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MEMBRANE REACTOR ADVANTAGES FOR METHANOL REFORMING AND SIMILAR REACTIONS

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MEMBRANE TECHNOLOGY SYMPOSIUM ARTICLE

Membrane Reactor Advantages for Methanol Reforming and Similar Reactions

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ABSTRACT

Membrane reactors achieve efficiencies by combining in one unit a reactor that generates a product with a semipermeable membrane that extracts it. One well-known benefit of this is greater conversion, as removal of a product drives reactions toward completion, but there are several potentially larger advantages that have been largely ignored. Because a membrane reactor tends to limit the partial pressure of the extracted product, it fundamentally changes the way that total pressure in the reactor affects equilibrium conversion. Thus, many gas-phase reactions that are preferentially performed at low pressures in a conventional reactor are found to have maximum conversion at high pressures in a membrane reactor. These higher pressures and reaction conversions allow greatly enhanced product extraction as well. Further, membrane reactors provide unique opportunities for temperature management which have not been discussed previously. These benefits are illustrated for methanol reforming to hydrogen for use with PEM (polymer electrolyte membrane) fuel cells.

INTRODUCTION

Membrane reactors achieve efficiencies by combining, in one unit, a reactor that generates a product with a semipermeable membrane that extracts it. The result is greater conversion as removal of the product drives equilibrium-limited reactions toward completion. This advantage is reviewed excellently by Armor (1, 2), but there is considerable confusion about what sort of reactions lend themselves to membrane reactors as opposed to sequential reactors and separators. There is also confusion about how best to run a membrane reactor so that the benefits are maximized. I plan to show that the advantage of a membrane reactor is not so much that you get higher conversion, as that you

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fundamentally change the way pressure affects the extent of reaction and product recovery. These benefits can be shown more clearly by following a typical application, steam reforming of methanol, a reaction that is being pursued as a source of hydrogen for PEM fuel cells. Other applications can then be discussed more generally.

PEM fuel cells are being pursued for mobile and remote electricity generation. They are silent and generate electricity at a much greater energy conversion than conventional engines and generators, in excess of 70% efficiency as opposed to 35% for a diesel generator. Methanol reforming and other similar processes are attractive mobile and remote sources of pure hydrogen since methanol and water are relatively easy to store and handle. A purifier of some sort is needed though since the power and efficiency of PEM fuel cells is greatly enhanced with pure hydrogen, but the reformer and purifier must be energy-efficient for fuel cells to retain their efficiency advantage over diesel generators.

A typical flow diagram for a methanol reformer and sequential purifier is shown in Fig. 1. The overall methanol reforming reaction is

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2 \qquad (1)$$

It can be modeled as occurring in two stages (3), an endothermic cracking reaction,

$$CH_3OH \rightarrow 2H_2 + CO \qquad (2)$$

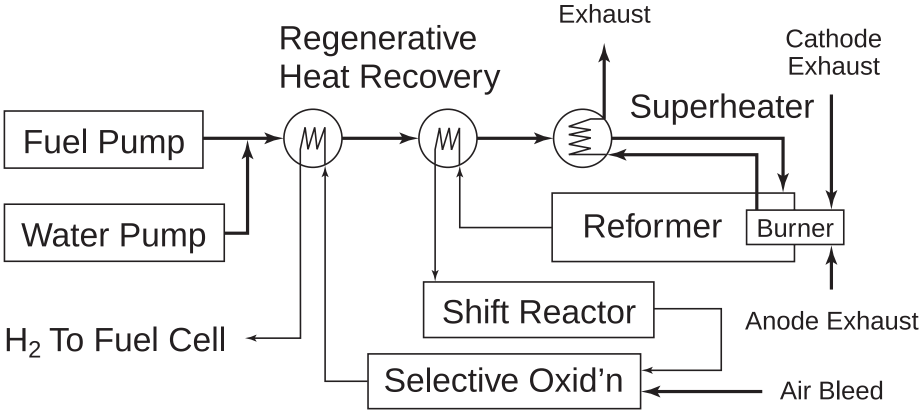

FIG. 1 Schematic of a hydrogen generator based on sequential methanol reforming and partial oxidation, from Amphlett et al. (9). As in Fig. 3, an internal burner provides the heat for reforming, but in this design the fuels are exhaust and air from the fuel cell cathode and anode. That large amounts of hydrogen are exhausted from the fuel cell results from the low purity of hydrogen in the reformer product.

followed by the exothermic water gas shift reaction,

$$CO + H_2O \rightarrow H_2 + CO_2 \tag{3}$$

Both reactions are performed over copper–zinc oxide catalyst to avoid methane formation. Methane is undesirable since, for each molecule of methane formed, four potential molecules of hydrogen are lost.

A membrane can be used to extract pure hydrogen from the reformate gas, or a partial oxidation reactor, as in Fig. 1, can be used to remove the most harmful component, the unconverted CO. The choice of purifier depends on the operating pressure; if the reaction is preformed at low pressures, less than 7 atm, this helps drive conversion to completion but leaves very little driving pressure to send hydrogen across a membrane. A PROX (partial oxidation) reactor is used, as in Fig. 1, and the product hydrogen is left with all the CO_2 and some nitrogen, but is cleaned of all but 20 ppm CO. Operating the reformer at high pressures, by contrast, hurts conversion efficiency but allows the use of a membrane purifier to remove all of the hydrogen impurities.

Hydrogen purification is a necessity since CO concentrations above about 100 ppm destroy current PEM fuel cells, and higher purity is better. Amphlett et al. have shown (4) that hydrogen containing 20 ppm CO results in a maximum power density that is $^1/_3$ of that with pure hydrogen. Thus, the fuel cell in Fig. 1 may have to be three times bigger and more expensive with PROX-purified hydrogen than with pure hydrogen, as purified through a metal membrane. Even this level of CO removal requires a big PROX reactor. For 3–5 bar operation, a PROX that reduces the CO to 20 ppm is the largest single component of Fig. 1, and weighs 10 to 20 times more than the reformer (4). The PROX also consumes some hydrogen, and leaves carbon dioxide, water, and nitrogen in the product hydrogen. Even if all the CO could be removed with a PROX, these gases would decrease system efficiency significantly by necessitating a bleed from the fuel cell electrodes.

For sequential reactor-separators, the alternative to a PROX is a membrane purifier using metal membranes. These exhaust a purer hydrogen stream but require the loss of a significant amount of the hydrogen produced in the reactor. The hydrogen partial pressure in the reject (bleed) steam must be at least as high as that in the purified output. A reformer product stream containing 70% hydrogen at 5 atm (absolute) starts with a hydrogen partial pressure of only 3.5 atm on the upstream side of the membrane. The purifier reject gas mixture containing all the CO_2 must also then contain about 2 atm hydrogen if the membrane outputs hydrogen at 1.5 to 2 atm (absolute). This 2 atm involves a loss of about 25% of the hydrogen in the reformer product stream beyond the hydrogen that is lost by the reaction not going to completion.

Heat transfer also presents problems for sequential reformer purifiers. Figure 1 shows an internal combustion heater used to drive the endothermic Reaction (2), while three external heat exchangers preheat the feed and provide cooling for Reaction (3). Some of these heat transfer problems, plus the conversion/recovery problem, are removed by using a membrane reactor as shown below.

THEORY

Conversion and Hydrogen Recovery with Idealized Reformers

Performing methanol (or similar) reforming reactions in a membrane reactor provides hydrogen purification simultaneously with the reaction. With an appropriate metal membrane, such a reactor will generate hydrogen at 100% purity and higher conversion than the sequential reactor/separator. There is also a fundamental change in the way pressure affects the extent of reaction and the percent hydrogen recovered, and this can provide even bigger advantages.

The equilibrium constant for the overall methanol reforming reaction, Eq. (1), is expressed in terms of partial pressure and mole fraction, respectively, as

$$K = [P_{H_2}]^3[P_{CO_2}]/[P_{H_2O}][P_{CH_3OH}] \tag{4a}$$

$$= P^2_{Tot}[y_{H_2}]^3[y_{CO_2}]/[y_{H_2O}][y_{CH_3OH}] \tag{4b}$$

where K is the equilibrium constant, $[P_{H_2}]$ is the partial pressure of H_2, P_{Tot} is the total pressure, and $[y_{H_2}]$ is the hydrogen component mole fraction. For a plug flow reactor with a feed of 1 mole each of methanol and water, we can define the "extent" of the reaction as the number of moles of output CO_2. Ignoring the observation that Reaction (1) progresses in two stages, the moles of hydrogen output at equilibrium will then equal "3-extent," while the moles of water and CH_3OH will be "1-extent" each. The total number of moles is thus "2 + 2-extent," and Eq. (4b) becomes

$$\frac{(27\text{-extent}^4)}{(2+2\text{-extent})^2(1\text{-extent})^2} = K/P^2_{Tot} \tag{5}$$

The higher the total pressure, P_{Tot}, the lower the extent of reaction as expected from Le Chatelier's principle.

In a membrane reactor the hydrogen partial pressure is no longer determined by the extent of reaction, but instead largely by the pressure in the pure hydrogen outlet. For an ideal membrane reactor where transport resistance is minimal, the hydrogen partial pressure in the reactor equals the pressure of this purified output, which we will call P_{H_2}. For use with PEM fuel cells, P_{H_2} will be 1 to 2 atm (absolute), which is much lower than the 3.5 atm leaving the plug reactor above; we thus expect a higher extent of reaction with the membrane reactor, even at a P_{Tot} of 5 atm. We can derive equations for the extent as a function of total reactor pressure by rearranging Eq. (4):

$$K = P_{\mathrm{H_2}}^3[y_{\mathrm{CO_2}}]/[y_{\mathrm{H_2O}}][y_{\mathrm{CH_2OH}}]P_{\mathrm{Tot}} \tag{6}$$

As before, consider a feed of 1 mole each of methanol and water, and define the extent of the reaction as equaling the mole conversion to CO_2. The number of moles of unpurified hydrogen leaving the reactor with the residual gases is

$$(\text{moles residual H}_2) = P_{\mathrm{H_2}}(\text{2-extent})/(P_{\mathrm{Tot}} - P_{\mathrm{H_2}}) \tag{7}$$

with the rest leaving as purified hydrogen. The total number of moles in the reactor is thus $\{\text{2-extent} + P_{\mathrm{H_2}}(\text{2-extent})/(P_{\mathrm{Tot}} - P_{\mathrm{H_2}})\}$, and Eq. (6) becomes

$$\frac{\text{extent}\left(\text{2-extent} + P_{\mathrm{H_2}}\dfrac{(\text{2-extent})}{(P_{\mathrm{Tot}} - P_{\mathrm{H_2}})}\right)}{(\text{1-extent})^2} = \frac{KP_{\mathrm{Tot}}}{P_{\mathrm{H_2}}^3} \tag{8}$$

Note that one can increase the reaction conversion (or extent) in this membrane reactor merely by increasing the total pressure P_{Tot} or by decreasing the pure hydrogen output pressure $P_{\mathrm{H_2}}$. This dependence of "extent" on P_{Tot} is counter that for the plug reactor, Eq. (5); not only is there a greater extent of reaction at a given pressure, there is a fundamental change in the way that pressure affects conversion.

There are two other significant advantages of increasing P_{Tot} or of decreasing $P_{\mathrm{H_2}}$ in a membrane reactor. For one, either of these changes decreases the amount of hydrogen exhausted with the impure bleed and thus increases the percent that is recovered pure, Eq. (7). Further, either of these changes decreases the average volumetric flow rate for a fixed molar feed rate. Thus, for any given volume reactor, these changes result in an increased residence time. Alternately, these changes can allow the use of less catalyst and smaller reactors, which would be advantageous for mobile and remote applications.

Thermal Uniformity and Heat Recovery

Membrane reactors can provide better heat transfer than standard plug-flow reactors since cold hydrogen that is removed from an endothermic region (e.g., Reaction 2) can be made to pass through an exothermic region (e.g., Reaction 3) before being collected. Simple shell-and-tube designs will do this, and two are shown in Figs. 2 and 3, with the difference being that the design in Fig. 2 includes an outer annulus for the feed flow while Fig. 3 includes a combustor to provide heat to the reactor. In both designs, hydrogen-permeable tubes run axially with hydrogen being collected in a header (the header is at the bottom in Fig. 2 and at the top in Fig. 3). In Fig. 2, entering methanol and

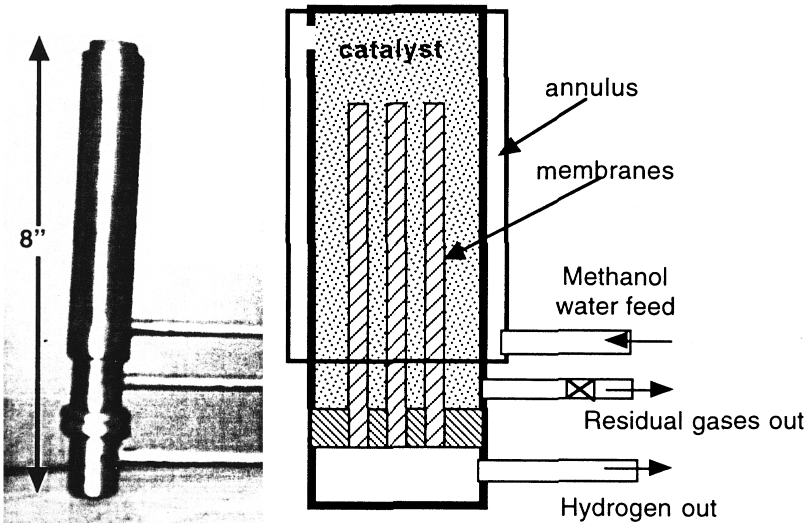

FIG. 2 Membrane reactor run at Tufts University. Heat is supplied by electrical heating tape wound around the outside. A methanol–water mixture was vaporized and fed at the bottom of the annulus where further heating occurred. Pure hydrogen exits at the bottom port, and residual gases from the middle port.

steam flows up through an outer annulus while being heated and flows down through a reactor core that contains catalyst and membrane tubes. Flow in the outer annulus has the same beneficial effect on temperature uniformity as flow in the tubes, providing convective heat transfer from the exothermic Reaction (Eq. 3) to the endothermic reaction (Eq. 2). Temperature uniformity is important in improving conversion and increasing catalyst life (4).

The membrane reactor in Fig. 3 provides heat to the reactor by combusting residual hydrogen and CO as well as combusting a start-up fuel, in this case methanol. As with the hydrogen purifier, a membrane reactor must exhaust a fraction of the hydrogen it produces because the hydrogen partial pressure in the exhaust gas must be at least as high as that in the pure stream. The minimal amount exhausted is the same as for the membrane purifier, Eq. (7):

$$\text{Minimal hydrogen exhaust} = P_{\mathrm{H_2}}(2\text{-extent})/(\mathrm{P_{Tot}} - \mathrm{P_{H_2}})$$

moles of hydrogen per mole of methanol, or about 0.05 mol/mol for an equimolar feed at 350 psi (24 atm). The design in Fig. 3 shows an open flame combustor for the residual gases plus a second flame used for start-up and control; an outer annulus is used to conserve heat and control the flame. Methanol and water enter at the bottom of the outer annulus, are heated and boiled, and pass to the membrane reformer section by going through the hole at the lower right. Most of the hydrogen formed leaves through the membranes, while the remainder is channeled to the combustor section, passing through a control valve shown at the upper left. The valve prevents backburning and can be adjusted to provide sufficient heat to the reactor. The valve also allows the combustor to operate at a lower pressure than the membrane reactor. It is possible to imagine a design that uses a catalytic combustor instead of an open flame; such a combustor employing platinum and rhodium could also minimize the CO and NO_x content of the exhaust. Such reactors should produce pure hydrogen at a high energy efficiency. There should be no electric use except for control, ignition, and liquid fuel pumping. This could be very useful for remote hydrogen production and mobile electric generation.

EXPERIMENTAL

The experimental reactor in Fig. 2 was built for Walter Judah's laboratory at Tufts University, and tested for steam reforming of methanol. The reactor was 1.25″ O.D., 0.8″ I.D., and 8″ in total length, and contained seven 5.5″ long

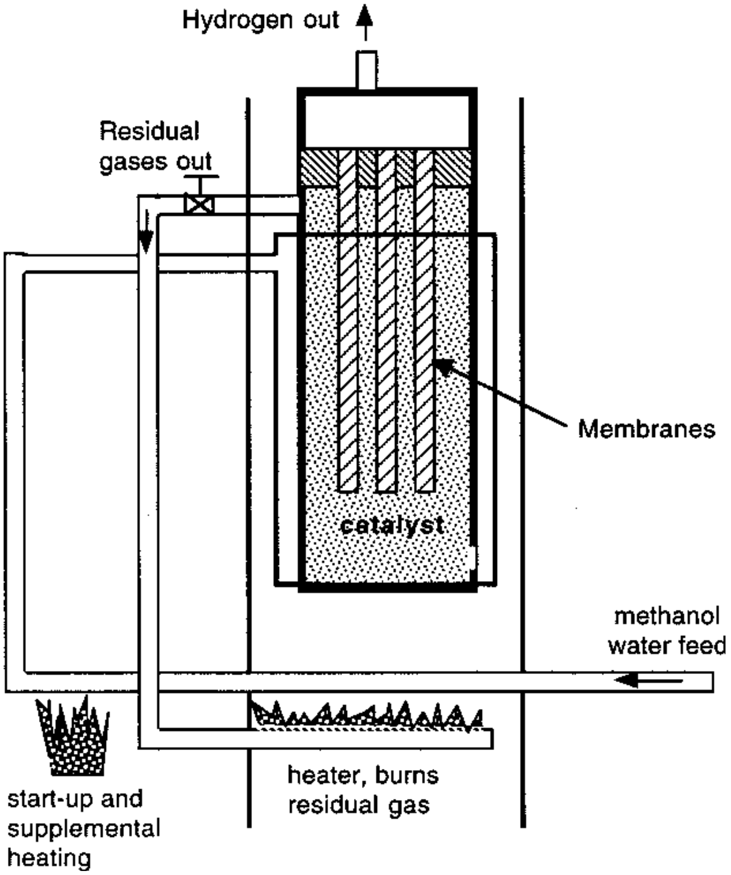

FIG. 3 A proposed membrane reactor, similar to that in Fig. 2, except that heat for the reactor is produced by combustion of the residual gases.

× 0.080″ diameter hydrogen purification membranes supplied by REB Research; these ran to within 1″ of the top of the reactor. The reactor was filled with 100 cm^3 of copper–zinc oxide catalyst, heated with electrical heating tape, and run continuously for 1 month at a pressure of 150 psig (16 atm) and a core temperature of 265°C. The observed hydrogen output averaged at 800 cm^3/min, and showed no significant deterioration over that time. In these tests, 80% of the stoichiometric hydrogen was recovered and the purity was 100%. A blown fuse prevented further tests, but further improvements should be possible with operation at 350 psi, as confirmed by a mathematical simulation by Amphlett et al. (5). The simulation also suggested that the relation between tube length and hydrogen recovery is weak, and that 4″ membranes could have worked as well as the 5.5″ membranes used here.

DISCUSSION

Other Reactions

The advantages of membrane reactor use is not limited to methanol reforming and have been observed in other reforming and cracking reactions. A group at The University of Calgary has built a fluidized membrane reactor using REB membranes and observed higher than equilibrium conversions for methane reforming at 600–700°C (6, 12). It is believed that the very high purity hydrogen produced by this membrane reformer may be cheaper than hydrogen produced by current sequential reformer–PSA units. Similarly, Wendell Rhine of Aspen Systems has used a membrane reactor from REB Research to convert octane and water to hydrogen at about 500°C instead of the typical 700°C; conversion was over 90% and more than 90% of this hydrogen was recovered through the membranes. Membrane reactors have also been used for cracking reactions, e.g., methane cracking at temperatures about 550°C (13), and ethane dehydrogenation to ethylene at 700°C instead of the typical 850°C by using a fixed-bed reactor and ceramic membranes (7).

Membrane Choices

REB Research membranes were used in most of the studies mentioned above, but the advantages of membrane reactors are independent of any specific type of membrane. Still, membrane choice is application-specific. Ceramic tubes seem most appropriate for high temperature hydrocarbon cracking applications because they combine a high flux and temperature stability in excess of 600°C with good H_2S tolerance. Ceramics, though, are destroyed by steam and thus are not acceptable for steam reforming. They are also unacceptable for applications requiring selectivities in excess of 100% (2).

Palladium–silver membranes are options for high value-added uses, including military, space, and nuclear. They are 100% selective, and fabrication and sealing technologies are well developed. The problem with palladium–silver is its high cost per flux, especially in the presence of CO or ppb levels of H_2S.

Several composite membranes have become available in the past few years. REB Research & Consulting Co. makes hydrogen permeable membranes by plating thin layers of palladium on lower-cost metallic substrates. These have been used in the majority of the studies described here because flux does not deteriorate in the presence of steam and CO. The manufacture and principles of these membranes are described elsewhere (6, 8) and the performance is shown in Fig. 4. The flux at 400°C is about 3 times that of palladium–silver, and it does not decrease drastically at the 260°C used in methanol reforming. The largest modules to date contain 1000 cm^2 of surface.

Carbon-coated ceramics (10) have shown good selectivity and water/sulfur tolerance, but they appear to work best at room temperature and show the cu-

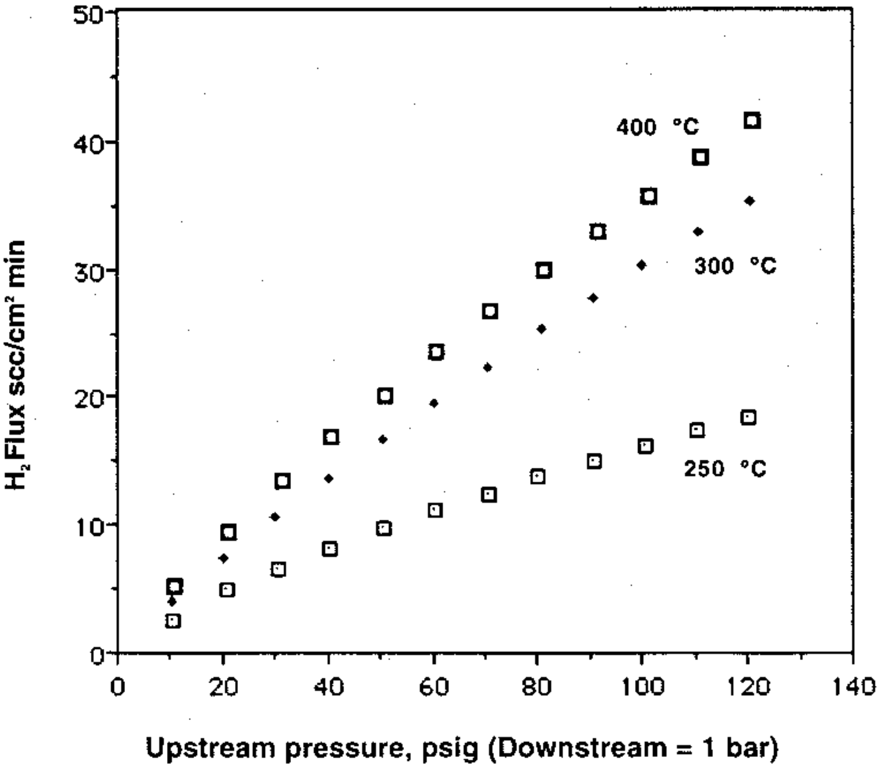

FIG. 4 Performance of REB Research membranes; flux as a function of temperature and pressure.

rious behavior that the hydrogen appears on the *high-pressure* side of the membrane. Palladium or palladium–silver coated ceramics have also been demonstrated, but current membranes are small and of poor durability (2, 11), especially when sealed into modules. As with unsupported palladium–silver, they poison in CO and H_2S, and selectivity appears to be about 1000 after 5–10 start–stop cycles. There are also exciting results with flat foil membranes of palladium–copper, palladium–ruthenium, and palladium–platinum–rhodium. Although the flux is lower than with palladium–silver, the CO and sulfur tolerance is greater. The main problem to date has been the difficulty of sealing the foils in a way that prevents leakage after a few cycles.

CONCLUSIONS

Membrane reactors appear most useful for equilibrium-limited cracking and reforming reactions where there are more moles of product than reactants. For such reactions, membrane reactors that remove a product can show both better conversions and improved product recovery by allowing operation at much higher pressures than would be possible otherwise. Membrane reactors also provide opportunities for heat transfer which may prove attractive for methanol or methane reforming to produce hydrogen for PEM fuel cells.

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