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METHANOL REFORMERS FOR FUEL CELL POWERED VEHICLES: SOME DESIGN CONSIDERATIONS

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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). The major motivations for developing fuel cell powered vehicles are as follows: 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.

The two most important operational requirements for a stand-alone fuel cell power system for a vehicle are the ability to start up quickly and the ability to supply the necessary power on demand for the dynamically fluctuating load. The rapid start-up requirement is obvious. An example of the dynamic performance requirement is given in Fig. 1, which shows the simulated velocity and power profiles for a small car, the IETV-1, operated on the Simplified Federal Urban Driving Schedule (SFUDS). On this schedule the power varies 15 times over 6 min; in actual driving the power fluctuations are typically more numerous and more complex.

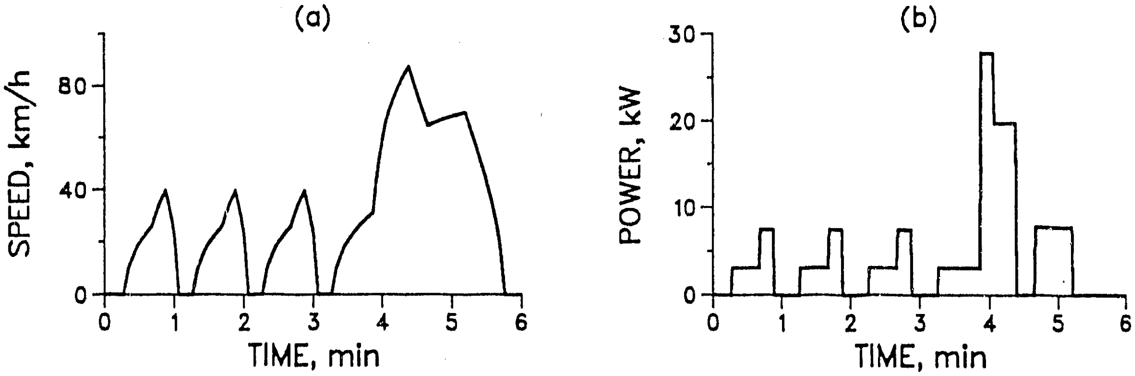

Fig. 1 Velocity and power profiles for the IETV-1 simulated on the SFUDS driving schedule: (a) Velocity vs. time; (b) Power vs. time.

Methanol is a likely fuel for use in fuel cells for transportation applications. It is a commodity chemical that is manufactured from coal, natural gas, and other feedstocks. For use in a fuel cell, however, the methanol must first be converted (reformed) to a hydrogen-rich gas mixture. The desired features for a methanol reformer include rapid start-up, good dynamic response, high fuel conversion, small size and weight, simple construction and operation, and low cost. In this paper we present the design considerations that are important for developing such a reformer.

Reforming of Methanol

Hydrogen may be produced from methanol by either partial oxidation or steam reforming, for which the overall reactions are:

$$CH_3OH(\ell) + \tfrac{1}{2}O_2(g) \rightarrow 2H_2(g) + CO_2(g) \qquad \Delta H^\circ_{298} = -154.86\,\text{kJ} \qquad (1)$$

$$CH_3OH(\ell) + H_2O(\ell) \rightarrow 3H_2(g) + CO_2(g) \qquad \Delta H^\circ_{298} = +130.99\,\text{kJ} \qquad (2)$$

$$CH_3OH(g) + H_2O(g) \rightarrow 3H_2(g) + CO_2(g) \qquad \Delta H^\circ_{298} = +49.48\,\text{kJ}. \qquad (3)$$

DISCLAIMER

Thus, partial oxidation reforming is exothermic, while steam reforming is endothermic.

Mechanism of Methanol Reforming

There are two schools of thought regarding the mechanism by which methanol is reformed to hydrogen. Amphlett et al. (3) believe that the methanol first dissociates into carbon monoxide and hydrogen, and the CO is subsequently oxidized, by oxygen in partial oxidation reforming and by steam in steam reforming. On the other hand, Springer et al. (4) and Vanderborgh et al. (5) feel 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.

Catalysts for Methanol Reforming

Variously supported oxides of copper and zinc have been used most often for the steam reforming of methanol, although additions of alumina (6), iron and chromium (7), and alkaline earth metals have also been employed successfully (8). A combination of oxidation catalysts, e.g., NiO-ZrO_2, NiO-Al_2O_3-CaO, and Cu-Pd-SiO_2, and reforming catalysts, such as NiO-Al_2O_3-MgO and Cu-SiO_2, is used for the partial oxidation reforming of methanol (9,10).

Partial Oxidation vs. Steam Reforming

Product Gas Composition

Both in partial oxidation and in steam reforming the product gas contains residual carbon monoxide. For use in a phosphoric acid fuel cell (PAFC), this CO must be reduced to less than 1%; for use in a proton exchange membrane (PEM) fuel cell, the residual CO must be reduced to trace amounts. The concentration of residual CO in the product gas can be reduced by injection of H_2O along with the CH_3OH in partial oxidation, and the use of excess H_2O in steam reforming. Even so, reducing the CO concentration to acceptable levels may require a follow-on selective oxidation step, using an appropriate catalyst (1).

In partial oxidation reforming, the product should nominally consist of 41% H_2, 21% CO_2, and 38% N_2, if all the CO is oxidized to CO_2. In practice, however, the addition of H_2O is required to reduce CO to low levels. Using a 1:1 molar mixture of CH_3OH and H_2O and selective oxidation of the residual CO, the product gas mixture contains 48% H_2, 20% CO_2, 11% H_2O, and 21% N_2. In steam reforming with 50% excess H_2O and after residual CO removal, the product gas composition is 63% H_2, 22% CO_2, 11% H_2O, and 4% N_2. The lower hydrogen concentration from the partial oxidation reformer compared to that from the steam reformer (48% vs. 63%) leads to a Nernst voltage decrease of $\sim$6 mV.

Energy Conversion

Partial oxidation reforming of CH_3OH produces excess thermal energy which can be used to vaporize the methanol and water and to heat the reformed product gas. The net energy effect is that, from the 726.5 kJ of the higher heating value (HHV) of one mole of the input CH_3OH, the partial oxidation reformer yields H_2 with a theoretical maximum electrochemically available energy of 474.4 kJ.

Steam reforming of CH_3OH requires the input of external energy. If the vaporizing and reforming energy is obtained from the fuel cell stack waste heat and the combustion of the spent fuel leaving the stack, the net effect is to convert the 726.5 kJ of the HHV of an input mole of CH_3OH to a theoretical maximum electrochemically available energy of 711.6 kJ as H_2. If the stack waste heat and spent gas combustion are not used to provide the vaporizing and reforming energy, then the maximum electrochemically available energy is 512.6 kJ.

Dynamic Response and Start-Up

The dynamic response and start-up performance of the partial oxidation reformer can be much superior to that of the steam reformer. This is because the partial oxidation reformer uses *direct* heat transfer, which provides very high heat fluxes, and therefore, the required heat transfer loads can increase or decrease rapidly. In contrast, a steam reformer must use *indirect* heat transfer, which limits heat fluxes. The high heat fluxes in *direct* heat transfer can make a partial oxidation reformer/fuel vaporizer start-up quickly; the lower heat fluxes in *indirect* heat transfer do not permit as rapid a start-up for a steam reformer/vaporizer, even if process gas recirculation is used to enhance the convective heat transfer.

Miscellaneous Features

The partial oxidation reformer is an intrinsically simple device due to the absence of burners, baffles, heat transfer surfaces, and combustion manifolding and ducting. In comparison, a steam reformer is relatively complex; it contains one or more burners, extended heat transfer surfaces, combustion air and exhaust ductwork, and perhaps even a process gas recirculator. Because of the high heat fluxes available, the partial oxidation reformer can be more compact than a steam reformer of equal methanol processing capacity. Also, since the combustion products form part of the reformed gas itself, there is no separate reformer combustion exhaust stream from the partial oxidation reformer.

Discussion

In a fuel cell power system it is possible to thermally integrate the fuel vaporizer, reformer, and the cell stack. Waste heat is available at ~80°C from the PEM stack and at ~190°C from the PAFC stack. In either fuel cell, the spent gas from the anode contains 10–30% of the H_2 in the anode feed, and its heat of combustion can also be used.

There are two major considerations in implementing such an integration. One is the quantity and quality of waste energy available, and the other is the dynamic relationship between the need for this energy and its availability. In a low temperature fuel cell system, such as the PEM, the stack waste heat is available at too low a temperature to vaporize water or pressurized methanol. In a higher temperature system, such as the PAFC, the stack waste heat can be used for this purpose. In either system, energy in the spent anode gas can be used.

In a dynamically varying automotive power system, the availability of the energy from the fuel cell stack and spent anode gas *lags behind* the demand for that energy. For instance, for a step increase in the power output required from the fuel cell stack, vaporizing and reforming of the additional fuel needs energy *before* the excess stack waste heat and the excess spent fuel become available; this only happens *after* the stack begins delivering power at the higher demand level. This temporal difference in the requirement and availability of thermal energy in the fuel cell power system suggests that the thermal subsystems of the stack should be independent of the vaporizer/reformer. In addition to being more responsive, the independent systems should be easier to operate and control.

Conclusion

A reformer developed for stand-alone fuel cell automotive power systems must be capable of rapid start-up and good dynamic response. To meet these requirements, it should incorporate: (1) a small catalyst bed for quick starting, small size, and low weight; (2) multiple catalysts for optimum operation of the dissociation and reforming reactions; (3) reforming by direct heat transfer partial oxidation for rapid response to fluctuating loads; and (4) thermal independence from the rest of the fuel cell system.

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