

PARTIAL OXIDATION FUEL REFORMING FOR
AUTOMOTIVE POWER SYSTEMS

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ABSTRACT

For widespread use of fuel cells to power automobiles in the near future, it is necessary to convert gasoline or other transportation fuels to hydrogen on-board the vehicle. Partial oxidation reforming is particularly suited to this application as it eliminates the need for heat exchange at high temperatures. Such reformers offer rapid start and good dynamic performance. Lowering the temperature of the partial oxidation process, which requires the development of a suitable catalyst, can increase the reforming efficiency. Catalytic partial oxidation (or autothermal) reformers and non-catalytic partial oxidation reformers developed by various organizations are presently undergoing testing and demonstration. This paper summarizes the process chemistries as well as recent test data from several different reformers operating on gasoline, methanol, and other fuels.

INTRODUCTION

The conversion of non-hydrogen fuels (gasoline, diesel, methanol, ethanol, propane, etc.) to hydrogen in fuel cell systems is a critical link in the chain of evolution of fuel cells from a scientific curiosity of one and a-half centuries ago, through niche applications in space beginning almost half a century ago, to widespread global use in the coming millennium. While steam reforming is most commonly used for the large-scale production of hydrogen from natural gas and other fuels, partial-oxidation (POX) and autothermal reforming offer particular advantages for automotive and small-scale fuel cell power systems. By eliminating indirect heat transfer at high temperatures, POX reforming makes possible designs that are compact and lightweight, and respond rapidly to fluctuating power demands after a rapid start from cold conditions. Several variations of the basic POX process are being developed. In general, preheated fuel, air, and water (or steam) are fed to the reformer in specific proportions such that the reaction energy provides all the heat needed to maintain the reaction temperatures. The reformat from the POX reformer consists of a mixture of hydrogen, carbon dioxide, carbon monoxide, nitrogen, water vapor, and small amounts of by-products, such as methane. The carbon monoxide is reacted with steam over a catalyst in a one or two stage water-gas shift (WGS) reactor to form carbon dioxide and additional hydrogen. The remaining carbon monoxide is reduced to trace levels by preferential oxidation (PROX) to carbon dioxide over a suitable catalyst.

Process conditions in the reformer have a significant bearing on the overall fuel cell system performance and efficiency. The POX, WGS, and PROX reactions are carried out at different temperatures, with the POX temperature being the highest (700–1500°C) and the PROX temperature being the lowest (100–180°C) in the sequence. Good thermal integration and low POX temperatures

increase reforming and system efficiency [1], but this requires the development of active catalysts for this reaction. This paper discusses the chemistry, thermodynamics, and engineering principles of partial-oxidation reformers for automotive power plants, as well as some of the recent developments in POX technology for automotive applications.

FUEL REFORMING PROCESSES AND CATALYSTS

For a fuel such as iso-octane (a surrogate for gasoline), the general (unbalanced) partial-oxidation reaction may be written as,



The value of x (and to a lesser extent y) determines the heat of this reaction. Water (or steam) is added to the feed stream to suppress carbon formation and to assist in the transformation of the hydrocarbons and carbon monoxide to hydrogen and carbon dioxide. The amount of water added can be selected by the process developer depending on the desired gas composition. Typically, one to two moles of water for every mole of oxygen are used.

For $x = 0$, reaction (1) becomes the steam reforming reaction, with a large endothermic heat of reaction (+1.685 MJ/g-mol of iso-octane for liquid feeds). As x increases, the reaction becomes less endothermic, becoming thermoneutral at $x = \sim 2.9$ (for all carbon converted to carbon dioxide). Typically, the process is operated at values of x between 3.1 and 3.9, so that there is a net heat generation to make up for the heat losses from the reformer. This reaction may be carried out at 1100–1500°C without a catalyst. With a suitable catalyst, the reaction temperature may be lowered to 700–800°C, which favors the formation of CO_2 relative to CO , increases reforming efficiency, and alleviates the materials problem in handling high temperature gases. Such catalysts are being developed by McDermott Technology, Inc., and Argonne National Laboratory, among others.

INTEGRATED FUEL PROCESSOR DEVELOPMENT

Several organizations are developing partial oxidation fuel reformers, with support from the U. S. Department of Energy (DOE) under the PNGV (Partnership for the Next Generation of Vehicles) program.

McDermott is developing a 50-kWe catalytic autothermal fuel processor system for automotive fuel cells [2]. This fuel processor will use a liquid-phase desulfurizer to reduce the sulfur in gasoline to less than 3 ppm by weight. The autothermal reformer will use a bifunctional catalyst operating at an average temperature of 800°C. The CO concentration will be reduced to about 2000 ppm (by volume) in a shift reactor, and further reduced to less than 100 ppm by preferential oxidation. Figure 1 shows a conceptual arrangement of the McDermott fuel processor system.

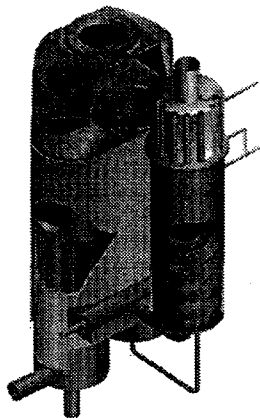
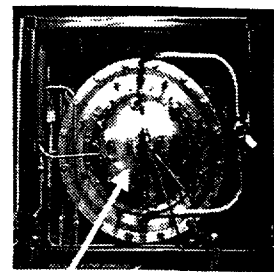


Fig. 1 Schematic drawing of the McDermott autothermal fuel processor system.



Top View with Test Frame
Side View with Test Frame

Fig. 2. Prototype assembly configuration for the HBT fuel-flexible fuel processor.

The fuel-flexible fuel processor (F³P) system being developed by Hydrogen Burner Technology is shown in Fig. 2 [3]. The fuel processor assembly includes several process steps, shown in Fig. 3, which have been thermally and physically integrated into the F³P. These F³P subsystems have been tested over 120 h, including about 60 start/stop cycles. Preliminary results from the testing with three fuels, methanol, natural gas, and gasoline, are summarized in Fig. 4. Additional testing is expected to establish higher operating capacities on natural gas and gasoline, and to yield higher efficiencies by operating at lower air-to-fuel ratios.

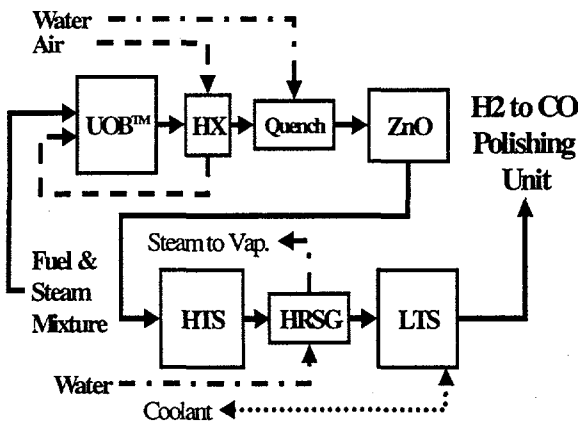


Fig. 3. Seven process units are thermally and physically integrated into the HBT fuel processor assembly.

	Methanol	Nat. Gas	Gasoline
Minimum SR	0.33	0.40	0.42 - 0.45
Efficiency	<76%	~70%	~68%
Max H ₂ , %dry	40%	33%	31%
Min CO, (LTS only)	0.3 to 0.1%	0.4 to 0.1%	0.5% to 0.1%
Tested Capacity, kWe**	38kWe	22kWe	15kWe

* Note preliminary performance based on ~120 hrs operation.
** Note Estimated Capacity based on Fuel Consumption and H₂ Concentration

Fig. 4. Summary of preliminary test results for the HBT fuel processor. SR = fuel stoichiometric ratio.

Epyx Corporation has developed a 20-kWe multi-fuel fuel processor [4]. Larger and smaller sizes are also being developed. Over 500 h of testing have been accumulated on a variety of fuels, including gasolines, methanol, ethanol, and natural gas. High conversion efficiencies of 76–80% with gasoline and 82–88% with methanol have been reported. Output from Epyx reformer was used to fuel a 10-kWe fuel cell stack from Plug Power. Preliminary measurements of system performance, efficiency, and emissions were in line with the targets developed by DOE and PNGV.

The Argonne partial-oxidation reformer (APOR) rated at 5–10 kWe is shown in Fig. 5, while Fig. 6 shows the schematic arrangement of the various process steps and temperatures within the APOR [5]. The main partial oxidation step is carried out at 700–800°C. This integrated reactor (reformer + sulfur removal + shift) has been tested with methanol, iso-octane, and gasoline. The H₂ concentration was

40% or higher (on a dry basis) during these tests. A mathematical model based on thermodynamic equilibrium, heat transfer, and material and energy balances is being used to develop reactor designs with improved performance. The present 5-10-kWe APOR has a volume of 7.5 liters. By improving catalyst configuration and reactor design, we anticipate that a 50-kWe reformer would be approximately 2 liters in volume.

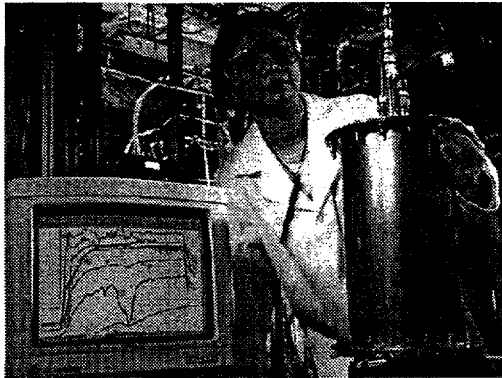


Fig. 5. The integrated Argonne partial oxidation reformer, APOR.

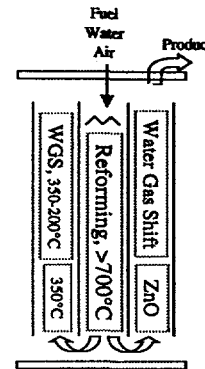


Fig. 6. Schematic arrangement of the various process steps in the APOR.

CONCLUSION

Several different approaches to partial oxidation reforming of gasoline and other transportation fuels are being pursued by various commercial organizations and a National Laboratory. Advanced catalysts are being developed that would enable these reformers to be used on-board light-duty vehicles powered by fuel cells. These reformers are presently being tested with conventional and alternative transportation fuels, such as gasoline and methanol. Preliminary results indicate that their performance will meet the objectives of the transportation application.

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