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# Methanol Steam Reforming for Hydrogen Production

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## 1. Introduction

### 1.1. Scope and Background

Recent years have seen an enormous amount of funding directed toward fuel cell research and development based on different fuel sources and fuel cell types. The number of small and large companies that are seriously working on fuel cell development is incredible, as seen in the roster maintained by *Fuel Cell Today* online.<sup>1</sup> One of the most popular fuels in these endeavors is methanol, whether used directly or preprocessed by reforming, partial oxidation, or decomposition. This review is intended to give the reader a broad look at the research and development activities being undertaken by groups from universities, government laboratories, nonprofits, small businesses, and large industrial interests. As would be expected in a research area of this type, where intellectual property is paramount, many of the details and much of the activity are not reflected in the open literature. We have sought to bring together the available published research activities along with what can be found of the ongoing industrial development efforts—which are, understandably, harder to come by.

The number of publications, conference presentations, and patents dealing with methanol steam reforming has grown tremendously in recent years,<sup>2</sup> as illustrated in Figure 1. The rapid increase in publications from about 1998 reflects the recent emphasis on fuel cell research undertaken by academics, government labs, and industry, and parallels the drastic increase in publications and conferences dealing with fuel cells, including the incorporation of fuel cell symposia within larger professional meetings of the AIChE, ACS, ASM, ECS, IECEC, IMRET, and others.

The purpose of this review is to give the reader an understanding of recent developments in this field relative to other fuels and reforming technologies. We provide an overview of methanol steam reforming from the perspective of catalyst development and mechanism understanding as well as reactor and system development and demonstration. Every application will have its own unique considerations and requirements, leading to different approaches to converting methanol to a suitable hydrogen stream.

In describing methanol steam reforming, we have limited our discussion almost exclusively to what is traditionally known as catalytic steam reforming (SR). Other methods, such as partial oxidation (POx), methanol decomposition, and autothermal reforming (ATR), are not covered in depth but are discussed only by way of contrast. In fact, the vast

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Daniel Palo received his Ph.D. in Chemical Engineering from the University of Connecticut in 1999, and since that time, he has been a Senior Research Engineer at PNNL. His research and project management work has involved various applications of catalytic and noncatalytic microchannel unit operations, with a particular focus on reforming of various fuels for portable fuel cell applications. Additional areas of interest include microchannel architectures for heat and mass transfer and chemicals production, microreactor-enabled system development, microfabrication, and the integration of micro- and nanotechnologies. Dr. Palo is currently Senior Research and Development Leader at the Microproducts Breakthrough Institute, a joint institute operated by Oregon State University (OSU) and PNNL. He serves as Courtesy Faculty in both Chemical Engineering and Industrial and Manufacturing Engineering at OSU. He has been honored with four PNNL Key Contributor awards and has over 20 peer-reviewed publications, including one U.S. Patent, with four additional U.S. and two foreign patent applications pending.

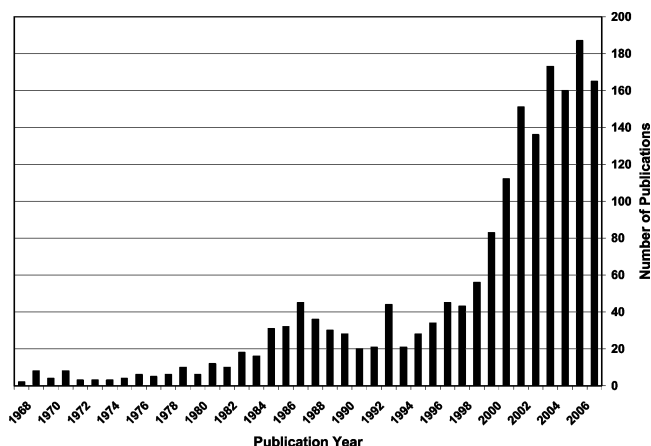


Robert Dagle joined PNNL as a research engineer in 2000 after having received his Bachelor's Degree in Chemical Engineering from Washington State University. He later obtained his Master's Degree in Chemical Engineering, also from Washington State University, in 2005. His Master's Thesis was titled Fuel Processing Catalysis for Microchannel Applications: Methanol Steam Reforming and Selective CO Methanation. In 2005, he became a Senior Research Scientist & Engineer. Robert has been granted one U.S. patent, and pending are eleven U.S. and four foreign patent applications. At PNNL, Mr. Dagle has performed research for both industrial and government clients. Much of his research has focused in the area of heterogeneous catalyst development for use in microchannel reactors. He has experience in various catalytic chemical unit operations, include steam reforming of various fuels, catalytic combustion, water-gas shift, selective CO methanation, preferential oxidation of CO, other fuel-processing related operations, oxidation reactions, and catalytic distillation.

majority of the investigations of hydrogen production from methanol have focused on steam reforming, as it offers specific advantages over POx, ATR, and decomposition, especially when considering hydrogen yield and CO production and subsequent mitigation. The advantage that SR has over the other methanol conversion methods in regard to low



Jamelyn (Jamie) Holladay received his Master's Degree in Chemical Engineering from Brigham Young University in 2000, and he has over seven years of research experience. His work involves process intensification and microchannel reactors for energy production. He has worked on miniature power supplies using a fuel processor and fuel cell, heterogeneous catalyst development, steam reforming, semiconductor processing, PEM fuel cells, and battery fabrication/testing. He is engaged in work for DOE (hydrogen production), NASA, DARPA, and other government and commercial clients. He has received two PNNL Key Contributor awards and many outstanding performance awards for his contributions. He has edited a book on process intensification and has over 20 peer-reviewed publications, including two issued U.S. patents and four additional U.S. patent applications.



**Figure 1.** Publications on methanol steam reforming by year, from 1967 through 2006, according to Chemical Abstracts Service.

CO production does not translate to other hydrocarbon fuels. The reason is that heavier fuels (i.e., those with C—C bonds) require a different conversion mechanism, so SR does not yield the same advantages over POx/ATR for these fuels. Put another way, methanol reforming can proceed through a non-CO-based mechanism, allowing for below equilibrium concentrations of CO in the reformer exit stream given the right catalyst and reaction conditions. This is described more fully in section 1.3.

Military interest in methanol-fueled fuel cells dates back at least to 1964, with the reported work by Heffner et al. of the M.W. Kellogg Company, who investigated hydrogen generation by methanol reforming for use on U.S. Navy submarines.<sup>3</sup> Since then, dozens of military fuel cell development and demonstration projects have been conducted, including everything from fundamental research on fuel cell components up to full system demonstrations and field trials. Military interest in fuel cell systems is based on a number of perceived advantages, including silent operation, higher efficiency/energy density, longer run time between “charges”,

**Table 1. World Methanol Supply and Demand History and Outlook for the Years 2004–2010, Expressed in 10<sup>3</sup> Metric Tons (Source: Jim Jordan and Associates, 2006, Used by Permission)<sup>13</sup>**

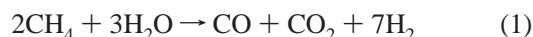
	2004	2005	2006	2007	2008	2009	2010
<b>DEMAND</b>							
formaldehyde	13476	13969	14449	15034	15363	15869	16414
MTBE	6481	5962	5258	3661	3439	3189	3214
acetic acid	3592	3781	3922	4190	4348	4428	4528
methyl methacrylate	1048	1086	1130	1164	1202	1234	1266
DMT	645	657	668	678	692	705	720
<i>total petrochemicals</i>	25242	25455	25427	24727	25044	25426	26142
gasoline/fuels	1165	1798	1941	3152	4302	5302	5850
solvents	1228	1274	1298	1331	1358	1387	1412
miscellaneous	5486	5745	5926	5723	5740	5711	7477
<i>total other uses</i>	7879	8817	9165	10206	11400	12400	14739
total demand	33121	34272	34592	34933	36444	37826	40881
<b>SUPPLY</b>							
capacity	37367	39556	42500	43439	46639	49439	50739
production	33121	34272	34592	34933	36444	37826	40881
total supply	33121	34272	34592	34933	36444	37826	40881
operating rate (demand/capacity)	89%	87%	81%	80%	78%	77%	81%

and lighter loads. Military applications range from subwatt (sensors) to multiwatt (soldier power, sensors), to 100+ watt (battery charging, auxiliary power), to multi-kilowatt (auxiliary power, silent watch, base power).<sup>4</sup> In smaller power levels, methanol has received a lot of attention despite the military's desire to deploy one fuel forward. For many in the military, methanol is seen as "tolerable" within this context for small power, because it can be prepackaged and treated much like other nonfuel logistics items (e.g., batteries, ammunition). For some decision makers, methanol is seen as a near-term opportunity to increase deployed energy density over current battery technology while waiting for solutions to come online that efficiently utilize logistics fuels such as JP-8 in fuel cell systems.<sup>5</sup> Where methanol is concerned, two main technologies have emerged in an effort to fulfill the military requirements for portable power, namely direct methanol fuel cells (DMFCs) and reformed methanol fuel cells (RMFCs). Commercial interest in methanol power to replace or augment lithium-based consumer batteries has also seen the competition between DMFCs and RMFCs, each of which has its advantages and disadvantages. We describe DMFCs and some other direct fuel cells briefly in section 2.

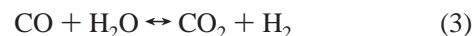
## 1.2. Methanol Production and Use

Methanol has a long history and is currently a worldwide commodity important in many respects. The first commercial methanol process, based on the destructive distillation of wood, dates back to 1830, and the first synthetic methanol plant was commercialized by BASF in 1923. Since then, methanol has become one of the largest volume commodity chemicals produced in the world.<sup>6</sup> Methanol can be produced from a variety of sources, including natural gas, coal, and biomass through a syngas-to-methanol route. Alternatively, the direct oxidation of methane also yields methanol, either thermocatalytically or through bioprocessing. However, due to low yields, these processes are not economical,<sup>6</sup> but increased interest has recently been shown in these alternative routes, driven by a desire to replace fossil fuels and address global climate concerns.<sup>7</sup>

For commercial purposes, methanol is primarily formed from natural gas through a syngas route. Steam reforming of methane produces a mixture of CO<sub>2</sub>, CO, and H<sub>2</sub> according to eq 1. Syngas is then converted to methanol at 200–300 °C over Cu/ZnO catalysts according to eq 2.



In the 1960s, very active Cu-based catalysts were developed, revolutionizing this process.<sup>8</sup> Today, a finely tuned CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> composition is used. Most researchers agree that, by using the commercial Cu catalyst, methanol is synthesized only from CO<sub>2</sub> (eq 2) and that CO does not directly take part in the synthesis.<sup>9</sup> However, CO is involved in the process through the water-gas shift (WGS) reaction:



Thus, the equilibrium reactions (eqs 2 and 3) must be considered simultaneously in methanol synthesis over Cu-based catalysts. The mechanisms involved for these reactions are quite complex, and the literature abounds with discussions concerning detailed kinetic and mechanistic studies for methanol synthesis.<sup>10,11</sup>

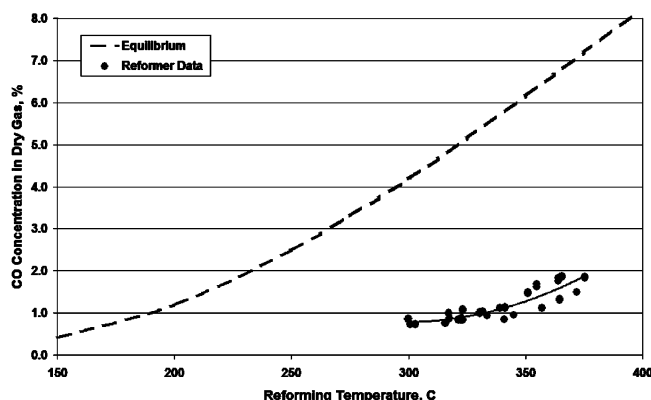
The effectiveness of Cu-based catalysts in the production of methanol naturally led to their investigation in the steam reforming of methanol, which can loosely be seen as the reverse of reaction 2, but with the addition of excess steam to drive reaction 3 to the right. Various catalysts used for converting methanol to hydrogen are described in detail in section 3.

World demand for methanol is driven by chemicals production applications, with the majority of methanol capacity going into the production of formaldehyde, MTBE (declining), acetic acid, fuels, and solvents.<sup>6,12,13</sup> Total world demand for methanol in 2005 was nearly 32 million metric tons, as shown in Table 1, and continues to rise, as seen in the projected values through 2010.<sup>13</sup> Over the period 2004–2006, world demand for methanol has slowly but steadily increased, while overall capacity has more than kept pace, indicated by the somewhat decreasing operating rates shown for the same time period. That is, worldwide capacity exists that could absorb additional demand from new applications.

## 1.3. The Case for Methanol

Methanol is a unique and advantageous fuel in many ways, which explains the large amount of interest in it as a hydrogen carrier for fuel cell applications. Methanol has a high H/C ratio (4:1), equal to that of methane. It is a liquid





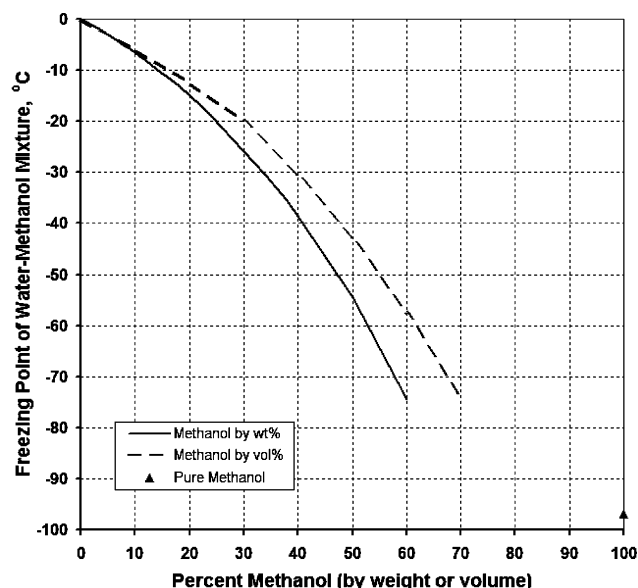
**Figure 2.** CO concentration in dry reformate as a function of reactor temperature. Equilibrium (solid dark line) and reactor results (data points) obtained for S/C = 1.2 at methanol conversions > 95%. (Reprinted with permission from ref 15. Copyright 2005 American Chemical Society.)

at atmospheric pressure and normal environmental temperatures, unlike methane or liquefied petroleum gas (LPG). It has a low boiling point (65 °C), which allows for facile vaporization in roughly the same temperature range as that for water.

In terms of environmental impact, methanol is readily metabolized by ambient organisms in the environment, and because it is miscible with water, methanol spills do not spread over wide areas of open water the way oil and gasoline spills do. An example given by Short reveals that an instantaneous release of 100,000 tons (300 million gallons) of methanol into the sea would result in a concentration of 0.1% within a 1-mile radius, at which point the methanol would be readily metabolized by marine life.<sup>14</sup> This effect is minimal when contrasted to the release of an equivalent amount of oil or gasoline.

Methanol can be converted to hydrogen at lower temperatures (150–350 °C) than most other fuels (>500 °C) because it contains no carbon–carbon bonds that must be broken, and unlike methane, it is easily activated at low temperatures. Low-temperature conversion leads to low levels of CO formation, even if the catalyst provides no special mechanism for selectivity of CO<sub>2</sub> over CO. However, it should be noted that operation at low temperature without a catalyst and at long residence times will lead to high levels of methane, which defeats the purpose of reforming the methanol in the first place. Given a sufficiently active catalyst that promotes the reforming of methanol at high space velocities, methane formation is not a concern. The effect of operating temperature on product selectivity is illustrated in Figure 2, which shows the equilibrium CO concentration in dry reformate (dashed line), based on a steam/carbon ratio (S/C) of 1.2.<sup>15</sup> The plot also indicates data points obtained by Palo et al. for a Pd-based reforming catalyst in a microchannel reactor at high throughput, showing the additional CO avoidance advantage that can be obtained using selective methanol reforming catalysts at higher operating temperatures. In this case, the kinetics could be increased 200-fold by operating at 300–325 °C, while maintaining CO concentrations equivalent to those predicted thermodynamically at less than 200 °C operating temperature. The low temperature of methanol conversion is important for system material selection as well as heating and insulation, all of which can lead to a smaller, more efficient system.

While not currently economically viable, bio-based sourcing of methanol is an intriguing possibility. Recent demon-



**Figure 3.** Freezing point depression behavior of methanol–water mixtures as a function of composition (data compiled from *Handbook of Chemistry and Physics*, 87th ed., 2006–2007, and *Ullmann's Dictionary*).<sup>16</sup>

strations, pilot plants, and production plants are producing methanol from such diverse bio-based resources as landfill gas, hog manure, sugar beets, driftwood, rice straw, and paper mill black liquor.<sup>7</sup> Methanol is most often produced from natural gas, but it could also be made from coal, which represents an abundant resource in the U.S. and has received much recent attention as an alternative to crude oil.

Methanol is miscible with water, which is a distinct advantage in terms of fuel handling in the system. For instance, if water recycling is not required, the fuel can be precisely premixed and prepackaged in fuel cartridges. Even if the fuel is not premixed, the miscibility of water and methanol allows the system to be simplified by providing a single inlet stream to the fuel processor, as well as the use of a single vaporizer. Another advantage of methanol's solubility in water is the depressed freezing point associated with methanol/water mixtures, as shown in Figure 3.<sup>16</sup> For the typical range of operation in methanol reforming (45–60 wt % methanol), the freezing point of the fuel mixture ranges from –44 °C to –74 °C, a distinct advantage for cold-weather deployment of methanol-fueled systems.

Because methanol is inherently a synthetic fuel, it does not suffer from sulfur contamination the way that typical automotive or residential fuels do. This is a big advantage when it comes to fuel reforming, as the system needs neither a front-end desulfurization operation nor sulfur-tolerant catalysts to operate on methanol.

Although the militaries of the U.S. and other countries (e.g., Canada, U.K., Australia) have shown interest in the use of methanol as a fuel for portable power systems, methanol suffers from a major flaw—methanol is not diesel fuel and methanol is not JP-8. The U.S. military has a less-than-fully implemented policy of “one fuel forward”, but a policy nonetheless.<sup>5</sup> For small power systems, the military has seen methanol as an initial entry point for portable power systems that can exceed the energy density of primary batteries and allow the insertion of fuel cell technologies into military applications before JP-8 fueled systems are ready for demonstration.

**Table 2. Calculated Hydrogen Yields Based on the Carried Weight (Adapted from Trimm and Onsan, Copyright 2001 from *Catalysis Reviews*. Adapted by Permission of Taylor & Francis Group, LLC, <http://www.taylorandfrancis.com>.)<sup>18</sup>**

fuel	indirect partial oxidation		direct partial oxidation	
	water/fuel <sup>a</sup>	yield <sup>b</sup>	water/fuel <sup>a</sup>	yield <sup>b</sup>
methane	2.8	690	0.8	1470
propane	3.9	1310	2.7	1300
iso-octane	10.1	1220	7.2	1250
methanol	1.0	1070	0.8	250

<sup>a</sup> Water/fuel = moles of water per mole of fuel fed to the reaction system. <sup>b</sup> Yield = volume of H<sub>2</sub> produced per mass of total fuel/water fed [mL g<sup>-1</sup>].

**Table 3. Fuel Energy Density and Fuel–Water Energy Density for Several Common Fuels Considered for Steam Reforming for Fuel Cell Systems**

fuel	fuel energy density (kW h kg <sup>-1</sup> )	fuel–water energy density <sup>a</sup> (kW h kg <sup>-1</sup> )
methane	13.9	4.3
propane	12.7	3.7
iso-octane	12.3	3.5
methanol	5.6	3.5

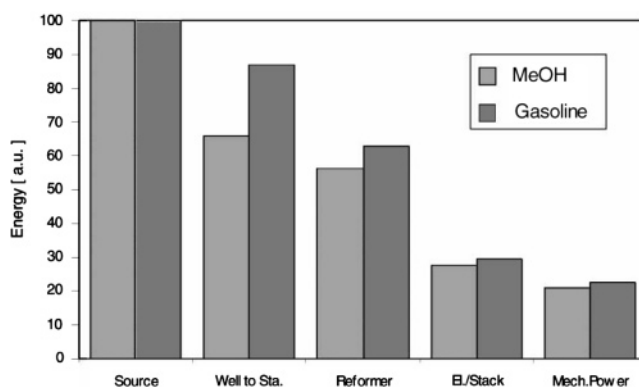
<sup>a</sup> Fuel–water mix represents the stoichiometric requirement for steam reforming, defined as a molar S/C ratio of 2.0 for hydrocarbons and 1.0 for methanol.

The tradeoffs among various fuels for hydrogen production are numerous, and decisions are made based on which parameter is deemed most important for the system being considered. From a health and toxicity point of view, methanol is worse than some but better than others. For instance, Short states that, broadly speaking, methanol is safer than gasoline but less safe than diesel.<sup>14</sup> Ingestion is the main concern with methanol, as it produces formic acid in the human body when metabolized. Unlike gasoline or diesel, methanol does not cause vomiting when ingested, so any ingestion that is not dealt with quickly will result in the formic-acid metabolism route internally. Short also cites a study by the Health Effects Institute regarding both liquid absorption through the skin and vapor absorption through the lungs.<sup>14</sup> The conclusion was that methanol's overall rate of absorption was much less than its rate of metabolism, even in a worst-case scenario of exposure.

For large-capacity consumer applications, such as automobiles, any fuel must be readily available in large quantities and have a distribution network that can support such a market. The same can be said for large stationary applications, where infrastructure-ready fuels such as natural gas and LPG are preferred.<sup>17</sup> For other niche applications, where a fuel is likely to be packaged in discrete quantities, other fuels can come into the picture.

As Trimm and Onsan point out, the choice of a fuel and a conversion system is not a trivial one.<sup>18</sup> In their review of on-board fuel conversion options, they compare methane, propane, iso-octane, and methanol for indirect partial oxidation (steam reforming) and direct partial oxidation, as listed in Table 2. In either case, the hydrogen yield for methanol is lower than that for the other fuels, except in the case of indirect partial oxidation of methane. The hydrogen yield was defined as milliliters of H<sub>2</sub> produced per gram of fuel/water utilized.

Another way to look at the issue is on a raw energy density basis, as shown in Table 3 for the same fuels that were investigated by Trimm and Onsan. This comparison of

**Figure 4.** Well-to-wheels efficiencies for methanol (from natural gas) and gasoline, without accounting for the penalty to polish gasoline to fuel processing grade. (Reprinted from ref 17, copyright 2002, with permission from Elsevier.)

energy density values reveals two important considerations. First, the energy density of methanol is about half that of typical hydrocarbon fuels. Second, the net energy density of methanol is roughly the same as that for the hydrocarbon fuels when the stoichiometrically required water is considered. This second point is important for systems that do not include active water recovery from the fuel cell and/or combustor, as would be the case for some of the simple portable systems under development. Obviously, though, if water recovery were implemented, the significant energy density disadvantage for methanol remains.

A similar analysis by Joensen and Rostrup-Neilsen<sup>17</sup> for onboard reforming applications compared methanol to gasoline on a well-to-wheels basis, as shown in Figure 4. They concede that methanol conversion is less complex than that of gasoline and is thus more efficient onboard a vehicle. However, since methanol requires more energy to manufacture, as from natural gas, the well-to-wheels analysis shows the two fuels being nearly equal in net energy.

An onboard hydrogen production study conducted at Los Alamos National Laboratory yielded similar results as mentioned above when considering several common fuels and the two main conversion methods of steam reforming and partial oxidation.<sup>19</sup> The study included methanol, ethanol, methane, gasoline, diesel, and jet fuel, and resulted in theoretical process energy needs assessments for each fuel. Important conclusions included the following:

(1) steam reforming of methanol required about the same theoretical energy input per kilogram of usable H<sub>2</sub> as that of any of the other fuels considered (145 J kg<sup>-1</sup> for methanol, 141–148 J kg<sup>-1</sup> for the others);

(2) this energy input was lower than was required for the partial oxidation route using gasoline, diesel, or jet fuel (169 J kg<sup>-1</sup>); and

(3) the reforming of methanol produced an order of magnitude less CO than the other fuels (0.8% versus 10–25%).

In conclusion, the author suggested that, for onboard reforming applications, methanol was the fuel of choice and should be processed with a combination of partial oxidation (for rapid startup and transient response) and steam reforming (for steady-state efficiency).<sup>19</sup>

If various fuels are compared on the basis of hydrogen content, methanol is at a distinct disadvantage, as shown in Table 4. The table lists the weight percent hydrogen contained in the neat fuel compared to the weight percent hydrogen per fuel when adding “free” water as recovered from the fuel cell cathode in an integrated power system.

**Table 4. Hydrogen Content and Reformed Hydrogen Content of Various Fuels Likely To Be Used as Hydrogen Carriers for Fuel Cell Applications**

fuel	hydrogen content (wt %)	reformed hydrogen content <sup>a</sup> (wt %)
methanol	12.6	18.9
ethanol	13.1	26.3
iso-octane	15.9	44.1
propane	18.3	45.7
methane	25.1	50.3

<sup>a</sup> Reformed hydrogen content indicates the amount of net H<sub>2</sub> produced as a percentage of the fuel weight, assuming complete conversion to CO<sub>2</sub> and H<sub>2</sub>, utilizing recycled (i.e., “free”) water within the fuel cell system. It represents a theoretical maximum hydrogen content for each fuel in an ideal steam reforming system.

This is the opposite assumption than was used to generate Table 3. It assumes a complex fuel processor/fuel cell system in which liquid water is recovered from combustion and/or fuel cell exhaust streams. The values of hydrogen content are calculated based on the idealized conversion of all carbon to CO<sub>2</sub> and all hydrogen to H<sub>2</sub> (that is, no methane production). In the case of a nonoxygenated hydrocarbon, the advantage comes in the addition of two moles of H<sub>2</sub>O per carbon atom, resulting in two additional moles of H<sub>2</sub> obtained per carbon atom in the steam reforming process. As a result, a fuel such as methane yields an effective hydrogen content of over 50%. In contrast, methanol has the lowest hydrogen content of any of the fuels listed, whether on a neat basis or on a reformed basis. This is a distinct disadvantage for methanol relative to typical hydrocarbons, or even ethanol.

Because of many specific advantages, and despite some major drawbacks, methanol has its place in the fuel cell arena, even if only in select applications. This is illustrated by the apparently waning interest in methanol as a fuel for transportation-oriented fuel cells compared to the continued strong interest in methanol as a fuel for small or portable power applications, whether DMFC or RMFC based. Ultimately the end users, whether the consumer market or the military, will decide the extent to which methanol is utilized as a hydrogen source for fuel cells, and this will depend on the weight given to the various system tradeoffs when considering which fuel to use.<sup>5,20</sup>

## 1.4. Previous Reviews

A search of the open literature revealed no previously published extensive and dedicated review of methanol steam reforming for hydrogen production. This is the case despite the fact that methanol steam reforming has been investigated for fuel cell applications since the 1960s<sup>3,21</sup> and early 1970s.<sup>22–24</sup> Some previous reviews were identified, however, that have relevance to the present work. A 1996 paper by Amphlett et al. introduces the reader to the various considerations for the fuel conditioning system (i.e., CO mitigation) for methanol-fueled terrestrial vehicle applications based on polymer electrolyte membrane (PEM) fuel cells.<sup>25</sup> The report assumes initial conversion to be achieved by the standard Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst and focuses on the various means of mitigating CO in light of the various PEM fuel cell anode specifications. Another review of onboard (vehicle) fuel conversion in 2001 by Trimm and Onsan,<sup>18</sup> referenced earlier, contains a section devoted to methanol reforming and provides 19 references in a discussion about catalyst formulations, activity, selectivity, and conversion mecha-

nisms. A year later, a review of fuel processing catalysts by Ghenciu<sup>26</sup> touched on methanol reforming, citing nine references, but providing little detail. From a materials perspective, researchers at Englehard Corporation provided an extensive review on “material needs for hydrocarbon fuel processing”,<sup>27</sup> but they dedicated only a few paragraphs and four references to methanol reforming catalysts in a publication that describes several fuels and various conversion and cleanup methods. In 2004, Holladay and co-workers published a review focused on portable (subwatt to several hundred watts) hydrogen production specifically using microreactor technology.<sup>28</sup> Since much of the portable power work in the literature has been based on methanol, there is some overlap with this current review, but only where microreactors and methanol reforming intersect. Similarly, another microtechnology review looking at industrial applications of microchannel reactors in the United States<sup>29</sup> provides a brief overview of methanol steam reforming as part of a much larger discussion.

Unlike any of the previous works mentioned above, we here seek to review methanol steam reforming progress as applied especially to fuel cell applications. Other similar processes, such as partial oxidation and autothermal reforming, are described by way of background information but are not the main focus of this discussion.

## 2. System Challenges

The development of a methanol-based power system involves much more than simply the steam reformer and associated process operations. There are specific system challenges that have great bearing on which type of system is selected, how it is operated, how it is deployed, and ultimately how it performs in practice. In this section we seek to bring together the technical challenges related to the system as a whole, contrast the military requirements to commercial needs, and briefly summarize the competing technologies. The focus of this section will be on challenges in the portable power applications, which is where most of the methanol steam reforming work is directed. The obvious need for a methanol distribution infrastructure and related issues regarding government regulations are beyond the scope of this work. Interested persons are referred to organizations such as the Methanol Institute ([www.methanol.org](http://www.methanol.org)) and the U.S. Fuel Cell Council ([www.usfcc.com](http://www.usfcc.com)) for more information.

### 2.1. Balance-of-Plant

Some typical system components for fuel cell balance-of-plant (BOP), along with their availability, are found in Table 5. For transportable (10 kW to ~250 W) and stationary systems, the components are readily available; however, reliable and inexpensive components for portable systems (<100 W) are more difficult to obtain, especially for the lowest power levels (<10 W). Table 5 contains a general listing of the components, and it is recognized that specific researchers and developers may or may not use all of these components and may add others specific to their applications. For the lower power applications, the components tend to be too large, too power hungry, or too expensive.<sup>28</sup> The old rule of thumb was that the BOP will account for one-third of the mass and volume of a fuel cell power supply while the fuel processor and fuel cell each account for one-third on their own. However, with new developments in fuel cells



**Table 5. Balance of Plant Considerations for Stationary, Transportable, and Portable Fuel Cell Power Systems<sup>a</sup>**

	stationary	transportable (10 kW to 250 W)	portable (<100 W)
fuel cells	expensive	expensive	expensive
pumps	X	X	expensive
flow meters	X	X	too large, power hungry, expensive
valves	X	X	X
air movers	X	X	inefficient, loud
filters	X	X	X
mufflers	X	X	relatively large
water management	X	X	need orientation independence
radiators	X	X (large)	too large
insulation/thermal management	X	X	X
hydrogen sensor	X	X	too large, expensive
CO sensor	X	X	too large, expensive
electronics	X	X	X
start-up battery	X	X	X

<sup>a</sup> An "X" indicates that a component is commercially available and well developed.

and fuel processors, this may no longer be true.<sup>28,30–33</sup> As fuel cells and fuel processors continue to shrink, the BOP may turn out to be the size-determining portion of the system.

The most consistent issue with the BOP components for most applications is that they are relatively expensive. Research has indicated that, even with a demonstrated increase in performance over batteries, many customers may not be willing to pay premium prices for fuel cell systems.<sup>31</sup> Therefore, it is necessary to reduce the number of components and to decrease their cost as much as possible. For example, design of the fuel processor such that there is only a small pressure drop on the air side of the system would enable the use of a less expensive and more efficient air blower rather than an air compressor. For a portable device, both mass and volume are at a premium. Many of the components are rather large, and further development is required to reduce their size. Multifunctional materials and unit operations will be key to the reduction in BOP component number, size, mass, and ultimately cost. Two additional issues that need to be addressed for fuel cell-based power systems include thermal management and water management.<sup>28,30,32</sup>

### 2.1.1. Thermal Management

Thermal management is important because it directly impacts the system efficiency. Often enthalpy balances are used to identify where energy is lost and how to improve the system; however, an exergy analysis has been shown to be more effective.<sup>34–37</sup> Exergy deals with the quality of energy in addition to the quantity available, and it can also be used to evaluate different forms of energy, such as chemical, thermal, and electrical, on a cohesive measure. For example, Ishihara et al.<sup>36</sup> performed both an enthalpy and exergy analysis on a methanol reformer/PEM fuel cell system and a DMFC. The enthalpy analysis indicated that an enthalpy efficiency of 100% was possible for the reformer/PEM system; however, the exergy analysis revealed that efficiency was limited to <50% due to the inability to recover waste heat from the fuel cell because of the low quality (80 °C) of the heat. In addition, this type of study can be used to identify where other thermal recuperation could occur and also the optimum voltage to operate the fuel cell for the sake of efficiency. For instance, a recuperative heat exchanger for the cathode air could be used to recover heat and increase the system efficiency. Interestingly, when the PEM system was compared to a DMFC system, the analysis revealed that

the DMFC would need to operate at 0.5 V at 600 mA cm<sup>−2</sup> in order to equal the efficiency of the PEM fuel cell system with methanol reforming. Current DMFCs operate at 0.4 V at 300–400 mA cm<sup>−2</sup>,<sup>38</sup> which, according to Ishihara, corresponds to an efficiency of 32%.<sup>36</sup> Since portable devices will be in close proximity to people, the thermal management is particularly important for safe operation. For portable fuel cells, the device not only needs to be well insulated to eliminate hot surfaces, but also the exhaust needs to be cooled sufficiently that it will not burn anyone. One of the weaknesses of the literature is that the majority of thermal management assumes an ambient temperature of 20–25 °C, but the actual ambient temperatures can reach as high as 50 °C.<sup>39</sup> Further development is required in this area for both methanol and non-methanol systems.

### 2.1.2. Water Management

Most reformers and fuel cells require water. Proper fuel cell performance requires good ionic conductivity between electrodes and catalyst surfaces. For most polymeric membranes, ionic conductivity is strongly dependent on the state of hydration of the membrane.<sup>40</sup> Strategies to manage water include humidifying the fuel and/or oxidant or using an active air blower to provide the oxidant and remove any excess water.<sup>41</sup> The water for steam reforming can either be carried, but with a significant weight penalty, or recycled from cathode and combustor exhaust, with a potential system penalty. For methanol reforming, the theoretical S/C requirement is 1.0. In practice, excess water is used to reduce the amount of CO produced and avoid coke formation.<sup>42</sup> Conventional water recovery uses a condenser and is dependent on gravity for the actual water separation from the gas. For portable and some aeronautical applications, it would be preferred that the device be orientation independent. There has been some development work in this area.<sup>43</sup> Condensing and phase separation using Microwick technologies, those using wicks to segregate liquids and gases in microchannel architectures, has been demonstrated in reduced gravity (<0.04 g) and hypergravity (>1.8 g) environments.<sup>43</sup> Measured performance indicated that the device was capable of operating independent of its orientation.

## 2.2. Military Requirements versus Consumer Needs

Both the military and the consumer electronics industry are interested in fuel cells for power supplies. Many fuel



**Table 6. Military and Consumer Needs (Adapted from Bolton<sup>5</sup>)**

feature	military		consumer	
	criticality <sup>a</sup>	comments	criticality <sup>a</sup>	comments
fuel	H	prefer logistics fuel and fuel flexibility, will accept methanol in some circumstances	L	need to be higher energy density than batteries
operation environments	H	−45 °C to 50 °C <sup>39</sup>	M	
power quality	H		M	
voltage	M	24 V preferred, US Mil Std 1332	L	
noise signature	H	US Mil Std 1332	M	
thermal signature	H	prefer <1 °C difference between surface temperature and ambient	L	meet safety regulations
weight	M	must be soldier portable	H	must be low weight
volume	M	must be soldier portable	H	must be compact
ruggedness	H	must be military hard, i.e., survive an electromagnetic pulse (EMP) etc.; see US Mil Std 1332	M–L	
high altitude operation	H	US Mil Std 1332	L	
air contaminants	H	must be able to filter out battlefield contaminants as well as regular contaminants <sup>58</sup>	M	must filter out emissions from consumer environments such as dust, low level sulfur, NO <sub>x</sub> , PM, etc.
reliability	H	soldiers' lives depend upon its operation	M	must meet consumers' expectations
operation	H	minimal operator input required	M	
cost	L		H	must be competitive
water management	H	make up water is relatively expensive	L	can add make up water
efficiency	M–L		H	

<sup>a</sup> Criticality is how important this feature is: H = high, M = medium, L = low.

cell providers view the military as a means to get their products into the market place (especially given the higher price tolerance of the military) and therefore are trying to develop dual use products (i.e., products that have essentially the same function in a military or commercial environment, but are generally ruggedized for military use). Conversely, the military often looks to leverage commercial availability with military needs to keep their own procurement costs down. Fortunately, there appears to be large overlap in the commercial and military needs, such as high-energy density (greater than currently available lithium ion technology), low parasitic power, simplified BOP, high degree of safety, and wide power range. For methanol-fueled power supplies, consumer applications range from <1 W to >10 kW, whereas military tolerance of methanol-based fuel cells extends only up to about 1 kW.<sup>28,44–49</sup> Indeed, there are some advocates of moving to a methanol economy rather than a hydrogen economy,<sup>50–52</sup> and not without reason, since methanol is an excellent hydrogen carrier and reasonable energy carrier, without the storage and transportation issues associated with hydrogen. However, methanol's high toxicity may pose a problem for large scale reformers and transportation uses. This debate will continue in the market and the halls of government, where the current focus is squarely on hydrogen and hydrogen storage.

The U.S. military has a great need for high-energy power supplies and is investigating fuel cells as one way to fill this need.<sup>4,39,53–55</sup> The U.S. Army currently uses 27 different types of batteries, 16 different chemistries, and 18 different voltages.<sup>5</sup> The average U.S. soldier in a Rifle Platoon for a 5 day mission carries 9 kg of batteries, not including batteries for contingencies and for personal electronic devices.<sup>56</sup> Of the batteries currently used by the U.S. military, 80% are primary (single-use) and only 20% are secondary (rechargeable).<sup>5</sup> The U.S. military would like to significantly increase the use of secondary batteries to reduce battery cost and improve logistics.<sup>4,39</sup> The power requirements for the U.S. military depend on the mission type, duration, and equipment to be used; therefore, it is difficult to determine an ideal power size for development. Logistics fuels are required for

power supplies over 1 kW in capacity and preferred for generators with lower capacity.<sup>5,39,57</sup> However, due to the difficulties with high sulfur levels (up to 3000 ppmw), high temperatures required for reforming and combustion, high acoustic signature for most internal combustion systems, and emissions, methanol and other prepackaged fuels are considered for use in military systems to fill the technological gap until systems are developed which can meet military specifications.<sup>5,39,57</sup> The lower capacity systems are typically divided into two categories: Soldier Advanced Power Sources (average 25 W) and Portable Field Rechargers (150–500 W).<sup>39</sup> Although there has been some development in methanol-powered auxiliary power units (APUs) and larger generator sets in the past,<sup>39</sup> the logistics fuel requirement has substantially decreased interest in these systems. The advanced power source is expected to be a hybrid system using fuel cells, batteries, and capacitors.<sup>39</sup> The power range of this system is close to the laptop power range (10–15 W) for consumers, and the military is hoping to leverage their systems with commercial development in an attempt to reduce acquisition cost.<sup>39</sup> The portable field rechargers are expected to be units which can be broken down into pieces to spread the weight among the soldiers.<sup>39</sup> Table 6 compares and contrasts the military and consumer requirements for fuel cell systems, and as was stated earlier, there is plenty of overlap in the requirements, though the priority of each requirement will differ between the two types of application.

### 2.3. Competing Technologies

Across each application space, various technologies are competing for the projected power markets that fuel cells compete in. Methanol reforming sees competition from other methanol conversion methods, especially DMFCs, but methanol as a fuel also sees competition from many other fuels and their associated conversion methods, whether hydrocarbons, ammonia, biomass, or even water by way of electrolysis. In the subsections below, we detail these competing technologies before moving on to discussions of methanol conversion catalysts and methanol reforming systems.

### 2.3.1. Low-Temperature Direct Fuel Cells

There has been great interest in low-temperature direct fuel cells primarily for portable electronics, such as cell phones, PDAs, and laptop computers, but also for larger applications, such as automotive and APUs. The appeal of this technology lies in its apparent simplicity in fuel storage and feed strategies.<sup>59</sup> Direct fuel cells process the fuel on the fuel cell anode to make protons and byproducts such as carbon dioxide. Unlike PEM fuel cells operating on hydrogen, there is no external fuel processing or hydrogen storage. DMFC technology has received the most attention, as described by many authors,<sup>59–64</sup> while other technologies, such as direct ethanol (DEFC),<sup>65–68</sup> direct formic acid (DFAFC),<sup>69–73</sup> and direct borane/hydrazine,<sup>74</sup> are also under development.

The challenges faced by the DMFC technology include methanol crossover; high catalyst usage, which results in higher cost; lower power density; lower efficiency (due to methanol crossover); and shorter operable life compared to direct hydrogen systems.<sup>59,61–64</sup> Since methanol is highly soluble in the electrolyte and the anode reaction kinetics are slow, a small amount passes from the anode to the cathode, where it leads to a reduction in fuel efficiency and reduces the efficiency of the cathode by causing a mixed potential effect (decreased voltage by 25 to 100 mV, a chemical short-circuit) and a mass transfer effect (> 100 mV, due to reduced gas permeability).<sup>60</sup> To minimize methanol crossover, the methanol is usually diluted with water (2–4 wt % methanol) either by feeding diluted methanol to the cell or by diluting a neat methanol stream in the cell.<sup>60</sup> The need to minimize the crossover effect results in either a reduction in power output or increased BOP complexity to control and monitor the methanol concentration.<sup>60</sup> Much effort is being given to decrease methanol crossover by improving the membrane which inhibits methanol crossover or allows for higher temperature operation to increase the anode kinetics<sup>75–77</sup> and to improve the anode and cathode catalysts and structure.<sup>38,78–80</sup> Current DMFCs typically use a Pt alloy catalyst at a loading of 2.0–8.0 mg cm<sup>−2</sup> on the anode.<sup>38</sup> This is much higher than the 0.2–0.3 mg cm<sup>−2</sup> for both anode and cathode in direct hydrogen PEMFCs.<sup>30,81</sup> Even with the higher catalyst loadings, DMFCs have a significantly lower power density (0.06 W cm<sup>−2</sup>) compared to PEMFCs (0.5 W cm<sup>−2</sup>) at ambient pressure.<sup>30,81</sup> Thus, more active area is required to achieve the same amount of power, ultimately resulting in a larger, more expensive stack. There has been relatively little research published on the long-term stability of DMFCs, with results showing a 2,000 h operation,<sup>82–84</sup> which is significantly less than that for PEMFCs, which have been shown to operate for more than 20,000 h.<sup>85</sup>

DEFCs are similar to DMFCs, in that they use similar catalysts and have many of the same challenges. Their advantage is that ethanol is not as toxic as methanol and that it has the potential for higher energy density, but currently DEFCs have lower power density. The primary research area for direct ethanol fuel cells has been the development of improved anode electrocatalysts.<sup>65–68</sup>

DFAFCs and direct borohydride fuel cells are more recent innovations that try to keep the advantages of the DMFC while addressing the low power and methanol crossover issues. Formic acid has a lower energy density than methanol (213 kJ mol<sup>−1</sup> versus 639 kJ mol<sup>−1</sup>). The DFAFCs have been shown to have 2 orders of magnitude smaller crossover flux through Nafion than methanol, which allows much higher

fuel concentrations (up to 75 wt %) to be used,<sup>69–72</sup> and they also have a higher open circuit potential (1.45 V) than methanol (1.24 V) or hydrogen (1.21 V).<sup>72</sup> However, unlike ethanol and methanol, formic acid is nonflammable, but it is also corrosive to skin at higher concentrations. One of the more significant challenges to this technology is that CO is formed at the anode as an intermediate in the decomposition of formic acid, which poisons the anode catalyst. Although this poisoning is reversible, it does limit the performance.<sup>73,86</sup> In addition, the catalyst, typically Pt/Ru or Pd/Pt alloy, loading is very high,<sup>86</sup> ranging from 2.4 mg cm<sup>−2</sup> to 8 mg cm<sup>−2</sup>.

Borohydride materials have been used for hydrogen storage, but since 2000, there has been increased interest in using them directly in fuel cells.<sup>74</sup> The advantages of the borohydride systems include a high open circuit voltage (OCV) of 1.6 V and high theoretical energy density. For example, solid sodium borohydride has an energy density of 9.3 kW h kg<sup>−1</sup>, which is higher than that of neat methanol, 5.5 kW h kg<sup>−1</sup>.<sup>74</sup> For practical systems, the NaBH<sub>4</sub> must be in a solution of typically 30 wt %, which reduces the net energy density considerably. Significant development is still required for this chemistry. For a recent review of direct borohydride fuel cells, the interested reader is referred to de Leon et al.<sup>74</sup>

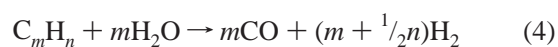
### 2.3.2. Nonmethanol Fuel Processing

The three traditional techniques used to produce hydrogen from hydrocarbon fuels include steam reforming (SR), partial oxidation (POx), and autothermal reforming (ATR). SR of hydrocarbons is highly endothermic; therefore, it favors high temperatures and requires an external heat source. POx is an alternative to steam reforming where the reaction heat is provided by the partial combustion of the hydrocarbon with oxygen. The third process, ATR, is thermally neutral, as it combines steam reforming and partial oxidation in a measured ratio. Since all three processes produce large amounts of carbon monoxide, one or more WGS reactors are used. Since the POx and ATR processes are exothermic, they do not need a complex, heated reactor. However, they either require an expensive and complex oxygen separation unit, or else the product gas is diluted with nitrogen from air. Steam reforming is typically the preferred process for hydrogen production, since it yields a high hydrogen content relative to the other methods.<sup>87</sup> The reader is referred to several in-depth review articles on hydrocarbon reforming for a deeper look into fuel processing than what will be presented here.<sup>27,87–90</sup>

Natural gas, propane, gasoline, and logistic fuels such as jet-A, diesel, and JP-8 are readily available. However, all of these fuels contain varying levels of sulfur, which must be removed prior to reformation by SR, POx, or ATR, though the sulfur tolerance varies with each reforming method. For liquid fuels, hydrodesulfurization is typically used to remove the sulfur.<sup>91–94</sup> For gaseous fuels, such as natural gas and propane, sorbents are typically employed.<sup>91–93,95</sup>

For hydrocarbon fuels, the SR, POx, and ATR reactions can be generalized as follows:

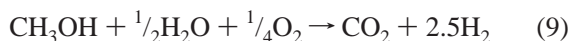
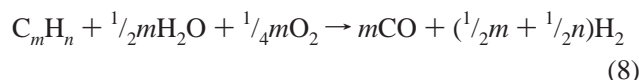
#### Steam Reforming



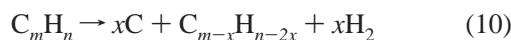
## Partial Oxidation



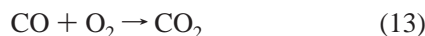
## Autothermal Reforming



## Carbon Formation



## CO Oxidation



By optimizing the operating conditions and using selective catalysts, fuel processing reactors are designed to maximize hydrogen production through reactions 3–9 while seeking to avoid reactions 10–12 and 14.<sup>27,30,87–90,96</sup>

Unlike methanol reforming, hydrocarbon fuel processing typically requires high temperatures (>500 °C).<sup>27,30,87–90,96</sup> The catalysts can be divided into two types—base metal (typically nickel) and noble metal (typically Pt or Rh based). Due to severe mass and heat transfer limitations, conventional steam reformers are limited to an effectiveness factor of catalyst which is typically less than 5%.<sup>97</sup> Therefore, the activity of the catalyst is rarely the limiting factor with conventional reactors,<sup>89</sup> so less expensive and less active nickel catalysts are used widely in industry.

**2.3.2.1. Partial Oxidation and Autothermal Reforming.** Hydrocarbon POx is being used in many of the larger scale hydrogen production systems, such as for automobile fuel cells.<sup>18,98–100</sup> The noncatalytic partial oxidation of hydrocarbons in the presence of oxygen and steam typically occurs with flame temperatures of 1300–1500 °C to ensure complete conversion and to reduce soot formation.<sup>89</sup> A catalyst is typically used in partial oxidation to reduce the operating temperature; however, it is proving hard to control because of coking and hot spot formation.<sup>18,90,96,98–100</sup> Krummenacher et al.<sup>99</sup> have had success demonstrating catalytic partial oxidation of decane, hexadecane, and diesel fuel. The high operating temperatures (800–1000 °C)<sup>99</sup> may make their use for practical portable devices difficult due to thermal management. Autothermal reforming adds steam to catalytic partial oxidation. Partial oxidation or catalytic partial oxidation is used to generate the heat needed to drive the steam reforming reactions in this process. Many of the technical issues of this type of reforming are discussed by Krumpelt<sup>101,102</sup> and Bellows.<sup>103</sup>

**2.3.2.2. Pyrolysis.** Pyrolysis is the decomposition of hydrocarbons into hydrogen and carbon in a water-free and air-free environment.<sup>104</sup> Pyrolysis can be done with any organic material. If no water or air is present, no carbon oxides are formed. Consequently, this process offers significant emissions reduction. Since no CO or CO<sub>2</sub> is present,

secondary reactors are not necessary. However, if air or water is present, then significant CO<sub>2</sub> and CO emissions will occur. The reaction, sans oxygen or water, can be written in the following form:



Typical unit operations required for this system include vaporizers/preheaters, a pyrolysis reactor, and recuperative heat exchangers. One of the challenges with this approach is the potential for fouling by the resulting carbon.<sup>105</sup> Due to concerns over CO<sub>2</sub> emissions, pyrolysis may play a significant role in the future, since it can be performed in such a way as to recover a significant amount of the carbon as a solid.<sup>104,105</sup>

**2.3.2.3. Plasma Reforming.** In plasma reforming, electricity is used to create a plasma which provides energy and the free radicals needed for reforming reactions.<sup>106–111</sup> When water or steam is injected with the fuel, H<sup>•</sup>, OH<sup>•</sup>, and O<sup>•</sup> radicals are formed with the electrons creating conditions where both reductive and oxidative reactions can occur.<sup>111</sup> Proponents maintain that plasma reforming offers many advantages, such as lack of catalyst, smaller system size and weight, lower temperature of operation, faster response time, fuel insensitivity, and lack of poisoning considerations.<sup>106–108,110</sup> The main disadvantages include the electrical requirements and significant electrode erosion at elevated pressures.<sup>107</sup>

**2.3.2.4. Aqueous Phase Reforming.** Aqueous phase reforming can also be used to process oxygenated hydrocarbons or carbohydrates to produce hydrogen.<sup>112–114</sup> These reactors operate at pressures up to 25–30 MPa and temperatures of 220–750 °C. The reforming reactions are rather complex but can be summarized to follow the reaction pathways in reaction 4 for reforming followed by reaction 3 for the WGS.<sup>114</sup> The research to date has been focused on supported group VIII catalysts, with Pt/Al<sub>2</sub>O<sub>3</sub> being the most active, but nickel-based ones are also attractive due to their low cost.<sup>114</sup>

**2.3.2.5. Ammonia Cracking.** Ammonia is an inexpensive fuel and has been proposed for use for fuel cells for portable power applications.<sup>28,54,115,116</sup> Pure ammonia has an energy density of 8.9 kW h kg<sup>−1</sup>, which is higher than that of methanol (5.5 kW h kg<sup>−1</sup>) but less than that of diesel or JP-8 (13.2 kW h kg<sup>−1</sup>).<sup>54</sup> Ammonia cracking is endothermic and is regarded as the reverse of the synthesis reaction. In industry, ammonia synthesis occurs at approximately 500 °C and 250 atm.<sup>116</sup>

Typical catalysts used in both ammonia synthesis and cracking include iron oxide, molybdenum, ruthenium, and nickel. Unlike synthesis, cracking does not require high pressures, and typically operates at temperatures around 800–900 °C.<sup>115,116</sup> Even though ammonia has a high energy density and decomposes to hydrogen and nitrogen, there has been relatively limited development of hydrogen production systems based on ammonia compared to hydrocarbon reforming systems.

## 2.3.3. Hydrogen from Other Sources

In addition to hydrocarbon reforming, hydrogen is produced by many other methods. A brief description of some of the most prominent is included here.

**2.3.3.1. Hydrogen from Biomass.** Biomass may be the only renewable organic substitute to petroleum currently known. In the United States it is second only to hydropower



as a primary energy source among renewable resources.<sup>117</sup> There are a wide range of biomass sources, such as animal wastes, municipal solid wastes, crop residues, short rotation woody crops, agricultural wastes, sawdust, aquatic plants, short rotation herbaceous species (e.g., switch grass), waste paper, corn, and many more. For hydrogen generation, the current biomass technologies include the following: gasification,<sup>118–121</sup> conversion to liquid fuels by supercritical extraction, liquefaction, hydrolysis, and biological hydrogen production.<sup>122,123</sup>

**2.3.3.2. Hydrogen from Water.** There has been a great deal of research in splitting water to make hydrogen and oxygen. In fact, its commercial uses date back to the 1890s.<sup>124</sup> It can be split into three categories: electrolysis, thermolysis, and photoelectrolysis. Water splitting in its simplest form uses an electrical current passing through two electrodes typically in a regenerative fuel cell. The most common fuel cell technology is alkaline based, but more PEMFC systems are being developed for this purpose.<sup>124–126</sup>

Thermolysis uses high temperature ( $\sim 2500^\circ\text{C}$ ) to decompose water to hydrogen and oxygen.<sup>124,127</sup> It is believed that overall efficiencies of close to 50% are achievable using thermolysis processes.<sup>128</sup> One of the significant problems with this technology is development of materials stable at this temperature and also sustainable heat sources.<sup>124</sup> Analysis of the different cycles has determined that although great progress has been made, they are still not competitive with other hydrogen generation technologies in terms of cost and efficiency.<sup>124,128</sup>

Photoelectrolysis uses sunlight to directly decompose water into hydrogen and oxygen, and it is similar to photovoltaics, except that the photocathode and photoanode are immersed in an aqueous electrolyte.<sup>124,129</sup>

**2.3.3.3. Chemical Hydrides.** Chemical hydrides are chemical compounds that when heated or reacted with other compounds, such as water, release hydrogen.<sup>130</sup> The hydrogen release rate is controlled either by temperature (hydride decomposition) or by mixing rate with water (hydrolysis).<sup>131,132</sup> There are many different types of chemical hydrides, but sodium borohydride seems to be the most developed.<sup>130</sup> Typically, the sodium borohydride is dissolved in water, and these solutions typically contain about 7–8% hydrogen by weight. To cause the hydrolysis reaction to occur, the borohydride solution is passed over a catalyst, such as cobalt or nickel borides, and ruthenium.<sup>131–134</sup> This chemistry has many advantages: it is nontoxic, stable at room temperature, safe, and odorless; the reactor bed operates at room temperature; and it is easy to control the hydrogen generation.<sup>131–134</sup> Its major drawbacks include the high cost of the material ( $\sim \$80/\text{kg}$ , which is approximately 50-fold higher than the energy equivalent price of gasoline) and the high energy requirements to fabricate and/or regenerate the material.<sup>130,131</sup>

### 2.3.4. Summary of Competitive Technologies

Obviously, the options for providing hydrogen to PEM fuel cells are numerous. The number of sources as well as the number of conversion methods are many and varied, and in some cases, the hydrogen is meant to be produced remotely from its point of use—in which case, the issue of hydrogen storage enters the picture. The choice of feedstock depends on the underlying motivation behind the developer or user. For instance, if reduction of local air emissions is the driving force, then the type of fuel may not be as

important as the ability to convert a fuel more efficiently and with low emissions. In contrast, military desire for fuel cells is driven by the need for higher energy density fuels and systems relative to primary batteries. This limits the search to militarily relevant fuels with high-energy density that can be converted efficiently in portable or transportable systems. From the perspective of agencies such as the DOE, the focus is on renewable fuel sources such as biomass and its associated products, like ethanol.

We next turn our attention to the development of active and selective catalysts for methanol, which is a unique fuel compared to the hydrocarbon fuels and, thus, has unique catalyst considerations.

## 3. Catalyst Development

Since low-temperature reforming of methanol is desired due to its favorable thermodynamics (low CO concentration), much emphasis has been placed on developing highly active catalysts that provide the desired fast kinetics at low temperatures. Most of this investigation has focused on Cu-based catalysts, mainly as an outgrowth of the extensive use of Cu-based catalysts in methanol synthesis.<sup>18</sup> However, because copper has some significant drawbacks, including deactivation, pyrophoricity, and high-temperature sintering, groups have sought to either modify the Cu-based formulations to address these issues or develop active and selective formulations from group VIII metals.<sup>135</sup> In this section on catalyst development, we cover these two main categories of catalyst for methanol steam reforming.

### 3.1. Copper-Based Catalysts

Methanol transformation into gaseous mixtures rich in hydrogen can be performed in two ways, by methanol decomposition,



or by methanol steam reforming according to reaction 5. Though the methanol synthesis (reaction 2), decomposition (reaction 16), and steam reforming (reaction 5) reactions are different, similarities exist in that the products for all three of these reactions are adsorbed strongly on the active sites.<sup>10</sup> While the decomposition and reforming reactions are less studied processes, the latter can be described as a reverse methanol synthesis. Over the Cu-based catalyst, similarities between the methanol synthesis and reforming mechanisms have been shown.<sup>10</sup>

#### 3.1.1. Reforming Mechanism

Methanol steam reforming over Cu-based catalysts was originally thought to have involved decomposition (reaction 16) followed by WGS (reaction 3).<sup>18</sup> However, in recent years, there is much evidence to suggest another pathway including a methyl formate intermediate. The presence of methanol methoxy reacts to produce methyl formate, which has been shown to be the rate-determining step in methanol steam reforming.<sup>18,136,137</sup> While some agreement exists in describing the existence of formate intermediates, involving a direct  $\text{CO}_2$  product pathway, there appears to be some discrepancy in explaining the involvement of the decomposition and WGS reactions.<sup>18,136</sup>

Some argue that WGS is somewhat unimportant, as competitive adsorption favors methanol rather than  $\text{CO}$ .<sup>18</sup>



Others have shown a significant amount of CO to form even when methanol conversion was incomplete.<sup>136</sup> This indicates that decomposition is taking place as well. It is argued that, while much slower than the reforming reaction, decomposition still must be accounted for in any kinetic model.<sup>136</sup> Such a model includes two prevalent active sites. One site activates the reforming and WGS reactions while the second activates decomposition. In this mechanistic explanation, decomposition occurs more slowly in the presence of water. Whatever the role that WGS may play in the reforming mechanism, its equilibrium and kinetics must certainly be taken into account.<sup>136</sup> WGS will occur perhaps to some degree, even before all the methanol is reacted, and to a larger degree once all the methanol is converted.<sup>9</sup> It should be noted that the mechanism for formation of the CO byproduct remains a controversial topic.

Whatever the source of CO, measures must be taken to minimize it as much as possible for fuel processing applications where CO is poisonous to the downstream fuel cell. Although mechanistic arguments are still in debate, it is generally observed that CO can be minimized by decreasing the contact time, increasing S/C to facilitate the WGS reaction, and decreasing the temperature, which acts to suppress CO thermodynamically.<sup>138</sup>

### 3.1.2. Composition and Active Components

It is generally agreed that the active component on the CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst for any of the reactions, including methanol synthesis, decomposition, or reforming, is copper. A good catalyst formulation contains well dispersed copper crystallites.<sup>8</sup> Generally, catalysts with high copper content give higher conversion and selectivities.<sup>139</sup> The role of ZnO is regarded to be relatively minimal, but it is needed as a textural support in segregating the Cu, which is highly susceptible to sintering. However, promotional effects of ZnO additives on Cu for the steam reforming reaction have been reported.<sup>140</sup> The use of alumina creates a high surface area support which serves to increase copper dispersion and decrease the susceptibility to sintering.<sup>141</sup> Just as there is dispute concerning the details for the mechanism, there is also dispute concerning the oxidation state of the active components. It is generally agreed that there is an optimum balance between metallic Cu<sup>0</sup> and oxidized Cu<sup>I</sup> for maximum activity/selectivity and this is a function of not only the catalyst preparation and composition but also the feed and reaction conditions.

### 3.1.3. Deactivation

Keeping an optimum oxidation state is an important feature of the commercial CuO/ZnO/Al<sub>2</sub>O<sub>3</sub>. This suggestion alone has allowed researchers to question the use of such a catalyst system in a fuel processing environment where changes in oxidizing condition are of concern.<sup>142</sup> However, the biggest problem with the Cu-based catalyst is the tendency for copper crystallites to readily sinter at temperatures > 300 °C,<sup>143</sup> although many claim that the temperature of operation should not exceed 260 °C for conventional copper-based catalysts.<sup>144</sup> For metals, the predominant sintering mechanism in the bulk is vacancy diffusion, which suggests a relationship with cohesive energy.<sup>143</sup> Hughs gave the following increasing order of stability for metals: Ag < Cu < Au < Pd < Fe < Ni < Co < Pt < Rh < Ru < Ir < Os < Re.<sup>143,145</sup> In this analysis lies the rationale for why copper-based catalysts are more susceptible to thermal

sintering. This explains why all modern copper catalysts contain one or more metal oxides to minimize thermal sintering.<sup>143</sup> It should be noted that the Cu-based methanol synthesis catalyst is relatively less susceptible to sintering. Differences include the higher temperatures usually needed for reforming and the differing partial pressures of reactants and products,<sup>143</sup> with the latter inducing different byproducts, such as methyl formate, that promote deactivation routes via pyrolysis.<sup>143</sup> It is generally thought that deactivation from the Boudouard reaction (reaction 11) via CO disproportionation appears unlikely. The CO<sub>2</sub>/CO ratios are quite high in methanol steam reforming, thus minimizing the thermodynamic driving force.<sup>143</sup> Sintering of the copper catalyst is also thought to be a function of steam concentration, as well as temperature. Steam strongly promotes sintering of most oxidic metals.<sup>143</sup> Also, the pyrophoric nature of copper when exposed to air is also a severe drawback.<sup>28</sup>

Thus, several routes for deactivation can occur on the copper-based catalysts. Copper crystallites are susceptible to thermal sintering or to high steam concentrations. Polymeric deposition can occur, which is also temperature dependent. Oxidation state changes of the Cu<sup>0</sup>/Cu<sup>I</sup> active sites can cause decreased activity or undesired changes in selectivity. Using the conventional methanol synthesis catalyst as a template, much research in the last several years has looked to optimize catalyst design for the methanol steam reforming reaction. The focus has been on improved activity, minimization of CO selectivity, and increased durability.

### 3.1.4. Promotion Effects

Ceria has been the subject of much research in a variety of reactions, including methanol steam reforming.<sup>146</sup> Ceria has been shown to affect the degree of dispersion as well as redox behavior and catalytic activity.<sup>147</sup> As such, Ce-based oxide catalysts have also been extensively reviewed for the WGS reaction.<sup>147</sup> Liu et al. were among the first to report the favorable effects of cerium promotion for methanol steam reforming. Cu/CeO<sub>2</sub> catalysts were compared with Cu/ZnO, Cu/Zn(Al)O, and Cu/Al<sub>2</sub>O<sub>3</sub> catalysts.<sup>146</sup> The higher activity of the Cu/CeO<sub>2</sub> catalysts was attributed to a higher dispersion of the Cu metal particles and strong metal-support interaction between the Cu metal and the CeO<sub>2</sub> support. Improved stability was also reported. Patel et al. has recently reported cerium-promoted Cu–Zn–Ce–Al-oxide catalysts to have improved activity as well as suppressed CO formation when compared to Cu–Zn–Al alone.<sup>147</sup> Cerium stabilization was also reported in a deactivation study. It was hypothesized that ceria enhanced stability due to its high oxygen storage capacity. The partially reduced ceria sites formed under the highly reducing environment of the reforming atmosphere produced the mobile oxygen that facilitated the coke gasification to inhibit coke deposition. Additionally, it is surmised that ceria increases the thermal stability against sintering.<sup>147</sup> Cheng et al. reported the promotional effects of yttria-doped ceria (YDC).<sup>148</sup> The addition of YDC to Cu/Al<sub>2</sub>O<sub>3</sub> catalysts drastically enhanced activity. The enhanced activity was attributed to the increase of oxidized copper sites, Cu<sup>+</sup>. These sites were suggested to be more active than the metallic copper, Cu<sup>0</sup>.<sup>148</sup> The role of yttria in the YDC is suggested to help facilitate the formation of the desired Cu<sup>+</sup> sites.<sup>148</sup> However, the addition of YDC decreased copper dispersion, so copper dispersion was enhanced by adding chromium oxide.<sup>148</sup>

The promotional effects of zirconium have also been the focal point for much research. Yong-Feng et al. reported ZrO<sub>2</sub>

promotion to increase conversion and improve selectivity.<sup>149</sup> ZrO<sub>2</sub> promotion was shown to increase copper dispersion and weaken the interaction between CuO and Al<sub>2</sub>O<sub>3</sub> to avoid the generation of a CuAl<sub>2</sub>O<sub>4</sub> spinel type compound.<sup>149</sup> Szizybalski et al. reported a different metal–support interaction resulting in a more stable CuZrO<sub>2</sub> catalyst when compared to Cu/ZnO.<sup>150</sup> Ritzkopf et al. also report higher methanol conversion and reduced CO formations over Cu/ZrO<sub>2</sub> catalysts prepared by a microemulsion technique.<sup>151</sup> Oguchi et al. reported enhanced catalytic behavior when ZrO<sub>2</sub> was added to CuO/CeO<sub>2</sub>-based catalysts.<sup>152</sup> Again, changes in the copper oxidation state are the results of a synergistic effect of cerium with zirconia.<sup>152</sup> With CeO<sub>2</sub> alone, metallic Cu<sup>0</sup> is present, but with ZrO<sub>2</sub>, copper is in the form of Cu<sub>2</sub>O. A mix of both CuO<sub>2</sub> and Cu<sup>0</sup> was present when supported on both ZrO<sub>2</sub> and CeO<sub>2</sub>. Velu et al. studied the oxidative steam reforming of methanol over reportedly active and selective CuZnAl(Zr)-oxide catalysts.<sup>153–155</sup> The addition of Zr to the CuZnAl catalyst was found to improve Cu reducibility and increase Cu metal surface area and dispersion. Through a mechanistic study it was found that CO<sub>2</sub> and CO were both produced as a primary product and CO was subsequently transformed into CO<sub>2</sub> by the WGS reaction and CO oxidation.<sup>153–155</sup>

Promotional effects of small amounts of Cr additives were reported by Huang et al. for both the methanol steam reforming and WGS reactions.<sup>140,156</sup> In the same study, the detrimental effects of Co additives were also reported. It was suggested that while Cr serves as both a catalytic and structural promoter, Co additives increased activity for the decomposition of methanol to CO.

Catalytic activity of Au-based<sup>157</sup> and Au-promoted catalysts<sup>158,159</sup> for methanol steam reforming has been reported. The use of Au offers interesting redox behavior for reactions such as steam reforming. Additionally, Takahashi et al. reported that Au may help increase copper dispersion.<sup>159</sup> However, other promoters may be more suitable, since Au is not very stable under reaction conditions<sup>143</sup> and has also been shown to have minimal activity.<sup>157,159</sup>

Papavasiliou et al. reported the performance of manganese-promoted Cu–Mn oxide catalysts to be higher than that of a CuO–CeO<sub>2</sub> catalyst prepared similarly.<sup>160</sup> A correlation of the formation of a Cu–Mn spinel phase with maximum activity was found.

### 3.1.5. Preparation Method

In addition to catalytic metal composition, the method of preparation has been shown to be extremely important to catalytic performance. Busca et al. reported the performance of CuZnAl catalysts for the oxidative methanol steam reforming reaction prepared from ex-hydrotalcite precursors.<sup>161,162</sup> It was found that the activities of such catalysts were more dependent on the oxidative nature of the Cu active sites, dependent on the synthesis technique. Furthermore, it was suggested that catalytic composition had less to do with activity than the nature of the oxidized Cu species. While these investigations were focused on *oxidative* methanol reforming, the importance of the synthesis procedure can be extended to methanol reforming without the addition of oxygen. Kniep et al. correlated increased activity of copper catalyst prepared from aged precipitates for the methanol steam reforming reaction.<sup>163</sup> Several preparation methods, including impregnation, coprecipitation, and hydrothermal synthesis, were studied by Shen et al. for methanol reforming

over Cu/Zn/Al-based catalysts.<sup>164</sup> It was found that the preparation method affects conversion and selectivity. In their study, a coprecipitation method yielded the best catalyst. Kawamura reported optimization of the coprecipitation temperature and pH, important in increasing Cu dispersion.<sup>165</sup> Valdés-Solís reported synthesis of nanosized spinel Cu-based catalysts by a silica template technique.<sup>166</sup> Compared to conventionally prepared catalysts, improved surface areas were reported, resulting in highly active catalysts. Deactivation due to coking was observed, although it appeared to be independent of the synthesis method.

## 3.2. Group VIII Metals

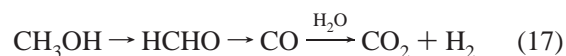
Group VIII metals such as Pd, Pt, and Ni exhibit different performance than copper-based catalysts.<sup>135</sup> Group VIII metals predominantly catalyze methanol decomposition, reaction 16, transforming methanol to CO and H<sub>2</sub>. In the presence of water, the kinetically slower WGS reaction (reaction 3) will occur. This secondary reaction of WGS converts some of the CO to CO<sub>2</sub>.<sup>135</sup> However, a significant amount of CO is produced via methanol decomposition. This makes the use of such metals an unattractive option for processes where hydrogen is desired.

Takahashi reported the addition of palladium to a CuZr catalyst, forming an amorphous CuZrPd alloy.<sup>159</sup> This particular CuZrPd alloy accelerated methanol conversion but facilitated methanol decomposition, thus producing more CO than CuZr alone.

### 3.2.1. Palladium–Zinc Alloy-Based Catalysts

Cu-based catalysts are active and selective for the methanol steam reforming reaction. However, sintering of the metal at temperatures > 280 °C and other deactivation issues remain problematic, including its pyrophoric nature when exposed to air. Precious metal and other group VIII metals are active for the conversion of methanol; however, they tend to *not* be selective for the reforming reaction. Other options include precious metal alloys, not containing copper, with Pd/ZnO being the most active and selective for this type of catalyst.<sup>18</sup>

Iwasa et al. were the first to report that Pd supported on ZnO and reduced at >300 °C has exceptionally high activity and selectivity to CO<sub>2</sub> and H<sub>2</sub>.<sup>144,167–170</sup> Combined TPR, XRD, and XPS methods revealed the formation of a PdZn alloy under reduction conditions higher than 300 °C.<sup>167,170</sup> It was shown that the reactions proceeded selectively toward methanol steam reforming over the catalysts having the PdZn alloy phase. Catalysts having the metallic Pd phase exhibited poor selectivities to CO<sub>2</sub>. Upon alloy formation, Iwasa's group proposed a reaction different than the decomposition reaction (reaction 16). The reaction in the case of group VIII metals, such as Pd alone, proceeds through the pathway in reaction 17,<sup>144,168</sup>



The HCHO species formed in the reaction is rapidly decarbonylated to CO and H<sub>2</sub>, and then partially transformed to CO<sub>2</sub> and H<sub>2</sub> through the secondary WGS reaction. When Pd is alloyed with Zn, however, a similar pathway to that over copper-based catalysts is suggested (reaction 18).<sup>168,170</sup>



The HCHO intermediate formed readily reacts with  $\text{H}_2\text{O}$  to produce a formate species. It has further been suggested that both reaction pathways (reactions 17 and 18) occur competitively over PdZn-based alloys, although reaction 18 is heavily favored, with reaction 17 producing less than equilibrium amounts of CO.<sup>170</sup>

It was suggested that the difference in the catalytic performance of these reactions was due to the difference in the reactivity of the aldehyde intermediate species formed in the course of the reactions.<sup>170</sup> Studies in surface science have revealed that the structures of aldehydes absorbed on Cu are greatly different from that on group VIII metals such as Pd.<sup>168</sup> In temperature-programmed desorption experiments, it was found that, on Cu, these aldehydes absorb preferentially in a  $\eta^1(\text{O})$ -structure (the oxygen in the carbonyl,  $\text{C}=\text{O}$ , is bonded to the Cu surface, maintaining its double bond). On group VIII metals, the aldehydes absorb as a  $\eta^2(\text{CO})$ -structure (the carbon loses its double bond and absorbs to the metal surface, as does the oxygen). Thus, on copper surfaces, the aldehyde preserves its molecular identity, whereas, on the group VIII surfaces, the bonds are ruptured.<sup>168</sup> Hence, Iwasa et al. hypothesized that the difference in the original catalytic functions of copper and group VIII metals for the steam reforming and dehydrogenation of methanol is ascribed to the difference in structures of the HCHO intermediates formed on these metals. Thus, the novel catalytic function typical of Cu emerges from PdZn systems as well.

Iwasa et al. expanded their work to other group VIII metals such as Co, Ni, Ru, Ir, and Pt on various supports such as  $\text{In}_2\text{O}_3$  and  $\text{Ga}_2\text{O}_3$ .<sup>144,170</sup> It was found that Pd and Pt both formed alloys with In, Ga, and Zn, improving the selectivity for methanol reforming once alloy was formed. However, of these different compositions, the Pd–Zn alloy appears to still be the most active and selective for the methanol reforming reaction. Also studied was a Pd/ZnO/ $\text{CeO}_2$  catalyst which had good thermal stability as well as good activity and selectivity. At an operating temperature of 350 °C, negligible activity loss was observed. Comparatively, a 20% loss in hydrogen exit concentration was observed over a Cu/ZnO catalyst under the same conditions.<sup>170</sup>

Work at the Pacific Northwest National Laboratory confirms that formation of a Pd–Zn alloy results in a highly selective methanol reforming catalyst.<sup>171</sup> Preparation studies indicated the use of highly acidic Pd nitrate aqueous precursors alters the textural properties such as porosity and crystalline structure, where dissolution is evident.<sup>172</sup> The use of an organic precursor in the preparation method can minimize these effects.<sup>173</sup> Pd loading and Pd/ZnO ratio optimization studies were done on  $\text{Al}_2\text{O}_3$ -supported catalysts.<sup>174</sup> On a Pd/ZnO/ $\text{Al}_2\text{O}_3$  catalyst, similar activities and selectivities were reported as on a conventional Cu-based catalyst at 220 °C,<sup>174</sup> although, due to higher stability of the Pd alloy, much higher operating temperatures can be used and the increased kinetics can be exploited.<sup>15</sup> Kinetic studies using a Pd/ZnO-based catalyst in a microreactor resulted in a reported power law expression suitable for the design of a miniature fuel processor.<sup>42</sup>

Other recent work has continued to examine the unique nature of the Pd–Zn type catalyst. Ranganathan et al. suggested that a Pd/ZnO catalyst favored the reforming reaction due to its higher density of acidic sites.<sup>175</sup> Comparatively, a Pd/ $\text{CeO}_2$  catalyst, which produced a high amount of CO, had a higher density of basic sites, which favors the decomposition reaction.

Tsai et al. have suggested that the unique catalytic function of Pd/ZnO for the reforming reaction is governed by the valence band structure of the catalyst. This is due to its similar band structure and catalytic performance to that of Cu.<sup>176</sup> It was hypothesized that an intermetallic compound may be logically designed by band structure calculations, replacing a selected metallic element without changing the catalytic function. Activity correlation for a PdZn catalyst was made to a PdCd catalyst.

Suwa et al. reported the performance of various supported Pd/ZnO-based catalysts.<sup>177</sup> While much more stable than Cu-based catalysts, deactivation of PdZn catalysts was reported. A Zn–Pd/C catalyst was found to have a much smaller deactivation rate.

Karim et al. reported crystallite size effects and alloy effects.<sup>178</sup> Lower selectivity was found when small crystallites were formed ( $\sim 1.5$  nm). However, these small particles were thought to be metallic Pd that was eventually alloyed with Zn upon increasing reduction temperature, resulting in increased selectivity. Furthermore, it was found that larger PdZn particles did not adversely affect the reforming reaction. Dagle et al. reported similar crystallite effects on selectivity,<sup>173</sup> where smaller PdZn crystallites can produce more CO. In fact, an optimum crystallite size which promotes the reforming reaction probably exists over Pd/ZnO type catalysts. Further reports by Agrell et al. confirm a correlation between Pd crystallite size and carbon monoxide selectivity.<sup>179</sup>

Penner et al. reported highly structured Pd–Zn on a mechanically stable  $\text{SiO}_2$  support.<sup>180</sup> As evidenced by TEM, the PdZn was thermally and structurally stable under reducing conditions up to 600 °C.

Work utilizing PdZn catalysts for use in microchannel reactors has also been done at the Institute for Micro Process Engineering. It appears that direct wash coating of the PdZn catalyst on microchannel walls resulted in high activity for the reforming reaction.<sup>181</sup> Kinetic investigations were made and compared microchannel reactor data to that of a “global model” kinetic expression.<sup>182</sup>

Several investigations of the PdZn type catalyst were made for the oxidative steam reforming of methanol (OSRM) reaction. Concerns related to use of the Cu-based catalysts in an oxidative environment made it necessary early on to find an alternative catalyst for oxidative reforming.<sup>183</sup> Fierro et al. were some of the first to report high reforming activity and selectivity of the Pd/ZnO catalyst for OSRM reactions.<sup>183</sup> A discussion of catalyst preparation and characterization accompanied reports of a finely dispersed and highly active Pd–Zn catalyst supported on alumina.<sup>184</sup> Chen et al. reported the use of a wall-coated, highly active Pd–Zn/Cu–Zn–Al mixed catalyst for the OSRM reaction in a microchannel reactor.<sup>185</sup> High hydrogen yields for the OSRM reaction in a microreactor were reported by Lyubovsky et al.<sup>186</sup> Liu et al. reported stability issues.<sup>310</sup> While Cu/ZnO lost its activity while maintaining a constant selectivity for CO formation, Pd/ZnO catalysts exhibited more stable activity but showed increasing CO selectivity. It was suggested that carbon deposits and surface oxidation break down the Pd–Zn alloy to produce elemental Pd. Catalyst regeneration in hydrogen was also demonstrated.

In summary, the ability to tailor Pd/Zn alloys to mimic the mechanistic behavior of Cu-based catalysts is noteworthy because Cu catalysts suffer from a lower-temperature operat-



**Table 7. Conversion Method Options for Methanol-Based Reforming Systems for Fuel Cells**

primary conversion	secondary conversion	CO mitigation	fuel cell
low-temperature steam reforming high-temperature steam reforming high-pressure steam reforming	water-gas shift	preferential oxidation selective membrane separations selective methanation CO adsorption approaches	standard PEM PEM with tolerant anode high-temperature PEM SOFC or other high temp FCs

ing window and have pyrophoricity issues. The ability to recreate the excellent selectivity of Cu catalysts in a more thermally and oxidatively robust formulation opens additional options for methanol reforming at higher temperatures and in less-than-ideal conditions while maintaining high H<sub>2</sub> output.

#### 4. Reactor and System Development

Given the foregoing discussion of system challenges, competing technologies, and catalyst development activities, we now turn to the subject of device demonstration and deployment. The vast majority of reactor and system demonstrations to be found in the literature have dealt with small and/or portable systems, such as would power portable electronic devices, battery chargers, backup/auxiliary power units, or recreational applications.

Our discussion of reactor and system development is categorized according to reactor types, which inevitably fall out from the system approach options that are described below. The reactor types are broadly separated in terms of system pressure. System pressure is most often dictated by the CO mitigation approach taken. If a catalytic approach is chosen, which converts CO to something more benign to the fuel cell (e.g., CH<sub>4</sub>, CO<sub>2</sub>), the system usually will operate at low pressures. If, on the other hand, the CO mitigation strategy includes a selective membrane separator, a high-pressure reactor is required.

Table 7 lists the system options from the perspective of conversion method, purification method, and fuel cell choice. Since methanol is an easily converted fuel, the low-temperature approach makes the most sense, unless there are other factors that would require deviating from this starting point, such as the availability of high-temperature waste heat to operate the reformer or the need to operate the reforming reaction at high temperatures to accommodate other downstream processes. As a result of low-temperature operation with selective catalysts, secondary conversion such as water-gas shift is generally unnecessary (see section 1.3, Figure 2). The next important consideration is CO mitigation. If the reformat is to be fed to a high-temperature fuel cell such as a high-temperature PEM or a solid oxide fuel cell, the CO mitigation step is unnecessary.<sup>30</sup> However, since most methanol reforming applications are intended for standard-temperature (60–80 °C) PEM fuel cells, CO mitigation to ppm levels is crucial for the proper operation of the fuel cell.<sup>30</sup> The most common CO mitigation approaches have included preferential CO oxidation, selective membrane separations, and selective CO methanation.<sup>30</sup> Each approach has its advantages and disadvantages, which is illustrated in the various applications and demonstrations described below. Additionally, some of the advantages become irrelevant given other system constraints—or conversely, some disadvantages become tolerable given other system constraints. For example, selective membrane separations give nearly 100% pure hydrogen, which is a distinct advantage for PEM stack operation. However, if a portable application is constrained

by its lack of capacity to generate the necessary pressures for the membrane, or if material cost is crucial, the membrane approach becomes undesirable. On the other hand, due to this low-pressure constraint, a developer must deal with the reduced hydrogen concentration and finite CO concentration (up to 100 ppm) present in the reformat stream exiting a preferential oxidation reactor, and its subsequent effect on PEM operation. Tradeoffs like these explain why various companies or research groups have approached similar system development targets with varying technology strategies, even for the same power level.

These system approaches have been deployed in various reactor embodiments, with the chosen configuration being dependent on the application. The main reactor body material has usually been stainless steel, ceramic, or silicon. The choice of reactor material is significantly affected by the reforming and cleanup approach taken, as well as having much to do with the background and experience of the investigators. This can be seen especially in the area of silicon-based reactors for small power applications. Since silicon has been the material of choice for microelectronics and subsequently MEMS, groups from this area have applied silicon processing techniques to the development of micro-reactors for fuel processing, including methanol as well as more complex fuels. For systems above about 10 W, though, silicon has not been used extensively.

While methanol steam reforming has been employed for nearly 100 years<sup>187</sup> and has been used in industrial applications for several decades, its application to portable power systems has required more creativity and innovation than is required for large industrial installations. Instead of the conventional industrial reactor that utilizes a large packed bed of extruded catalyst and indirect reactor heating, these smaller applications require better deployment options in order to more effectively utilize the catalyst and avoid the large pressure drops that would result from a small packed bed (with analogously small particle sizes). The new approaches also seek to more closely integrate the heat source (electrical resistance or combustion) with the endothermic operations of methanol/water vaporization and methanol steam reforming. These new approaches are illustrated in the work conducted by the groups described below, taking the form of wall-coated catalysts, interleaved combustion and reforming operations, microchannel architectures, integrated systems, and novel materials that would not be economical for larger applications.

Illustrated in the reactor and system development examples of this section are the various independent and dependent variables for methanol steam reformers. These considerations are listed in Table 8, and they go well beyond the effects of temperature and pressure on conversion and selectivity, with each variable change affecting several aspects of the system. Each group of investigators has approached the subject based on their own application concept and the weight of various tradeoffs. The result is a variety of reactor sizes, concepts, materials of construction, and purification methods.



**Table 8. Independent Variables Relevant to Methanol Steam Reforming and the Affected Dependent Variables for Reactors and Systems**

independent system variables	dependent variables
temperature	methanol conversion
pressure	CO selectivity
catalyst composition	hydrogen purity
catalyst form	hydrogen yield
residence time	hydrogen utilization
S/C	reactor size
reactor material	reactor weight
construction method	reactor pressure drop
power level	system efficiency
heating method	system energy density
flow geometry	system cost
sweep gas use	failure mode
	catalyst lifetime
	catalyst stability/attrition
	BOP implications
	fuel cell type
	fuel cell lifetime

As was stated earlier, the vast majority of methanol reforming applications are focused on some form of portable power. Much of this development work has been driven by the military,<sup>4,5,39,44,45,57,188,189</sup> with an emphasis on powering the war fighter with devices that offer significantly higher energy densities than batteries. In parallel, much commercial interest has driven this area of development, with the most prominent commercial players being Motorola,<sup>48,190–194</sup> Casio,<sup>195–200</sup> Idatech,<sup>201,202</sup> Genesis Fueltech,<sup>203</sup> and Ultracell.<sup>204,205</sup> These commercial applications include battery replacement or recharging for portable electronics and portable power for recreational uses.

#### 4.1. Low-Pressure Reforming Systems

Because of the variety of approaches and power levels, groups have employed various types of materials and fabrication methods in the production of the reformers that are employed in low-pressure systems. The discussion of low-pressure reforming, then, is entered into based on reactor type, according to fabrication material—namely metals, glasses, and ceramics. All of these materials have been employed in attempts to develop low-pressure reforming systems that provide good metrics, such as small volume, low mass, high throughput, high efficiency, rapid startup, and rapid transient response.

##### 4.1.1. Metal Reactors

Metals such as stainless steel, FeCrAlY (“Fecralloy”), aluminum, and copper have been extensively employed in the production of methanol steam reformers and supporting components. This represents the largest category of methanol systems and includes much of the work in what are known as microchannel-based reactors. As will be seen, the vast majority of devices described are microchannel-based. A more thorough discussion of microchannel reactors in general can be found elsewhere.<sup>28,29,206,207</sup>

Under a DARPA-sponsored micropower program, researchers at Pacific Northwest National Laboratory (PNNL) demonstrated an integrated subwatt fuel processor based on methanol steam reforming.<sup>28,33,44,45,208,209</sup> The system was heated by methanol combustion and contained several unit operations (reformer, combustor, vaporizers, CO cleanup) in an integrated stainless steel unit the size of a transistor, 0.3 cm<sup>3</sup> in volume and weighing less than one gram (Figure



**Figure 5.** Sub-watt integrated methanol steam reformer developed at PNNL, without selective methanation (left) and with selective methanation (right). (Reprinted from ref 208, copyright 2004, with permission from Elsevier.)

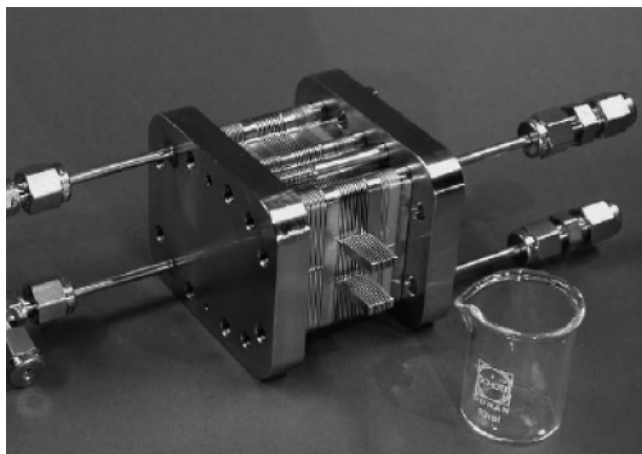
5).<sup>208</sup> Demonstrated efficiencies were measured at 10–33% (based on lower heating values), depending on how the system was operated. The investigators conducted steam reforming of a 60 wt % methanol feed stream at 300–350 °C, heated by methanol combustion. In some embodiments, the device included a selective methanation reactor that reduced the CO concentration to less than 100 ppm.<sup>44</sup> Along with collaborators at Case Western Reserve University, the PNNL researchers demonstrated the production of power from this reformat stream using a PEM fuel cell based on a phosphoric acid-doped polybenzimidazole membrane, to produce 23 mW of electric power.<sup>33</sup>

One of the most important conclusions from this investigation was that even though the fuel processor and fuel cell could be developed for such low power applications, and even have a very low footprint, the necessary BOP equipment that would support such a system appeared to be the biggest hurdle. Innovative methods of moving fluids and controlling the process would need to be employed to make such a system deployable as a self-contained power source.

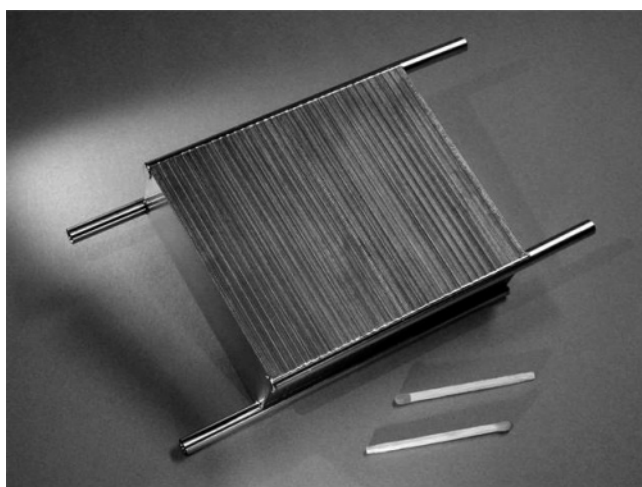
A series of papers published by the group at Germany's Institut für Mikrotechnik Mainz (IMM) describes their development of microchannel-based fuel processing components for methanol steam reforming<sup>46,210–213</sup> and supporting reactions (PrOx, WGS).<sup>211–213</sup> Early work by this group describes a stainless steel microreactor with dimensions of 75 mm by 45 mm by 110 mm, utilizing a wall-washcoated Cu/Zn catalyst and having an estimated capacity of 90 W (net electric output, based on certain system assumptions).<sup>46,210</sup> Actual demonstration results indicated a net output of about 30 W, with 65% methanol conversion, and 4500 ppm CO content. Operation at these conditions would not be acceptable in a final system, especially if efficiency is a consideration at all.

Further developments reported by the same group included an increase in output power to 100 W and integration of the methanol reformer with a combustor, and integration of a PrOx reactor with high- and low-temperature recuperative heat exchangers.<sup>211,212,311</sup> The integrated units are shown in Figures 6 and 7. Estimates of a complete power system based on this integrated processor and including methanol and oxygen tanks and a 100 W fuel cell yield an overall size of 280 mm by 100 mm by 400 mm.<sup>210,211</sup>

A forthcoming publication from IMM reports a miniaturized version of this concept, with a 20 W net power output, including a dual-stage PrOx unit.<sup>213</sup> The group reports



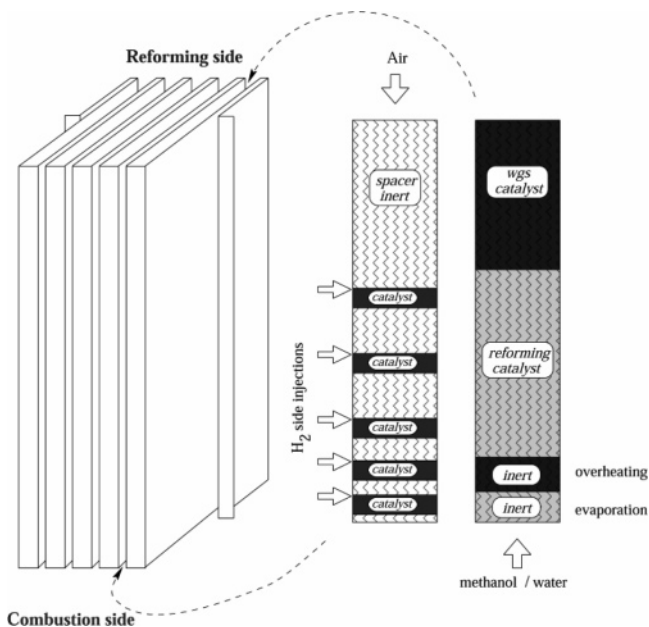
**Figure 6.** Microstructured integrated selective oxidation reactor/heat exchanger prototype developed at IMM. (Reprinted from ref 311, copyright 2005, with permission from Elsevier.)



**Figure 7.** Combined steam reformer/catalytic combustor for the methanol steam reforming system developed at IMM. (Reprinted from ref 212 with permission of ASM International, all rights reserved, www.asminternational.org.)

dimensions for the integrated reformer/combustor unit as 120 mm by 36 mm by 25 mm and the PrOx reactor as 104 mm by 80 mm by 15 mm. Utilizing  $S/C = 2.0$ , and operating at  $275\text{ }^{\circ}\text{C}$  and a throughput of  $350\text{ mL min}^{-1}\text{ g}_{\text{cat}}^{-1}$ , they report full methanol conversion, 0.35% CO out of the reformer, and 18 ppm CO out of the PrOx.<sup>213</sup> This represents a suitable product stream composition for standard PEM fuel cell use, but improvements on the device sizes should be possible and are probably necessary for portable use at 20 W.

In work related to the IMM developments, in that both projects are part of the MiRTH-e program of the European Union, researchers at Eindhoven University of Technology in The Netherlands have conducted a modeling investigation that compares microreactor technology to conventional fixed-bed technology for portable hydrogen production.<sup>214</sup> The group investigated two reactor types (methanol steam reforming and selective oxidation) for two system sizes (100 W and 5 kW) for both the microreactor and the fixed-bed reactor. The microreactor design was based on patterned plate construction (laser welded or diffusion bonded), where the catalyst was wall coated on the respective plates.<sup>214,215</sup> The fixed-bed reactor was a shell and tube design with reforming catalyst packed on the shell side of the reactor.



**Figure 8.** Folded-sheet reactor concept developed at the Institute for Chemical Process Engineering, indicating the staged combustion concept and a dual catalyst bed on the reforming side. (Reprinted with permission from ref 217. Copyright 2004 American Chemical Society.)

In conclusion, they found the microreactor design to be smaller and lighter for both power level cases but that the microreactor advantage disappears as system output is increased. This is due to scaling factors. For the microreactors, scaling factors were generally found to be 1.0 or greater for both volume and mass. On the contrary, and in line with conventional engineering heuristics, the fixed-bed reactor design was found to have scaling factors of 1.0 or less for both volume and mass.<sup>214</sup> Because of the nature of microchannel architecture, the scaling factor will always be around 1.0, as the way of scaling up is to number up. So, while the advantage of microchannels is an ability to minimize heat- or mass-transfer limitations, once a certain throughput-per-volume is established, this will hold at both small and large scales.

The integrated reactor concept was also investigated by a group at the University of Stuttgart's Institute for Chemical Process Engineering.<sup>216–218</sup> The concept, called a folded-sheet reactor, seeks to integrate the exothermic oxidation reaction with the endothermic vaporization and methanol steam reforming operations, as others have also attempted. In the folded-sheet reactor concept, pictured in Figure 8, the investigators utilize an interleaved geometry, where the endothermic and exothermic sections are alternated. Additionally, for the purpose of proper temperature control, the exothermic combustion sections are designed with a staged fuel feed system.<sup>217</sup>

The group conducted extensive modeling work, followed by demonstration of 1 kW<sub>th</sub> and 10 kW<sub>th</sub> demonstration devices. In the case of the 10 kW<sub>th</sub> device, 16 reforming and 17 combustion layers were employed. Testing results over the 5 kW<sub>th</sub> to 10 kW<sub>th</sub> range with this device yielded methanol conversions from 70% to 90%, with CO levels increasing with increased conversion, which is to be expected.<sup>219</sup> Overall, the group found the experimental results to agree quite well with the simulation calculations performed,<sup>217</sup> but operation of this device should be improved to achieve complete methanol conversion in order to improve



system efficiency. Given the ease of reforming methanol, this is not a difficult goal to achieve.

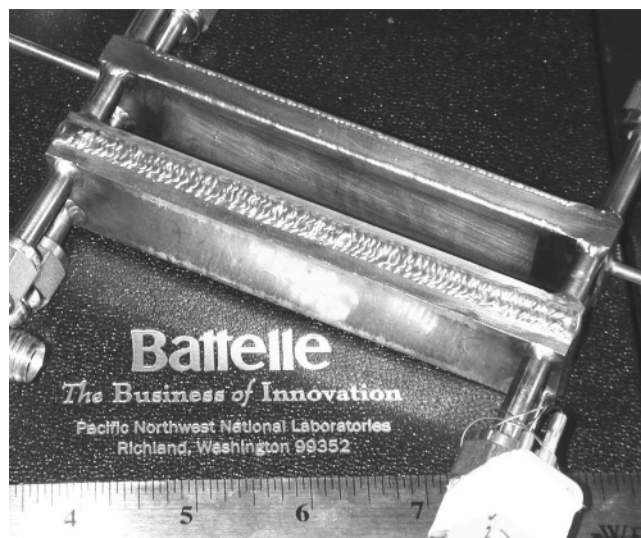
Pfeifer and co-workers at the Karlsruhe Research Center have developed methanol reforming technology based on microstructured reactors aimed at automotive applications.<sup>181,220,221</sup> Much of the work has been to investigate catalyst issues, but reactor demonstrations are also reported. Using Pd-based methanol reforming catalysts and microstructured reactors, the group has demonstrated >85% conversion at 310 °C using a S/C = 1.9. CO concentrations were quite low as well (0.2–0.5%), but this is to be expected when conversion is less than complete. The 200 W reactors were electrically heated and were mainly used to investigate the issues of durability and selectivity<sup>220,221</sup> and the effect of washcoating.<sup>181</sup>

In addition to the subwatt reforming work conducted at PNNL and described above, researchers there have also developed larger integrated reforming units based on similar microchannel architectures.<sup>15,189,222</sup> Early work described a breadboarded fuel processing system constructed from stainless steel that included vaporizers, steam reformer, and catalytic combustion.<sup>189</sup> The system was demonstrated as thermally self-sustaining after initial startup with electric heat. Demonstration of this system, with the reformer operating at about 350 °C, and using S/C = 1.8, yielded >99% conversion of methanol, roughly 0.8% CO in the dry reformat, an estimated 13 W of power (27 W<sub>th</sub>), and a net thermal efficiency of 45% for the base case. The system was further demonstrated over a range of 14 to 80 W<sub>th</sub>, with net thermal efficiencies of 53–58% for the upper range of operation.<sup>189</sup>

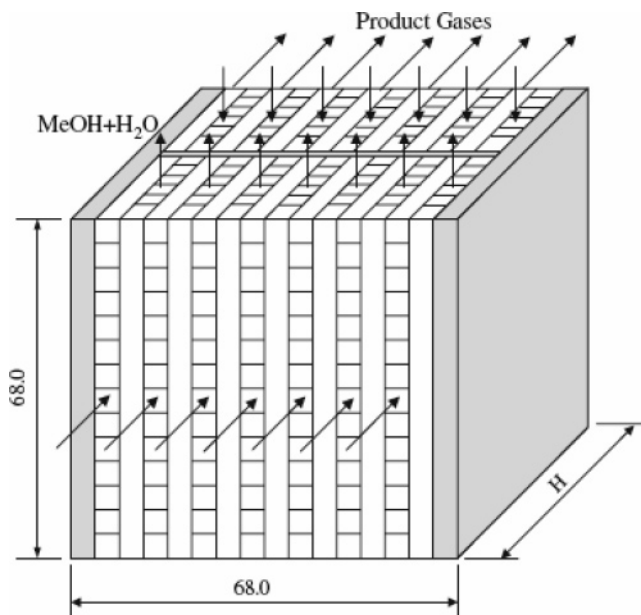
Subsequent work by the same group resulted in an integrated reformer containing the same unit operations as in the breadboard system.<sup>15</sup> Integration of the unit operations yielded devices with higher thermal efficiency, and the PNNL researchers demonstrated the integrated units at nominal sizes of 20, 50, 100, and 150 W. The demonstrated thermal efficiencies of these units were reported at up to 85% based on lower heating values, and S/C was reduced to 1.2.<sup>15</sup> Additional system development saw the integration of some of these units with catalytic selective methanation technology to reduce the CO concentration in the reformat to PEM-tolerant levels, such as the device shown in Figure 9.<sup>223,224</sup> The group demonstrated this integrated fuel processor at up to 180 W, at about 70% thermal efficiency and yielding a CO concentration in the dry reformat of 30–100 ppm. The reformer technology was also demonstrated as part of a semipackaged battery charger system for the U.S. Army.<sup>223,225</sup>

Researchers at East China University of Science and Technology have recently reported on a compact 10 W methanol reformer based on microchannel architecture. The diffusion-bonded “FeCrAlY” reactor was heated by an electric furnace in a laboratory setup. Most of the work was conducted to look at catalyst compositions for the Cu/Zn system, and the estimated power output of the device, which measured 40 mm by 40 mm by 10 mm, was about 10 W.<sup>226,227</sup>

Another embodiment of the integrated combustor/reformer concept has been reported by researchers at China’s Dalian Institute of Chemical Physics. Labeled a plate-fin reformer, or PFR, the device incorporates methanol steam reforming with catalytic combustion of (simulated) anode off gas.<sup>228–230</sup> Figure 10 illustrates the reactor concept, which included packed-bed catalyst for both the reformer (Cu/Zn/Al<sub>2</sub>O<sub>3</sub>) and



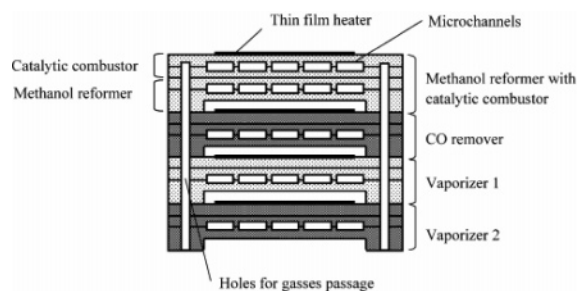
**Figure 9.** Integrated methanol steam reformer developed by researchers at PNNL. The unit includes vaporization, catalytic combustion, catalytic steam reforming, and selective methanation reactors. (Photo courtesy of PNNL.)



**Figure 10.** Plate-fin type methanol fuel processor developed by Pan and Wang, indicating flow patterns in the device for reforming and heat exchange. (Reprinted from ref 230, copyright 2006, with permission from Elsevier.)

the combustor (Pt/Al<sub>2</sub>O<sub>3</sub>), with particle sizes of about 1 mm diameter.

High methanol conversions were demonstrated, using pressures up to 0.04 MPa, temperatures of 210–270 °C, S/C of 1.2 to 1.6, and throughputs of 1200–1600 h<sup>−1</sup>. Under these conditions, CO concentrations from the reformer were below 1%, except for the 1200 h<sup>−1</sup> throughput condition (resulting from increased WGS conversion at the slower throughput).<sup>229</sup> Demonstration of the PFR over time showed a steady 100% conversion level over 100 h, but the CO concentration steadily increased over this time from 0.4% to 1.2%. A second test, conducted on a larger unit, showed a steady CO concentration (1.5% ± 0.5%, higher than the 100-h test) over the course of 1000 h of operation. However, during this same time, the methanol conversion decreased from 100% to 93%.<sup>229</sup>



**Figure 11.** Casio-developed multilayered microreactor: (a) schematic cross-section of the reactor body indicating the various sections, and (b) picture of the device with a U.S. quarter for scale. (Reprinted from ref 195, copyright 2005, with permission from Elsevier.)

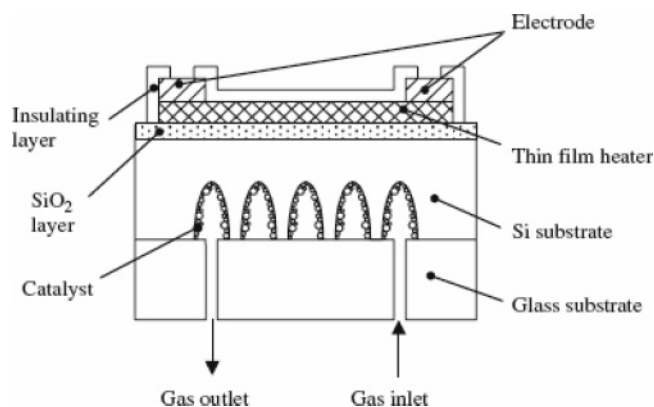
Subsequent work by the team demonstrated an integrated system that included a preferential oxidation (PrOx) reactor.<sup>230</sup> The size of the final system, including the control system, was 680 mm by 500 mm by 400 mm, with a mass of 40 kg. Using  $S/C = 1.5$ , this system processed  $70 \text{ mL} \cdot \text{min}^{-1}$ , which corresponds to an estimated electrical output on the order of 5 kW. The authors also report thermal efficiencies for this system of 75% and greater.<sup>230</sup>

Researchers at the Korean Advanced Institute of Science and Technology have demonstrated a plate type methanol reformer in the 5.5 W range.<sup>231,232</sup> Using Cu/ZnO catalyst coated on the plate walls, they first demonstrated an electrically heated device,<sup>231</sup> followed by an internally heated device based on interleaved combustion and reforming.<sup>232</sup> The latter device was operated at 210–290 °C and achieved high methanol conversion only at temperatures > 250 °C, with  $S/C = 1.5$ .<sup>232</sup> However, the CO level of 1.2–1.4% is higher than would be expected based on the temperatures and catalyst employed. This is likely due to the higher residence times, which allow for the reverse water-gas shift reaction to occur to a significant extent.

At the Korean Institute of Energy Research, investigators have developed microchannel-based reformers for methanol processing and demonstrated them at 33  $W_{th}$  and 59  $W_{th}$ .<sup>233–236</sup> For the 33  $W_{th}$  case, the reactor measured 70 mm by 40 mm by 30 mm and was heated by electric heating rods. While the CO concentration in the dry gas was held generally below 1%, greater than 90% methanol conversion was achieved only at low throughput and at higher temperatures (240 and 260 °C).<sup>233,236</sup> For the 59  $W_{th}$  case, internal combustion was integrated into the design. Operating over roughly the same temperature range as the previous reactor, methanol conversion was demonstrated at >99%, but the CO concentration was considerably higher, at 2.2% in the dry gas.<sup>234,235</sup> This higher CO concentration creates significant challenges for any CO cleanup step located downstream.

#### 4.1.2. Glass and Silicon Reactors

Several publications issued by CASIO Computer Company of Japan describe development work on a glass multilayered microreactor for PEM fuel cells for portable electronic device applications.<sup>195,197,199,200</sup> Figure 11 shows a schematic and picture of the device they developed, which includes a methanol reformer, a catalytic combustor, a CO remover (PrOx), and two vaporizers, and has dimensions of 22 mm by 21 mm by 11 mm.<sup>195</sup> Wall-coated Cu/Zn and Pt/ $\text{Al}_2\text{O}_3$  catalysts were utilized for the reformer and combustor units, respectively, and a commercial PrOx catalyst was employed. The device also incorporates thin film heaters that are used for startup. Demonstration of the device yielded 2.5 W of electric power, operating at a 280 °C reforming temperature



**Figure 12.** Electrically heated methanol steam reforming microreactor developed by Casio. (Reprinted from ref 200, copyright 2006, with permission from Elsevier.)

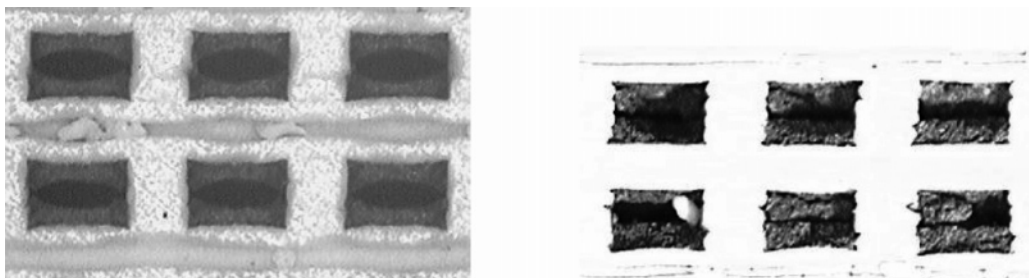
and using  $S/C = 1.2$ .<sup>199</sup> Electric heat for start up was required for the first 30 min of operation as the combustor was brought online and the temperatures were stabilized.

A subsequent redesign reported by CASIO yielded an electrically heated methanol reformer measuring 25 mm by 17 mm by 1.3 mm and constructed from glass and silicon (Figure 12).<sup>200</sup> The developers found sandblasting to be a suitable technique for producing microchannels in the plate materials, and catalyst adhesion to the wall was enhanced by the resultant surface roughness. The noninsulated device consumed several watts in the electric heaters to yield 1 W of electric power, but based on previous demonstrations, the group expects to rectify this problem. Other future work identified included the need to achieve 100% methanol conversion, increase thermal efficiency, and demonstrate durability.<sup>200</sup> The work described by the CASIO researchers has also resulted in at least two issued patents.<sup>196,198</sup>

This work represents the type of integration and “system approach” that is required for such small reforming systems. It is one thing to demonstrate methanol steam reforming in a packed tube in a furnace. It is quite another to develop an integrated processing unit that is self-heating, is multichanneled, and incorporates all the necessary unit operations such as vaporization, reformation, and CO mitigation, along with built-in heat generation.

Researchers at Lehigh University have developed silicon-based methanol fuel processors at the 8–20 W range, fabricated using photolithography and deep-reactive ion etching.<sup>237–241</sup> Early work by the group utilized a packed-bed serpentine channel configuration employing the Sud-Chemie Cu/Zn catalyst.<sup>238</sup> The device was heated electrically using patterned platinum resistance heaters. Reactor demonstrations at 190–200 °C and  $S/C = 1.5$  yielded hydrogen production of  $0.176 \text{ mol h}^{-1}$  at about 88% methanol





**Figure 13.** Photos of two different fuel processors made by Motorola using the cofired process. In both cases, the catalyst layer is  $\sim 125$   $\mu\text{m}$  thick, but the volume fraction of catalyst in the channel differs, being  $\sim 66\%$  in (a) and  $>90\%$  in (b). (Copyright 2006, Motorola, Inc., used by permission.)

conversion. The corresponding CO concentration was reported at less than 1%, but no CO cleanup operations were conducted. The hydrogen power was estimated at 9.5 W.

Because of the long serpentine channel design of this reactor, the corresponding pressure drop through the unit was found to be 70–100 psig.<sup>240</sup> As a result, the same team developed a new embodiment of the small silicon-based reactor, utilizing a radial flow pattern.<sup>240</sup> As expected, the new geometry resulted in a much lower pressure drop through the catalyst bed, and the reactor was demonstrated at 98% methanol conversion and about 20 W of hydrogen production operating at 230–250 °C. However, the CO concentration was significantly higher than previously reported, being in the range of 2.1–3.1%, depending on S/C.<sup>240</sup> Significant improvement in the CO concentration would be required for this system to be useful for common CO mitigation techniques and standard PEM fuel cells.

Researchers at LLNL demonstrated an electrically heated silicon-based packed-bed microreactor for methanol steam reforming in the temperature range of 180–300 °C. They conducted extensive modeling, which was confirmed by experiments at very low processing rates ( $10 \mu\text{L min}^{-1}$ ).<sup>204,242</sup>

Another silicon-based reformer was reported by researchers at Seoul National University in South Korea. The group employed the popular Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> reforming catalyst formulation but introduced a new loading method that they call “fill-and-dry coating”.<sup>243</sup> Thin film heaters were built into the device, which included two steam reformer sections and a vaporizer. Nearly full conversion was reached at select conditions, and the maximum output of the device was an estimated 20 W<sub>e</sub>, with a corresponding CO concentration of 2100 ppm. Drastic differences in device performance were observed depending on the method of catalyst application, with the water-based fill-and-dry method being superior.<sup>243</sup>

Researchers at Tohoku University fabricated a silicon-based microreactor for methanol steam reforming, with an emphasis on thermal isolation through suspended structures. Good thermal isolation was achieved, evidenced by a 100 °C gradient from the reaction area to the outer wall of this very small device. However, methanol conversion of  $<1\%$  was achieved due to temperature distribution issues and reactant bypass.<sup>244</sup> The same group reported elsewhere the demonstration of a silicon-based reformer/fuel cell combination wherein the reformer produced the equivalent of 0.2 W at a total efficiency of 6%. Details are few, as this result is reported in the context of a paper focused on propane and butane conversion.<sup>245</sup>

A separate group from KAIST has demonstrated a MEMS reformer based on glass construction.<sup>246,247</sup> The reported work is concerned mainly with catalyst properties and issues related to deploying the catalyst as a washcoat on the reactor

walls. In a demonstration, using electric heat, the device was operated at up to 350 °C, with a calculated power output of 0.35 W.<sup>247</sup>

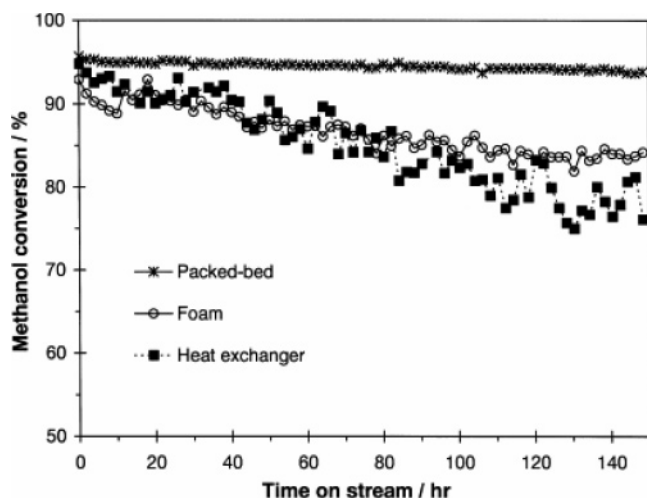
An investigation of kinetic measurements and thermal integration in microchannel devices conducted at Stevens Institute used methanol reforming as a model reaction. As part of this work, an electrically heated silicon based reactor was demonstrated at 2.5 W.<sup>248</sup>

#### 4.1.3. Ceramic Reactors

Utilizing their expertise in ceramic processing, researchers at Motorola conducted a development effort to produce a ceramic-based methanol reformer for small electronic applications.<sup>48,190–194</sup> A catalytic combustor was integrated with a methanol steam reformer and a methanol/water vaporizer. The reforming catalyst (Cu/Zn/Al<sub>2</sub>O<sub>3</sub>) was deployed as a packed bed while the combustion catalyst (Pt) was washcoated on the ceramic walls.<sup>190</sup> Thick film heaters were also incorporated into the ceramic structure. A device measuring 15 mm by 35 mm by 5 mm housed a reactor measuring just 5 mm by 15 mm by 1 mm.<sup>48</sup> The reported feed stream had S/C between 0.95 and 1.05, and the reformer was operated at 180–230 °C. These S/C values and reforming temperatures are lower than is generally reported for methanol reforming, but the Motorola system employed a high-temperature (150–225 °C) PEM fuel cell that could utilize a hydrogen rich stream containing significant amounts of CO and unreacted methanol. It was reported that the sum of these two impurities could acceptably be up to 5% by volume.<sup>48</sup> Motorola holds at least two patents relative to this technology.<sup>191,192</sup>

Recent developments reported by Motorola include a switch to a Pd-based catalyst, including wall-coating of both the reforming and combustion catalysts on green ceramic before firing.<sup>194</sup> The structural results of this process are illustrated in Figure 13. Motorola reports that their Pd-based formulation, developed in cooperation with BASF Catalyst, LLC, could survive the 850 °C ceramic firing temperature with only 12.7% loss in activity. The activity loss for the typical Cu-based catalyst for the same processing conditions was 47.5%, which is not surprising based on the nature of the two catalysts.<sup>194</sup>

Like the CASIO example described earlier, this effort by Motorola illustrates the integrated approach to reforming. In this case, the approach was to integrate the fuel cell directly with reformer unit, which is expected to lead to a more compact and more efficient system. Furthermore, the investigation of catalyst deposition on the green ceramic demonstrates an understanding of the need for production-friendly processing methods.



**Figure 14.** Comparison conducted by de Wild et al. for steam reforming of methanol in three different reactor configurations: packed-bed reactor, foam monolith filled reactor, and catalyst wall-coated heat exchanger. (Reprinted from ref 251, copyright 2000, with permission from Elsevier.)

A ceramic microreactor was developed by researchers at Yonsei University in South Korea, which incorporated a feed vaporizer and a packed-bed catalytic steam reformer ( $\text{Cu/ZnO/Al}_2\text{O}_3$  catalyst) in an electrically heated ceramic structure fabricated from low-temperature cofired ceramic (LTCC).<sup>249</sup> High conversion of methanol was achieved only at 280–340 °C. Subsequent CO preferential oxidation was demonstrated, which reduced the CO level to about 50 ppm, but few details are given in terms of selectivity, and only 12 h of durability are reported.<sup>249</sup>

Researchers at the University of Michigan have also demonstrated a LTCC-fabricated methanol steam reformer. The group coupled two LTCC devices together, one for methanol steam reforming using a Cu-based catalyst and the other for hydrogen combustion with a Pt-based catalyst to heat the reformer. Performance in this wall-coated device was found to be similar to that of a packed-bed reactor.<sup>250</sup> It would be expected, then, that the wall-coated device would yield a lower pressure drop for the same performance—a distinct advantage in practice.

#### 4.1.4. Reactor Comparisons

A comparison of catalyst deployment options was conducted by researchers at The Netherlands Energy Research Foundation for the case of methanol reforming with Cu-based catalyst in the multi-kilowatt power range.<sup>251</sup> They compared three different reactor options—packed bed, monolith foam, and washcoated channel—and the results are shown in Figure 14. Due to enhanced heat transfer, the foam and washcoat configurations showed much higher weight-specific activities than the packed bed, and the washcoated reactor achieved >95% conversion at a temperature 50 °C less than was required for the packed bed. However, a 150-h test showed that the foam and washcoat deactivated much more rapidly, losing 10% and 15% of their conversion, respectively. During the same period, the packed bed saw a conversion decrease of only 1.5%.<sup>251</sup> The results of this study demonstrate the kinds of tradeoffs that are often pondered by developers of portable catalytic reactors. From a pressure drop standpoint, the washcoated wall would be favored; from a shock and vibration standpoint, the monolith might be favored; and from a simplicity of catalyst manufacturing standpoint, the packed

bed might be favored. However, each of these methods of catalyst deployment has its disadvantages, such as keeping a packed bed in place, avoiding reactant bypass when using a monolith foam, and dealing with flaking or attrition when using a washcoated wall. As was mentioned earlier, which disadvantages can be tolerated and which advantages are most desired will depend on the application in terms of duty cycle, price point, operator training, and expected device lifetime.

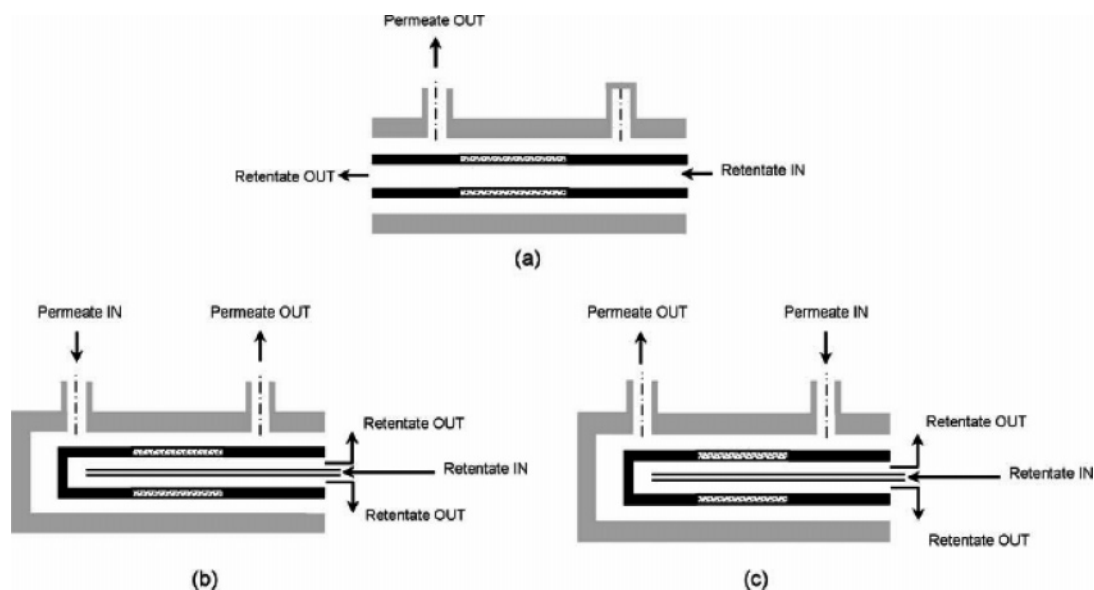
Researchers from Nippon Telegraph and Telephone Corporation conducted a similar comparison between a plate-fin type reactor and a packed bed for the reforming of methanol with a Cu-based catalyst.<sup>252</sup> The comparison was made between two reactors constructed of aluminum, with the same overall dimensions, and each containing a steam reforming side and a catalytic combustion side. The plate-fin type reactor was found to have a 28% shorter startup time, a 16-fold higher heat transfer coefficient, and only one-ninth of the catalyst volume relative to the packed bed.<sup>252</sup>

In the area of small glass-based reactors, Datye and co-workers at the University of New Mexico have conducted extensive studies comparing wall-coated and packed-bed catalyst arrangements in quartz tube reactors for methanol reforming.<sup>253–255</sup> The group not only demonstrated good adhesion of a catalyst coating to a nonporous wall,<sup>253</sup> but also quantified the difference between wall-coated and packed-bed reactors, revealing that packed-bed reactor diameters in excess of 300  $\mu\text{m}$  would suffer from significant thermal gradients.<sup>254,255</sup> In contrast, their wall-coated reactors up to 4.1 mm diameter suffered from neither heat transfer nor mass transfer issues, and as others have shown, the wall-coated catalyst demonstrates higher specific activity than typical packed-bed catalysts.<sup>255</sup>

An interesting comparison was conducted by Samms and Savinell at Case Western Reserve University, where methanol reforming in an idealized plug flow reactor was compared to the same reaction in an internal reforming fuel cell (IRFC).<sup>256</sup> Despite lower catalyst utilization in the IRFC, mainly due to nonuniform flow, the researchers verified that consumption of  $\text{H}_2$  by the fuel cell actually accelerates the methanol conversion, leading to an overall reduced catalyst requirement for the IRFC compared to an external reformer.<sup>256</sup> This is similar to the effect seen when utilizing a selective membrane to remove hydrogen during reforming operations, and this is described in the next section.

## 4.2. Membrane-Based Systems

Membrane-based methanol reforming systems have been extensively demonstrated by several research and development organizations. These systems offer a number of advantages over the low-pressure systems that employ catalytic CO mitigation. They've been shown to require less sophisticated temperature and pressure control than their catalytic counterparts,<sup>257</sup> and they provide a hydrogen stream that is nearly 100% pure, allowing for dead-ended operation of the fuel cell anode and eliminating the poisoning effects of CO and methanol, and the dilution effects of  $\text{CO}_2$ ,  $\text{CH}_4$ , and other byproducts. All of this adds up to higher hydrogen utilization in the fuel cell. Also, because of the physical removal of  $\text{H}_2$  from the reactor zone, the exact CO selectivity in the reformer is not quite as important, except as it relates to  $\text{H}_2$  yield by reaction 5. Additionally, the continuous removal of  $\text{H}_2$  from the reaction mixture can result in any number of advantages, including higher conversion, higher



**Figure 15.** Geometries used by Basile et al. in their modeling work for methanol steam reforming, showing two cocurrent geometries (a and b) and one countercurrent geometry (c). (Reprinted from ref 261, copyright 2006, with permission from Elsevier.)

selectivity, lower operating temperatures, and reduced catalyst requirements.

Membrane reactors also have their drawbacks, namely the requirement to operate at high pressure and the often-encountered fragile nature of thin metal foils, which are also quite expensive. Steam reforming helps to alleviate this first requirement, in that only liquids need to be fed at the membrane working pressure. This at least avoids the need for air compressors, which can be heavy, noisy, and highly parasitic. The second issue has been investigated by many groups, but deployment of membrane-based systems is the ultimate test of Pd and Pd-alloy membrane durability. Additionally, membrane-based systems have tended to be quite heavy, but this issue is being addressed as well, as seen by the demonstration activities reported by companies like Idetech and Genesis, described below. Finally, cost is a potential barrier for membrane-based systems entering the marketplace. With Pd being intrinsically expensive, the need to operate very thin membranes reliably is crucial, and much progress has been made in the area of thin Pd membrane durability. Ultimately, the higher cost of a Pd membrane needs to be weighed against the advantages that membrane-based systems provide. In recent years, most methanol reforming demonstration units have been membrane-based, mainly for the advantageous reasons listed above, and in spite of the higher cost and increased weight that the membrane units impose on the system. The general approach tends to be aimed at first getting demonstration units in front of the potential users as quickly as possible and then addressing the cost and weight issues as interest in these applications increases.

For a general review of Pd membrane reactors, the interested reader is directed to the extensive review of Paglieri and Way,<sup>258</sup> especially section 3 and references therein. In the following subsections, we detail the progress achieved and demonstrations conducted by various research and development groups in this well-researched approach to methanol utilization.

#### 4.2.1. Modeling and Simulation

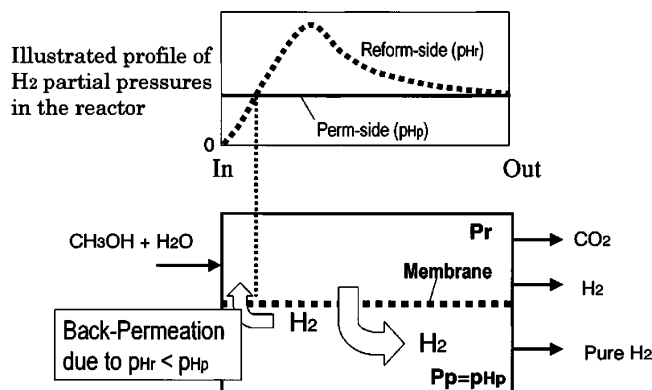
Some of the earliest high-pressure methanol reforming and Pd membrane separation work was that conducted by

researchers at the W. H. Kellogg Company and reported at the 1964 American Chemical Society meeting.<sup>3</sup> With application to a U.S. Navy submarine, they designed a hydrogen generating system at  $9.1 \text{ kg h}^{-1}$  (200 kW) with a maximum output of  $31.8 \text{ kg h}^{-1}$  (700 kW). The design incorporated a Pd/Ag membrane unit and an undetermined methanol conversion catalyst. Overall, they estimated the system to provide energy densities of  $2.2 \text{ kW h kg}^{-1}$  and  $1962 \text{ kW h m}^{-3}$ . Suggested follow-on work included development of a suitable catalyst, providing a throughput of  $\sim 2000 \text{ h}^{-1}$  and a useful life of 240 h, both of which have been exceeded in subsequent work by various groups.

Basile and co-workers have conducted extensive modeling and experimental work on methanol reforming in membrane reactors. In their initial simulation work, they sought to fill some gaps they had identified in the literature, namely the analysis of membrane-based methanol reformers according to variables other than temperature and pressure.<sup>259</sup> The Basile group compared membrane reactors and traditional packed-bed reactors by investigating the parameters of temperature, pressure, time factor (residence time), feed S/C, and sweep gas flow rate. The membrane was a Pd/Ag alloy with a thickness of  $50 \mu\text{m}$ . At any given condition, the membrane reactor was found to be superior to the traditional reactor in terms of conversion, selectivity, and productivity, all of which are driven by the constant removal of product hydrogen from the reactor zone.<sup>259</sup> These results were later confirmed by experimental studies comparing the two types of reactors<sup>260</sup> and further refined by the use of counter-current sweep gas operation, as illustrated in Figure 15(c) along with two cocurrent geometries, (a) and (b).<sup>261</sup>

Previous work by Itoh et al. sought to address the back-permeation effect that occurs at the front end of the reforming bed in membrane reactors, as illustrated in Figure 16.<sup>262</sup> This issue arises from a reverse concentration gradient that develops due to low hydrogen production at the beginning of the reformer bed. Using simulation and experimental studies, Itoh concluded the best hydrogen recovery option was the use of a sweep gas in co-flow orientation. However, this introduces the disadvantage of diluting the permeate hydrogen, and this is not a practical solution for most nonstationary applications.





**Figure 16.** Illustration of the back-permeation phenomenon that occurs in membrane reactors, where a reverse hydrogen concentration gradient develops at the inlet side of the reactor. (Reprinted with permission from ref 262. Copyright 2002 American Chemical Society.)

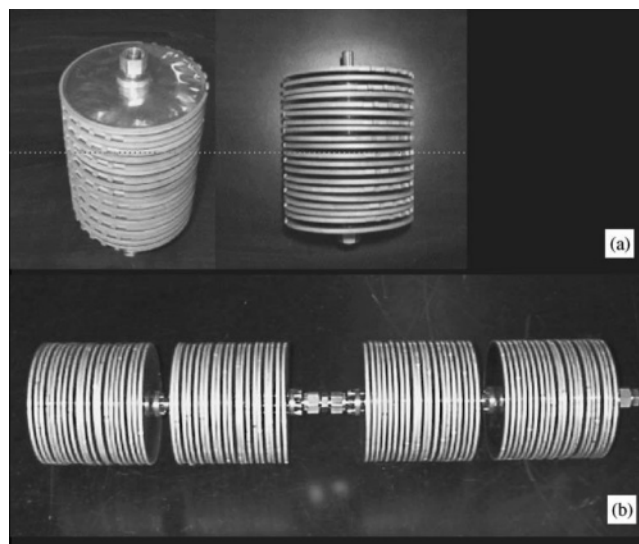
In additional work, the Basile group began looking at the effect of adding small amounts of oxygen to the reformer feed, a process known as oxidative steam reforming. They found that such operation could increase methanol conversion and hydrogen production and reduce CO selectivity.<sup>263,264</sup>

A modeling study by Nair and Harold agrees with previously reported comparisons where the membrane reactor provides enhanced conversion and productivity relative to a conventional packed-bed reactor.<sup>265</sup> Their study investigated parameters such as particle size, membrane thickness, space velocity, and surface-to-volume ratio at 260 °C and 10 atm. They found a tradeoff between hydrogen utilization and overall productivity. Additionally, they found catalyst particle size, membrane thickness, and membrane surface-to-volume ratio to be coupled and thus subject to a variety of tradeoffs, such that the controlling factor varied depending on the relative values of these three parameters.<sup>265</sup>

#### 4.2.2. Membrane Reactor Development

Researchers at the Research Center Julich have demonstrated a packed-bed reformer based on a tube-in-tube design operating at 3.8 bar, and they have quantified many of the relevant parameters for such a system in automotive applications.<sup>266–270</sup> The reactors they describe are meant to be supported by downstream Pd membrane separation of the hydrogen from the reformat, but the focus of the work has been on the catalyst issues. Working with partners Haldor-Topsoe A/S and Siemens AG, Julich quantified catalyst deactivation issues, especially in light of required lifetimes of 3000 h or more.<sup>269,270</sup> Additional investigations quantified the relationship of CO formation to extent of methanol conversion<sup>267,269</sup> and highlighted the sometimes conflicting boundary conditions faced by commercial applications of this sort, such as cost ceilings, required yields, high rates, dynamic response, partial load behavior, and catalyst lifetime.<sup>267</sup> They found considerable deactivation (linear) of the copper-based catalyst, with most of the losses occurring on the inlet end of the bed. Accounting for such deactivation, and sizing the reactor bed accordingly, they projected the possibility of a 4000 h lifetime with no more than 20% loss relative to original performance.<sup>269,270</sup>

Lin and co-workers also found significant rate improvements in membrane reactors relative to traditional packed-bed reactors.<sup>271</sup> They demonstrated an integrated unit, heated by combustion of the membrane retentate, and measured up



**Figure 17.** Integrated membrane reactor module (a) and multi-module (b) developed by Han et al. for methanol steam reforming at up to 10 kW power output. (Reprinted from ref 277, copyright 2002, with permission from Elsevier.)

to 74% efficiency and up to 70% hydrogen yield.<sup>272</sup> Other experiments demonstrated up to 97% hydrogen yield, but such operation does not leave enough combustion fuel to thermally sustain the integrated unit. Operation at about 74% hydrogen recovery was found to provide a system energy balance.<sup>273</sup>

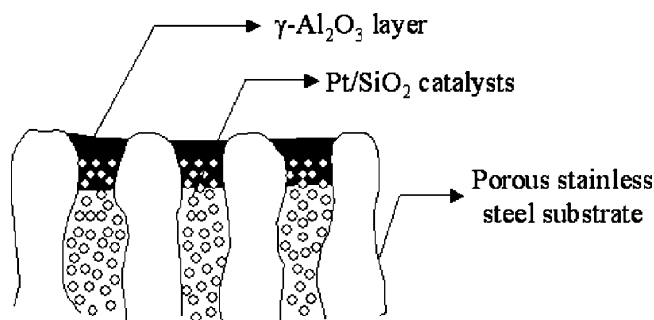
Mechanistically, they theorize that a reverse spillover mechanism is responsible for the improved reaction rates obtained in Pd membrane reactors containing Cu-based catalysts. In essence, the newly formed hydrogen from the reforming reaction is able to migrate directly from the active Cu site to the Pd membrane surface.<sup>274</sup> Such mechanistic studies of Pd membrane reactors are beyond the scope of this discussion, but the interested reader is referred to the subsequent work by Rei et al.<sup>275</sup>

Han and co-workers at SK Corporation have demonstrated several integrated membrane reactors for processing methanol. Their first reported unit was a 2-kW device with an 89% thermal efficiency (based on *higher* heating values)<sup>276</sup> and a power density of about 0.77 kW L<sup>-1</sup>.<sup>276</sup> Similar to the work of Lin, they operated their devices at about 75% hydrogen recovery to achieve thermal energy balance within the system.<sup>277</sup> A second generation device, this time operating at 10 kW, was demonstrated and is shown in Figure 17.

More recently, Han et al. demonstrated a nominal 25-kW unit operating at 70–75% recovery and about 75% thermal efficiency.<sup>278</sup> Peak production on the reformer unit was up to 40 kW electric. The device is planned for demonstration with a PEM stack (Hyundai Motors) and eventual integration into a hybrid vehicle.<sup>278</sup>

Buxbaum details the advantages of membrane reactors, with specific reference to methanol steam reforming. In addition to the removal of pure hydrogen from the reactor, he further claims that temperature management can be enhanced through the inherent counter-current flow of a shell-and-tube design and that pressure can be used to drive a reaction that would not otherwise benefit from increased pressure operation.<sup>279,280</sup> REB Research offers several membrane reactors for purchase, as well as complete hydrogen generators for lab/stationary use, based on methanol reforming.<sup>281</sup>





**Figure 18.** Schematic diagram of the cross-sectional structure of the Pt-loaded microporous membrane developed by Lee et al. (Reprinted from ref 284, copyright 2006, with permission from Elsevier.)

Wieland and co-workers compared three different Pd alloy membranes, Pd/Ag, Pd/Cu, and Pd/V/Pd.<sup>257</sup> Pd/V/Pd was found to have high permeation rates but suffered from instability and could not be tested above 6 bar due to failure. The Pd/Cu membrane was found to be much more stable but exhibited the lowest permeation of the three.<sup>257</sup> The group also found the presence of CO or methanol to significantly affect the hydrogen flux, decreasing it by up to 70%, a phenomenon also reported by Arstad et al. for Pd/Ag membranes.<sup>282</sup> The decrease is ascribed to competitive adsorption by CO or methanol—a process that is reversible but is problematic for systems of this sort that inevitably contain significant concentrations of both CO and methanol. Wieland further reports methanol steam reforming conversion in excess of the equilibrium prediction due to removal of the product hydrogen. However, this was only observed at pressures above 20 bar.<sup>257</sup>

Recent work reported by Zhang et al. describes the use of a carbon membrane reactor in much the same way as Pd-based membrane reactors.<sup>283</sup> The carbon membrane was used as a 6-mm i.d. tube with a wall thickness of 20–30  $\mu\text{m}$  and sealed inside a stainless steel tube. As expected, methanol conversion was higher for the membrane reactor compared to the fixed-bed reactor over the temperature range 200–250  $^{\circ}\text{C}$ , but the  $\text{H}_2$ ,  $\text{CO}_2$ , and CO yields were virtually the same. The data were obtained at very low throughput (1.0  $\text{h}^{-1}$ ), with  $\text{S/C} = 1.5$  and a reactor pressure of 0.2 MPa. The authors report a permeate stream consisting of 96.9–97.6%  $\text{H}_2$  and 2.4–3.1%  $\text{CO}_2$  with “almost no CO”, but the CO levels were not quantitatively reported.

Lee and co-workers have developed a membrane reactor based on Pt-loaded microporous silica supported on porous stainless steel, as illustrated in Figure 18.<sup>284</sup> While the device showed significant improvement in conversion and a high  $\text{H}_2/\text{CO}$  selectivity, the net hydrogen recovery was very low, ranging from 2.8% to 9.1% depending on the type of membrane used. The authors speculated that use of mesoporous membranes would increase hydrogen permeability but would also result in decreased CO removal efficiency.<sup>284</sup>

A comparison of Cu, Ni, and Ru reforming catalysts by Kikuchi et al. demonstrated that Ni-based catalysts had the most stable activity but suffered from the methanation side reaction. However, they found that operation within the Pd membrane reactor suppressed methanation for this catalyst and led to a higher hydrogen yield than the Cu or Ru catalyst systems.<sup>285</sup> They reported deactivation of the Cu catalyst at  $>200\text{ }^{\circ}\text{C}$  and of the Ru catalyst at  $>250\text{ }^{\circ}\text{C}$ , while the Ni catalyst remained stable up to 450  $^{\circ}\text{C}$ .



**Figure 19.** A command and control combat vehicle with a 2kW Idatech fuel cell APU mounted on the front portion of the roof. (Reprinted from ref 39, copyright 2004, with permission from Elsevier.)



**Figure 20.** IdaTech's iGen Fuel Cell System generates 250 W at 12/24 VDC using a methanol/water mixture in a fully automated system about the size of two lunch boxes. (Copyright 2002–2006, Idatech, LLC, used by permission.)

#### 4.2.3. Membrane-Based Power System Development

Developers at Idatech, LLC (formerly Northwest Power Systems, LLC) have been reporting on fuel processors and complete power systems based on methanol reforming since as early as 1997<sup>286,287</sup> and have developed an extensive patent portfolio around their systems, which incorporate high-pressure reforming with metal membrane purification of the hydrogen.<sup>288–291</sup> The Idatech reformer is a compact, integrated unit that includes a packed-bed steam reformer coupled with internal combustion and a selective membrane made of a proprietary Pd alloy. Downstream of the membrane, they have also included a catalytic methanation bed that catalytically removes any trace CO that may pass through the membrane.<sup>286,290</sup>

U.S. Army CERDEC reported in 2004 the demonstration of an Idatech unit operating on methanol/water and providing 2 kW for a silent watch application.<sup>39</sup> The unit was somewhat ruggedized and mounted on top of a command and control vehicle (see Figure 19), where it was used in somewhat realistic environments of wind, dust, cold, heat, and vibration.

While most of the early work conducted by Idatech was focused on multi-kilowatt systems, more recently they have demonstrated a 250 W unit for battery charging applications for the U.S. military.<sup>202</sup> The complete device (Figure 20), containing the integrated reformer, fuel cell, and balance of plant, measures 36 cm by 50 cm by 16 cm and provides 250 W continuous output at 12 or 24 VDC with an estimated fuel consumption rate of 500  $\text{mL h}^{-1}$ . The fuel processor module is reported to have nearly 2000 h of operational time

demonstrated, including 229 thermal cycles. Extensive balance-of-plant validation has also been conducted by Idatech, showing thousands of operating hours and hundreds of on/off cycles for components such as cooling fans, air pumps, liquid pumps, and solenoid valves.<sup>202</sup> According to an Idatech product brochure, the iGen device operates on a 64 wt % methanol solution, can start up in less than 10 min, and can operate at  $-22$  to  $122$  °F ( $-30$  to  $50$  °C). At full load (250 W net), the device consumes  $9\text{ mL min}^{-1}$  of fuel, which translates to a net fuel-to-electricity efficiency of 15% based on the lower heating value of methanol.

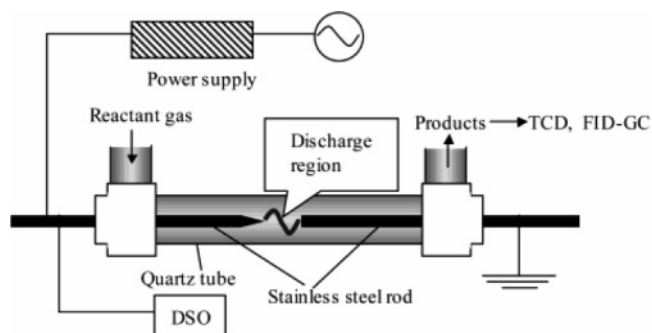
In the late 1990s, Ledjeff-Hey and co-workers reported their demonstration of a Pd-based membrane reactor utilizing the standard Cu-based reforming catalyst.<sup>292</sup> They described an integrated device that included the vaporizer, reformer, membrane, and catalytic burner in a package measuring 14 cm diameter and 60 cm long and weighing 15.5 kg. The commercial Pd/Ag membrane they employed was 7.5 mm thick—much thicker than most membranes recently reported. Operation of the device over a range of temperatures demonstrated between 40% and 62% hydrogen recovery at 5 atm. Increased pressure (7 atm) yielded higher recovery rates and a maximum overall efficiency of 54%, with some identified areas for improvement on thermal performance. Due to leakage issues, the permeate contained between 50 and 80 ppm CO and from 500 to 750 ppm CO<sub>2</sub>.<sup>292</sup>

Development work reported by Genesis Fueltech, Inc. includes a reforming system that produces 20 slpm of H<sub>2</sub> (3.6 kW<sub>th</sub>) in an integrated unit that measures 45 cm by 20 cm by 46 cm and weighs 22.7 kg.<sup>203</sup> The net thermal efficiency of the fuel processor ranges from ~20% at low outputs to over 75% at high outputs, based on LHVs. They further report 0–100% output capacity with rapid transition between output levels. Genesis reports development of a proprietary methanol reforming catalyst that replaces the typical Cu/ZnO formula. This provides better high-temperature operation (390–450 °C) to more closely integrate with the membrane temperature, and they report 13,000 h of reformer operation without degradation.<sup>203</sup> The reformer operates at 150 psig and uses 150 mL of catalyst at the 20 slpm design level. Integrated heat exchange provides a 100 °C exhaust temperature despite reformer bed operation at ~400 °C. The reported air-side pressure drop through the burner is 0.2–1.0 in. of water,<sup>293</sup> which is a major consideration for integrated systems, as every parasitic load must be absorbed by the fuel cell gross power output, reducing the overall efficiency of the device.

### 4.3. Other Methods of Reaction Enhancement

In addition to catalysis, thermal heating, and membrane separations, some groups have investigated other methods of enhancing the methanol steam reforming reaction. This includes methods such as acoustic field application, microwave-enhanced heating, plasma reforming, supercritical reforming, and the liquid-phase reaction, as detailed below. In some cases, the method is meant to enhance the rate of reaction. In others, such as liquid-phase reforming, the product selectivity is enhanced.

Recently, Erickson demonstrated the enhancement of reaction rate in a catalytic methanol steam reformer by applying a controlled acoustic field to the reactor.<sup>294</sup> The enhancement of rate was more pronounced at higher throughput, while the rate enhancement was almost negligible at low throughput.



**Figure 21.** Experimental setup for nonequilibrium pulsed discharge reforming of methanol. (Reprinted with permission from ref 296. Copyright 2004 American Chemical Society.)

Perry and co-workers demonstrated through modeling and experimental investigations that the use of microwave energy could provide a more uniform temperature distribution in a packed-bed methanol steam reformer.<sup>295</sup> In essence, the even heating provided by the microwave energy avoided the common convective and conductive limitations that often result in cold spots in an endothermically operating packed-bed reactor. This is definitely an intriguing concept but requires the integrated generation of microwave power for the system.

The use of plasma to conduct methanol reforming reactions without catalyst was investigated by Sekine et al.<sup>296</sup> as well as Futamura and Kabashima.<sup>297,298</sup> While the work of Sekine et al., illustrated in Figure 21, demonstrated the use of pulsed discharges for reforming a variety of fuels, and both groups demonstrated conversion at low temperatures, both demonstrations yielded very high CO concentrations in the methanol reformat—much higher than expected from thermodynamic equilibrium, and a great disadvantage relative to catalytic routes. This is not unexpected, as, without a catalyst present, the reaction proceeds through very nonselective means. Similar behavior is observed when noncatalytic methanol reforming or methanol decomposition reactions are conducted thermally. Much CO is formed initially, and if insufficient time is allowed for the WGS reaction to convert the CO to CO<sub>2</sub>, then the CO concentration exiting the reactor will be considerably higher than the equilibrium prediction.

Like plasma reactors, supercritical water reactors can be operated in methanol steam reforming without a catalyst (although the metal reactor walls provide at least some catalytic activity). This approach has been demonstrated by a number of research groups, but due to the higher temperatures required for supercritical operation (400–700 °C), the resulting CO levels are much higher than those in the traditional catalytic steam reforming approach. In addition, methanation of the carbon species is also favored by the high pressures and longer residence times characteristic of the supercritical reactors. More details on the reactors and experiments can be found by consulting the works of Gupta,<sup>299–301</sup> Boukis,<sup>302–304</sup> and Rice.<sup>305,306</sup> The overall subject of methanol oxidation in supercritical water was recently reviewed by Vogel et al.<sup>307</sup>

Liquid-phase reforming of methanol has also been proposed as a means of hydrogen generation. The work of Dumesic and co-workers has demonstrated the utility of liquid-phase reforming of several oxygenated bioderived molecules, such as glucose, sorbitol, and glycerol.<sup>113</sup> Within the conduct of this work, they also demonstrated the liquid-phase reforming of methanol at 225–275 °C and 29–56 bar,

with no reported CO formation in the product gas. The reaction was conducted over a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst at very low space velocity (0.008 g<sub>CH<sub>3</sub>OH</sub> g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>).<sup>113</sup> In batch experiments with various silica-supported catalysts, Miyao et al. experienced similarly long reaction times, on the order of 300 min.<sup>308</sup> Unlike the Dumesic group, though, they saw significant quantities of CO produced, even at the low temperatures of operation (77–102 °C). Additionally, a European patent describes the liquid-phase reforming of methanol at 0.1–24 MPa and 50–240 °C over a Cu catalyst that includes oxides of Zn, Al, and Cr.<sup>309</sup>

## 5. Summary and Future Prospects

Methanol steam reforming for hydrogen production continues to be an active area of research. With much progress already achieved, there are still many problems yet to solve. While interest in methanol as a PEM fuel cell fuel has remained strong, there seems to be a shift of focus away from automotive applications and a sustained emphasis on portable and small power applications. In the higher power range (>>1 kW), methanol has several disadvantages relative to logistics fuels (e.g., JP-8, diesel) or infrastructure fuels (gasoline, LPG, NG), especially with regard to distribution network and energy density. On the low power side (<100 W), where the simplicity of methanol provides an advantage, RMFCs must compete with advanced battery technology and DMFCs, both of which are further developed than RMFC units in general. Furthermore, at these low power levels, BOP considerations become increasingly important. As a result, RMFC units are likely to make their mark on the portable power space in the 100–1000 W power range, where the fuel can be treated like a prepackaged consumable and where BOP availability is not as limited. The military will continue to show interest in RMFC devices, even if only as a short-term solution, with the longer-term focus being on heavy fuels like JP-8 and diesel. Commercial markets may accept RMFCs (and DMFCs, for that matter) only if price points can be brought down considerably.

Continued technical advancements will be needed in either case. As seen in section 3, catalyst development has been a big focus area for methanol reforming researchers, but much more work remains. If Cu-based catalysts are to be used successfully in the long term, the deactivation and sintering issues need to be addressed. Alternatively, the Pd alloy formulations being developed could solve many of these problems. However, regardless of the catalyst formulation used, other tangential factors need to be addressed, such as potential poisoning or passivation of the catalyst due to trace contaminants over long operational times. These contaminants could come from several sources, including the methanol fuel, the water (carried or recycled), and even the environment in which these devices are stored and operated.

Reactor and system development activities by groups around the world have demonstrated the ability to conduct methanol reforming at small and large scale, at high efficiencies, and for a host of applications. Consequently, material selection and system design vary widely, from the very small metal, glass, or ceramic microreactors to the large-scale, high pressure, membrane-based hydrogen generators. Catalyst deployment methods used have included traditional packed-bed reactors, monolith reactors, and wall-coated channels, each with its demonstrated advantages and disadvantages. In this case, one size does not fit all. For each application, the method of catalyst deployment will depend

on a number of factors, including price, application, user, reactor type, power output, and the developer's predispositions.

Efforts in developing microchannel-based devices for methanol steam reforming and its associated unit operations have proven successful. The interleaving of combustion and reforming channels has been shown to provide a very compact device with high efficiency. In this type of deployment, though, fabrication can become quite complex and expensive if not designed for manufacturing from the early stages. Likewise, several developers have shown the promise of methanol reforming in a Pd–membrane reactor configuration, with the resultant pure H<sub>2</sub> to feed to the fuel cell. These developers will need to address cost and weight issues before full deployment and acceptance can be expected, but they have definitely made an impression through the public demonstration of prototype units at the various conferences and expos that relate to fuel cell power.

Methanol reforming will continue to be an active area of research, even if it only serves as an initial step on the road to fuel cells powered by gasoline, diesel, or JP-8. Military interest continues to be driven by a need for higher energy density power sources, as they must provide the soldier with more power without increasing his already large burden. Methanol reforming is a step to get there. Commercial applications, if successful, could see methanol become the next “propane”, where it is sold in single-use containers at retail outlets for use in portable fuel cell units. This scenario is still years away, but if developers can establish an acceptance of methanol as a useful fuel and can establish a market for personal and recreational fuel cell power systems, then this is not an outlandish idea. Ultimately, the market, both military and commercial, will determine where methanol reforming goes from here. In the meantime, researchers and developers will continue to explore the possibilities, hoping to hit upon an additional breakthrough that will bring this important technology closer to commercial application.

## 6. Acronyms

APU	auxiliary power unit
ATR	autothermal reforming
BOP	balance of plant
DARPA	defense advanced research projects agency
DEFC	direct ethanol fuel cell
DFAFC	direct formic acid fuel cell
DMFC	direct methanol fuel cell
LHV	lower heating value
LPG	liquefied petroleum gas
mA	milliamps
MEMS	microelectromechanical systems
mV	millivolts
MTBE	methyl <i>tert</i> -butyl ether
NG	natural gas
OCV	open circuit voltage
OSRM	oxidative steam reforming of methanol
PDA	personal digital assistant
PEM	polymer electrolyte membrane
PEMFC	polymer electrolyte membrane fuel cell
POx	partial oxidation
RMFC	reformed methanol fuel cell
S/C	steam-to-carbon ratio
slpm	standard liters per minute
SOFC	solid oxide fuel cell
SR	steam reforming
TPR	temperature-programmed reduction
V	volts



$W_e$	watts electric equivalent
$W_{th}$	watts thermal
WGS	water-gas shift
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
YDC	yttria-doped ceria

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