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FUELS PROCESSING FOR TRANSPORTATION FUEL CELL SYSTEMS*

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FUELS PROCESSING FOR TRANSPORTATION FUEL CELL SYSTEMS

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Abstract

Fuel cells primarily use hydrogen as the fuel. This hydrogen must be produced from other fuels such as natural gas or methanol. The fuel processor requirements are affected by the fuel to be converted, the type of fuel cell to be supplied, and the fuel cell application. The conventional fuel processing technology has been reexamined to determine how it must be adapted for use in demanding applications such as transportation. The two major fuel conversion processes are steam reforming and partial oxidation reforming. The former is established practice for stationary applications; the latter offers certain advantages for mobile systems and is presently in various stages of development. This paper discusses these fuel processing technologies and the more recent developments for fuel cell systems used in transportation. The need for new materials in fuels processing, particularly in the area of reforming catalysis and hydrogen purification, is discussed.

1. INTRODUCTION

Fuel cells combine hydrogen and oxygen electrochemically to produce electricity cleanly, efficiently, and quietly. While the oxygen is typically obtained from the air (in terrestrial applications), the hydrogen may be extracted from a variety of primary fuels, such as natural gas, petroleum-derived distillate fuels, or alcohols (methanol, ethanol), by a process called reforming, whereby the primary fuel is converted to a hydrogen-rich gas mixture. This fuel reformer is usually part of the fuel cell system. Of course, hydrogen may also be produced remotely from the fuel cell, for example, in space or submarine applications. In this paper, however, we focus on the conversion of a fuel such as methanol or natural gas within the fuel cell power system. One of the major aspects of such hydrogen production is the potential for the chemical and thermal integration of the fuel processor with the fuel cell stack and the balance of the plant [1].

The technology for reforming natural gas and other primary fuels into hydrogen has been employed in the chemical industry for decades. The potential application of fuel cells to transportation, however, has imposed new constraints on the fuel conversion processes. The fuel processor design is influenced by several factors, including the type of fuel cell it feeds, the primary fuel available, and the application. High-temperature fuel cells such as the solid oxide fuel cell (SOFC), operating at a nominal 1000°C, and the molten carbonate fuel cell (MCFC), operating at about 650°C, produce high quality waste heat that can be used effectively for the energy requirements of fuel processing. The waste heat from the low-temperature polymer electrolyte fuel cell (PEFC), operating at 80°C, is available at too low a temperature to be useful in fuel processing.

There are two major reaction pathways for converting fuels to hydrogen. One process is steam reforming, which combines a carbon-containing fuel with steam to produce carbon dioxide and hydrogen. These reactions are catalyzed and are endothermic. The second process is partial oxidation reforming, where the fuel is combined with sub-stoichiometric oxygen and steam to produce carbon dioxide and hydrogen. The partial oxidation reaction is exothermic and can be either catalytic or non-catalytic. Varying amounts of carbon monoxide are also produced in either fuel conversion process. This carbon monoxide is typically reacted with steam in a water-gas shift reactor to produce carbon dioxide and additional hydrogen in the fuel processor's product gas. Even small amounts of carbon monoxide in the fuel gas poison the platinum electrocatalyst in the PEFC. Therefore, the carbon monoxide content of the reformate must be reduced to only a few parts per million for use in the PEFC.

The high-temperature fuel cells (SOFC, MCFC) are being developed for stationary applications involving central and distributed power generation. These high-temperature systems offer significant fuel flexibility and high quality waste heat for cogeneration applications. Transportation applications, on the other hand, are leaning toward the lower temperature fuel cells, such as the 200°C phosphoric acid fuel cell (PAFC) and the PEFC. The U. S. Department of Energy (DOE) is developing a small fleet of three buses operating with a phosphoric acid fuel cell/battery hybrid system operating with methanol fuel. Each of the big three U. S. automakers (under DOE sponsorship) is developing PEFC systems for passenger cars. A PEFC-powered bus is being tested in Vancouver, British Columbia, while a PEFC-powered van has been demonstrated in Germany, but these two vehicles carry hydrogen as the fuel on-board and do not incorporate a fuel reformer in the fuel cell power system.

2. THE PRIMARY FUEL

Certain features are desirable in the primary fuel for fuel cell applications. These include high energy density; low reforming temperature; low levels of sulfur, chlorine, and other contaminants; and a relatively high hydrogen-to-carbon ratio. The conversion of the primary fuel to hydrogen is preferred at low temperatures; this permits heat recovery from other heat-releasing processes in parallel, lowers heat losses, allows use of a wider choice of hardware materials, and enables shorter start-up times. Since catalysts are used at various stages in the fuel processor and in the fuel cell, the fuel should be free of, or have a very low level of, contaminants such as sulfur and chlorine, which generally have a poisoning effect on catalysts. For example, natural gas must be desulfurized to prevent poisoning of the nickel and copper catalysts used in natural gas reformers and shift reactors, respectively. A reformate rich in hydrogen enhances fuel cell performance — this is facilitated by a fuel with a high hydrogen fraction (e.g., a high H/C ratio in the hydrocarbon). A high carbon content in the primary fuel results in higher carbon dioxide in the reformate, which reduces the mole fraction of hydrogen.

Methanol shows considerable promise as a primary fuel because it is a liquid at ambient conditions, and can therefore be stored and transported via a network similar to that existing for gasoline. Furthermore, it is a commodity chemical and is widely available; it can be produced from natural gas, biomass, or coal; and it is easy to reform. Although more difficult to carry out, reforming of conventional fuels such as gasoline or diesel is also attractive because of their high energy content and their existing production, distribution, and retailing infrastructure. Natural gas also has an extensive network (which may need upgrading to meet widespread use in transportation), but it has a lower energy density than liquid fuels, and requires high reforming temperatures of above 700°C.

3. DESIRABLE FEATURES OF THE FUEL PROCESSOR

The fuel processor represents a major step in the chain of converting fuel to power. While specifics of the reformer design are determined by the type of fuel cell to be supplied and the primary fuel to be converted, there are a number of desirable features for all fuel reformers.

The fuel processor must yield high hydrogen concentration in the reformate and a high conversion efficiency. Steam reformers for methanol and methane can theoretically produce up to 75% and 80% hydrogen on a dry basis, respectively. The conversion efficiency of the fuel processor should be high, that is, the energy content of the hydrogen in the product reformate should be a high percentage of the total energy input to the processor. The fuel processor must also remove from the reformate all species that may poison the electrocatalysts in the fuel cell.

When the fuel processing involves a catalyzed reaction, the catalyst should be active (i.e., process a large amount of fuel per unit weight, volume, and surface area); selective (i.e., catalyze the desired reaction(s) while suppressing undesirable reactions and byproducts); rugged (i.e., possess a high crush strength); resistant to deactivation; and inexpensive. The conversion of alcohols often results in the formation of methane, which once formed can only be converted to hydrogen at temperatures above 700°C. Each molecule of methane formed from methanol reforming represents a significant loss in reformer efficiency because it corresponds to two molecules of hydrogen that could have been used in the fuel cell.

The type of application also presents unique constraints and imposes additional requirements on the fuel processor. For example, applications which involve frequent start-ups and shutdowns, such as passenger cars, require a rapid start-up capability. In principle, this would be available with a simple, lightweight system (with few components and no recycle loops) operating at a low temperature. The start-up time is determined by the thermal mass of the critical elements in the system which governs the time required to reach the reformer operating temperature.

Mobile applications impose weight and volume constraints. Simple, compact fuel processors are desirable for these applications. Since the weight of the fuel processor adds to the total weight of the vehicle, a heavy fuel processor in turn requires a larger fuel cell with greater fuel consumption, leading to a propulsion system that is less fuel efficient.

If the application requires fuel cell operation at steady state for long periods with few or gradual power transients, as in a stationary power plant, effective system integration (material and energy) is possible and can result in efficient power generation. However, if the application requires numerous power transitions between brief steady states, as in transportation, then slow processes (e.g., indirect heat exchange) should be avoided to prevent long response times, even if some process integration must be eliminated.

The reformer design is significantly affected by the type of fuel cell. Because of their high operating temperatures, MCFC and SOFC, when designed to do so, can reform some fuels internally. In such cases, the job of the fuel processor may be limited to fuel purification or to initiation of the conversion reaction. These higher temperature fuel cells are more resistant to contaminants and can provide high quality waste heat to the fuel processor. On the other hand, the PEFC, operating at 80°C, is extremely sensitive to carbon monoxide. To bring this contaminant level to below 10 ppm involves conversion to carbon dioxide in a water-gas shift reactor, followed by selective oxidation over a catalyst. These additional processing steps, however, increase the complexity, weight, and volume of the fuel processor.

4. STEAM REFORMING OF METHANOL

The steam reforming of methanol is represented by the following reaction,

$$CH_3OH(l) + H_2O(l) = CO_2 + 3H_2 \qquad \Delta H_{298} = +131\ \text{kJ} \qquad (1)$$

This reaction can deliver a product stream that contains 75% hydrogen and 25% carbon dioxide on a dry basis. The reaction is strongly endothermic, requiring 131 kJ of energy per gmol of methanol reformed. Of this, 82 kJ (63%) is required for the vaporization of the liquid reactants. In practice, a steam-to-carbon ratio of 1.2 or higher is used, in which case the energy requirement increases to 140 kJ or more. The steam reforming of methanol is a well-studied reaction, and commercial catalysts (containing copper zinc oxide) can catalyze this reaction at the relatively low temperatures of 200–250°C with good selectivity. The steam reformer is typically not limited by the reaction-rate, rather by the rate at which the required heat of reaction can be transferred to the catalyst. Consequently, these reformers, with their large heat transfer area, resemble heat exchangers more than catalytic reactors. The energy required to vaporize the liquid feeds, preheat the vapors, and supply the heat of reforming reaction is obtained from hot gases flowing on the other side of a wall. The hot gases are generated by burning unreacted hydrogen in the anode effluent and supplemental fuel. The "steam reformer" usually houses the various components (vaporizer, preheater, reactor, burner) within a single unit. Such a design, although complex, maximizes the thermal efficiency of the reformer.

The unit operations of such a fuel processor in a PEFC system are illustrated in Fig. 1. The methanol feed from the fuel tank is initially split into two streams: the smaller stream goes to the burner as supplementary fuel to generate heat by combustion, while the other is mixed with water (in the desired proportion, 1.2 in this case) and becomes the process stream. The liquid mixture is preheated, vaporized, and further heated to the reformer inlet temperature of 200°C. The reforming reaction takes place while the heat of reaction is transferred to the process stream from the combustion gases across a wall. Some incidental heat loss (Q_l) to the ambient atmosphere occurs at this unit. The product gas leaves the reformer at 150°C containing 71% hydrogen. It is partially cooled as it passes through the liquid preheater and is then further cooled to the fuel cell (PEFC) inlet temperature of 80°C, before it enters the anode chamber. Air is fed to the fuel cell cathode chamber. The hydrogen in the anode gas reacts electrochemically with the oxygen in the cathode gas, generating electricity. At a fuel (hydrogen) utilization of 80% and a cell efficiency of 55%, the fuel cell produces 285 kJ of electricity and 233 kJ of waste heat. To maintain the fuel cell and the effluents at 80°C, 214 kJ of heat must be removed from the stack. The anode effluent, containing 33% hydrogen, and the cathode effluent, containing 12% oxygen, are fed to the burner. The oxidation of the supplementary methanol and the unreacted hydrogen generates heat and raises the temperature of the product gases to 496°C. Some heat loss (Q_4) also occurs in this unit. The hot gases from the burner transfer part of their sensible heat to the process stream in the steam reformer and the heat exchanger, before leaving the system as exhaust. The overall system efficiency (based on the lower heating value of methanol) under the specified conditions was calculated to be 44.6%. Efficiency calculations based on more rigorous system designs, operating under pressure have been reported by Kumar et al [2].

5. PARTIAL OXIDATION REFORMING OF METHANOL

The partial oxidation process combines methanol with oxygen (air) to oxidize the carbon to carbon oxides and release hydrogen. A typical partial oxidation reaction for methanol, using an oxygen-to-methanol molar ratio of 0.5, is represented by,

$$CH_3OH(l) + 0.5O_2 = CO_2 + 2H_2, \qquad \Delta H_{298} = -155\ \text{kJ} \quad (2)$$

The product can contain up to 66% hydrogen and 33% carbon dioxide. This is an exothermic reaction, releasing 155 kJ of energy. The exothermic nature of this reaction offers many advantages:

- These reactors are easy to start-up — once ignited, the reactors warm up to operating conditions quickly.
- These reactors permit direct liquid feed — when injected as a spray, the liquid vaporizes on contact with the hot gases and surfaces (direct heat transfer). This eliminates the need for separate vaporizers.
- The partial oxidation reformers do not require any heat exchange and, therefore, can be designed as simple adiabatic reactors which are much more compact and lightweight than steam reformers.
- These reactors are dynamically responsive to changes in the load, i.e., the hydrogen demand. During times of vehicle acceleration, when the fuel cell requires additional hydrogen, only the feed rate to the reformer needs to be increased. As long as the total feed rate is within the reactor's rated capacity and the oxygen-to-methanol ratio is maintained, the reactor will continue to process the additional feed and produce the additional hydrogen.

The use of air, as the source of oxygen, for the partial oxidation reaction leaves nitrogen as an inert gas in the reformate. This reduces the hydrogen concentration in the product gas. For example, if the oxygen in equation (2), where an oxygen-to-methanol molar ratio of 0.5 is used, is taken from air, then the maximum hydrogen concentration achievable is 41%. This is considerably lower than that available with the steam reformer and affects the fuel cell performance by reducing the Nernst potential of the cell. However, the hydrogen concentration in the reformate depends on the oxygen-to-methanol ratio in the reformer feed. It is possible to operate a partial oxidation reformer with an oxygen-to-methanol ration less than 0.5. This results in the formation of some carbon monoxide, which can be subsequently reacted with steam to produce carbon dioxide and additional hydrogen via the water-gas shift reaction:

$$0.5CH_3OH(l) + 0.25O_2 + 0.94N_2 = 0.5CO_2 + H_2 + 0.94N_2 \qquad \Delta H_{r,298} = -77\text{ kJ} \quad (3)$$

$$0.5CH_3OH(l) = 0.5CO + H_2 \qquad \Delta H_{r,298} = +64\text{ kJ} \quad (4)$$

$$0.5CO + 0.5H_2O(l) = 0.5CO_2 + 0.5H_2 \qquad \Delta H_{r,298} = +1.4\text{ kJ} \quad (5)$$

so that the net reaction is:

$$CH_3OH + 0.25O_2 + 0.5H_2O + 0.94N_2 = CO_2 + 2.5H_2 + 0.94N_2 \qquad \Delta H_{r,298} = -11.6\text{ kJ} \quad (6)$$

If the partial oxidation is conducted at an oxygen-to-methanol molar ratio of 0.25, the resulting product stream has a maximum hydrogen concentration of 56%. Figure 2 shows the maximum hydrogen concentration obtainable from partial oxidation as a function of the oxygen-to-methanol molar ratio. As anticipated, the hydrogen concentration increases linearly with decreasing oxygen. At the limiting molar ratio of zero, no partial oxidation takes place, and the reaction sequence becomes equivalent to the steam reforming reaction, producing a hydrogen concentration of 75%. The oxygen/methanol ratio is ultimately determined from an energy standpoint, where sufficient oxygen must be provided to generate heat via reaction (3) to support the endothermic dissociation reaction (4).

The actual oxygen-to-methanol molar ratio to be employed will ultimately be determined by such factors as the desirable operating temperature, the heat losses from the reactor, the amount of excess steam needed to accomplish the water-gas shift conversion, the location of water/steam feed (before partial oxidation or before shift conversion), the type of feed (liquid water or steam) into the system.

Figure 3 shows the temperature of the reformate after the partial-oxidation and the water-gas shift reactions as a function of the oxygen-to-methanol ratio, assuming water and steam. Adiabatic operation and stoichiometric feed of water and steam are assumed. The lower curve represents a process with liquid water injection, while the upper curve represents injection of saturated steam at 100°C. At an oxygen-to-methanol ratio of 0.5, the product temperature is 1027°C for both curves. There is sufficient oxygen available to convert all the carbon to carbon dioxide, and therefore, the water-gas shift reaction is not required. As the oxygen-to-methanol ratio is reduced below 0.5, the product temperature decreases, because less heat is generated via the partial oxidation reaction and more water or steam is needed for the water-gas shift reaction. The curve for liquid water is more sensitive to the oxygen-to-methanol ratio because of the additional heat required to vaporize the water. At a ratio of 0.25, the product gas temperature is 107°C with liquid water injection and 271°C with steam injection.

While reaction kinetics are favored by higher temperatures (faster reactions at higher temperatures), thermodynamic (e.g., product distribution) or catalytic (product distribution, catalyst deactivation) conditions may be favored at lower temperatures. For an operating temperature of, say, 200 °C the oxygen-to-methanol ratio is 0.275 with liquid water injection, which yields a hydrogen concentration of 55%. With steam injection, the same temperature can be achieved at a lower oxygen-to-methanol ratio of 0.23, giving a hydrogen concentration of 58%. This example illustrates the importance of the energetics on reaction stoichiometry and product control.

Figure 4 shows the schematic of a simplified PEFC system with a partial oxidation reformer for the fuel. The reformer feed, consisting of methanol, air, and water, enters the reactor unit at 25 °C. This simulation uses an air feed corresponding to an oxygen-to-methanol molar ratio of 0.25. The steam-to-methanol molar ratio is 0.55. The reactions generate heat, of which 1% is considered lost through the walls (Q_1). The product emerges at 90 °C, containing 56% hydrogen, 22% carbon dioxide, 21% nitrogen, and 1% water. The gas stream is cooled to 80 °C, the inlet temperature for the polymer electrolyte fuel cell. Air is fed to the fuel cell cathode. As in the steam-reformed methanol system described earlier, the fuel cell is considered to operate at a cell efficiency of 55% and consume 80% of the hydrogen feed. This generates 266 kJ of electric power. To maintain the fuel cell and effluent temperatures at 80 °C, 200 kJ of heat must be removed from the fuel cell. The waste gas from the anode contains 20% hydrogen; the cathode effluent contains 12% oxygen. The overall system efficiency (based on the lower heating value of methanol) was calculated to be 42%.

The unreacted hydrogen in the anode effluent represents a major source of energy loss from the system. If the anode and cathode effluents were combined and the hydrogen allowed to oxidize, the heat generated would raise the temperature of the resulting gases to 342 °C. This energy can be recovered and used in an auxiliary system that requires heat, e.g., heating (or cooling) of the passenger cabin.

6. STEAM REFORMING VS. PARTIAL OXIDATION REFORMING

A methanol steam reformer can produce a reformate containing up to 75% hydrogen. The maximum hydrogen concentration possible from a partial oxidation reformer is determined by the oxygen-to-methanol molar ratio (e.g., 41% hydrogen at $O_2/CH_3OH = 0.5$). The higher hydrogen concentration afforded with the steam reformer yields a slightly higher Nernst potential in the fuel cell. Increasing the hydrogen concentration from 41% to 75% results in a Nernst voltage advantage of 9 mV (~0.8%).

The fuel cell system employing the partial oxidation process is simpler in that it uses fewer components, a once-through flow pattern, and only two heat exchangers (Fig. 4). In contrast, the system using the steam reformer (Fig. 1) has flow splitting, recycle loops, and multiple heat exchangers. The steam reformer unit itself, because of its large heat transfer area, tends to be large and heavy.

The exothermic partial oxidation process enables direct injection of liquid feed, while steam reformers require pre-vaporization. The exothermic reaction warms the reactor up rapidly during start-up, while steam reforming is slower because the catalyst has to be heated from across a physical boundary.

The partial oxidation process is inherently suited for load following [3]. During times of increased hydrogen demand, only the feed rates need to be increased. As long as the feed proportions are maintained and the feed rate is within the reactor's rated capacity, the reactor will respond with increased product. With the steam reformer, both the feed rate and the heat transfer rate must be increased simultaneously. The transfer of heat across a physical boundary is a slower process. Another significant concern with the load following capability of the steam reformer system (Fig. 1) is that part of the heat for the reforming reaction is obtained by burning the unreacted hydrogen in the anode effluent. During a step increase in hydrogen demand, vaporizing and reforming of the additional fuel require energy *before* the excess unreacted hydrogen becomes available, which happens *after* the stack begins delivering electricity at the higher power level. In other words, the heat required to process additional fuel is not immediately available from the anode effluent because the additional hydrogen (which must be burned to generate the additional heat) is not present in that stream. This results in a lag between heat demand and supply in the steam reformer. This phase difference in the requirement and availability of thermal energy in the fuel cell system suggests that the thermal subsystems of the stack and the endothermic vaporizer/reformer should be independent of each other to obtain good dynamic performance for the system as a whole.

The anode effluent from a fuel cell system using the partial oxidation reformer carries unreacted hydrogen with it. The energy associated with this hydrogen is not recoverable within the fuel cell system and thus decreases the overall system efficiency. The steam reforming system, on the other hand, permits effective recovery of the unreacted hydrogen in the anode effluent. However, during step increases in hydrogen demand, the additional energy is not available when needed and, thus, additional methanol must be burned. During this sequence, the system efficiency drops. Thus the higher system efficiencies of steam reformers are possible only during steady-state operations. Applications which encounter numerous load changes, such as typical transportation applications, cannot achieve these high system efficiencies. Such systems are likely to be better served by the simpler, more compact, and more dynamically responsive partial oxidation reformer.

Fuel cell systems with partial oxidation reformers lose energy with the anode effluent, significantly decreasing system efficiency. The efficiency can be improved if the fuel cell can be operated at higher fuel utilizations so that the amount of unreacted hydrogen leaving the fuel cell stack is reduced. A plot of the efficiency of fuel cell systems with partial oxidation reforming and steam reforming as a function of the electrochemical fuel utilization is shown in Fig. 5. The steam reformer system has an efficiency of 44% at a fuel utilization of 70%, increasing to 45.1% at 90% fuel utilization. The two curves for the partial oxidation system show strong sensitivity to the fuel utilization. The lower curve represents an oxygen-to-methanol ratio of 0.5 and varies from 29.2% to 37.5% efficiency as the fuel utilization is increased from 70% to 90%. The upper curve, representing an oxygen-to-methanol ratio of 0.25, shows an efficiency increase from 36.5% at 70% fuel utilization to 46.9% at 90% fuel utilization. Thus, for the conditions used in these simulations, the system efficiency is higher for partial oxidation than steam reforming at fuel utilizations above 87%.

7. TRANSPORTATION STEAM REFORMERS

The DOE fuel cell bus is presently using a methanol steam reformer developed by Fuji Electric Co. for use with a phosphoric acid fuel cell. A schematic of this design is shown in Fig. 6 [4]. It is rated for use with a 50 kW(e) fuel cell, weighs 266 kg, has a volume of 0.4 m^3, operates at a steam-to-methanol ratio of 1.5, and can produce up to 47 Nm^3/hr of hydrogen. At steady state, the product stream contains (on a wet basis) 65% hydrogen and less than 2% carbon monoxide. The heat for the endothermic process is provided by burning supplemental methanol and fuel cell exhaust gas in the reformer burner.

A 60 kW(e) methanol steam reformer [5] has been proposed for the GM-Allison passenger car, to be powered by a polymer electrolyte fuel cell. The feed methanol and water (steam-to-methanol ratio of 1.3) will be vaporized with heat from the burner exhaust and then injected into a heterogeneous recirculating gas catalytic converter (steam reformer). This reformer is being developed, at a 10 kW(e) level, by Los Alamos National Laboratory. The heat transfer section is separate from the catalyst section, and a gas recirculation rate of 20–50 times the net fuel processing rate is used to prevent significant reactant cooling during the endothermic reaction.

8. TRANSPORTATION PARTIAL OXIDATION REFORMERS

A. D. Little, Inc. is pursuing the development of a multifuel reformer under the sponsorship of the U.S. Department of Energy [6]. The objective of that program is to develop a 50 kW(e) ethanol fuel processor for possible use in one of the DOE fuel cell (PAFC) buses. A. D. Little is presently testing a half-scale bench-top reformer. This reformer is operated with ethanol and air, preheated to ~250°C, with the air flow rate at an equivalence ratio of 3. The equivalence ratio is defined as the ratio of the stoichiometric mols of oxygen required for complete combustion to the actual moles of oxygen used. The reactor consists of a non-catalytic region near the injectors where the oxidation reactions take place, followed by a catalyzed section. Nickel reforming catalysts and three-way automotive catalysts have both been tried and found to be effective.

A 10 kW(e) catalytic partial oxidation reformer for methanol is being developed at Argonne National Laboratory [7]. A schematic of the reformer is shown in Fig. 7. Liquid methanol is sprayed in as a fine mist at the top and is mixed in and carried down with the oxidation air. The mixture first passes through an electrically heated igniter coil. The reactant mixture ignites and generates sufficient heat to vaporize some methanol and raise the mixture temperature so that the reaction can continue in the catalyst section that follows. The catalyst is copper zinc oxide supported on honeycomb disks. The product gas is cooled and analyzed. Testing of the reformer has shown that the reactor can reach operating temperatures (≥200°C) and exceed 10% hydrogen (dry basis) in well under a minute. Operating at an oxygen-to-methanol ratio of 0.25, the reactor produced a gas stream that contained (on a dry basis) 36–40% hydrogen, 16–18% carbon monoxide, 7–9% carbon dioxide, and less than 0.5% methane at steady state. This gas stream should produce over 45% hydrogen after converting the carbon monoxide in the water-gas shift reactor. There are a number of ways to obtain the steam for the shift reaction, the simplest being to co-inject some water with the methanol feed at the reformer inlet. Indeed, this water co-injection should be beneficial by providing more uniform temperatures. Studies of transient response of the reactor are in progress.

9. RESEARCH AND DEVELOPMENT NEEDS

The production of hydrogen from hydrocarbons has been practiced in the chemical process industries for many years. The potential use of fuel cells in the transportation sector brings opportunities for new fuels and processes, and also imposes new constraints for the processes.

Reforming at temperatures close to or below the fuel cell temperature is beneficial from the standpoint of overall efficiency. Although steam reforming of methanol can be achieved at relatively low temperatures (250°C), other fuels such as natural gas or ethanol, which are also promising as primary fuels, require considerably higher temperatures. The development of lower temperature reforming catalysts for these fuels, which can provide high activity and good product selectivity, will significantly advance the overall fuels processing by helping to improve fuel conversion efficiencies as well as widening the choice of alternative fuels.

At the present stage of fuel processing technology for fuel cells, considerable effort is being directed toward the post-processing of reformate. Instead of removing the contaminants, such as carbon monoxide, from the product gas, the potential advantages are much greater if efforts focus on extracting hydrogen in the reformate stream economically. This is particularly true in fuel cells where the product water is formed at the cathode, e.g., the PEFC. The channel containing the extracted hydrogen can then end at the anode, resulting in zero hydrogen wastage. The use of pure hydrogen in the anode will enable 100% fuel utilization and increase system efficiencies resulting from higher Nernst potentials. Current hydrogen permeation technologies (membranes, transfer through palladium, etc.) are either limited in the permeation rate or require excessive temperature and/or pressure.

10. CONCLUSION

The design of the fuel processor is ultimately determined by three important considerations: the primary fuel, the type of fuel cell, and the application. While all fuel processor designs are driven by some performance criteria, transportation applications using low temperature fuel cells, especially the PEFC, set the most demanding constraints on process conditions and deliverable products. These requirements and restrictions are best served by partial oxidation systems because they are simple, compact, and responsive. Operation of partial oxidation reformers at an oxygen-to-methanol ratio of 0.25 can provide 56% hydrogen in the reformate after the water-gas shift reactor. The energy associated with the unreacted hydrogen in the anode exhaust can be recovered by parallel energy-consuming processes. This fuel processing technology will be advanced significantly with better catalysts and materials for hydrogen purification/enrichment.

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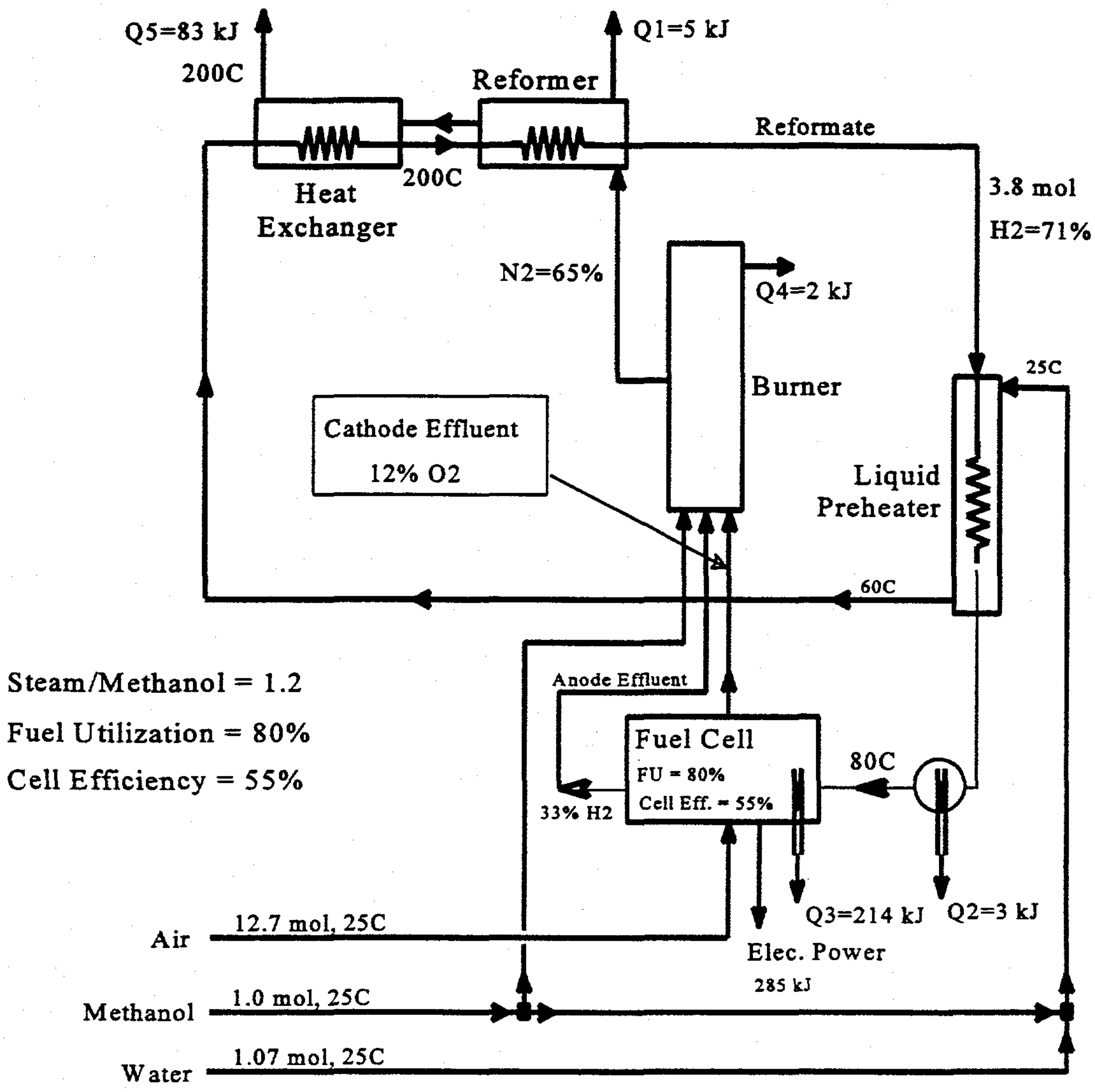

Fig. 1. Schematic of a methanol steam reformer in a polymer electrolyte fuel cell system.

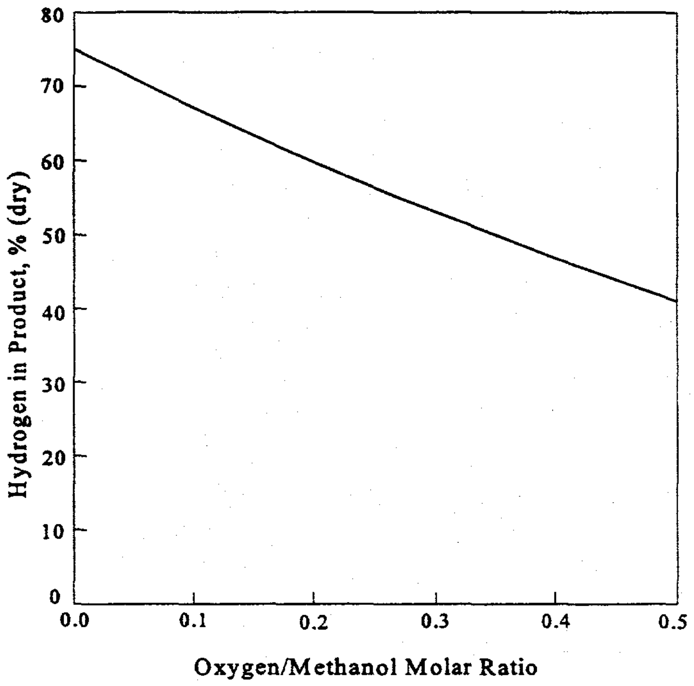

Fig. 2. Hydrogen concentrations in product (dry) from a partial oxidation reformer, as a function of the oxygen-to-methanol molar ratio.

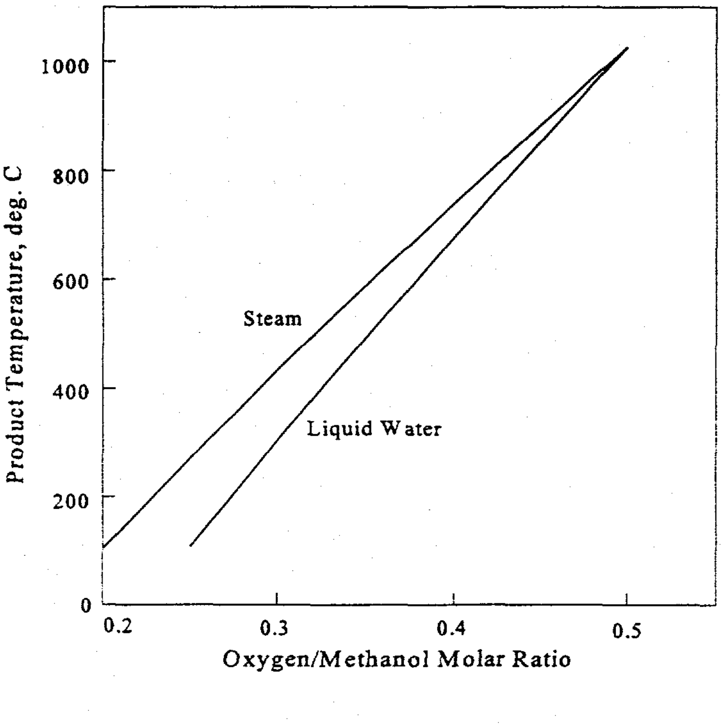

Fig. 3. Product temperatures from a methanol fuel processor (partial oxidation and water gas shift reactors) operating adiabatically, as a function of the oxygen-to-methanol molar ratio.

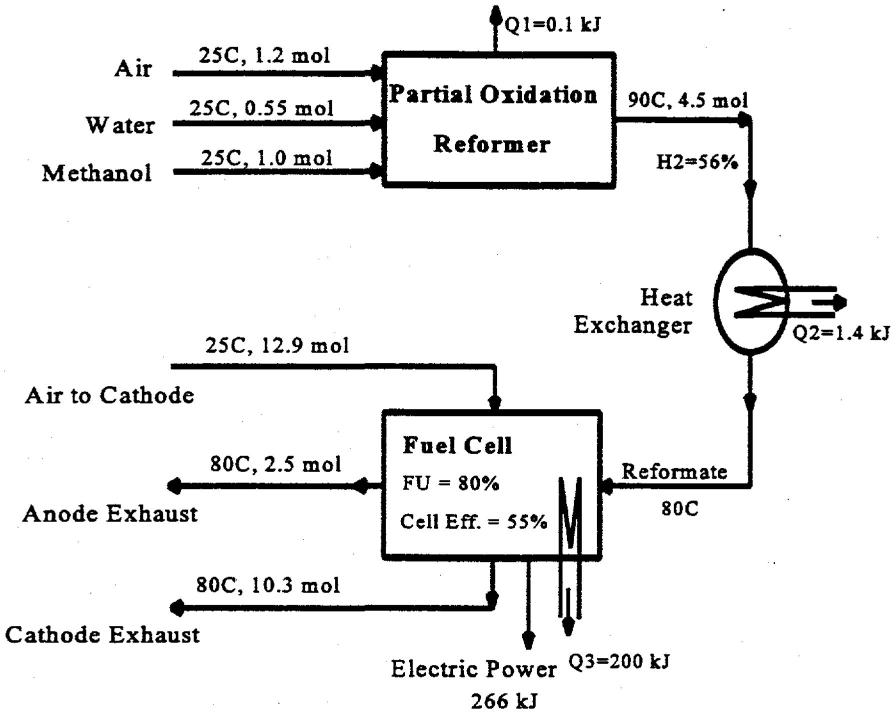

Fig. 4. Schematic of a methanol partial oxidation reformer in a polymer electrolyte fuel cell system.

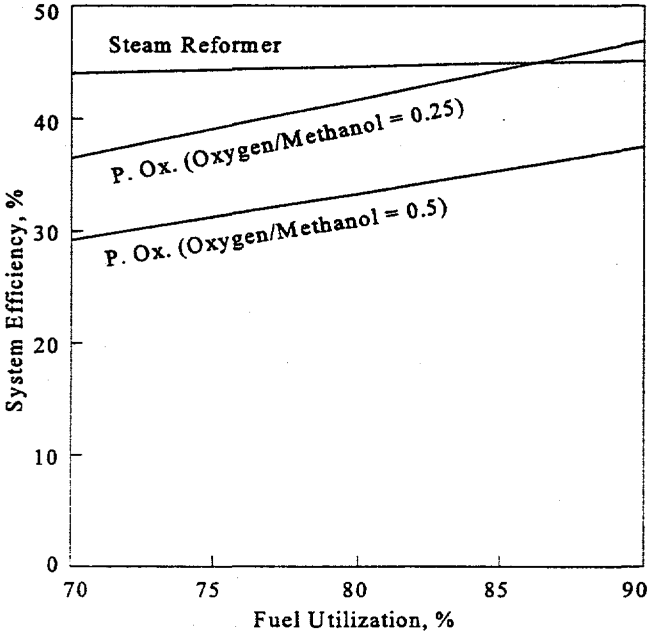

Fig. 5. Comparison of system efficiencies obtainable with steam reformer and partial oxidation reformer (at two oxygen/methanol ratios), as a function of hydrogen utilization in the fuel cell.

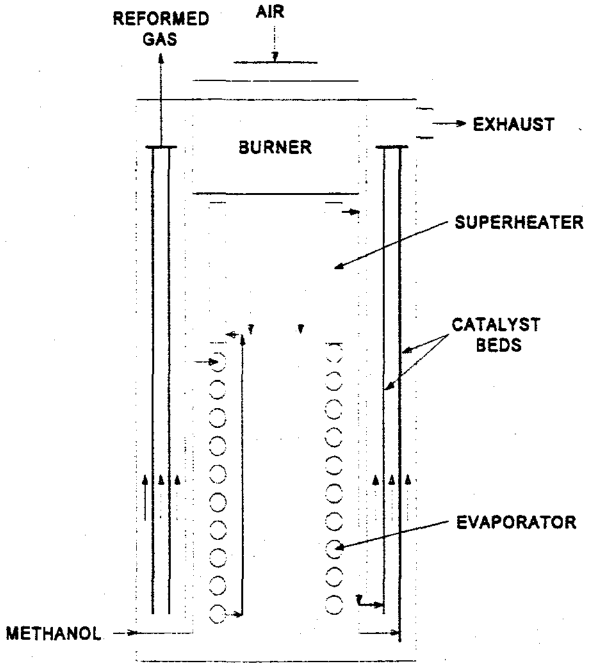

Fig. 6. Schematic of a methanol steam reformer designed for a DOE fuel cell bus.

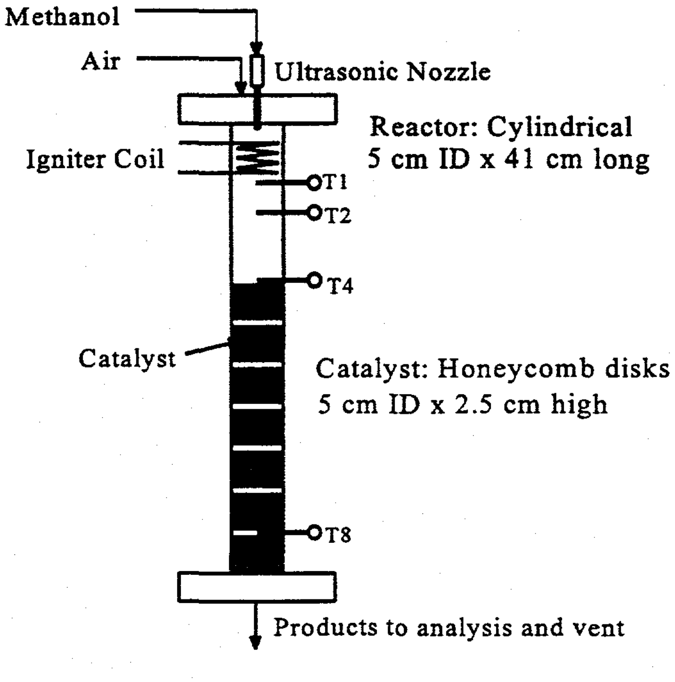

Fig. 7. Schematic of a 10 kW(e) methanol partial oxidation reformer being developed at Argonne National Laboratory.