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Review

A review of recent advances in numerical simulations of microscale fuel processor for hydrogen production

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HIGHLIGHTS

- Reviews models for microscale reactors for hydrogen production (<5 W) for fuel cells.
- Reviews materials and fuels for microscale reactors.
- Summarizes 1D, 2D and 3D models over the past 15 years.

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ABSTRACT

Microscale (<5 W) reformers for hydrogen production have been investigated for over a decade. These devices are intended to provide hydrogen for small fuel cells. Due to the reformer's small size, numerical simulations are critical to understand heat and mass transfer phenomena occurring in the systems and help guide the further improvements. This paper reviews the development of the numerical codes and details the reaction equations used. The majority of the devices utilized methanol as the fuel due to methanol's low reforming temperature and high conversion, although, there are several methane fueled systems. The increased computational power and more complex codes have led to improved accuracy of numerical simulations. Initial models focused on the reformer, while more recently, the simulations began including other unit operations such as vaporizers, inlet manifolds, and combustors. These codes are critical for developing the next generation systems. The systems reviewed included plate reactors, microchannel reactors, and annulus reactors for both wash-coated and packed bed systems.

1. Introduction

Over the past decade we have witnessed an unprecedented increase in the use and functionality of small personal electronic devices such as smart phones and tablet computers. With each generation, the power demand of these devices has increased. While there has been substantial improvement in batteries over the recent years, batteries still fail to yield the desired energy density for long duration usage. Fuel cells have been proposed to meet the increasing power demands [1]. The primary challenge for a small scale fuel cell is how to safely store hydrogen fuel. To this end many groups have developed microscale fuel processors which can convert a hydrocarbon or ammonia based fuel to a hydrogen rich stream for use in proton exchange membrane (PEM) or solid oxide fuel cells [1–12]. As part of the microscale fuel processor research, various models have been developed as design tools and to better understand the system physics. This paper reviews the microreactor models developed for small scale (<5 W) hydrogen production suitable to power low power personal electronic devices.

1.1. Microreactor general characteristics

The main factors in considering the microreactor design include: fuel cell choice, fuel choice, fuel processing approach, operating temperature, catalysts, reactor architecture and materials of fabrication. Fuel cell choice determines constraints on gas constituents to the fuel cell. A polymer electrolyte membrane (PEM) fuel cell (FC) operates at low temperatures, typically less than 363 K. The low temperature operation causes the fuel cells to be very sensitive to carbon monoxide poisoning. Therefore fuel processing systems for PEMFC must produce a hydrogen rich gas

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stream with less than 100 ppm CO, or preferably less than 10 ppm CO [12]. Several higher temperature fuel cells have been proposed for small scale power supplies including phosphoric acid doped polybenzimadole (PBI), which operates at 388–423 K and solid oxide fuel cells (SOFC), which typically operate >973 K [13–15]. PBI FC and SOFC both can tolerate CO at higher concentrations (>1% and >10% respectively), making the fuel processing requirements less stringent [13–15]; however, PBI FC and SOFC have some loss in performance compared to PEMFC and the higher temperature operation makes thermal management much harder.

By far the most popular fuel for small scale hydrogen production is methanol. While lacking the high energy density compared to paraffinic hydrocarbons, methanol can be reformed to hydrogen at lower temperatures than paraffinic hydrocarbons; 473–573 K compared to greater than 775 K [2]. The low temperatures have two advantages, first the lower temperatures make thermal management easier and second the lower temperatures favor higher hydrogen production due to thermodynamic equilibrium. For steam reforming there is an added benefit for methanol compared to other hydrocarbon fuels. Steam reforming requires water. Ideally, water produced by the fuel cell can be recycled for use in the reformer. This works for larger applications, but for these miniature applications, the added balance of plant may become problematic. Therefore it is likely that the water will be carried. Methanol steam reforming requires significantly less water than paraffinic hydrocarbons (1.2:1 steam: carbon compared to 3:1 or more) to mitigate coke formation on the catalysts. If water is included in the energy density, methanol actually has a slightly higher energy density than other hydrocarbons, and is only slightly less than that of methane (Table 1). Other fuels of interest include: ammonia [16], methane [17–19], butane [14], and ethanol [20–22].

For reformers producing less than 5 W equivalent hydrogen there are three main classes of fuel processing used: steam reforming (SR), partial oxidation (POx), and autothermal reforming (ATR). Steam reforming is an endothermic process where the fuel mixed with water is decomposed over a catalyst to produce a hydrogen rich product gas. In partial oxidation, the fuel is mixed with oxygen and, as the name indicates, is oxidized. The partial oxidation rips apart the molecule producing mostly hydrogen, methane, CO, CO_2, and water. POx can be done with or without a catalyst. ATR is a combination of the two processes where the POx reaction provides heat for the endothermic SR. Table 2 lists some advantages and disadvantages for each of the reforming approaches. More details on the reforming approaches, including catalysts, can be found in review articles by Holladay et al. [2], Song [23], and Bartholomew and Farrauto [24].

The small nature of low power reactors lends itself to a microchannel or plate architecture; however, small packed bed reactors and membrane reactors have also been examined [12,27,28]. Microchannel and plate architectures have high heat and mass transfer rates with the potential to enable high thermal integration and therefore higher efficiencies. Membrane reactors allow for process intensification by integrating multiple unit operations into one reactor. While a packed bed is simplistic in design and fabrication, it must be combined with other approaches, a membrane, microchannels or both, for implementation. Initially, the main material for construction was silicon due to ease of fabrication, or ceramics since they have a low thermal conductivity. However, more designs based on metals are appearing. Table 3 lists advantages and challenges for various classes of materials.

Due to the small nature of these reactors, models (one-dimensional, two-dimensional and three-dimensional) have been developed to aid in understanding the performance and to aid in design. This paper reviews the modeling work that has been reported on this scale of microreformer. While there has been great interest and many papers involved with modeling microchannel and small reactors, there are relatively few reported results from modeling reactors at the low power (<5 W range).

2. One dimensional models

One dimensional models are the simplest models to develop and require less computational power. They can be useful to determine trends in performance. However, many assumptions are required for one dimensional models. For example, they assume

Table 1
Fuel and Fuel–Water mix energy density for several common fuels.

Fuel	Fuel energy density (kW-hr kg^{-1})	Fuel-water energy density (kW-hr kg^{-1})[a]
Methane	13.9	3.8
Propane	12.7	3.2
Iso-octane	12.3	3.05
Methanol	5.6	3.7

[a] Fuel-water mix represents the stoichiometric requirement for steam reforming, defined as a molar S/C of 3.0 for paraffinic hydrocarbons and 1.2 for methanol. Fuel-water energy density is based upon the lower heating value of the hydrogen produced from reforming the mixture with 100% conversion to CO_2 and H_2. (i.e. $CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$).

Table 2
Comparison of reforming technologies (adapted from Refs. [2,12,25,26]).

Technology	Advantages	Disadvantages
Steam Reforming	Most extensive industrial experience Oxygen not required Lowest processing temperature Best H_2/CO ratio for H_2 production	Highly endothermic
Autothermal reforming	Lower process temperature than POX Low fuel slip	Limited commercial experience Requires air or oxygen
Partial oxidation	Decreased desulfurization requirement No catalyst required (although sometimes used) Low fuel slip	Low H_2/CO ratio Requires air or oxygen Very high processing temperatures Soot formation/handling adds process Complexity

Table 3
Microreactor material advantages and challenges (adapted from Ref. [12]).

Material	Advantages	Challenges
Metal	Conventional fabrication techniques Durable Low to modest costs No clean room required	Poor compatibility with ceramics and glass
Silicon and silicon type of materials	Well characterized silicon fabrication techniques High precision manufacturing Low cost, high volume manufacturing	Fragile material Requires a clean room
Low Temperature Co-Fired Ceramics	Flexible fabrication Refractory and durable materials Low cost No clean room required	Non-standard fabrication Sealing
Polymers	Low cost Flexible fabrication	Chemical compatibility Thermal stability Sealing