Praxair, the OTM can operate at temperatures between 850^oC and 1100^oC. Since it is feasible to operate both the OTM and the HTM in the temperature range of 850 - 900^oC, the actual operating temperature will be fixed by economic optimization. For current analysis, the operating temperature of 900^oC was selected.

Membrane Selectivity

It is known that some proton conductors exhibit oxygen permeation in addition to hydrogen. This phenomenon can result in loss of hydrogen. In the reaction zone, there is oxygen activity due to presence of H_2O, CO and CO_2. The decomposition of any of these compounds on the HTM's surface can produce oxygen ions, which can pass through the HTM and react with hydrogen on the permeate side to produce steam. In the experiments carried out by ANL so far, there is no evidence of moisture in the permeate, which indicates there is no oxygen transport across the HTM.

Effect of Syngas Components on HTM

Some of the ceramic membrane materials decompose in the presence of CO_2 and H_2O. Initial tests conducted at ANL in the presence of simulated syngas mixtures indicate that the ceramic material used in this CRADA (cooperative research and development agreement) decomposes in the presence of a large concentration (30%) of CO_2. Finding suitable membrane material that can survive in the syngas environment will be a critical element of the future development program. The research at ANL shows that it is feasible to develop such materials.

Other technical issues for using ceramic membranes are identified below. The work done so far lead to the conclusion that these issues can be adequately addressed by further development. The next phases of the development program will begin addressing the issues of operating pressure, compatibility of catalysts with the OTM and the HTM, long-term stability and reliability, seals, diffusion limitation, heat transfer, reactor design, and tolerance to thermal cycling.

Experimental Studies for HTM

The ANL-2 membrane (the ANL's proprietary material) was used throughout this study. This membrane consists of a proton-conducting material (yttrium-doped $BaCeO_3$) with metal additive to provide high electronic conductivity and enhance the hydrogen flux. The membrane disks, with varying thickness (200 - 1200 microns), were prepared by conventional ceramic pressing, sintering, and polishing.

Hydrogen Flux

The experiments were carried out to study the effects of hydrogen partial pressure, membrane thickness, and temperature. Gas mixtures consisting of hydrogen and helium were used as feed gases. Both dry as well as wet (containing 3% moisture) feed mixtures were used. The presence of moisture was found to enhance the hydrogen flux by 30 to 50%. Since the syngas mixture in the reactor will contain steam, only experimental results with wet feed mixtures are presented below.

Effect of Hydrogen Partial Pressure

The hydrogen flux through purely mixed conducting ceramic membranes is reported to be proportional to $\ln(p_2/p_1)$, where p_2 and p_1 are partial pressures of hydrogen on feed and permeate sides, respectively. Initial experiments were planned to see if ANL-2 exhibits flux characteristics that are similar to those of other proton conductors. Two sets of experiments (with 1 and 4% hydrogen in the feed) were carried out by varying sweep gas flow to achieve different p_2/p_1 ratios. When flux was plotted against $\ln(p_2/p_1)$, the results were not conclusive. Due to low hydrogen concentration in the feed, absolute flux values were also low, and the likelihood of measurement error was high. Therefore, another set of experiments was conducted at 900°C using ~0.45mm thick membrane with the hydrogen concentration in the feed from 1 to 100%. The hydrogen concentration in the permeate was kept below 1%. The results from these experiments clearly demonstrated that for the ANL-2 membrane, flux was not proportional to $\ln(p_2/p_1)$. It was found that the hydrogen flux is proportional to $(p_2^n - p_1^n)$ (Figure 2). This type of correlation is observed for metal membranes, where a solution diffusion mechanism is responsible for hydrogen transport. It appears that the metal additive in the ANL-2 membrane is a major contributor to the observed hydrogen flux.

Effect of Temperature and Membrane Thickness

The flux measurements were made at temperatures between 600 and 900°C and for membrane thickness between 0.28 and 1.2 mm. Hydrogen concentration in the feed gas was held constant at 77.6% (with 3% moisture and balance being helium). The sweep gas on the permeate side was nitrogen with 92 ppm hydrogen in it. The sweep flow was adjusted to achieve constant hydrogen concentration (~0.8%) in the permeate. Figure 3 shows the results from this study.

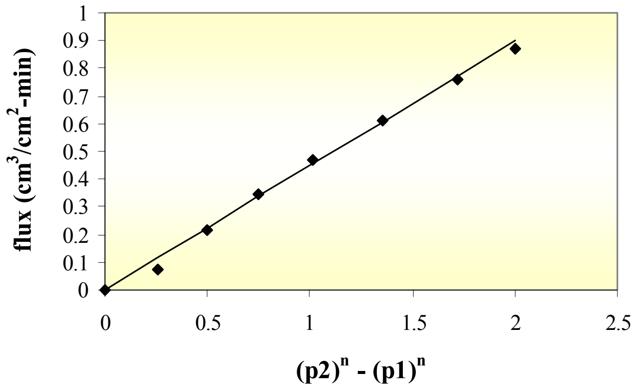

Figure 2. Effect of Hydrogen Partial Pressure on Flux

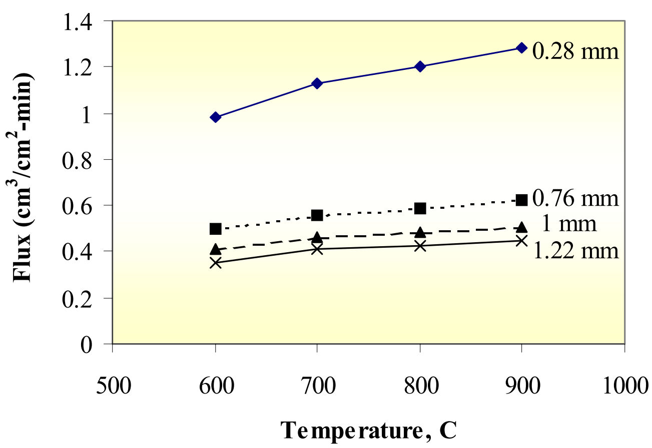

Figure 3. Effect of Temperature on Flux through Membranes of Various Thickness

The flux was found to increase only slightly with temperature. Again, this behavior is more typical of a metal membrane than of a proton conductor. This finding further strengthens the supposition that the metal additive in ANL-2 is the major factor that affects hydrogen transport, and that the contribution from the proton conductor is small.

As membrane thickness decreases the resistance due to bulk transport decreases. However, other mass transport resistances, such as diffusion through the boundary layer and surface exchange reactions, remain constant. It has been reported in the literature that for very thin membranes, surface exchange reactions exerts a dominant effect on flux. To gauge the magnitude of these resistances, 1/flux vs. thickness was plotted (Figure 4).

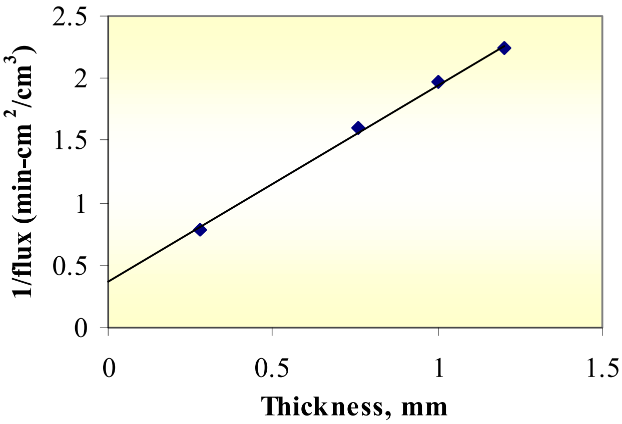

Figure 4. Plot of 1/flux vs. membrane thickness

The intercept on the y-axis represents other mass transport resistances. Thus, for a hypothetical thickness of zero, the limiting flux for a given set of process conditions is ~2.5 $cm^3/cm^2/min$. Based on these results, a flux equation was proposed to predict flux in the reactor and to estimate the membrane area in the reactor. The average flux in the reactor was estimated to be 1.5 $cm^3/cm^2/min$. A preliminary cost estimate indicated that the reactor cost will be more than 75% of the total equipment costs. A literature review indicates that flux as high as 40 $cm^3/cm^2/min$ is reported with certain composite metal membranes (Peachey 1998). Consequently, the process economics were developed based on the fluxes that are expected to be achieved as opposed to the fluxes that were measured in this program.

Flux with Syngas Mixtures

The results of experiments with syngas mixtures are shown in Figure 5. Three syngas compositions were tested. These compositions represent conditions at the entrance and exit of different reactor configurations. Solid lines on the graph are values predicted by the flux equation and the markers are measured flux values. For Mixtures 1 and 2, the flux remained steady for the duration of the test (4 to 6 hours). Also, the predicted values agreed well with experimental values. With Mixture 3, which represented conditions at the exit of the reactor, the flux values declined rapidly. Mixture 3 contained 30% CO_2 (by vol.) and a high level of CO_2 may have caused degradation of the membrane surface.

Economic Feasibility Analysis

A process that uses the integrated OTM-HTM reactor was selected for the economic analysis. For the transportation sector, a production capacity of 1,000 scfh will be desirable. The demand in the industrial sector varies widely between 200 and 35,000 scfh (Heydorn 1998). Plants with the production rates in the range between 1,000 and 5,000 scfh could serve majority of customers in this sector. The hydrogen plant capacity was fixed at 1,000 scfh for the cost estimation. The capital costs for 2,000 and 5,000 scfh were estimated by using appropriate scale-up factors. For each capacity, costs were estimated for 10, 100, and 1,000 plants built/year. The product costs were estimated and compared with two competing supply options: liquid hydrogen and electrolysis. Market projections were made for the industrial and transportation sectors. Estimation of preliminary development costs and a business case analysis will be performed by May 2001.

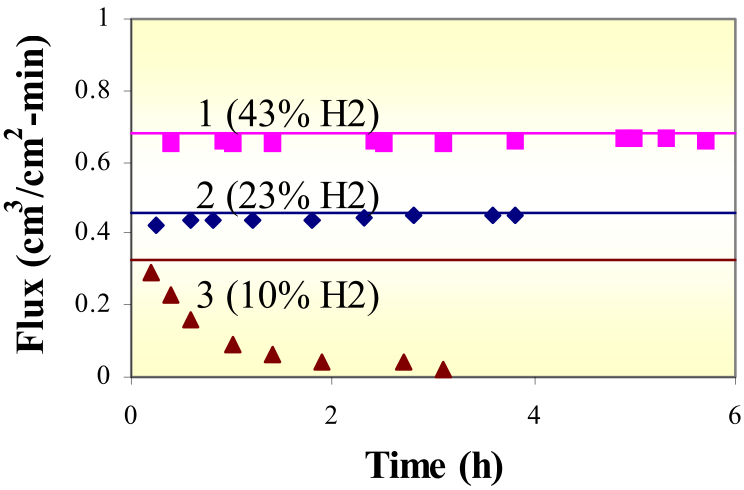

Figure 5. Hydrogen Flux with Syngas Mixtures

Overall Product Costs

The cost to manufacture the membrane reactor was developed based on the reactor design and costing techniques for similar systems under development at Praxair. The cost of the balance of the plant equipment (natural gas compressor, water treatment system, air compressor, heat exchangers, steam generator, and desulfurization unit) was based on purchasing major components from qualified suppliers. The quotes were obtained for multiple-unit purchases (in quantities of 10, 100 and 1,000) when available. Where quantity discount data were unavailable, reasonable cost reduction was assumed based on our experience. A P&ID (process and instrumentation diagram) was developed for controls and instrumentation that are necessary for safe operation, safe startup, and shutdown procedures. The cost of control valves and instruments were estimated based on volume pricing available to Praxair.

A three-dimensional plant layout, with details of piping, skids, and assembly was developed. Based on this layout, the cost of complete assembly was developed including the costs of piping, insulation, equipment, and instrument mounts, electrical, and metal enclosure. Finally, the costs of engineering and design, shipping, installation, and startup costs were estimated. All of these costs were included in the estimate of total capital investment.

The product costs were estimated by adding annual operating, M&R (maintenance and replacement), and capital recovery costs. To estimate capital recovery costs, the method described in the Hydrogen Infrastructure Report (Thomas 1997) was used. The report has suggested the financial parameters listed in Table 2.

Table 2. Financial Parameters

10% after–tax rate of return
26% corporate tax rate
15-year plant life
2.7% inflation rate

These parameters lead to capital-related charges of 18.5% of capital investment/year. In addition, the assumptions listed in Table 3 were made.

Table 3. Cost Estimation Assumptions

Natural gas	$3/MMBtu (HHV)
Power	$0.05/kWh
Water	$0.1/1000 gal.
M & R	3% of capital investment/year
Capacity Utilization	80%

Figures 6 and 7 show capital and product costs for various cases. As seen from Figure 7, a significant reduction in capital costs will be required to achieve the DOE target of $8/MMBtu. At 1,000 scfh, it is highly unlikely that we can achieve the necessary cost reduction. At a 5,000 scfh capacity and a production rate of 100-1000 units per year, a capital cost reduction of 50-65% will be required. To achieve this level of cost reduction, the flux target will have to be set at a much higher level than the value assumed for the cost estimation. However, improvement in membrane performance alone will not be sufficient to achieve a 50-65% reduction in total capital. Thus, a development program that focuses on reducing the cost of the balance of the plant and assembly costs will be required in addition to membrane reactor development. We are currently assessing the potential impact of cost reduction areas to estimate the probability of meeting the DOE targets.

The projected costs of hydrogen from OTM/HTM technology are lower than the costs of liquid hydrogen and electrolytically produced hydrogen. Liquid hydrogen costs $30-$45/MMBtu, depending on the consumed volume, location and contract length (Chemical Marketing Reporter 2001). The projected capital and M&R costs for mass produced electrolysis equipment (Thomas 1997) and power costs assumed in this study results in the cost of electrolytically produced hydrogen to be $25/MMBtu for a 5,000 scfh plant.

Market Assessment

The potential market in the industrial sector was assessed based on Praxair's internal information and based on the SRI report (Heydorn 1998). According to the SRI report, 19 billion scf of hydrogen was used as gas by small-volume customers in 1996. These customers are currently supplied by liquid hydrogen and they represent conversion opportunities for on-site plants. It was assumed that a fraction of the liquid volume will be replaced by on-site plants and that additional customers currently served by ammonia dissociation and electrolysis will also become available for on-site OTM/HTM plants. Furthermore, an average long-term growth rate of 3% was assumed for the small-scale industrial market. Based on these assumptions it was estimated that Praxair will have the opportunity to build 15-50 plants per year, depending on the plant size that is manufactured.

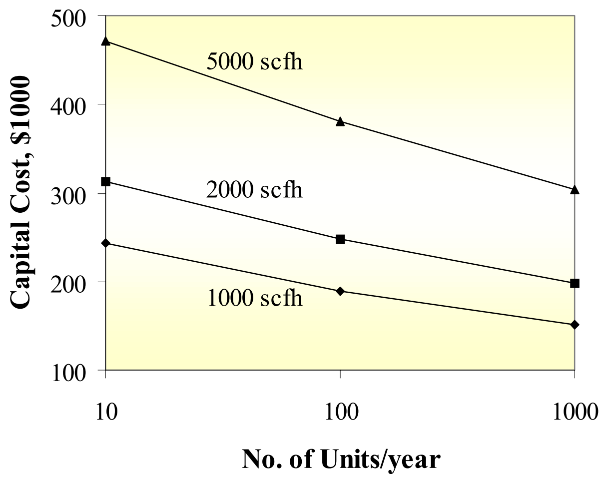

Figure 6. Capital Costs at Various Production Capacities

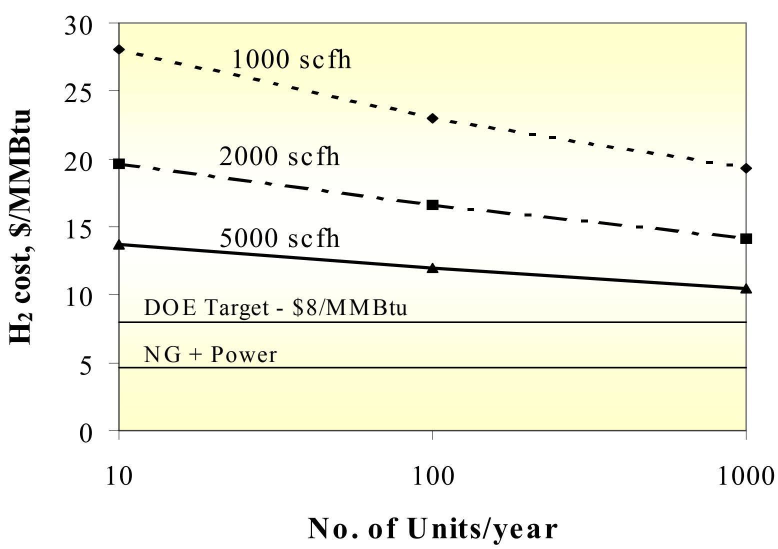

Figure 7. Hydrogen Costs at Various Production Capacities

The estimation for passenger cars powered by fuel cells was based on a modification of the California Air Resources Board (CARB) mandate released in January 2001 on their web site (CARB 2001) for zero emission vehicles (ZEVs). Table 4 lists the assumptions that were made for passenger cars.

Table 4. Assumptions for Fuel Cell Cars Market

No. of cars sold in California in 2003		1.5MM
Percentage share of large/intermediate volume manufacturer		65%
Annual car sales growth		1.5%
Average H_2 consumption by car (this implies 12000 miles driven/yr and 65 mpgge (miles per gallon of gasoline equivalent) efficiency (HHV) or 5.84 scf H_2/mile)		8 scfh
Market Parameters for Fuel Cell Cars:	Conservative	Optimistic
ZEVs as % of total vehicles sold by large/intermediate manufacturer in 2003	0.5%	0.5%
ZEVs as % of total vehicles sold by large/intermediate manufacturer in 2020	5%	10%
% of ZEVs that are based on H_2 fuel cells in 2003	10%	10%
% of ZEVs that are based on H_2 fuel cells in 2020	80%	100%
Ratio of no. of new H_2 FCVs in US/California in 2003	1	1
Ratio of no. of new H_2 FCVs in US/California in 2020	5	10

Figure 8 shows the potential number of hydrogen fuel cell cars to be sold in the U.S. per year, based on the optimistic scenario. New hydrogen production capacity required every year was estimated based on the total FCVs (cars only) sold every year and the assumptions for hydrogen mileage and miles driven per year listed in Table 4. With the assumption of 80% capacity utilization, the number of hydrogen plants required at the three capacities (1,000, 2,000, or 5,000 scfh) was estimated. If all plants have a 1,000-scfh capacity, more gas stations can be equipped with a hydrogen supply than with a 5,000-scfh plant. Figure 9 shows the projected percent of gas stations that will be equipped with a hydrogen supply for the optimistic scenario.

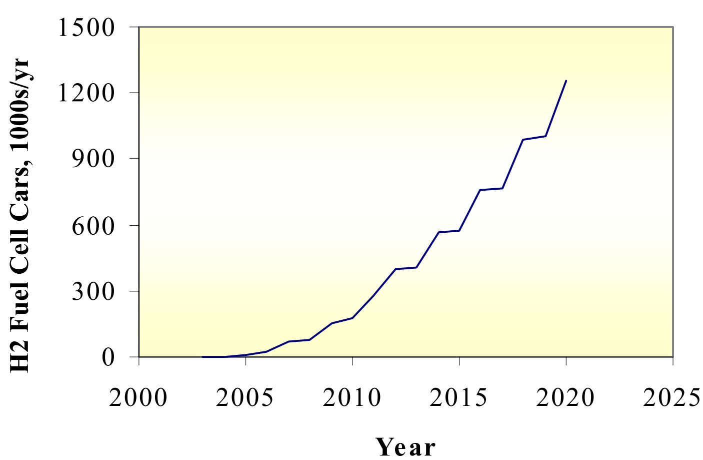

Figure 8. Optimistic Projections for Hydrogen Fuel Cell Cars in the U.S.

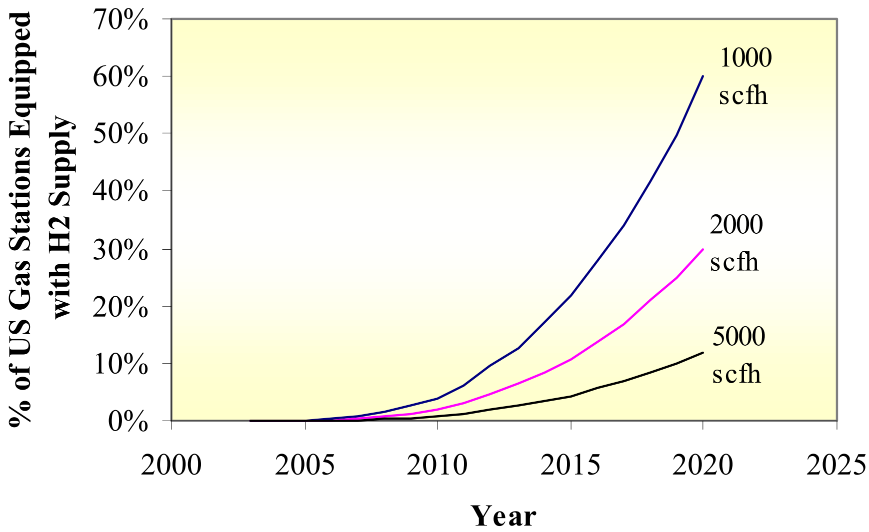

Figure 9. Gas Stations Equipped with Hydrogen Supply at the Three Plant Capacities for Optimistic Projections

Based on the economic analysis, the 5,000-scfh plant has the best chance to offer low-cost hydrogen. However, if gas stations are equipped with 5,000-scfh plants, the percentage of gas stations with hydrogen fueling capabilities will reach only 12% according to optimistic scenario. The larger plants will also likely experience lower utilization, which will drive up the cost of hydrogen. The average consumer would ideally like to see 1/2-2/3 of the gas stations with a hydrogen supply. Smaller plants (such as 1000-scfh) will result in a higher percentage of gas stations with hydrogen fueling capabilities, but the cost of hydrogen from these stations will be high. Thus, there are significant challenges that must be met if the transportation sector market is to materialize. A more aggressive conversion to FCVs may be necessary to satisfy the need of the consumers to reduce the cost of the vehicle and the fuel and increase fuel availability.

Conclusions

Integration of the OTM and the HTM in one reactor is technically feasible. The process based on the integrated reactor will be able to achieve an efficiency that is comparable to the conventional steam methane reformer process. The projected hydrogen costs are lower than the competing supply options, such as electrolysis and liquid hydrogen. Current projections indicate that to achieve an $8/MMBtu target, the capital cost must be reduced by 50-65%. A multi-pronged development program will be required to achieve such cost reductions. The primary focus will be to develop a low-cost membrane with high hydrogen flux and tolerance for syngas components. Additional efforts must be directed toward reducing the balance of the plant costs.

Acknowledgments

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