Fuel processing for PEM fuel cells: transport and kinetic issues of system design

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Abstract

In light of the distribution and storage issues associated with hydrogen, efficient on-board fuel processing will be a significant factor in the implementation of PEM fuel cells for automotive applications. Here, we apply basic chemical engineering principles to gain insight into the factors that limit performance in each component of a fuel processor. A system consisting of a plate reactor steam reformer, water–gas shift unit, and preferential oxidation reactor is used as a case study. It is found that for a steam reformer based on catalyst-coated foils, mass transfer from the bulk gas to the catalyst surface is the limiting process. The water–gas shift reactor is expected to be the largest component of the fuel processor and is limited by intrinsic catalyst activity, while a successful preferential oxidation unit depends on strict temperature control in order to minimize parasitic hydrogen oxidation. This stepwise approach of sequentially eliminating rate-limiting processes can be used to identify possible means of performance enhancement in a broad range of applications.
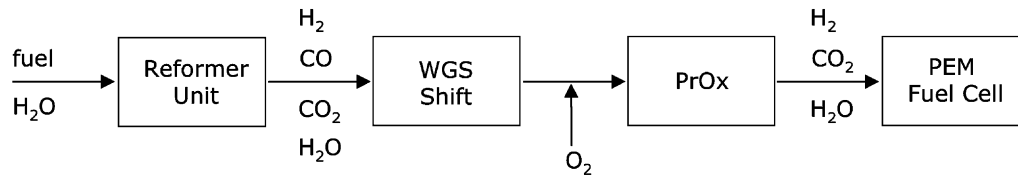© 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Fuel cell power systems for transportation applications have received increased attention in recent years because of their potential for high fuel efficiency and lower emissions. A fuel cell converts hydrogen and oxygen into water, directly generating electrical energy from chemical energy without being restricted by efficiency limits of the Carnot thermal cycle [1]. Proton exchange membrane (PEM) fuel cells are preferred for automotive applications, because their low operating temperatures (around 80 °C) allow for rapid startup; other potentially attractive features include relatively low projected cost and maintenance needs. Lacking a hydrogen fuel delivery system, a fuel processor may be required to generate a hydrogen-rich stream using infrastructure fuels such as gasoline or diesel. Fuel processors for automotive applications are usually rated for 50 kW electric output. This figure may seem low (50 kW = 67 Hp) when compared with the power ratings of today's vehicles; yet, because electric engines deliver maximum torque at all rpm while internal combustion engines deliver maximum torque only at an optimum rpm, internal combustion engines operate at a fraction of their nominal power rating most of the time while electric motors operate at their rated power at all times.
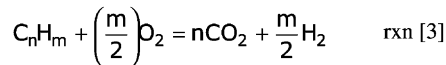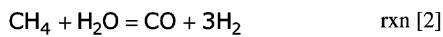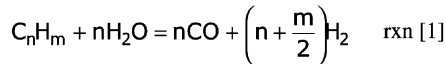
Aside from the ubiquitous issue of cost, the automotive environment imposes several performance constraints on a 50 kW fuel processor. The system must be fully operational within a minute or so of a cold-start and able to respond rapidly to varying loads. Significant load transients occur frequently as a result of acceleration, hills, highway cruising, etc. The use of a large-capacity battery storage system to serve as an energy reservoir between the fuel processor and fuel cell would increase cost and weight. Although increasingly aggressive size and weight targets are proposed by various groups (DOE, PNGV, CARAT, etc.), the physical and chemical processes occurring inside each of the unit operations comprising a fuel processor place lower bounds on the corresponding catalyst weights and reactor volumes.

It is the goal of this communication to investigate the primary components of an automotive fuel processor for PEM fuel cells and show how basic chemical engineering principles can be applied to reveal the role of heat transport, mass transport, and reaction kinetics in the component designs. The results can be useful for estimating the minimum and relative sizes of the component reactors and, more importantly, understanding the sources of performance limitations. This knowledge can suggest a means of process enhancement (lower weight and cost, higher overall efficiency) from the perspective of reactor configurations, catalyst formulations, and process integration.
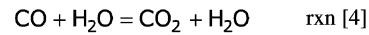
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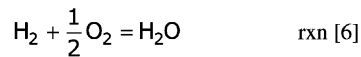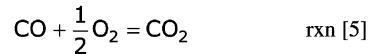E-mail address: dloffler@idatech.com (D.G. Löffler).

Fig. 1. Schematic drawing of an automotive fuel processing system and listing of relevant chemical reactions.

2. Overall description of a fuel processor

In order to generate a hydrogen-rich stream from an automotive fuel processor, fuel (e.g. gasoline or diesel) is converted in a reforming unit that involves steam reforming (feed is composed of fuel and steam), or autothermal reforming (i.e. feed is fuel, steam, and air). In Fig. 1, a schematic drawing of the overall process is shown for the case of steam reforming, which is a mature technology for hydrogen, ammonia and synthesis gas production facilities that are large, steady-state operations. In conventional tubular steam reforming, the energy to drive the endothermic reforming reactions ((1) and (2)) is supplied by external heating through the tube wall, generally through combustion of a portion of the fuel. It should be noted that reforming reactions are shown separately for methane and for higher hydrocarbons, because the reaction is considered to be irreversible for higher hydrocarbons while it is reversible in the case of methane.

In autothermal reforming, the heating process is internal as a portion of the fuel is catalytically combusted to yield heat necessary for the reforming process. In general, autothermal reforming has a better capacity for start-up than steam reforming, because the unit can be quickly brought up to desired operating temperature by running in combustion mode for a short time. However, comparisons between fuel processors based on these two approaches are complex, since quantitative comparisons of overall efficiency and cost depend on details of system integration and control.

Although the specific composition of the reformer effluent depends on the reforming technology and operating conditions chosen, we can take a representative steam reforming outlet as containing 55% H_2, 10% CO, 5% CO_2, and 30% H_2O on a molar basis. The example calculations presented here are based on using methane as the fuel because in practice liquid fuels are converted to predominantly CH_4 in a pre-reformer unit.

Because CO is a poison to the fuel cell electrocatalyst, its presence in the product stream must be reduced to less than 50 ppmv. This task is partially accomplished by a water–gas shift (WGS) reactor (reaction (4)). Chemical equilibrium limits the conversion achieved in the WGS reactor, thus, final CO cleanup occurs in a preferential oxidation (PrOx) unit in which the desired reaction is the oxidation of carbon monoxide (reaction (5)); however, life is complicated by the presence of the undesirable combustion of hydrogen (reaction (6)). Selectivity is a serious issue in the PrOx unit, because the oxidation of hydrogen leads to diminished process efficiency and increased water management issues.

This brief overview of a fuel processor focuses on the main reaction vessels and neglects the desulfurizer unit, heat exchangers, controls, etc. that would be included in a detailed process diagram. The reforming, water–gas shift, and preferential oxidation reactors represent a large fraction of the volume and cost, and pose the greatest technical challenges.

3. Reforming unit

Beginning with a tubular packed bed steam reformer, a simple drawing of which is shown in Fig. 2a, we will use data from the literature and results of correlation calculations to illustrate the relative effects of heat transfer, mass transfer, and reaction kinetics on component performance. A series of reactor designs will be evaluated, in which the reactor configuration evolves to successively alleviate the limiting factors; the final incarnation represents a reasonable lower bound for the unit specifications.

3.1. Fixed bed tubular reformer: reactor volume based on heat transfer rate

Assuming a 40% efficiency for the PEM fuel cell stack, a 50 kW device requires a hydrogen production of around
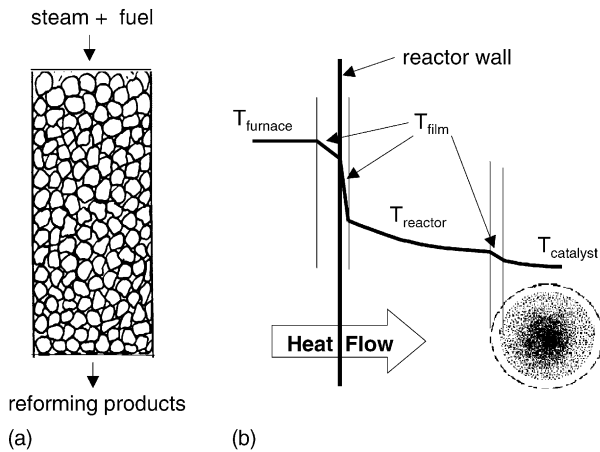
Fig. 2. Illustration of conventional tubular steam reformer (a) and associated heat transfer resistances (b).

31 mol/min based on the lower heating value of hydrogen. In order to determine the fuel feed required to produce this level of hydrogen from steam reforming, we can assume that the methane reforming reaction proceeds far to the right and that most of the CO that is produced is converted in the WGS reactor; in this case, the approximate overall stoichiometry is $CH_4 + 2H_2O = 4H_2 + CO_2$. Accordingly, a feed of 7.75 mol/min of methane is needed to generate 31 mol/min of hydrogen. Based on a heat of reaction of about 165 kJ/mol for methane steam reforming, the heat duty of the reformer is 21.3 kW. Although heat fluxes in industrial tubular steam reformers can be several times greater, those in smaller-scale units containing 3 mm catalyst particles in a single 1 in. diameter pipe will be around 17.4 kW/m^2 [2] These values of heat duty and heat flux result in a required heat transfer area of 1.22 m^2, a tube length of 15.3 m, and tube volume of 7.75 l. A similar estimate of internal tube volume can be obtained using a fixed bed wall heat transfer coefficient correlation [3,4], in which Nusselt number is given as a function of Reynolds and Prandtl numbers, and taking the temperature difference between the tube wall and the bulk fluid to be around 200–250 °C.

3.2. Fixed bed tubular reformer: reactor volume based on chemical reaction rate

Based on a detailed kinetic model [5] of methane steam reforming over a Ni-based catalyst, the intrinsic rate of methane conversion can be computed to be around 12.0 mol/kg$_{cat}$ s at a temperature of 750 °C, a pressure of 2.5 bar, and a steam-to-methane ratio of 3. This pressure was chosen because PEM fuel cells operate at or slightly above atmospheric pressure and there will be some pressure drop downstream of the reformer. Because the effectiveness factor can be expected to be around 0.001 [6] for our current reactor configuration, approximately 10.8 kg of catalyst are needed to process 7.75 mol of methane per minute. If we

suppose the catalyst bulk density is 1.5 kg/l, then the catalyst volume is 7.2 l.

This example yielded a higher tube volume based on heat transfer than on apparent reaction rate. Heat transfer is a serious issue in steam reforming processes because the reaction is highly endothermic and, as shown in Fig. 2b, the heat flow must overcome resistances at the furnace/external tube wall interface, inside the tube wall, at the tube wall/gas and gas/catalyst pellet interfaces, and within the catalyst pellet.

3.3. Fixed bed plate reformer: reactor volume based on heat transfer rate

Next, we shall attempt to reduce the reformer volume by designing a reformer based on a plate heat exchanger. Plate heat exchangers provide higher heat transfer area per unit volume than tubular heat exchangers. Also, since the plate surface is easily accessible during manufacturing, it can be easily roughened with corrugations, dimples, or other protuberances to reduce the thickness of the heat transfer boundary layer.

Consider a reformer design based on a plate heat exchanger, as shown in Fig. 3, which consists of a series of alternating combustion and reforming channels. Heat generated by an exothermic chemical reaction in the combustion channels is transferred through the channel walls to drive the endothermic reforming process. The combustion and reforming catalysts can either be loaded as pellets in the channel or directly deposited on the channel walls, which is the situation depicted in Fig. 3. We first consider the situation in which the reforming channels are loaded with 1/8 in. catalyst pellets. If there are 50 reforming channels and each is 3 in. wide and 1/8 in. high, the Reynolds number will be around 70. By assuming a ΔT of around 250 °C and using available plate heat exchanger Nusselt number correlations [7] based on Reynolds number, Prandtl number, and ratio of channel height to plate length, we can solve for the plate length that matches the heat flow into the reforming channels with the heat duty. Rough calculations reveal that a plate length of 7.3 in. is needed for this sample configuration. This length corresponds to a total volume of 2.2 l for the reforming passages in the plate configuration and represents a
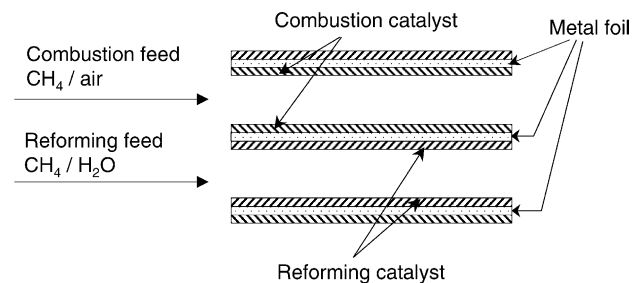

Fig. 3. Drawing of a steam reformer based on a plate heat exchanger with catalyst-coated plates.

factor of 3.5 improvement over the heat transfer volume for the tubular design. The estimated catalyst volume now exceeds the heat transfer volume, an observation that is not surprising considering the low effectiveness factor associated with 1/8 in. pellets of reforming catalyst. The low effectiveness factor is due to both pore diffusion resistances and the low temperatures in the pellet core induced by the endothermic reaction.

3.4. Coated-catalyst plate reformer: reactor volume based on mass transfer rate

We shall consider next a plate reactor configuration in which the reforming catalyst is directly deposited onto the heat exchange plates. The effectiveness factor of the coated catalyst is now orders of magnitude larger than that of the 1/8 in. pellets, because the characteristic length of the catalyst is over two orders of magnitude shorter for the coated catalyst and the heat supplied from the back of the plate provides uniform temperature over the thickness of the coating. The mass of coating needed is about 20 g, which translates in a density of approximately 5 mg/cm^2. This is well within the range of thickness found in coated catalysts.

In the coated-catalyst plate reformer, the heat of reaction is transferred directly from the solid plate to the catalyst, thus, eliminating the solid–fluid heat transfer resistance that limited the volume of the plate reformer packed with catalyst pellets. In addition, the catalyst volume needed is now insignificant. The reformer volume is controlled now by the rate of mass transfer from the bulk of the fluid to the catalyst surface.

Using the Chilton–Colburn analogy [8] and a similar argument as was used for the plate reactor with catalyst-packed passages, the gas–solid mass transfer coefficient can be estimated to be around 1.75 mol/m^2 s for a reasonable catalyst-coated plate reactor geometry with a plate corrugation depth of 1/8 in. The resulting total volume of reforming channels is now only 1.2 l.

3.5. Coated-catalyst plate reformer: volume of reforming and combustion channels

The intrinsic rate of reforming is comparable to that of combustion, hence the volume of the combustion channels can be taken to be the same as the volume of the reforming channels. Then, the minimum total internal volume of a 50 kW plate-type methane steam reformer is about 2.4 l. The reactor volume is controlled by the film mass transfer resistance between the gas streams and the catalyst surfaces.

We have built and tested a plate reformer for methane steam reforming. The device consisted of a single reforming channel with a combustion channel on either side. Almost complete methane conversion and near-equilibrium product composition were maintained for 400 h on-stream. Based on our experimental results, the total reforming plus combustion channel volume for 50 kW productivity is 5 l; this value is only a factor of two higher than the value previously estimated. The agreement is remarkable given the assumptions introduced in the calculations.

The plate reformer has shown an extremely fast response to load transients; the device is able to reach a new steady-state only a fraction of a second after a step change in the flowrates of the reforming and combustion gas mixtures. This behavior occurs because the thermal mass and the heat transfer resistance between the combustion and reforming channels are low. The foil properties dominate the transient response with the reactor frame introducing only a second-order effect. Because of its short thermal transients, the plate reformer promises to achieve the fast start-up times required for transportation applications. Furthermore, we observed that the plate reactor could accommodate changes of about a factor of two in load simply changing the flow rates in the reforming and combustion channels. Larger load variations might be met by varying the number of channels open to flow. Plate reactors could be built including manifold and switching systems to direct process flows to a given number of channels at a certain time, according to load.

4. Water–gas shift reactor

The water–gas shift reactor provides primary CO cleanup, as well as secondary H_2 production. This reaction is moderately exothermic with a heat of reaction, ΔH_{rxn}, of −40 kJ/mol. Lower temperatures favor high equilibrium CO conversion while high temperatures favor intrinsic kinetics. A target carbon monoxide conversion of 90–95% in the WGS unit would translate into a carbon monoxide level of 30 000–100 000 ppm being reduced to 1000–10 000 ppm. Thermodynamics mandates that the WGS outlet gas temperature be no more than 220–250 °C to achieve such conversion levels. Indeed, low-temperature catalyst activity and stability are the main issues related to the water–gas shift reactor. Most industrial water–gas shift catalysts have been developed for operation at higher temperatures. A viable water–gas shift catalyst for an automotive fuel processor must demonstrate sufficient activity over a reasonable temperature window, have 2000–5000 h stability, be non-pyrophoric (a feature not possessed by conventional Cu-based WGS catalysts), and not require a lengthy in situ pre-reduction procedure. Because the intrinsic rate of current water–gas shift catalysts [9,10] is orders of magnitude lower than that of steam reforming, the WGS unit can be expected to be the largest component of the automotive fuel processor.

Computer simulations were used to illustrate the impact of temperature profile on the reactor performance. Using representative kinetics, curves of CO conversion as a function of catalyst space velocity, (W/F_{CO}^0) where W is the catalyst mass and F_{CO}^0 is the inlet molar flow rate of CO, were generated for various temperature profiles.
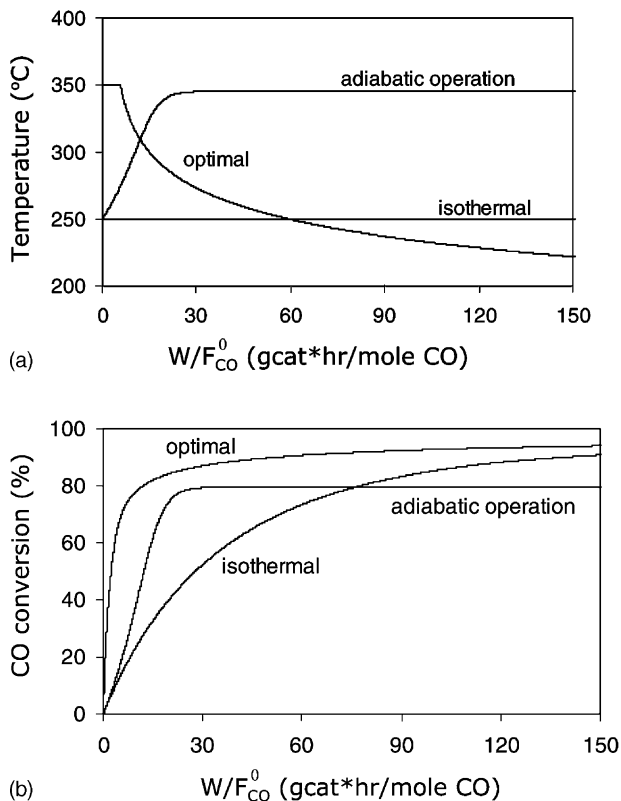
Fig. 4. Water–gas shift reactor. Isothermal, adiabatic, and optimal temperature profiles are shown in (a) for a sample WGS catalyst. Carbon monoxide conversion profiles are presented in (b) to convey the impact of temperature control on the progress of the reaction.

Three temperature profiles were considered, as shown in Fig. 4a: isothermal operation at 250 °C, adiabatic operation with an inlet temperature of 250 °C, and an optimal temperature profile. The optimal temperature profile was determined by choosing a temperature to maximize the local rate of CO conversion at each axial position along the reactor, while limiting the temperature to a suitable maximum value corresponding to limits of catalyst stability. Profiles of carbon monoxide conversion versus catalyst space velocity are shown in Fig. 4b for the temperature profiles depicted in Fig. 4a. Adiabatic operation with an inlet temperature of 250 °C yields poor performance because the temperature of the process stream increases to a point at which equilibrium conversion is low (<80%). Isothermal operation initially yields conversions lower than those obtained adiabatically, but the conversion curve for the isothermal case continues to increase well beyond the point at which the conversion profile for the adiabatic case reaches a plateau. Yet, significantly better performance can be achieved by operating at a relatively high temperature and exploiting reaction kinetics when the gas composition is far from equilibrium and then lowering the temperature as thermodynamics begins to limit the CO conversion. Indeed, the conversion curve corresponding to the optimal temperature profile results in far better performance than either the isothermal

or adiabatic modes. Assuming the reformate stream is around 65 mol% H_2 at the end of the WGS unit, and recalling that 31 mol/min of hydrogen are required, then the total flow rate entering the WGS unit must be 48 mol/min, 4.8 mol/min of which are CO. For the optimal temperature profile, 90% carbon monoxide conversion is attained at a catalyst space velocity of 60 g_{cat} h/mol of CO, which translates into a catalyst mass of 17 kg, or catalyst volume of 11.3 l assuming a bed density of 1.5 kg/l.

Excessive volume of low-temperature water–gas shift catalyst is certainly one of the major technical obstacles to the production of a commercial automotive fuel processor. The optimal temperature profile provides the minimum reactor volume. In practice, this profile could be approached by implementing a plate-type reactor configuration, similar to that previously described for the reformer unit. Here, the alternate channels through which reformate is not flowed would be used to pre-heat other process gas that is passed counter-current to the reformate and extracts heat from it.

5. Preferential oxidation reactor

Final carbon monoxide cleanup is accomplished in the PrOx reactor, to which the process stream and a small flow of oxygen (or air) are fed. The critical issue in the design of the PrOx reactor is to achieve a high level of CO conversion (<50 ppmv CO in effluent) while minimizing hydrogen loss. This may seem a daunting task, given that the inlet concentration of hydrogen is two orders of magnitude greater than the CO concentration, and the rate of hydrogen oxidation is also orders of magnitude higher than that of CO oxidation. However, the difference in the heats of chemisorption of H_2 and CO on noble metals [11] enables the design of a PrOx process based on platinum catalysts demonstrating reasonable selectivity of oxygen to CO oxidation. On a Pt/γ-alumina catalyst, CO displaces hydrogen from the metal surface at temperatures lower than 150 °C. Consequently, carbon monoxide is oxidized before hydrogen because chemisorbed CO is far more abundant on the catalyst active sites. At higher temperatures, the surface coverage of CO decreases, allowing for hydrogen adsorption and oxidation [12].

Fig. 5 shows simulated CO conversion (a) and oxygen selectivity to CO oxidation (b) profiles as functions of the catalyst space velocity for isothermal operation at several temperatures. The results are for an inlet CO level of 1 mol% and an inlet O_2/CO ratio of 1.0. As seen in Fig. 5a, nearly complete CO conversion is achieved for operating temperatures up through 200 °C, beyond which, the maximum conversion decreases rapidly with increasing temperature. Results show that final CO conversions are 100% at 200 °C, 98% at 250 °C, and 70% at 300 °C. The initial selectivity of oxygen to CO conversion decreases with increasing temperature in Fig. 5b, because the surface coverage of
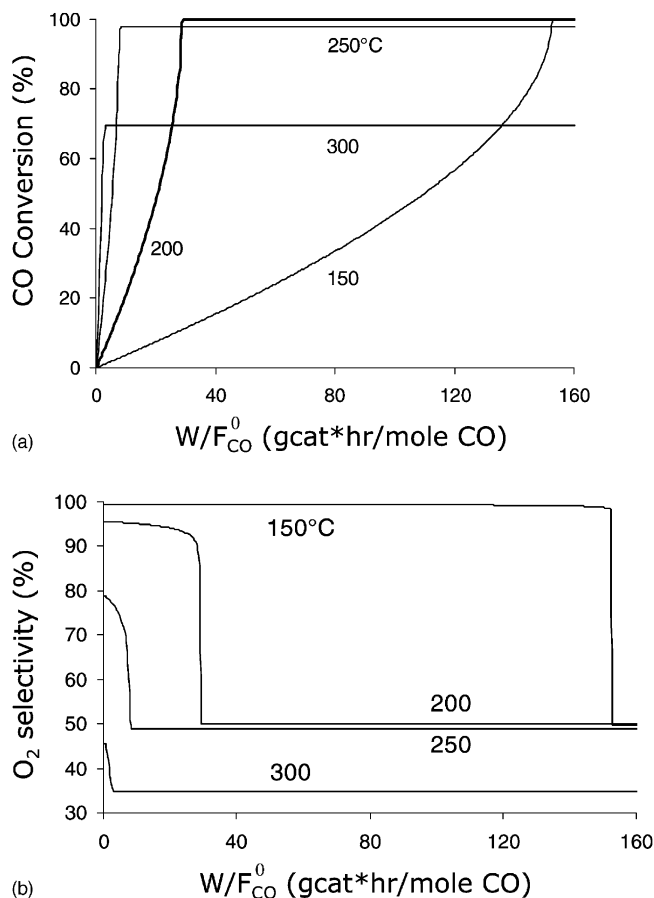
Fig. 5. Preferential CO oxidation reactor. Profiles of carbon monoxide conversion (a) and oxygen selectivity to CO (b) are shown as functions of catalyst space velocity for various cases of isothermal operation.

CO decreases as the temperature increases. For any given temperature, the selectivity also decreases with increasing catalyst space velocity and reaches a plateau once all of the oxygen is consumed. At low temperatures, the selectivity remains high until the CO is virtually depleted and then the remaining oxygen reacts with hydrogen.

The kinetics of the PrOx reactions reveal that temperature control in the reactor is the predominant technical challenge, because poor selectivities primarily result from excess reactor temperature; as in the case of the WGS unit, adiabatic operation in a single-stage reactor can be expected to yield poor performance. An effective reactor design will involve a means of temperature control, such as supporting the catalyst on a heat exchange-type device, using staged air or water injections, or a combination of these ideas.

Simulations of non-isothermal PrOx configurations suggest that approximately 5 kg of 0.5 wt.% Pt on γ-alumina are needed to reduce a 1 mol% CO reformate to less than 50 ppm of carbon monoxide. The bulk volume of this catalyst mass is around 3.5 l, indicating that although the volume of catalyst needed for the PrOx unit is larger than plate reformer volume, it is several times smaller than for the WGS reactor.

6. Conclusion

Operating requirements and component design issues have been explored for an automotive fuel processor for PEM fuel cells. We applied basic chemical engineering principles to show how conventional industrial technology could be scaled down effectively by alleviating the limiting factor (heat transfer, mass transfer, reaction kinetics) in a series of evolving reformer designs. It was determined that the minimum reasonable volume for a compact steam reformer for a 50 kW system is about 2.5 l and that only tens of grams of reforming catalyst are needed. Using a plate-type reactor configuration in which the catalysts are directly deposited on metal plates, mass transfer between the process stream and the catalyst surface limits the size of the reformer. Next, investigations of the water–gas shift and preferential oxidation reactors revealed the importance of good temperature control. Achieving sufficient carbon monoxide conversion in the WGS reactor depends on having good catalyst activity at low (200–250 °C) because thermodynamics severely restricts conversion at higher temperatures. The WGS unit is currently the largest primary component of the fuel processor, requiring an estimated 11.5 l of bulk catalyst volume. Temperature control also plays a pivotal role in the preferential oxidation unit, because the selectivity of oxygen to carbon monoxide oxidation deteriorates at temperatures higher than about 225 °C in platinum-based systems. Roughly, 3.5 l of catalyst are needed for the PrOx unit in a 50 kW fuel processor.

We conclude that the minimum total volume of the process stream reactors in a 50 kW fuel processor is 17 l. This figure depends heavily on a water–gas shift unit that operates with an optimal temperature profile and a strictly isothermal preferential oxidation reactor. Practical fuel processors should exhibit considerably larger volumes.

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