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**REFORMERS FOR THE PRODUCTION OF HYDROGEN
FROM METHANOL AND ALTERNATIVE FUELS
FOR FUEL CELL POWERED VEHICLES**

by

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**Electrochemical Technology Program
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MASTER

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ABSTRACT

The objective of this study was (i) to assess the present state of technology of reformers that convert methanol (or other alternative fuels) to a hydrogen-rich gas mixture for use in a fuel cell, and (ii) to identify the R&D needs for developing reformers for transportation applications.

Steam reforming and partial oxidation are the two basic types of fuel reforming processes. The former is endothermic while the latter is exothermic. Reformers are therefore typically designed as heat exchange systems, and the variety of designs used includes shell-and-tube, packed bed, annular, plate, and cyclic bed types. Catalysts used include noble metals and oxides of Cu, Zn, Cr, Al, Ni, and La.

For transportation applications a reformer must be compact, lightweight, and rugged. It must also be capable of rapid start-up and good dynamic performance responsive to fluctuating loads. A partial oxidation reformer is likely to be better than a steam reformer based on these considerations, although its fuel conversion efficiency is expected to be lower than that of a steam reformer. A steam reformer better lends itself to thermal integration with the fuel cell system; however, the thermal independence of the reformer from the fuel cell stack is likely to yield much better dynamic performance of the reformer and the fuel cell propulsion power system.

For both steam reforming and partial oxidation reforming, research is needed to develop compact, fast start-up, and dynamically responsive reformers. For transportation applications, steam reformers are likely to prove best for fuel cell/battery hybrid power systems, and partial oxidation reformers are likely to be the choice for stand-alone fuel cell power systems.

SUMMARY

The objective of this study was to assess the present state of technology of reformers for converting methanol and other alternative fuels to a hydrogen-rich gas mixture for use as the anode gas in a fuel cell. A related objective was to identify the R&D needs for developing reformers that achieve the start-up, steady-state, and transient/dynamic performance requirements necessary for fuel cell powered vehicles.

Methanol and other alternative fuels must be converted (reformed) to a hydrogen-rich gas for such fuels to be used in fuel cells. The reforming of methanol requires temperatures of 200°C or higher, while the reforming of ethanol or hydrocarbons requires temperatures $\geq 450^\circ\text{C}$. For the proton exchange membrane fuel cell (operating temperature $\sim 80^\circ\text{C}$) and the phosphoric acid fuel cell (operating temperature $\sim 190^\circ\text{C}$), this fuel processing must be carried out in an external reformer, i.e., outside the fuel cell stack. For the higher temperature fuel cells, such as the molten carbonate (operating temperature 650°C) and the solid oxide (operating temperature 1000°C) fuel cells, this fuel conversion may be carried out within the fuel cell stack.

There is a variety of reformer designs, including shell-and-tube, packed bed, annular, plate, and cyclic bed reformers. Catalysts used include noble metals and the oxides of Cu, Zn, Cr, Al, Ni, and La, both as pellets and as monolithic blocks. Such reformers can produce hydrogen-rich gases from a variety of fuels, including methanol, ethanol, natural gas, propane, hexane, gasoline, diesel, and naphtha.

An external fuel reformer must process the methanol or other alternative fuel at the rate necessary for the fuel cell's maximum load. In addition, the reformer must be capable of fast response to the rapidly and widely fluctuating load on the fuel cell in a transportation application. Further, since the fuel processing occurs at an elevated temperature, the reformer must reach its operating temperature and produce hydrogen-rich fuel gas within a few seconds from cold start for general automotive applications; longer start-up times may be acceptable for fleet and mass transport applications.

Partial oxidation and steam reforming are the two basic types of reforming processes available for the conversion of methanol and other alternative fuels to a hydrogen-rich gas mixture. Partial oxidation reforming of methanol is exothermic overall (i.e., yields excess heat in the process) and produces a reformed gas containing 48% H₂, 20% CO₂, 11% H₂O, and 21% N₂. Steam reforming of methanol is endothermic overall (i.e., requires the input of external thermal energy) and yields a product gas containing 63% H₂, 22% CO₂, 11% H₂O, and only 4% N₂.

From thermodynamic analyses, we have estimated that a fuel cell system with a partial oxidation reformer has a gross energy efficiency of 29.4%. In a fuel cell system with a steam reformer, the gross energy efficiency ranges from 31.7% to 44%, depending on whether or not the waste heat from the fuel cell stack can be used to vaporize the methanol and water and/or to provide the heat of reaction. The lower efficiency of the partial oxidation reformer is offset, however, by its potentially much superior load following dynamic performance, as discussed below.

Commercial processes have long been employed in the petroleum and petrochemical industries for the manufacture of hydrogen by steam reforming and partial oxidation of hydrocarbon feedstocks, such as natural gas, propane, butane, and naphtha. Similarly, technology has been developed for the steam reforming of methanol for steady load conditions in stationary applications and in hybrid power transportation applications. For example, methanol reformers have been developed by Energy Research Corp. and by Booz, Allen and Hamilton, Inc., for a program to develop a fuel cell/battery powered bus. These reformers give high conversion and good product quality when operated under design conditions. However, they have poor response to variable load requirements, and are not likely to be acceptable for transportation use in stand-alone fuel cell systems. Even for hybrid systems, it is desirable to reduce their size, weight, and start-up times.

Some reformers are being developed specifically for transportation applications. An example is the reformer with a high gas recirculation rate being developed by Los Alamos National Laboratory. That design substantially improves the reforming system's dynamic performance. Issues of fast enough start-up and adequately high heat transfer rates, however, have not yet been resolved fully.

In a generic sense, for use in transportation applications, a partial oxidation reformer is likely to have start-up and dynamic performance characteristics superior to those of a steam reformer because of the exothermic versus endothermic reaction, and because of the rapid and efficient direct heat transfer between the combustion products and the process gas. Also, a partial oxidation reformer is likely to be mechanically simpler and more compact than a steam reformer, making it more desirable for transportation applications.

The fuel reformer can be thermally integrated with the rest of the fuel cell system, or operated independently. In a thermally integrated system, the thermal energy requirements of the reformer are met, at least in part, by the excess heat generated in the fuel cell stack; in a thermally independent reformer, heat required by the reforming process is provided by the combustion of the fuel methanol itself. For fuel cell/battery propulsion systems, where the fuel cell operates at essentially constant power output, thermal integration is practical. For stand-alone fuel cells in automotive applications, where the fuel cell output must vary widely and rapidly, including periods of operation at idle or standby conditions, thermal integration of the reformer with the rest of the fuel cell system is likely to be impractical. For thermally independent systems, partial oxidation and steam reforming offer comparable energy efficiencies.

None of the methanol reformers presently available has demonstrated the performance capability needed for an automotive system powered by a stand-alone fuel cell. It is recommended that a reformer capable of processing 15-25 kg/h (33-55 lb/h) of methanol be developed for this specific application. Such a reformer should incorporate a small and lightweight multiple-catalyst bed, direct heat transfer (partial oxidation), and water injection. It should be designed to operate thermally independently from the rest of the fuel cell system. Even for fuel cell/battery systems, it is recommended that the presently available steam reformers be improved further to reduce their size, weight, and start-up times by incorporating design features that enhance heat transfer.

I. OBJECTIVE

The objective of this study was to assess the present state of technology of reformers for converting methanol (and other alternative fuels) to a hydrogen-rich gas mixture to be used as the anode gas in a fuel cell and to determine their adaptability to use in a fuel cell powered vehicle. To this end, we examined the requirements for a stand-alone fuel cell and reformer in transportation applications, investigated the thermodynamics involved in the reforming of methanol (as well ethanol and methane), reviewed the literature on catalysts for the production of hydrogen from methanol, reviewed the literature on current reformer designs and applications, and determined the advantages and disadvantages of the two basic kinds of reformers (partial oxidation and steam reforming). On the basis of this information, we provide recommendations for use of reformers with fuel cell powered vehicles and give some suggestions for future technology development needs.

II. REQUIREMENTS FOR FUEL CELLS AND REFORMERS IN TRANSPORTATION APPLICATIONS

Fuel cells are being developed for use in automotive propulsion systems as alternatives for the internal combustion engine in buses, vans, and passenger cars.^{1,2} Low emissions of pollutants, high fuel energy conversion efficiencies, superior acceleration, low noise and vibration, and the possibility of using coal- or biomass-derived alcohols rather than petroleum-based fuels are the major motivations.

Adaptation of fuel cells to vehicle use, however, poses some severe challenges. In addition to being cost-competitive with current and projected conventional technology, the fuel cell power subsystem must be able to provide acceptable dynamic response to power demand fluctuations, high enough power density to fit within the weight and space limitations of vehicle design, and quick start up. It must also satisfy other considerations, such as ruggedness, drivability, safety, and long operating lifetimes.

These challenges are being met, at least in a limited sense. A multiyear program is underway to demonstrate a small bus powered by a methanol-fueled fuel cell/battery for urban transportation.³ For this bus, the fuel cell subsystem provides the average power requirement of 50 kW on an essentially steady basis, while the battery subsystem provides the surge power needed for acceleration and hill climbing.

One issue that has a great bearing on the adaptability of fuel cells to transportation applications is the conversion of the primary fuel to hydrogen or a hydrogen-rich gas mixture suitable for use in a fuel cell. Hydrogen can be produced from methanol and other alternative fuels by reforming (with or without steam) or catalytic oxidation. The desired features for such a portable reformer include rapid start-up, dynamic performance responsive to fluctuating loads, efficient and complete fuel conversion, small size and weight, simplicity of construction and operation, long life, and low cost.

For a stand-alone fuel cell system for a vehicle, perhaps the most important operational requirement is the ability to supply the necessary power on demand for the dynamically fluctuating load. For example, the simulated velocity and power profiles for a small car, the IETV-1, operating on the SAE J227aD driving schedule are shown in Fig. 1.

As the vehicle accelerates from 0 to 72.4 km/h in 28 s, the power demand increases rapidly to 21.7 kW at 14 s, followed by a gradual reduction to 15.1 kW by 28 s. During vehicle cruise at 72.4 km/h the power demand is 6.9 kW for the next 50 s, followed by a drop to 0 kW as the vehicle slows to a stop. The Federal Urban Driving Schedule (FUDS) and its simplified version, the SFUDS, are more demanding in terms of both the power fluctuations and the peak power required for the same vehicle. The velocity and power profiles for the IETV-1 simulated on the SFUDS are shown in Fig. 2. In addition to a more complex velocity and power profile than was the case for the J227aD, the peak power requirement rises sharply to 29.3 kW. The nominal cruise power is 10–30% of peak power demand, while sustained power is ~75% of peak power. On the SFUDS schedule the vehicle's power demand undergoes 15 step changes in 6 min; in an actual urban driving situation, the fluctuations are typically more numerous, more complex, and, of course, more irregular.

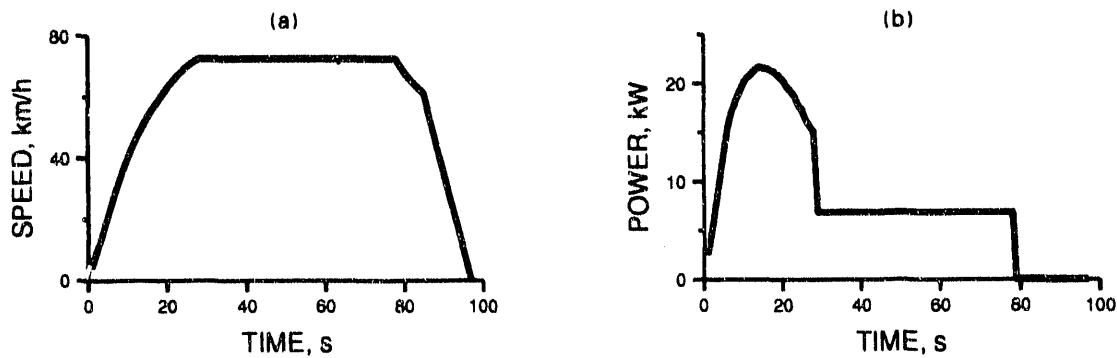


Fig. 1. Velocity and Power Profiles for the IETV-1 Simulated on the SAE J227aD Driving Schedule: (a) Velocity vs. Time and (b) Power vs. Time

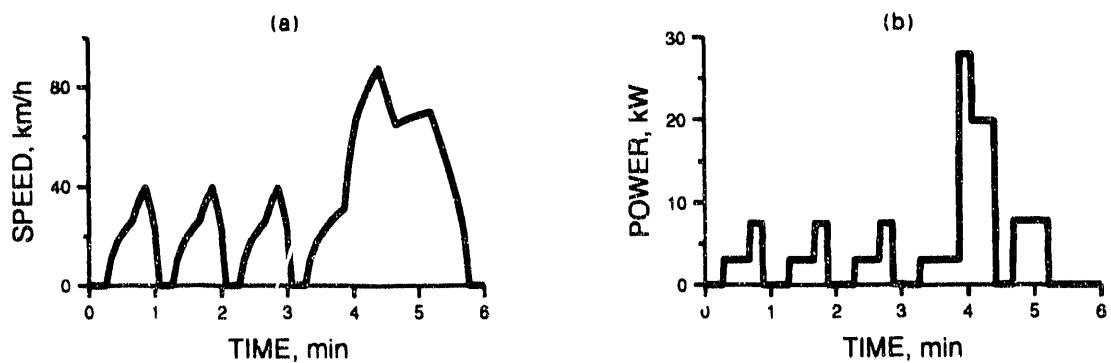


Fig. 2. Velocity and Power Profiles for the IETV-1 Simulated on the SFUDS Driving Schedule: (a) Velocity vs. Time and (b) Power vs. Time

To be suitable for transportation applications, therefore, the fuel cell power system must respond rapidly to wide fluctuations in power demand, as well as operate in the nominal idle, cruise, and sustained high-power conditions. The fuel reformer must, in turn, operate

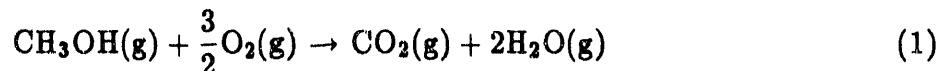
with highly variable fuel flow rates yet maintain high conversion yields and efficiencies at all points in the typical driving profiles.

In addition, the reformer must be capable of rapid start-up, so that the hydrogen-rich gas mixture is available at least as quickly as the fuel cell stack is ready to deliver power from a cold start. For fleet operations, it may be possible to maintain the reformer and the fuel cell stack in stand-by conditions to eliminate start-up times. For other applications, the reformer must be able to begin delivering useful concentrations and amounts of hydrogen within several seconds, assuming that the fuel cell stack can also begin delivering electric power in the same time frame. There is some flexibility in this start-up time if the system includes a suitable battery and/or hydrogen storage to meet the initial starting needs.

III. REFORMING OF METHANOL, ETHANOL, AND METHANE

When considering different fuels for use in fuel cell powered vehicles, methanol has clear advantages in terms of fuel storage and distribution because it can be used with minimal disruption to the present liquid fuel (gasoline, diesel) distribution network.⁴ Methanol is a commodity chemical; it can be manufactured from coal, natural gas, or other feedstocks; and it can be easily reformed to hydrogen at low temperatures. Higher molecular weight hydrocarbon or alcohol contaminants in commercial grade methanol can, however, reduce the reforming efficiencies by raising the reforming temperature and by producing esters, ethers, alkenes, and higher alcohols in the product gas.⁵ Even with clean methanol, trace amounts of dimethyl ether, methane, and formaldehyde may be formed.

For a fuel cell system operating on vaporized methanol as the fuel, the overall reaction is

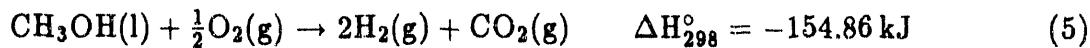


where the enthalpy (ΔH_{298}°) and free energy (ΔG_{298}°) are -676.1 kJ and -689.1 kJ , respectively, for this reaction. Thus, if methanol could be used directly in a fuel cell, theoretically 689.1 kJ of energy could be obtained from a mole of methanol; however, direct electrochemical oxidation of methanol has not yet been demonstrated on any significant scale. Therefore, the methanol (or any of the other alternative fuels) must first be converted to hydrogen or a hydrogen-rich gas mixture before it can be effectively used in a fuel cell.

Hydrogen may be produced from methanol by either partial oxidation or steam reforming. In a partial oxidation or auto-thermal reformer, the methanol is first vaporized and then dissociated into carbon monoxide and hydrogen. The carbon monoxide is then preferentially oxidized by using a suitable catalyst:



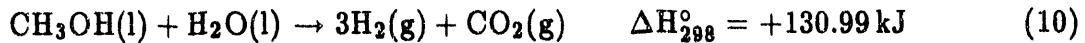
Thus, overall,



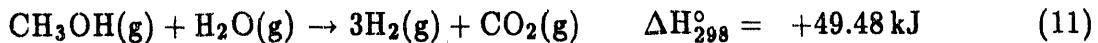
In a steam reformer, the methanol and water are vaporized, the methanol is dissociated, and the carbon monoxide is oxidized by steam:



Thus, overall,



For reforming pre-vaporized methanol and water, the overall reaction is



Thus, the net reaction in partial oxidation reforming (Eq. 5) is exothermic, i.e., excess heat is generated, even after the endothermic vaporization and dissociation steps (Eqs. 2 and 3) are taken into account. Since the absorption of thermal energy and the emission of thermal energy both occur in the same process gas stream, and since the overall reaction is exothermic, *direct* heat transfer between the heating and the heated fluids can be used. In *direct* heat transfer there is no physical boundary or interface between the hot and the cold media. An example of *direct* heat transfer is the heating of water by injecting steam into it. In such a heat exchanger the heat flux can be very high, leading to a compact heat exchanger. Moreover, the temperature difference between the two fluids leaving the heat exchanger can approach zero (and usually does), resulting in a very efficient mode of heat transfer. Thus, in partial oxidation, the entire heat of combustion can be used to vaporize and reform the reactants in a compact unit with minimum loss of energy from the system.

On the other hand, the overall reaction in steam reforming (Eqs. 10 or 11) is endothermic and requires the input of external thermal energy. The energy requirements are less if the methanol and/or the water are vaporized when fed to the reformer; nevertheless, heat must be supplied to the process gas in a steam reformer. Since in this case the heating medium must necessarily differ from the process gas, *indirect* heat transfer must be used. In *indirect* heat transfer, the heating fluid is kept separate from the heated fluid by a physical barrier impervious to either fluid. As a result, the heat flux in *indirect* heat exchange is relatively small, leading to the requirement of a relatively large heat exchange surface area (and consequently heat exchanger size). Also, the temperature difference between the two fluids must not approach zero, resulting in relatively inefficient heat transfer between the two fluids. Indeed, because of the overriding heat transfer considerations, steam reformers are typically designed as heat exchangers and often incorporate special design features to enhance the heat transfer in them.

Both in partial oxidation and in steam reforming the product gas contains residual carbon monoxide. For use in a phosphoric acid fuel cell, this CO must be reduced to less than 1%; for use in a proton exchange membrane fuel cell, the residual CO must be reduced to trace amounts. The concentration of residual CO in the product gas is reduced by injection

of H_2O along with the CH_3OH in partial oxidation, and by the use of excess H_2O in steam reforming. Even so, the CO concentration may have to be reduced to acceptable levels in a follow-on processing step of selective oxidation by using an appropriate catalyst.¹

For methanol, the dissociation occurs at temperatures $\geq 400^\circ\text{C}$. The selective oxidation of CO to CO_2 occurs at all temperatures from room temperature to 400°C or higher in the presence of a suitable catalyst. The oxidation of CO by H_2O occurs at $\sim 200^\circ\text{C}$ over a suitable catalyst.

For ethanol, the dissociation occurs at $500\text{--}700^\circ\text{C}$, with subsequent oxidation of the CO to CO_2 occurring at $\sim 200^\circ\text{C}$ for steam reforming and at essentially all temperatures from room temperature and up for partial oxidation reforming.

For methane, the dissociation reaction occurs at $\geq 800^\circ\text{C}$; the subsequent carbon oxidation occurs at lower temperatures.

Steam reforming and partial oxidation reforming have been demonstrated for methanol, ethanol, natural gas, gasoline, diesel, naphtha, and other hydrocarbons.

IV. CATALYSTS

Based on models containing selected species, Amphlett et al.⁶ have shown that the most favorable thermodynamic conditions for the production of hydrogen from methanol are a temperature of 225°C , low pressure, and the presence of excess water. At these conditions, however, the formation of carbon (soot) and methane are also favored thermodynamically, and these undesirable products must be inhibited by using an appropriate selective catalyst. Kinetic studies⁷ have shown that the dissociation of methanol (Eqs. 3 and 8) is the rate-determining step.

A. Mechanism of Methanol Catalysis

There are two schools of thought regarding the mechanism by which methanol is reformed to hydrogen. Amphlett et al.⁸ believe that Eqs. 8 and 9 represent the true mechanism. On the other hand, Springer et al.⁹ and Vanderborgh et al.¹⁰ contend that the reaction occurs through an alternate oxidation and reduction of active sites on the catalyst, where the methanol first reduces a site by taking away the lattice oxygen and producing CO_2 and H_2 . The reduced site is then oxidized by water to produce H_2 . This is supported by the observation that methanol cracking, which uses the same catalyst, occurs at temperatures near 400°C , while steam reforming of methanol can occur at temperatures as low as 200°C . Further, the catalyst activity appears to be affected by the hydrogen-to-steam ratio, perhaps controlled by the rapid reaction of hydrogen with the lattice oxygen atoms.

B. Catalysts Used

There is wide consensus that the oxides of copper and zinc give satisfactory methanol conversion, although some researchers have included alumina,¹¹ iron, and chromium¹² in their catalyst formulations. Lee et al.¹³ found that the addition of an alkaline earth metal to the copper and zinc oxides provides greater selectivity toward CO_2 (over CO) but with a slight decrease in catalyst activity. The highest selectivity for CO_2 was observed with Ba-Cu-Zn at 250°C .

Engelhard Corp.¹⁴ tested a copper/zinc oxide catalyst (T2107RS) and a zinc/chromium oxide catalyst (C70-2RS), both manufactured by Union Carbide for methanol reforming. The T2107RS catalyst contains 27.5% Cu, 1.0% Cr, 11.6% Zn, and 29.9% Al₂O₃; the C70-2RS catalyst contains 22% Cr and 55% Zn (for each catalyst, the balance is oxygen; compositions are given in weight percent). The T2107RS showed far greater activity than the C70-2RS for methanol reforming at 250–300°C. On the other hand, the C70-2RS was more effective at 350–400°C and exhibited good tolerance to impurities such as ethanol.

Mitsubishi Electric Corp.¹⁵ has patented a monolithic Y-type zeolite supported catalyst. This zeolite was impregnated with hydroxides of Cu, Zn, Al and La, and then oxidized by firing for 3 h at 300°C. The resulting catalyst contained the metals Cu, Zn, Al, and La in the ratio 10:7:1:1 and yielded a methanol conversion of 94% without significant pressure drop.

For the partial oxidation reforming of methanol, Jenkins and Shutt¹⁶ used a copper/silica catalyst along with a mixture of copper/silica and palladium/silica near the outlet from the reactor. Essentially complete conversion of the methanol was obtained, although in the absence of water in the fuel feed, roughly equivalent amounts of CO and CO₂ were produced; with the addition of water to the fuel input stream, most of the CO was converted to CO₂ by the water gas shift reaction. For ethanol, Jenkins and Shutt used a Pt/La₂O₃ catalyst coated with γ -Al₂O₃, but no details on catalyst performance were provided.

A metal-supported monolithic nickel catalyst for reforming methane has been discussed by Rohatgi and Voecks.¹⁷ With this catalyst operated at ~800°C, the catalyst activity and pressure drop performance were found to be superior to conventional packed-bed catalysts.

V. REFORMER DESIGNS AND APPLICATIONS

Fuel reformers are commonly used in industrial practice for the manufacture of hydrogen needed in the petroleum refining and chemical process industries. The common feedstocks are natural gas, propane, butane, and naphtha, and two most commonly used processes are steam reforming and partial oxidation in the presence of steam.¹⁸

Fuel reformers for the production of hydrogen for use in fuel cells have been developed more recently. Much of this development work, however, has concentrated on stationary applications, with essentially constant system load and process throughput. Reformers have been built and tested for converting methanol and natural gas to a hydrogen-rich fuel gas. Reforming of a variety of other fuels (including ethanol, gasoline, diesel, and naphtha) has also been demonstrated. For constant-load, stationary applications, steam reforming is preferred over partial oxidation reforming because the reformer provides a higher overall system efficiency. As discussed above, steam reforming is endothermic and requires the input of thermal energy. As a result, heat transfer to the reaction zone of the reformer is a principal design consideration, and the reformer size and its dynamic performance are primarily determined by heat transfer rather than catalytic activity.

Thus, most of the reformers developed to date have been designed around heat exchange equipment configurations. These include the conventional shell-and-tube, plate, packed-bed, and double-pipe heat exchangers, as well as modified versions of these types.

A. Shell-and-Tube Reformers

A conventional shell-and-tube type reformer is typified by the 50-kW methanol reformer developed by Engelhard Corp. for On-site Integrated Energy Systems.¹⁴ The reformer subsystem is shown schematically in Fig. 3a, while details of the baffle arrangement within the shell are shown in Fig. 3b. The 17-in. (43-cm) dia reformer shell contains 120 tubes [4-ft (1.2-m) long, 1-in. (2.5-cm) dia] packed with 1/8-in. (0.3-cm) pellets of the T2107RS catalyst (see Sec. IV.B). The reformer provides cocurrent flow of the combustion gases in the shell and the process gas in the tubes.

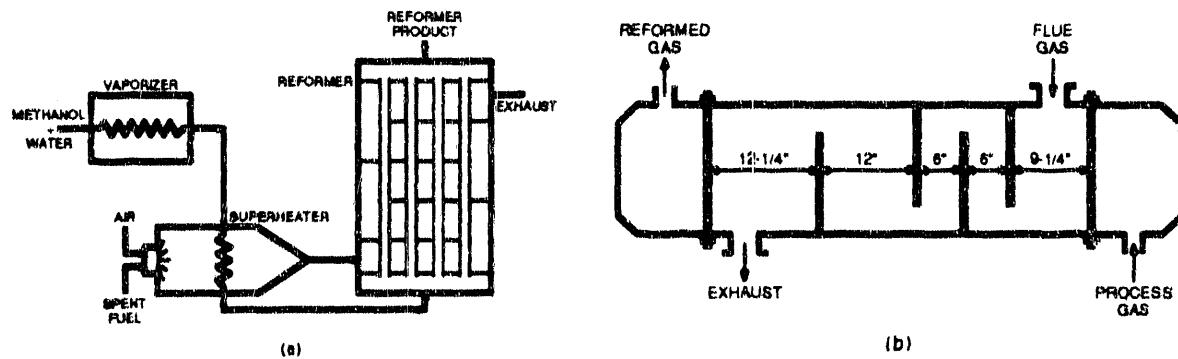


Fig. 3. Engelhard Corp. 50-kW Methanol Reformer:¹⁴ (a) Schematic Diagram of the Reformer Subsystem and (b) Baffle Arrangement within the Reformer Shell

From preliminary studies, Engelhard found that increasing the tube diameter increased the temperature gradients within the tubes and decreased the fuel conversion. Mathematical modeling of the reactor showed that the process gas temperature dropped sharply within the first 10% of the tube length, where most of the conversion took place. The tube-side heat transfer coefficient increased with increasing concentration of H₂ in the process gas; however, the limiting heat transfer coefficient was found to be the one on the shell side. The shell-side heat transfer coefficient increased as the number of baffles was increased, but this also sharply increased the shell-side pressure drop. The optimized design, shown in Fig. 3b, used close spacing of baffles in the fast reaction zone at the inlet end, with increased spacing between the baffles downstream.

At the design feed rate of the process gas containing steam/methanol in the ratio 1.3:1, with inlet temperatures of 452°C for the feed gas and 481°C for the combustion gas, the reformer provided 99.8% conversion and yielded a product containing 74.6% H₂, 23.9% CO₂, and 1.4% CO on a dry basis. Increasing the feed rate by 33% decreased the methanol conversion to 92.3%, illustrating the importance of sustaining the design operating conditions for this type of reformer.

A similar reformer using a dual-catalyst system has been patented by Fuji Electric Co., Ltd.¹⁹ A high temperature catalyst (e.g., Cu-Cr-Zn) at the reactor inlet provides fast kinetics, while a low temperature catalyst (e.g., Cu-Zn) at the outlet end provides high conversion. A fast-start reformer, incorporating additional burners within the shell as independent heat sources, has also been patented by Fuji.²⁰

Kawasaki Heavy Industries, Ltd., has also developed a shell-and-tube reformer for methanol.²¹ In this reformer the tubes are packed with the reforming catalyst, and the shell side is packed with metal or ceramic particles for improved shell-side heat transfer, resulting in a compact design. The process gas is split between the shell and the tubes. The bulk of the gas flows through the tubes and is converted to the reformat; the portion of the raw gas fed to the shell side is mixed with air and burned. This combustion on the shell side provides the heat of reaction for the reforming reactions. A reformer of a similar design has been patented by Toshiba Corp. for the conversion of natural gas and other hydrocarbons to hydrogen.²²

A version of shell-and-tube heat exchange reformer incorporating extended surfaces (fins) in the tubes and Rasching rings on the shell side was developed by Union Carbide for the steam reforming of natural gas.²³ In a later development the fuel dissociation and reforming steps were physically separated but were still carried out in one internally insulated vessel;²⁴ a catalyst-free reaction zone was included between the primary and secondary reforming beds.

B. Packed-Bed Reformers

A variety of packed-bed configurations have been developed for natural gas and methanol reformers. Even in these, however, the primary consideration is heat transfer between the heating medium and the process gas. Versions of packed-bed reformers have also been tested for the partial oxidation reforming process.

A packed-bed reformer using an annular catalyst bed with concentrically located vaporizer and burner has been developed by Energy Research Corp.²⁵ and is shown in Fig. 4a. A somewhat similar reformer developed by Booz, Allen & Hamilton, Inc.,²⁶ is shown schematically in Fig. 4b. Each of these designs uses a concentric down-flow burner. The methanol/water fuel mixture is vaporized, superheated, and then passed through the catalyst bed. Although in principle the two reformers are similar, they use different combustion gas and process fluid flow schemes to achieve the requisite thermal energy input into the process gas.

A packed-bed methanol reformer with a high gas recirculation rate is being developed at Los Alamos National Laboratory.¹ The structural design is shown schematically in Fig. 5. An internal fan recirculates the reformat through the catalyst bed at a rate of 20 to 50 times the net fuel processing rate to maintain the bed at the desired reaction temperature and to provide high convective heat transfer rates. In this fuel processing scheme, the reforming step is followed by a shift converter (to reduce the CO concentration to less than 0.6%) and a preferential oxidation unit (to reduce the CO to less than 10 ppm).²⁷

Haldor Topsoe, Inc., has developed a heat exchange reformer for natural gas that uses two separate catalyst beds housed in a single vessel.²⁸ The heat exchange processes within

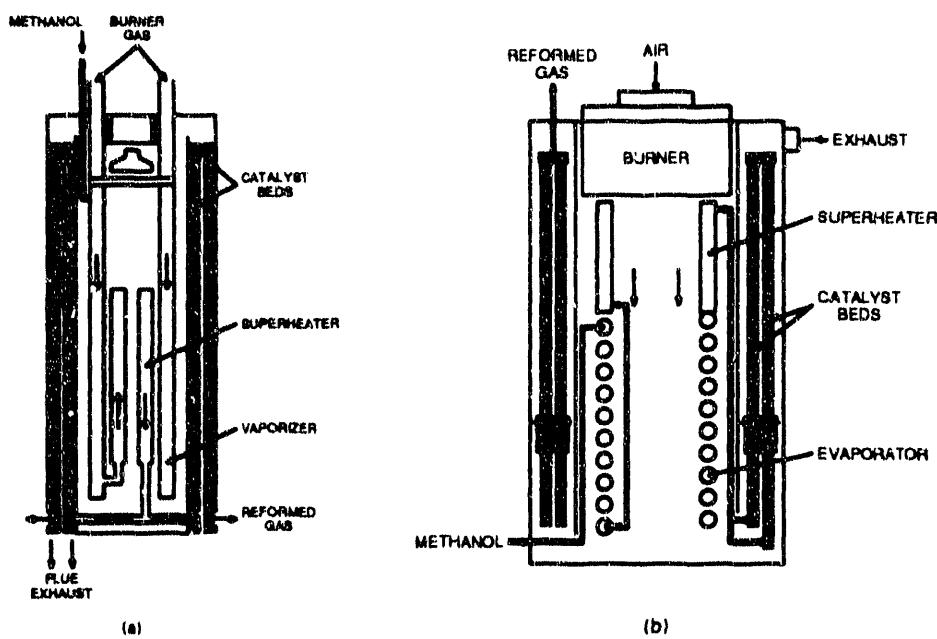


Fig. 4. Schematic Diagrams of the Packed-Bed Methanol Reformers Developed for the Fuel Cell/Battery Powered Bus System: (a) Energy Research Corporation Design²⁵ and (b) Booz, Allen & Hamilton Design²⁶

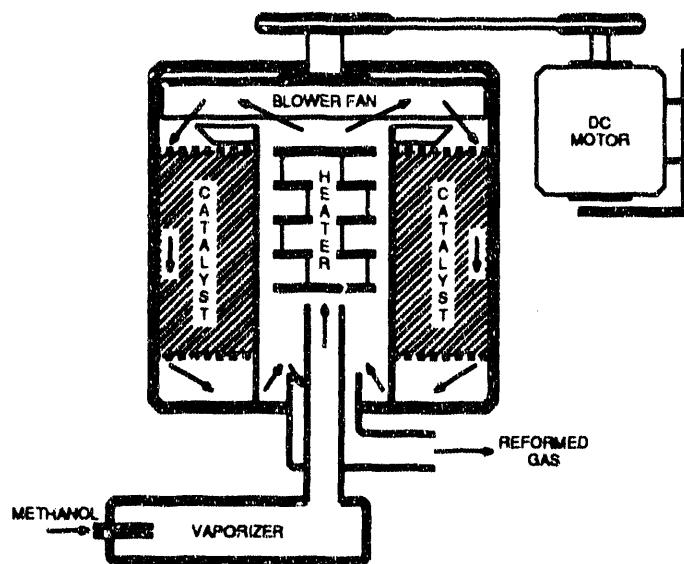


Fig. 5. Schematic Diagram of the Recirculating Methanol Reformer Developed at Los Alamos National Laboratory¹

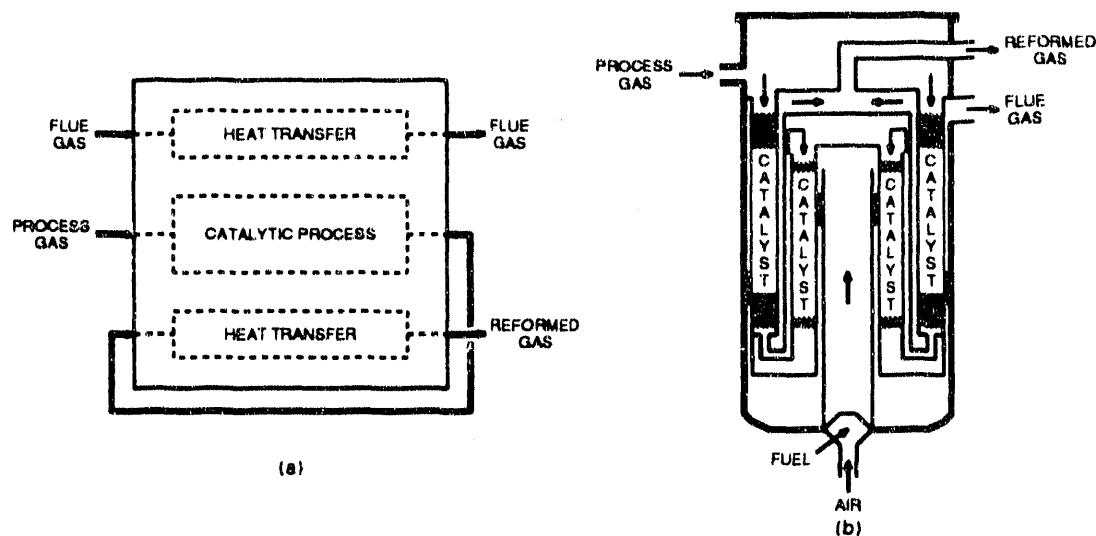


Fig. 6. Heat Exchange Reformer Developed by Haldor Topsoe.²⁸
 (a) Schematic Diagram of the Heat Exchange Processes
 and (b) Structural Design of the Reformer

this reformer are shown schematically in Fig. 6a, while Fig. 6b shows the structural design of the reformer. The burner for the heat of reaction is placed within the reformer. The two catalyst beds are in series. The first bed is heated by countercurrent flow of hot flue gases and the effluent from the second bed, while the second bed is heated by cocurrent flow of flue gases. Test data during proof of concept and demonstration runs were presented at Fuel Cell Seminars.^{29,30}

A packed-bed reformer incorporating fuel recycle and hydrogen purification has also been developed by Haldor Topsoe.³¹ The processing steps described consist of catalytic reforming at 1.5–2.5 atm and 250°C followed by condensation and recycle of unconverted methanol and water. Hydrogen is separated from the reactor effluent by pressure swing adsorption on molecular sieves.

A compact-design packed-bed methanol reformer incorporating an isothermal reaction zone followed by an adiabatic reaction zone has been patented by Asahi Engineering Co., Ltd.³² The lower isothermal zone is packed with alumina catalyst balls, while the upper adiabatic zone is packed with Cu-Cr catalyst pellets.

Another dual-section packed-bed reformer has been developed by Hitachi, Ltd.³³ A fraction of the feed gas is burned in the upper bed, which is packed with a combustion catalyst. The heat generated is used for the steam-reforming reaction in the lower bed, which is packed with a reforming catalyst.

A packed-bed reforming process that uses co-injection of CO₂ with the process feed gas has been developed at the Institut Francais du Petrole.¹² In this process methanol, water, and carbon dioxide are passed over a fixed bed of CuO-Fe₂O₃-Cr₂O₃ catalyst at 150–400°C. Co-injection of carbon dioxide is claimed to increase methanol conversion.

A combination evaporator/reformer has been developed by Mitsubishi Electric Corp.³⁴ In this device the packed catalyst bed is placed parallel to the methanol evaporator. Heat is supplied to both by a common burner. Heat distribution to each is varied by moving the burner nozzle and by adjusting a combustion baffle to redirect the gas flow within the vessel. With this arrangement cold-start times are significantly reduced.

A three-catalyst packed-bed reformer that employs partial oxidation has been tested by Jet Propulsion Laboratory (JPL) for the production of hydrogen for use in fuel cells,³⁵ and a dual-catalyst packed-bed reformer that also employs partial oxidation has been developed at the Johnson Mathey Technology Center.¹⁶ The two reformers are shown schematically in Fig. 7.

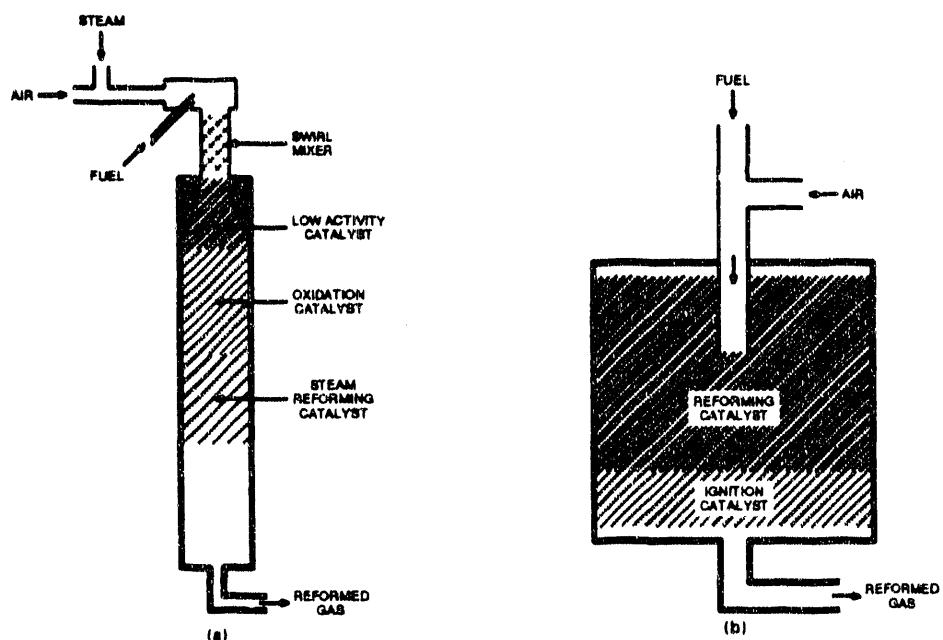


Fig. 7. Schematic Diagrams of Packed-Bed Partial Oxidation Reformers: (a) The JPL Autothermal Reformer³⁵ and (b) The Johnson Mathey Hot SpotTM Reformer¹⁶

In the JPL reformer the fuel is injected into a premixed stream of air and steam just ahead of a swirl mixer at the inlet to the reformer. A conical refractory-lined entrance zone in the reactor eliminates any dead spots. A combination of three different catalysts is used: at the entrance, a NiO-ZrO_2 catalyst with low activity effects a gradual increase in the reactant temperature and suppresses carbon formation; in the middle zone, a $\text{NiO-Al}_2\text{O}_3-\text{CaO}$ type of oxidation catalyst with high void fraction oxidizes the fuel; and in the last zone, a $\text{NiO-Al}_2\text{O}_3-\text{MgO}$ steam-reforming catalyst with high activity maximizes hydrogen production.

The Johnson Mathey Hot SpotTM reactor contains a Cu-Si catalyst in the main reaction zone, and a mixture of Cu-Si and Pd-Si in the last 20% of the bed. The palladium makes the reactor capable of self-ignition. The feed gas mixture consisting of methanol,

water, and air is injected into the middle of the main reaction zone. At start-up the methanol is oxidized at the reformer exit. The reaction zone then moves upstream toward the point of injection. The feed inlet velocity stabilizes the reaction front well inside the packed bed, where the heat of methanol oxidation effectively provides the heat of reforming for the bulk process gas by direct heat transfer. In addition to reforming methanol, this reactor has been tested successfully with methane (natural gas), propane (LPG), n-hexane, petroleum ether, lead-free gasoline, and commercial grade diesel fuel (the last using a 1% Pt-3% Cr-Si catalyst formulation).

C. Other Types of Reformers

In addition to the above reformer designs, plate-and-frame, multistage, and other types of reformers have been discussed in the literature.

A plate-and-frame type of reformer similar in concept to a filter press has been developed by Ishikawajima-Harima Heavy Industries (IHI).³⁶ The reformer is designed around a series of heat transfer plates that have a reforming catalyst on one side and a combustion catalyst on the other side. In addition to efficient heat transfer, the design provides for low thermal stresses in the structure due to matched temperature gradients in the reforming and combustion sides.

During the early development of the solid polymer electrolyte (SPE) fuel cell, General Electric Co. designed a methanol reformer that uses an annular two-pass catalyst bed enclosed in an air preheater chamber.³⁷ Vaporized methanol is catalytically cracked into hydrogen and carbon monoxide using the heat generated by fuel combustion as the combustion gases pass through the core of the reactor. The cracked gases are mixed with steam (from the fuel cell exhaust) and fed to the shift reactor, which reduces the CO to less than 0.2% in the product gas.

Imperial Chemical Industries has developed a two-step reforming process,^{38,39} where the preheated feedstock (natural gas, naphtha, or methanol) and steam mixture is first adiabatically reformed, yielding the partially reformed gas. This gas is then passed through the annular catalyst in a double-tube reformer. The heat for the secondary reforming is supplied by passing a hot gas stream through the central tube.

International Fuel Cells has demonstrated a two-column cyclic reformer for producing hydrogen from diesel fuel.⁴⁰ Each column alternates between hydrogen production and bed regeneration modes. Packed with catalyst and other material of high thermal mass, the column is first heated by burning spent anode gas within the column. On attaining the desired temperature, the column is switched to reforming duty. The catalyst bed acts as a very effective heat exchanger, storing heat during regeneration and supplying it during the reforming cycles (2-4 min each) with minimum bed temperature swings, eliminating the need for heat exchange with external sources. This reformer concept offers fast transient capability and recovers automatically from off-design operating conditions. In addition, any carbon deposited in the catalyst bed during the reforming cycle is burned off during the regeneration (combustion) cycle.

A multistage reformer has been developed by JGC Corp.,⁴¹ where the steam-to-methanol ratio is kept below 1.0 and the reaction temperature in each reactor is kept 10–50°C above the dew point. The product from the first stage is mixed with additional steam before going into the second stage. Thus, the overall excess steam is greatly reduced in this process without adversely affecting product quality.

Finally, a methanol reformer incorporating several advanced features has been developed by Chemical Energy Specialists.⁴² Its design is said to provide exceptional conduction heat transfer within both the catalyst bed and an integral feed vaporizer, improved convection heat transfer in the catalyst bed with internal recirculation obtained without moving parts, a unique internal burner with rapid and high turn-down capability, and a simplified overall control methodology.

VI. PARTIAL OXIDATION VERSUS STEAM REFORMING

Each of the two basically different kinds of fuel reforming has certain advantages as well as disadvantages from the perspective of potential application to automotive systems.

A. Product Gas Composition

Nominally, the product of partial oxidation reforming should consist of 41% H₂, 21% CO₂, and 38% N₂, if all the CO is oxidized to CO₂. In practice, however, CO and CO₂ appear in roughly equal proportions in the product gas, which thus contains ~13% each of CO and CO₂, 50% H₂, and 24% N₂. With the addition of H₂O, such reforming occurs as a combination of partial oxidation and steam reforming. With a 1:1 molar mixture of CH₃OH and H₂O as the reactant, this mode of partial oxidation reforming can yield a gas mixture containing approximately 51% H₂, 19% CO₂, 10% H₂O, 1% CO, and 19% N₂ as the product.

With steam reforming, the nominal product composition is 75% H₂ and 25% CO₂ if a stoichiometric amount of water is used. In practice, an excess of water is necessary to reduce the amount of CO in the product gas. With 50% excess H₂O, the product gas composition is 67% H₂, 21% CO₂, 11% H₂O, and 1% CO.

For the low temperature proton exchange membrane (PEM) fuel cell, a final CO removal step is required to avoid poisoning of the noble metal catalyst in the anode. This may be done using selective oxidation at $\geq 400^\circ\text{C}$ with a small amount of air over a suitable catalyst, such as platinum. 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 reformed gas containing 48% H₂, 20% CO₂, 11% H₂O, and 21% N₂; selective oxidation of 1% CO from a steam reformer product would produce a gas containing 63% H₂, 22% CO₂, 11% H₂O, and 4% N₂. These product gas compositions are summarized in Table 1. For both the low temperature PEM and the higher temperature phosphoric acid fuel cells, the difference in hydrogen concentration of 48% versus 63% leads to a Nernst voltage penalty of 6 mV ($\sim 0.5\%$) for the partial oxidation reformer versus the steam reformer.

B. Energy Efficiency

Partial oxidation reforming of CH₃OH produces excess thermal energy, which can be

Table 1. Reformer Product Gas Compositions

Reforming Process	Gas	Gas Composition, %		
		Nominal	With Excess Water	After CO Removal
Partial Oxidation	H ₂	41	51	48
	CO ₂	21	19	20
	H ₂ O	—	10	11
	CO	—	1	—
	N ₂	38	19	21
Steam Reforming	H ₂	75	67	63
	CO ₂	25	21	22
	H ₂ O	—	11	11
	CO	—	1	—
	N ₂	—	—	4

used to vaporize the methanol and to heat the reformed product gas by *direct* heat transfer, a very rapid and efficient means of heat transfer. The net energy effect is that, from the 726.5 kJ of the higher heating value (HHV) for one mole of the input CH₃OH, the partial oxidation reformer yields H₂ with a theoretical maximum electrochemically available energy of 474.4 kJ. If the fuel cell system is operated with an electrochemical fuel utilization of 75% and a cell voltage of 0.7 V, its gross efficiency would be 29.4%, based on the HHV of the input fuel methanol.

Steam reforming of CH₃OH requires the input of external energy by *indirect* heat transfer, a relatively slow and inefficient means of heat transfer. If the vaporizing and reforming energy is provided from the rest of the fuel cell system itself (i.e., from the fuel cell stack waste heat and the energy in the spent fuel leaving the stack), the net effect is to convert the 726.5 kJ of the HHV for an input mole of CH₃OH to a theoretical maximum electrochemically available energy of 711.6 kJ as H₂. With an electrochemical fuel utilization of 75% and a cell voltage of 0.7 V, the gross efficiency for the fuel cell system would then be 44%. On the other hand, if the vaporizing and reforming energy is provided by the combustion of additional methanol, then the gross efficiency for the fuel cell drops to 31.7%, which is only a little higher than the efficiency of the system with a partial oxidation reformer.

C. Start-Up and Variable Load Operation

The start-up and performance under varying loads can be much superior for the partial oxidation reformer compared to that of the steam reformer. This is because direct heat transfer in the partial oxidation reformer is much more efficient than the indirect heat transfer in a steam reformer. The partial oxidation reformer can be much more compact than a steam reformer of equal methanol processing capacity due to the absence of heat transfer surfaces. Also, since the combustion products form part of the reformed gas itself, no separate reformer combustion exhaust stream is needed for the partial oxidation reformer.

In addition, with the use of suitable oxidation catalysts, the partial oxidation reformer can be self-starting without the use of an ignition source.

D. Miscellaneous Features

The steam-reformer product gas leaves the reformer at ~ 180 - 200°C , which is comparable to the stack temperature in the phosphoric acid fuel cell. This reformate would need to be cooled to $\sim 80^\circ\text{C}$ for use in a PEM system. The product gas from a partial oxidation reformer would be at a much higher temperature, perhaps 400°C , and would require an appropriate heat exchanger to cool it down to the fuel cell stack temperature.

The hydrogen concentration in the partial oxidation product is lower than that in the steam reformer product. As a consequence, for the same power output from the fuel cell system, a 20-25% greater flow rate of the anode gas would be needed in the fuel cell stack. This does not necessarily mean a higher input rate of methanol to the fuel cell system, however. The methanol fuel input rate is a function of the overall system efficiency and, for a given system power output, is only slightly greater for the partial oxidation system than for the steam reforming system if the latter is operated without using the stack waste heat for fuel and water vaporization.

Both the partial oxidation and the steam reformer require the addition of water to the process gas for good product quality; however, a partial oxidation reformer requires one-third less water for the same amount of methanol than is used in a steam reformer. The product of either reformer may require additional CO removal if it is to be used in a low temperature fuel cell.

The partial oxidation reformer is a mechanically simple system due to the absence of burners, baffles, heat transfer surfaces, and combustion manifolding and ducting; in it, process kinetics are not limited by heat transfer considerations. A steam reformer is relatively complex; it contains one or more burners (for spent fuel and fresh fuel), extended heat transfer surfaces, and combustion air and exhaust ductwork. In a steam reformer the limiting kinetic factor is the rate of heat transfer from the burner and the combustion product gases to the process gas stream. The partial oxidation reformer may, however, be subject to coking (deposition of carbon on the catalyst, rendering it inactive), particularly with higher hydrocarbons.

VII. DISCUSSION

As discussed in Sec. II, a small passenger car driven on the SFUDS profile requires a power system capable of delivering up to ~ 30 kW for at least several seconds. For the fuel cell/battery small urban bus, the fuel cell subsystem is required to provide ~ 50 kW of power at essentially steady state. For system efficiencies of ~ 30 - 45% , the corresponding methanol consumption rate is ~ 10 - 16 kg/h (22-35 lb/h) for the 30 kW system and ~ 18 - 27 kg/h (40-60 lb/h) for the 50 kW system.

Both partial oxidation and steam reforming of methanol (and other alternative fuels) have been discussed at some length in the literature. Most of the recent literature on the subject is in the form of patents in the U. S. and abroad. Steam reformers for methanol

and natural gas for use with fuel cell systems have received considerable attention; partial oxidation reformers, while commercially used in industrial hydrogen manufacture, have not seen much development for fuel cell applications, presumably due to the lower efficiency of fuel cell systems employing such reformers. Enough information does exist in the literature, however, to reasonably assess the merits of each type of reformer for use in fuel cell powered automotive applications.

Most of the fuel reformers discussed in the literature were developed for use in power systems operated at essentially constant load, primarily for stationary applications, where efficiency is of primary importance. As a result, much of the effort has been devoted to development of steam reformers which, when thermally integrated with a fuel cell system, can yield gross system efficiency of 44% (for the fuel cell operating conditions discussed above). For automotive applications, however, rapid start-up, ability to handle varying loads, small size, and low weight are equally as important as the system efficiency, or perhaps even more so. To meet these performance requirements, the reformer may have to be thermally independent of the rest of the fuel cell system, in which case the gross system efficiency decreases to ~30%.

Since thermal integration of the reformer with the rest of the fuel cell system has such a marked effect on the system efficiency, the factors involved in devising an integrated system must be considered carefully. There are two major considerations in integrating a fuel reformer with the balance of the fuel cell power system for use in automotive applications. One is thermal integration, and the other is coupling of the dynamic performance of the reformer with that of the fuel cell stack. The two considerations are interrelated and can only be discussed in conjunction with each other.

For an automotive application, dynamic performance of the total system under widely and rapidly fluctuating loads is of primary importance, and thermal integration may be sacrificed, if necessary. On the other hand, for a fuel cell power system operating at essentially constant load, thermal integration of the reformer with the fuel cell stack and the rest of the power system is the only significant concern; dynamic performance of either the reformer or the fuel cell stack is unimportant.

In a fuel cell power system incorporating a steam reformer, energy is required to vaporize the methanol and water and to reform the vaporized fuel. Excess thermal energy is available in the system in the form of stack waste heat and as spent fuel. In principle, therefore, the energy requirements of vaporizing and reforming the fuel can be provided from this excess energy. In a dynamically varying system, however, the availability of this excess energy lags behind the demand for it.

For instance, consider a step increase in the power output required from the fuel cell stack. Vaporizing and reforming of the additional fuel require energy before the excess stack waste heat and the excess spent fuel become available. This happens after the 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 the thermal subsystems of the stack and the vaporizer/reformer should be independent of each other. The vaporizer and reformer can be combined into one thermal subcomponent (indeed, a partial oxidation reformer performs both functions in one piece of hardware). In addition

to being more responsive, the independent systems should be easier to operate and control. This independence does mean, however, that the power system would have to operate at a lower overall fuel use efficiency, as compared to a thermally integrated system. The excess energy is not necessarily wasted. It can be used to provide passenger compartment heating and cooling.

Even in a thermally independent system, a steam reformer is slightly more efficient than a partial oxidation reformer. The latter, however, is inherently more responsive to dynamic load fluctuations due to direct heat transfer for fuel vaporization and conversion, although design approaches such as process gas recirculation as used in the Los Alamos reformer¹ can improve the dynamic performance of the steam reformer.

Considerable research effort has been devoted to developing the steam reformer for automotive use, in particular in maximizing the fuel-to-hydrogen conversion selectivity and efficiency. Prototypical steam reformers have been developed by ERC²⁵ and BAH²⁶ for the fuel cell/battery bus propulsion system. Although these reformers have been successfully tested for a constant load application, their start-up times and dynamic performance are unacceptable for stand-alone fuel cell systems that provide automotive power. The Los Alamos recirculating reformer design¹ attempts to provide rapid start-up and good dynamic performance, but relevant test data have not yet been published. Due to the indirect heat transfer, however, even this design is not likely to be as dynamically responsive as a partial oxidation reformer. Chemical Energy Specialists⁴² claims that its steam reformer provides rapid start-up and quick response to load changes; however, no design details or operating data have been published.

In comparison, much less effort has been devoted to the development of partial oxidation reformers. A fuel processing system somewhat similar to the partial oxidation reformer was used in an earlier program sponsored by DOE through the National Renewable Energy Laboratory (formerly, the Solar Energy Research Institute).⁴³ Under the alcohol fuels program in the early 1980s a Ford Escort and its internal combustion engine were modified to run on methanol converted to a H₂/CO mixture by partial oxidation. Although in that approach the CO content of the reformed gas was of no particular concern, the tests did demonstrate that a partial oxidation reformer can provide adequate dynamic performance. More recently, the Johnson Mathey Hot SpotTM reformer¹⁶ was described in the literature. The test results did not indicate an acceptably short start-up time; no dynamic performance data were reported.

VIII. R&D RECOMMENDATIONS

Among all the methanol reformers described and discussed in the literature, none has been demonstrated to possess the requisite performance capability for rapid start-up and dynamic response necessary for use in a stand-alone fuel cell system for automotive applications. The published information does strongly suggest, however, that by appropriately combining selected features of the various designs, it should be possible to develop a reformer that has the required start-up and operational characteristics. The desirable features of such a reformer include:

- a platinum-group metal catalyst for self-ignition of the reformer;
- multiple catalysts for optimum operation of the oxidation, dissociation, and shift reactions;
- a small catalyst bed for a quick starting, light, and compact reformer;
- direct heat transfer (partial oxidation), perhaps combined with process gas recirculation, for rapid response to fluctuating loads;
- water injection for improved product quality; and
- a fuel processing scheme thermally independent of the rest of the fuel cell system.

In addition, further efforts are needed in the area of product quality, i.e., CO minimization, particularly for use of the reformer with the low temperature PEM fuel cell system.

For fuel cell/battery automotive applications, where the fuel cell is expected to operate at an essentially constant power output, a steam reformer can provide high efficiency by thermally integrating the reformer with the balance of the fuel cell system. The prototype reformers developed by ERC²⁵ and BAH,²⁶ although adequate for the present fuel cell bus program,³ can be improved further to reduce their size, weight, and start-up times by design modifications that enhance heat transfer. Such modifications might include the process gas recycling successfully used in the Los Alamos reformer¹ or the design approaches claimed to be effective in the reformer developed by Chemical Energy Specialists.⁴² Such improvements in heat transfer are likely to result in substantial improvements in start-up and dynamic performance of the reformer and the entire fuel cell system.

It is recommended that DOE sponsor the development of a steam-injected, partial-oxidation methanol reformer incorporating the features identified above, capable of processing 15–25 kg/h (33–55 lb/h) of methanol along with the appropriate amount of co-injected water. Such a reformer would be prototypical of the type and size of reformer needed for a stand-alone fuel cell system for automotive power. The objective of this effort should be to build a compact, lightweight, quick starting, and dynamically responsive reformer. The product gas from the reformer must be essentially free of carbon monoxide or must contain amounts of CO small enough to be reduced to a few parts per million by processes such as catalytic selective oxidation.

It is also recommended that DOE should continue efforts to improve the currently available steam reformers for use in hybrid power systems, with the objective to reducing their size, weight, and start-up times.

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