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OVERVIEW OF FUEL PROCESSING OPTIONS FOR POLYMER ELECTROLYTE FUEL CELL SYSTEMS*

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OVERVIEW OF FUEL PROCESSING OPTIONS FOR POLYMER ELECTROLYTE FUEL CELL SYSTEMS

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Introduction

The polymer electrolyte fuel cell (PEFC) is being developed for use in heavy- and light-duty transportation applications. While this fuel cell has been used successfully in buses and vans with compressed hydrogen as the on-board fuel [1,2], the fuel cell system must incorporate fuel processing (reforming) for any other on-board fuel to produce the hydrogen or hydrogen-rich fuel gas to be fed to the fuel cell stack. This is true even for alternative methods of storing hydrogen, such as use of a metal hydride or liquefied hydrogen. For example, Fig. 1 shows a simplified schematic diagram of a compressed hydrogen-fueled PEFC system; the same system with magnesium hydride as the fuel storage option is shown in Fig. 2. The "fuel processing" needed to recover the hydrogen includes providing the heat of dissociation of the hydride and cooling the hydrogen to the temperature of the fuel cell stack. Discussed below are some of the options being considered for processing of on-board fuels (other than compressed hydrogen) to generate the fuel cell anode gas, and the effects of fuel processing on system design, efficiency, steady-state and dynamic performance, and other factors.

On-Board Fuels and Fuel Storage Options

The entire spectrum of alternative and conventional fuels is being considered for transportation PEFC systems. These include hydrogen as compressed gas, liquefied gas, and metal hydrides; alcohols, such as methanol and ethanol; natural gas as a compressed or liquefied gas; and petroleum-derived hydrocarbon fuels. Of the hydrides, magnesium hydride offers a relatively high gravimetric energy storage density. However, the high dissociation temperature of magnesium hydride (about 300°C) requires that some of the recovered hydrogen be burned to provide the heat of dissociation, thereby reducing the system efficiency. The low temperature hydrides, such the iron-titanium hydride (with a dissociation temperature of about 25°C), offer a high system efficiency but only a low gravimetric energy storage density. Of the alcohols, methanol can be reformed to hydrogen and carbon dioxide under relatively mild conditions, but ethanol is more refractory, requiring high temperatures for the conversion. Natural gas and other hydrocarbon fuels also require rather severe reforming conditions.

Conventional Fuel Reforming Processes

Reforming of hydrocarbons and other compounds to hydrogen and/or synthesis gas (a mixture of hydrogen and carbon monoxide) is widely practiced in the petroleum refining and the petrochemicals industry. The two most common reforming processes are steam reforming and partial-oxidation reforming; the latter is usually carried out as a combination of oxidation (with substoichiometric amounts of oxygen or air) and steam reforming. The major reactions (unbalanced) are

$$C_nH_{2n+2} + H_2O \rightarrow H_2 + CO + CO_2 \qquad \text{(Endothermic)}$$

and

$$C_nH_{2n+2} + O_2 \rightarrow H_2 + CO + CO_2 \qquad \text{(Exothermic)}$$

The steam reforming reaction is highly endothermic, requiring the input of thermal energy into the reaction process. The partial-oxidation reaction is exothermic, requiring no input of external energy. The effects of this difference in the sign of the enthalpy of reaction on reformer and process design are discussed further below.

For the production of hydrogen in industrial processes, the reformate is reacted with steam (the water-gas shift), first at a high temperature (to obtain better kinetics) and then at a low temperature (to obtain favorable thermodynamics). This converts the carbon monoxide to carbon dioxide and generates additional hydrogen:

$$CO + H_2O(g) \rightarrow CO_2 + H_2 \qquad \Delta H^{o}_{298} = -41.2 \text{ kJ}$$

$$CO + H_2O(l) \rightarrow CO_2 + H_2 \qquad \Delta H^{o}_{298} = +2.8 \text{ kJ}$$

The water-gas shift reaction is exothermic at standard conditions when steam is used and slightly endothermic when water is used.

Fuel Reforming in the Transportation Application

Carbonaceous On-Board Fuels

Liquid fuels, i.e., fuels that are liquid at atmospheric pressure and room temperature, are attractive for heavy- and light-duty transportation applications due to their ease of storage, distribution, handling, and vehicle refueling. Indeed, it may be possible to use the existing fuel distribution and retailing infrastructure, perhaps with only relatively minor modifications. That is a major reason, therefore, for the interest in methanol fuel for fuel cell propulsion systems in buses and light-duty vehicles [3,4], even though the energy content of methanol is only half that of an equal volume of gasoline.

Fuels that contain carbon, however, give rise to a special problem for use with PEFC systems. The anode electrocatalyst in the PEFC is readily poisoned by even traces of carbon monoxide, such that the performance of the fuel cell is greatly diminished by the presence of even a few parts per million of CO in the fuel gas supplied to the anode. This effect is discussed at length in the following paper [5]. Suffice it to say that means must be provided to reduce the level of carbon monoxide to less than 10 ppm by volume gaseous product from the fuel processor in the PEFC system. Typically, the reformate after the shift reaction contains one-half to one percent of carbon monoxide, a level too high to be fed to the fuel cell stack. One engineering approach that is being pursued to reduce carbon monoxide to trace levels is to convert it to carbon dioxide by reaction with air on a suitable catalyst that oxidizes CO in preference to, and in the presence of a large concentration of, hydrogen [6].

Another issue with carbonaceous fuels is the presence of contaminants, primarily sulfur in natural gas and petroleum-derived fuels, and small amounts of byproducts in synthetic fuels, such as commodity methanol. Catalysts typically used in the reforming process and/or the water-gas shift reaction are susceptible to sulfur poisoning. One approach applied in industrial practice to address this problem is to use an excess of catalyst to permit rated operation throughout the design life of the catalyst bed(s).

Reforming Energies for Methanol, Ethanol, and Natural Gas

The standard reaction energies (ΔH^{o}_{298}) for the steam reforming of methanol, ethanol, and methane (surrogate for natural gas), assuming complete conversion of the fuel to hydrogen and carbon dioxide, are:

$$CH_3OH(l) + H_2O(l) \rightarrow CO_2 + 3H_2 \qquad \Delta H^{o}_{298} = +131.0\text{ kJ}$$

$$CH_3OH(g) + H_2O(g) \rightarrow CO_2 + 3H_2 \qquad \Delta H^{o}_{298} = +49.5\text{ kJ}$$

for liquid and prevaporized methanol and water;

$$C_2H_5OH(l) + 3H_2O(l) \rightarrow 2CO_2 + 6H_2 \qquad \Delta H^{o}_{298} = +348.1\text{ kJ}$$

$$C_2H_5OH(g) + 3H_2O(g) \rightarrow 2CO_2 + 6H_2 \qquad \Delta H^{o}_{298} = +157.0\text{ kJ}$$

for liquid and prevaporized ethanol and water; and

$$CH_4 + 2H_2O(l) \rightarrow CO_2 + 4H_2 \qquad \Delta H^{o}_{298} = +253.0\text{ kJ}$$

$$CH_4 + 2H_2O(g) \rightarrow CO_2 + 4H_2 \qquad \Delta H^{o}_{298} = +165.0\text{ kJ}$$

for methane with water and steam. In each case, the energy needed to vaporize the reactants is more than half of the total energy required for the steam reforming of the liquid fuels with water. As will be discussed below, this requirement for the input of thermal energy into the process constrains the start-up and dynamic performance of steam reformers.

For the partial-oxidation reforming of these fuels, again assuming complete conversion of the fuel to hydrogen and carbon dioxide, the reaction energies are:

$$CH_3OH(l) + \tfrac{1}{2}O_2 \rightarrow CO_2 + 2H_2 \qquad \Delta H^{o}_{298} = -154.9\text{ kJ}$$

$$C_2H_5OH(l) + 1\tfrac{1}{2}O_2 \rightarrow 2CO_2 + 3H_2 \qquad \Delta H^{o}_{298} = -509.4\text{ kJ}$$

$$CH_4 + O_2 \rightarrow CO_2 + 2H_2 \qquad \Delta H^{o}_{298} = -318.7\text{ kJ}$$

Thus, the partial-oxidation reactions release energy, which is generally used to carry out some steam reforming to increase the yield of hydrogen. In that case, since the emission of thermal energy and the absorption of thermal energy both occur in the same process gas stream, *direct* heat transfer between the heating and the heated fluids can be used, resulting in very high effective heat transfer rates.

Reformate Compositions

The product composition depends on the reforming process used. In the steam reforming of methanol, for example, the nominal reformate composition is 75% H_2 and 25% CO_2 if a stoichiometric amount of water is used. In practice, however, an excess of water is necessary to reduce the amount of CO in the product gas. Even with 50% excess H_2O, some CO is produced; the gas composition of the steam-reformed product gas is typically 67% H_2, 21% CO_2, 11% H_2O, and about 1% CO. In the case of partial-oxidation reforming of methanol, the nominal product composition is 41% H_2, 21% CO_2, and 38% N_2 (for oxygen derived from air), if no carbon monoxide is formed. In practice, however, particularly in the high temperature (~700°C) partial-oxidation process, CO and CO_2 appear in roughly equal proportions in the product gas, which may then contain approximately 13% each of CO and CO_2, 50% H_2, and 24% N_2. If enough water is added to the partial oxidation process to achieve a thermally neutral reaction, and the same level of CO is assumed as in steam reforming, the product gas mixture will contain approximately 51% H_2, 19% CO_2, 19% N_2, 10% H_2O, and 1% CO.

For the low temperature PEFC, a final CO removal step is required to avoid poisoning of the noble metal catalyst in the fuel cell anode. This may be done using preferential oxidation at ≥400°C with a controlled, small amount of air over a platinum-based catalyst. Then, for a steam-injected partial oxidation reformer, the removal of 1% CO, using twice the amount of air necessary to oxidize the CO, would produce a final reformate containing 48% H_2, 20% CO_2, 11% H_2O, and 21% N_2. Selective oxidation of 1% CO from a steam reformer product would produce a gas containing 63% H_2, 22% CO_2, 11% H_2O, and 4% N_2. The difference in hydrogen concentration, 48% versus 63%, results in a Nernst voltage penalty of ~6 mV for a fuel cell operating on the partial-oxidation reformate as compared to the steam reformate.

Examples of PEFC Systems with Different Fuel Processing Options

The design and performance of PEFC systems fueled by hydrogen, methanol, and natural gas, have been analyzed for various fuel processing options [7]. In the case of hydrogen, the fuel processing needed depends on the hydrogen storage option used. Schematic system diagrams for compressed hydrogen and for hydrogen stored as magnesium hydride are shown in Figs. 1 and 2. The compressed-hydrogen-fueled PEFC system requires no fuel processing, other than perhaps occasional purging of the dead-ended anode gas to remove any inert contaminants. With hydrogen stored as magnesium hydride, on the other hand, the thermal energy of dissociation of the hydride must be added to the hydride bed to release the hydrogen for use in the fuel cell stack. Since the dissociation temperature of magnesium hydride, 300°C, is greater than that of the waste heat available from the PEFC stack, some of the generated hydrogen must be burned in the fuel processor. As an alternative method for on-board storage and generation of hydrogen, the steam-iron reaction has been proposed; a schematic system diagram based on this option is shown in Fig. 3. In this case, energy is needed to raise steam, again requiring that some of the generated hydrogen be burned within the fuel processing section of the PEFC system.

A methanol-fueled PEFC system with a steam reformer is shown schematically in Fig. 4. The energy for the endothermic steam reforming reaction is obtained by burning the spent anode gas. However, since the PEFC operates under pressure, the burner exhaust is also pressurized, and some energy is recovered from this exhaust by means of a turbine expander. Thus, the fuel processor in this system acts as the burner in a gas turbine cycle, in addition to producing the anode feed gas for the PEFC. Finally, Fig. 5 shows a PEFC system with compressed natural gas as the on-board fuel, reformed by the partial-oxidation process. In this system there is no recycle of the spent anode gas to the fuel processor. However, the spent anode gas contains hydrogen, which must be oxidized to water before being emitted to the environment. The energy available from this oxidation of waste hydrogen is not used within the PEFC system, but may well be used for the heating and/or cooling of the passenger cabin.

Effect of Fuel Processing on PEFC System Performance

The choice of on-board fuel, fuel storage, and fuel processing options greatly affects the efficiency, start-up and dynamic performance, and other operational parameters of the PEFC system. These factors also effect the design of the fuel cell/battery hybrid propulsion power system.

System Efficiency

As shown by the illustrative schematic system diagrams above, different fuels and fuel processing options can affect the efficiency of the PEFC system operated under steady state, at some selected design operating point. This is discussed in greater detail in Reference 7. Table 1, adapted from that work, summarizes the comparative efficiencies of the various options.

Table 1. Summary of system efficiencies for different fuels, fuel storage, and fuel processing options

Fuel, Storage, and Processing Option	**System Efficiency, %***
H_2, 200 atm	52.3
H_2, Mg Hydride	32.3
H_2, Fe-Ti Hydride	52.6
H_2, Glass Microspheres	51.2
H_2, Steam-Iron Generator	42.9
Methanol, Steam Reformer	44.8
Methanol, Partial-Oxidation Reformer	40.2
Natural Gas, Steam Reformer	41.1
Natural Gas, Partial-Oxidation Reformer	40.9

*Based on the lower heating value of the on-board fuel. Does not include the energy consumed in refueling the on-board fuel tank.

As is evident from this table, the compressed hydrogen and the low temperature iron-titanium hydride offer the highest design-point efficiencies of any of the options considered. It is not coincidental that these two options need the least fuel processing among the PEFC systems evaluated. As the complexity of the fuel processing subsystem increases, the efficiency of the fuel cell system decreases. Thus, the methanol, natural gas, and the steam-iron hydrogen production options have significantly lower energy conversion efficiencies, primarily because part of the fuel's energy is consumed in the fuel processing subsystem.

Start-up and Dynamic Performance

The discussion above has related, for the most part, to system operation at steady state and a defined design point of power generation. For heavy- and light-duty transportation applications, the start-up and dynamic performance of the fuel cell system are of equal, or perhaps greater, importance than just the energy conversion efficiency under steady-state operation. Some of these issues have also been discussed elsewhere [8].

Some aspects of the start-up of a methanol steam reformer were presented in an earlier paper [9]. Depending on the design geometry (e.g., diameter of the catalyst tubes), and the start-up protocol, it may take several minutes for the reformer to achieve the design amount of methanol conversion and hydrogen concentration in the product gas from the reformer. For example, Fig. 6 shows methanol conversion during cold start-up for 5-cm and 1-cm dia catalyst tubes, using hot combustion gas at 623°C (1160°F). The conversion increases more rapidly in the 1-cm dia tubes than in the 5-cm dia tubes, but even with the thinner tubes, it takes almost 10 min to get up to 50% conversion. The corresponding concentrations of hydrogen in the product gas are shown in Fig. 7. It takes the steam reformer several minutes to begin producing hydrogen, almost 5 min for the reformer with 5-cm dia tubes and 3 min for the reformer with 1-cm dia tubes. The profiles of methanol conversion along the length of the 1-cm dia catalyst tubes during cold start-up are shown in Fig. 8. Up to the first 10 min or so, only the first 20% of the catalyst is effective in converting the methanol-water feed.

In addition to the time for a cold start, the design of a fuel processor will affect the efficiency and the emissions from the PEFC system over a drive cycle. Any fuel consumed during the start-up will have a negative effect on the fuel economy. Similarly, emission of any regulated pollutants during start-up (i.e., before the design temperatures and temperature profiles are achieved) will contribute to the total emissions from the PEFC system. In general, the shorter the start-up time and the lower the thermal mass of the reformer, the less impact there will be on fuel economy and emissions.

Of the two major types of fuel reforming processes, the partial-oxidation reformer can be much superior in dynamic performance to the steam reformer, for two reasons. One reason is that the direct heat transfer in the partial-oxidation reformer is much more rapid and more efficient than the indirect heat transfer in a steam reformer. The other reason is that, in the case of the steam reformer, the energy needed to vaporize the fuel and water and to carry out the reforming reactions is obtained by burning the spent anode gas. With a dynamically varying system load, however, the availability of the spent anode gas *lags behind* the need for it at the reformer burner. Thus, for example, if a step increase is desired in fuel cell power output, vaporizing and reforming the additional fuel require energy *before* the excess spent anode gas becomes available; this spent anode gas becomes available only *after* the fuel cell stack begins delivering power at the higher demand level. This phase difference in the requirement and availability of thermal energy in the fuel cell power system suggests that for good dynamic performance, the thermal subsystems of the fuel cell stack and the vaporizer/reformer should be decoupled from each other. This is inherently so in a PEFC system with a partial-oxidation reformer since there is no recycle of the spent anode gas to the fuel processor.

Operating Logic of Hybrid Systems

The design, start-up and operating protocol, and dynamic response of the fuel processor can also influence the operating logic and trade-offs in fuel cell/battery (or other energy storage device) hybrid systems developed for transportation. Since the fuel cell stack can begin delivering electric power as soon as hydrogen becomes available to it, the start-up time of the complete PEFC system is governed primarily by the start-up time of the fuel processor. The start-up time of the fuel cell system has a direct bearing on the required energy capacity of the battery/energy storage device needed to provide the selected performance capability of the propulsion system during cold start. The issue of how a fuel cell is operated during the running of the vehicle is also affected by the dynamic behavior of the fuel processor and, in turn, the entire fuel cell system. While it is clear that the fuel cell must provide the total energy used by the vehicle over any given driving cycle, it is not known *a priori* whether the fuel cell should be used in a load-following manner, at a fixed power generation level with the battery providing for the load fluctuations, or perhaps in a "damped" load-following manner with both the fuel cell and the battery providing for the primary load variations. The dynamic performance of the fuel processor selected for the PEFC system essentially imposes a boundary condition on the hybrid system's operating logic.

Other Factors

The reformate in the system diagrams in Figs. 2–5 leaves the fuel processor at a temperature too high for feeding the gas directly to the fuel cell stack. This gas must be cooled to about 80°C, requiring a heat exchanger or direct cooling by water injection (this water, in turn, must be recovered from the fuel cell or reformer burner exhaust by means of a heat exchanger). Heat exchangers add weight and volume to the PEFC system, which are already severely constrained, particularly for light-duty vehicles.

For a given on-board fuel, the concentration of hydrogen in the partial-oxidation reformate is lower than that in the product gas from a steam reformer. Consequently, for the same power output from the fuel cell stack, a 20–25% greater mass flow rate of the anode gas is needed, perhaps requiring redesign of the anode gas flow fields within the polymer electrolyte fuel cells. The higher anode gas flow rate does not necessarily mean a higher net fuel consumption rate, however. The fuel economy is determined by the overall system efficiency, of which the fuel processor efficiency is only one component.

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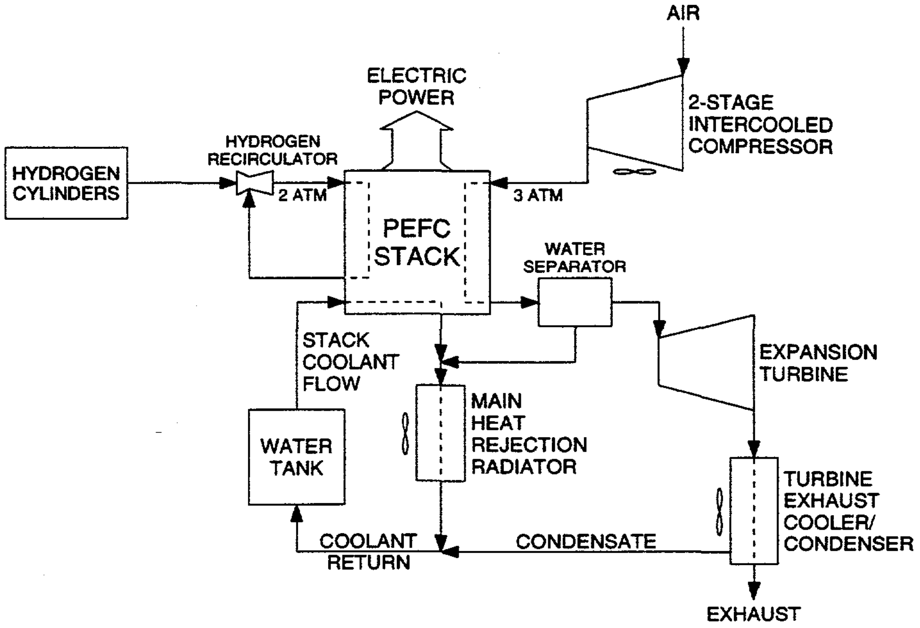

Fig. 1. Schematic diagram of a PEFC system with compressed H_2 on-board.

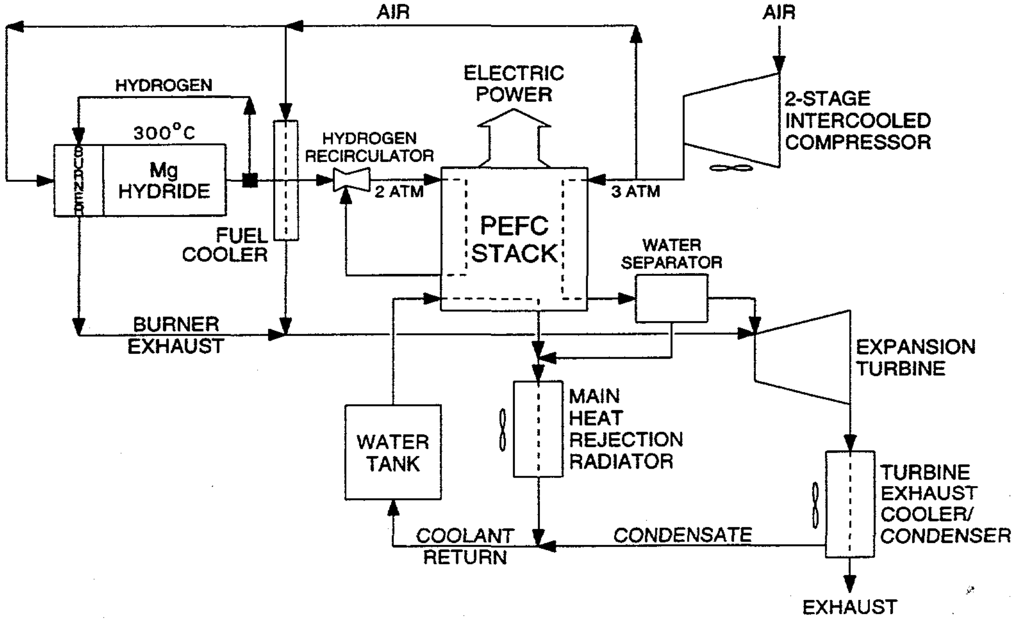

Fig. 2. Schematic diagram of a PEFC system with magnesium hydride storage of H_2.

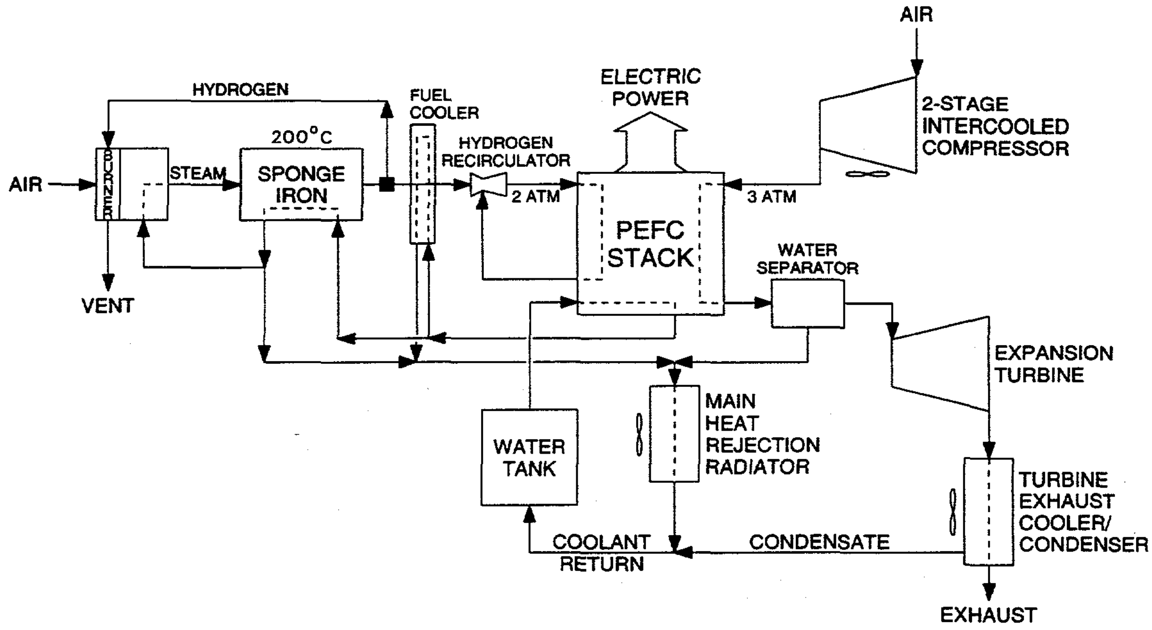

Fig. 3. Schematic diagram of a PEFC system with the steam-iron reactor for the on-board generation of H_2.

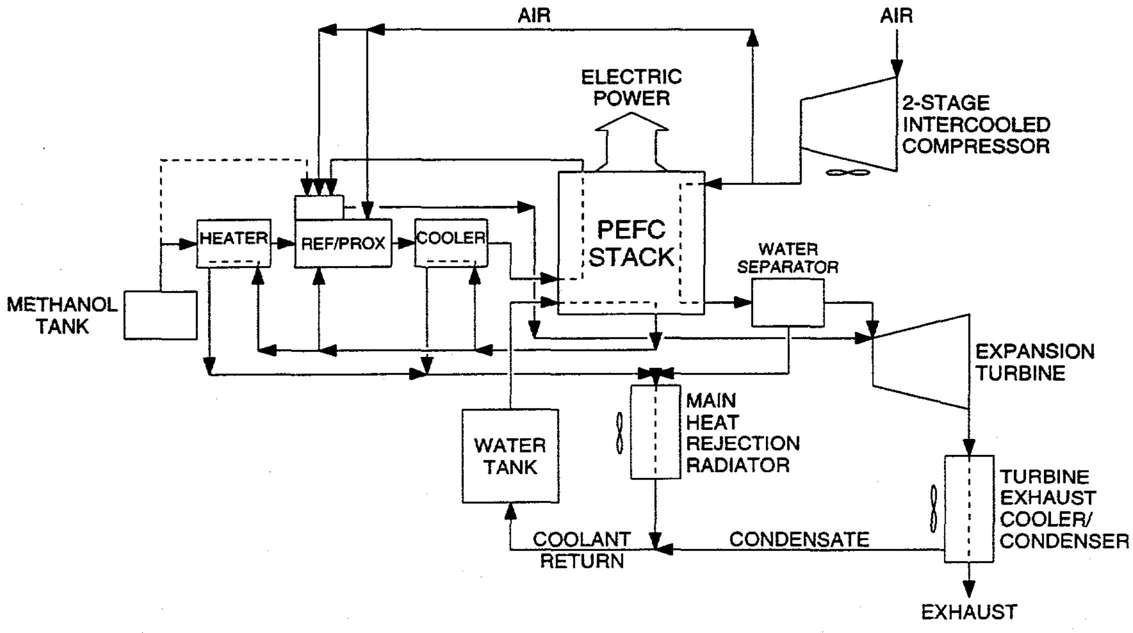

Fig. 4. Schematic diagram of a methanol-fueled PEFC system with a steam reformer.

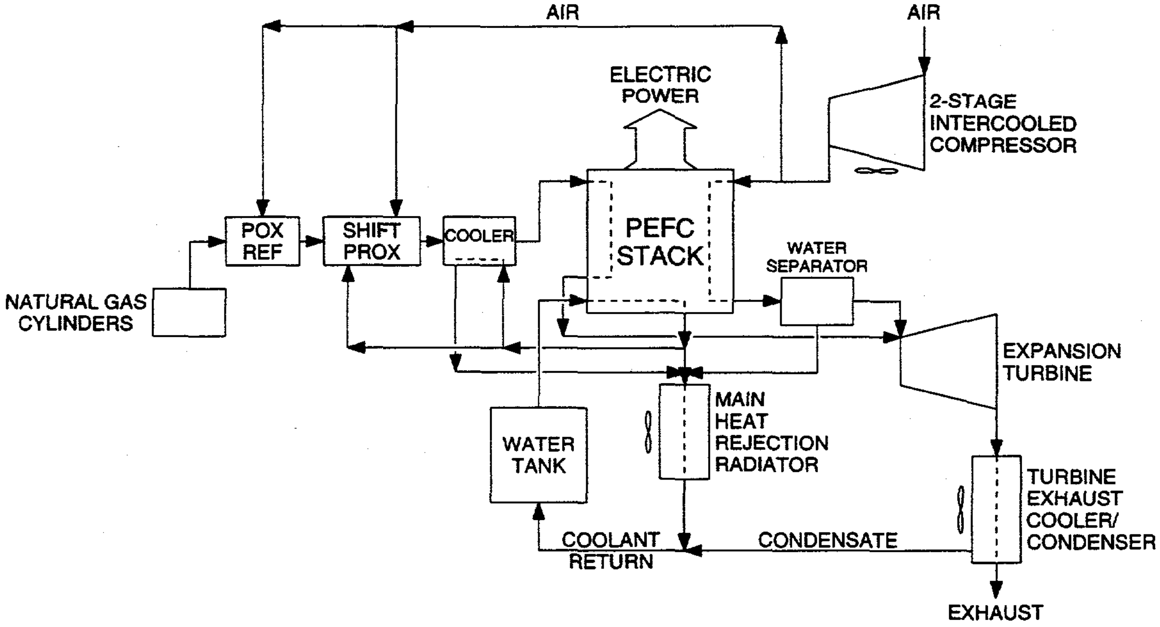

Fig. 5. Schematic diagram of a natural gas-fueled PEFC system with a partial-oxidation reformer.

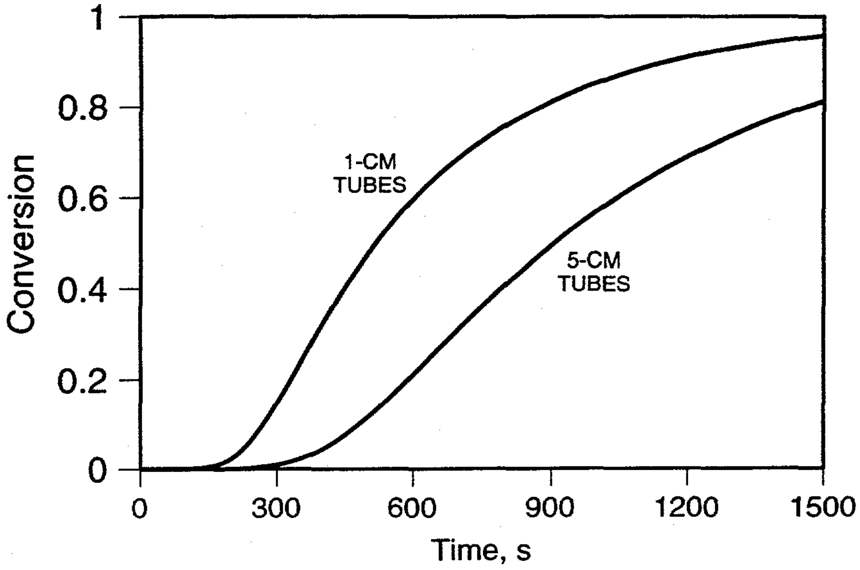

Fig. 6. Methanol conversion during start-up of a steam reformer for two different catalyst tube diameters.

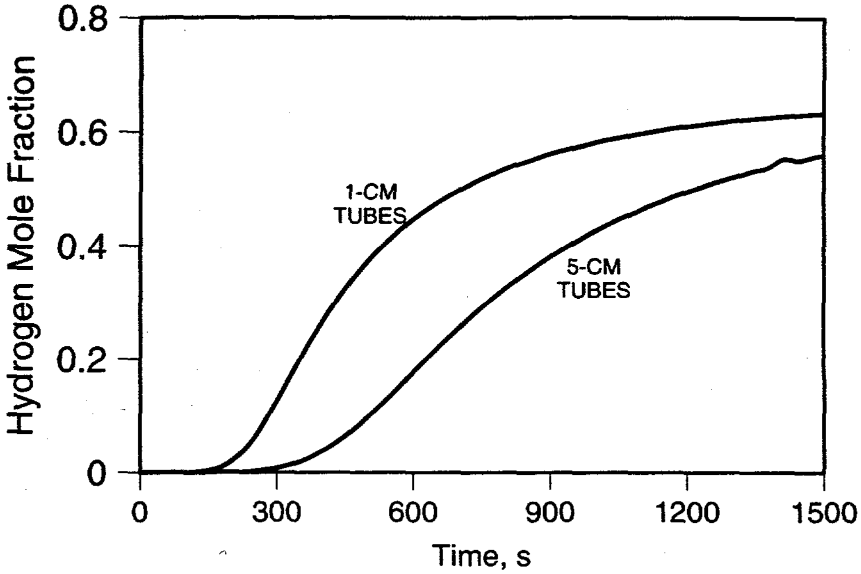

Fig. 7. Hydrogen concentrations in the steam reformer product gas during start-up.

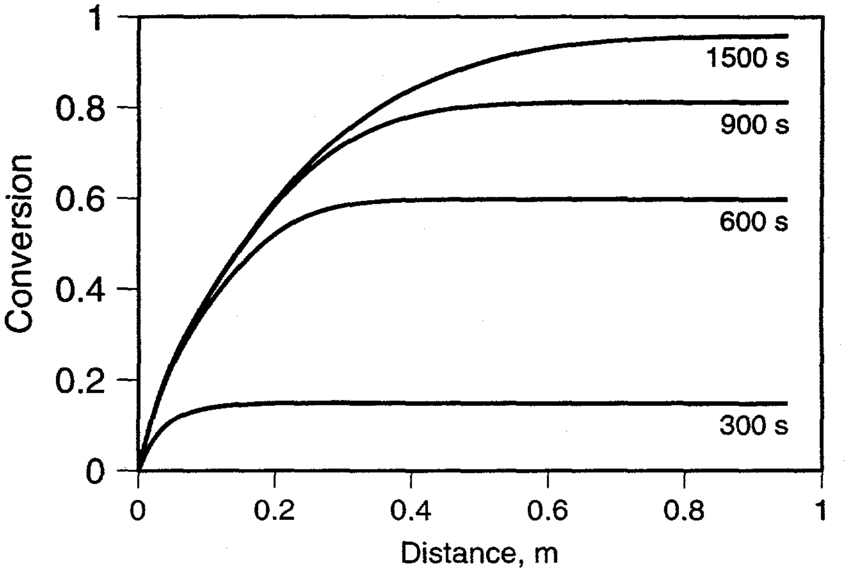

Fig. 8. Methanol conversion along the length of the 1-cm diameter catalyst tube in a steam reformer during start-up.