

Integrated Fuel Processor Development Challenges*

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Abstract

In the absence of a hydrogen-refueling infrastructure, the success of the fuel cell system in the market will depend on fuel processors to enable the use of available fuels, such as gasoline, natural gas, etc. The fuel processor includes several catalytic reactors, scrubbers to remove chemical species that can poison downstream catalysts or the fuel cell electrocatalyst, and heat exchangers. Most fuel cell power applications seek compact, lightweight hardware with rapid-start and load-following capabilities. Although packaging can partially address the size and volume, balancing the performance parameters while maintaining the fuel conversion (to hydrogen) efficiency requires careful integration of the unit operations and processes. Argonne National Laboratory has developed integrated fuel processors that are compact and light, and that operate efficiently. This paper discusses some of the difficulties encountered in the development process, focusing on the factors/components that constrain performance, and areas that need further research and development.

Introduction

The implementation of fuel cells in a host of applications will be greatly enhanced by the availability of fuel processors that enable fuel cell systems to operate on currently available fuels. Recognition of this need has led to a broad range of research and development efforts to develop suitable fuel processors and their supporting technologies (e.g., catalysts). Of the various fuel cell applications, few are as more constrained as the on-board fuel processor for the light-duty fuel cell vehicle.

Light-duty fuel cell vehicles are being developed that use the low temperature polymer electrolyte fuel cell. These fuel cells operate best on hydrogen; however, in exchange for some loss in power output, these units can operate with reformat gas, if the levels of certain contaminants (e.g., carbon monoxide, sulfur, ammonia) that may be present are limited to a few ppm (or lower). The size, weight, and response of these fuel cell systems are constrained by the performance of the subsystems that remove these contaminants. The various components of the processor operate at different temperatures. The size and location of heat exchangers also constrains the system. Consequently, fuel processors for this application are restricted in their size, weight, and response by the components, processes, and heat exchangers that are present in the fuel processor.

Fuel cells offer the potential for high fuel efficiency and low emissions. In order to maintain those characteristics of the fuel cell power plant, the fuel processor must be efficient over a broad power range and maintain a clean exhaust gas. In addition, the automotive fuel processor is severely limited in terms of size (limited space under the hood), weight (reduces the mileage achievable), and cost. Furthermore, the fuel processor must not limit the vehicle's start-up and load-response capabilities.

All of these demands make for a very challenging design problem, which has forced researchers to take a fresh look at the wizened art of making hydrogen. Various organizations are developing design alternatives that include different reforming processes (e.g., steam reforming, autothermal, etc.), sulfur removal methods, CO

management processes, membrane processes, etc. Argonne National Laboratory (ANL) is studying a pathway (see Figure 1) that is based on the catalytic autothermal process. Our process relies on limited sulfur-tolerant catalysts and thermal integration to achieve an efficient^a conversion within a compact, lightweight enclosure.

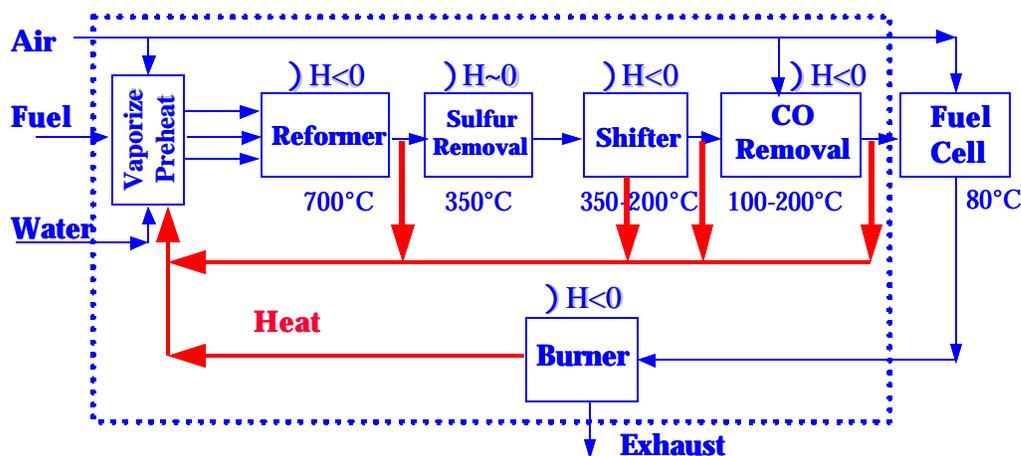


Figure 1. Schematic of a fuel processor showing the various unit processes, fluid flow and temperatures, and flow of thermal energy. Dotted box represents the fuel processor.

Component Challenges

The first step in the conversion of hydrocarbon fuels usually involves a reforming reaction. The catalytic autothermal process has received wide acceptance because of its potential for a compact, lightweight, and responsive unit. Because of significant advances in catalyst and reactor designs for the autothermal reactor that this is no longer considered the most demanding unit in the fuel processor. These reactors are now small enough that the reforming can be conducted at space velocities that are of about 10^5 per hour. Issues that remain include controlling the oxidation reactions (with oxygen as the limiting reactant), which leads to a hot zone in the catalyst. Reducing the temperature in the hot zone would be beneficial because it would relax the choice of materials of construction and would also lead to greater selectivity for hydrogen (less CO formed.)

Most petroleum-derived fuels contain sulfur. Future gasolines, which are slated to have lower sulfur levels, will still contain tens of parts per million of sulfur. If the reforming catalyst is sulfur tolerant, the task of dealing with the sulfur is considerably simplified because the reforming reaction converts the various forms of organosulfur to hydrogen and carbonyl sulfides, which are easier to trap. One of ANL's reforming catalysts has demonstrated sulfur tolerance and therefore allows this pathway. Other processes using reforming catalysts that are susceptible to the sulfur poisoning must either remove sulfur before the reformer or operate at over 1000°C , since many catalysts show some sulfur tolerance at these high temperatures.

Removal of sulfur after reforming is typically done with reagents, which react with the H_2S and COS , like zinc oxide,. The level of sulfur removal is limited by

^a Efficiency is defined as the lower heating value of hydrogen produced as a percentage of the lower heating value of the fuel.

equilibrium, which, at the conditions between the reformer and the shift reactor, still leaves 2-3 ppm of sulfur in the reformat [1]. This level of sulfur poisons many of the shift catalysts that are being considered for fuel cell applications. Since the fuel cell anode electrocatalyst usually has a very low (ppb) tolerance [2] for sulfur, further removal of sulfur is necessary.

As shown in Figure 1, the reformat gas from the reformer needs to be cooled from its exit temperature of 700°C to 350°C as it enters the zinc oxide bed. The shift reaction itself is an exothermic process and the reformat requires a declining temperature profile as it progresses through the shift reactor. A typical exit temperature from the low-temperature water gas shift reactor is ~200°C. Maintaining the desired temperature profile requires significant heat removal and, therefore, heat transfer surfaces. With careful and innovative designs, it is possible to avoid large weights and volumes that typify the more traditional heat exchangers (e.g., tubular).

For example, the reformat gas from the autothermal reformer is at 700°C and contains 7.9% carbon monoxide. The gas must exit the shift reactor at 200°C containing 1.5% carbon monoxide. The heat removal needed to achieve this in a 50 kW(e)^b fuel processor is ~26 kW.

Table 1 compares two simplistic options for this heat exchange, where the heat is removed by a cooling medium passed through a tubular coil. In the first case, the heat is removed by a gaseous cooling medium that picks up sensible heat. In the second case, the heat is removed by a phase change of the cooling medium. This has a significant impact on the log mean temperature difference (LMTD), as shown in the table. It has been assumed that for both cases the overall heat transfer coefficient is limited by the reformat side at 50 W/m²·°C. Case I requires a heat transfer surface area of 7.2 m², which translates to a 0.635-cm. diameter tube that is 353 m long. That tubing alone would weigh 42 kg.

Case II with its higher LMTD requires less (27% of Case I) heat transfer surface area. Case II also uses a bigger diameter tube and thus requires a length of 64 m, which weighs 12 kg. At 0.24 kg/kW(e), tubular heat exchangers are clearly not attractive for automotive fuel processors, especially since the target proposed by the Partnership for a New Generation of Vehicles (PNGV) is 1 kg/kW(e) for the entire fuel processor (including the balance of plant components: pumps, pipes, gauges, etc.)

^b The lower heating value of the hydrogen in the reformat should be 125 kWt, assuming a fuel utilization of 80% and a stack efficiency of 50%.

Table 1. Comparison of Tubing Length and Weight Required to Remove Heat[°] Using Sensible Heat of a Gaseous Cooling Medium (Case I) and by Phase Change of the Cooling Medium (Case II)

	Case I	Case II
Log Mean Temperature Difference, °C	75	275
Overall Heat Transfer Coefficient, W/m ² ·°C	50	50
Required Heat Transfer Area, m ²	7.0	1.9
Tube Diameter, cm	0.635	0.95
Tube Length, m	353	64
Tube Weight, kg	42	12

The water gas shift reactor is an essential component in the fuel processor, since the reforming of most fuels will yield significant quantities of carbon monoxide. Since equilibrium at lower temperatures allows lower levels of CO, a low temperature shift reactor is needed. But the low temperature severely limits the reaction rate and requires a large catalyst bed. With the conflicting constraints between equilibrium and kinetics, it is possible for a given catalyst(s) system and inlet/outlet CO concentrations, to calculate an optimum temperature profile that will result in the smallest catalyst volume. Figure 2 shows such a temperature profile and concentration of CO that would result along the length of the shift reactor.

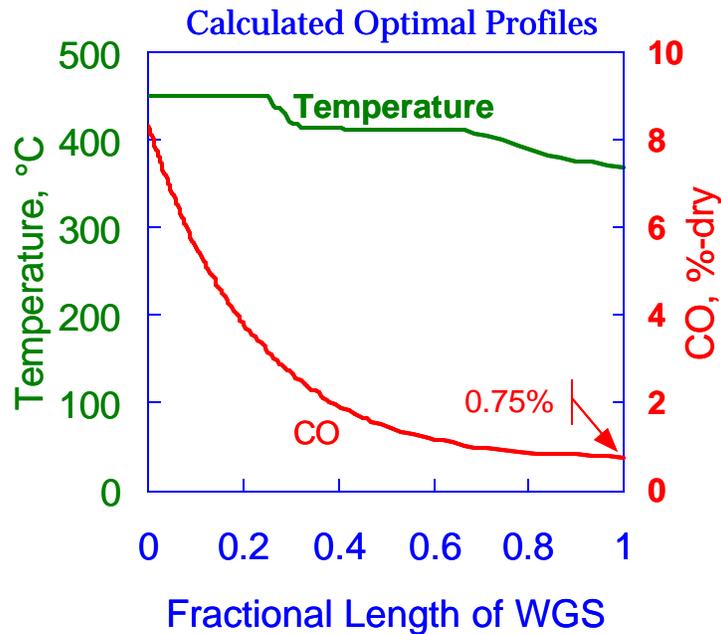


Figure 2. Optimized temperature profile within a water gas shift reactor and the resulting CO concentration.

[°] Heat Load: 26 kW; Reformate Inlet/Outlet Temperatures: 700/200°C; CO Concentration in Reformate Inlet/Outlet: 7.9/1.5 %-dry.

Although difficult, it is possible to design the water gas shift reactor to operate at the optimum profile at the design point. Since automotive fuel processors with their transient needs will rarely operate at any specific design point, it becomes even more difficult (and perhaps impractical) to try to achieve such a profile at all loads.

Even with an optimally designed shift reactor, the reaction rate in the low-temperature zone is much too slow. Until more active catalysts become available, this zone of the reactor is destined to remain the largest zone and thus be the component that limits the power density of the fuel processor. This challenge has been recognized and many academic, government, and industrial enterprises have committed to identifying new catalysts for this reaction. Alternative engineering approaches are also being investigated to reduce the importance of the low-temperature shift reactor. These include the use of various membranes [3] that extract one or more of the gas components to offset the equilibrium limitations.

Conclusion

The past decade has seen significant advances in the development of the fuel processor for light-duty fuel cell vehicles. The new generation of fuel processors is much closer to the desired weight, volume, and performance characteristics. The experience associated with these advances has highlighted the need for some further developments in the components. They include the ability to limit high temperatures in the reformer, sulfur removal or tolerance, development of compact heat exchangers and careful thermal integration, and development of new generation catalysts with higher activity and durability.

Eventually the individual components must be optimized with respect to the total fuel processor, such that its weight, volume, and transient performances do not limit or compromise the performance of the vehicle.

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