Thermally integrated fuel processor design for fuel cell applications

William F. Northrop [a,d], **Sang Ok Choi** [b], **Levi T. Thompson** [a,b,c,*]

[a] Department of Mechanical Engineering, University of Michigan, Ann Arbor, MI 48109, USA
[b] Hydrogen Energy Technology Laboratory, University of Michigan, Ann Arbor, MI 48109, USA
[c] Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109, USA
[d] Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN 55455, USA

ARTICLE INFO

ABSTRACT

Effective thermal integration could enable the use of compact fuel processors with PEM fuel cell-based power systems. These systems have potential for deployment in distributed, stationary electricity generation using natural gas. This paper describes a concept wherein the latent heat of vaporization of H_2O is used to control the axial temperature gradient of a fuel processor consisting of an autothermal reformer (ATR) with water gas shift (WGS) and preferential oxidation (PROX) reactors to manage the CO exhaust concentration. A prototype was experimentally evaluated using methane fuel over a range of external heat addition and thermal inputs. The experiments confirmed that the axial temperature profile of the fuel processor can be controlled by managing only the vapor fraction of the premixed reactant stream. The optimal temperature profile is shown to result in high thermal efficiency and a CO concentration less than 40 ppm at the exit of the PROX reactor.

1. Introduction

Hydrogen has potential to be a flexible energy carrier for a variety of current and future energy applications. Due to concerns about climate change and the depletion of hydrocarbon fuel resources, increased energy efficiency and diversification of fuel sources are essential. Small, distributed stationary electricity generation from natural gas using proton exchange electrolyte (PEM) fuel cells is emerging as a viable alternative to grid-provided electricity. With proper design, these have potential to decrease greenhouse gas emissions compared with centralized generation and offer opportunities for local waste heat recovery thus providing additional energy savings [1].

To use hydrocarbon fuels with PEM fuel cells, a largely CO-free hydrogen-rich syngas, here called reformate, must be produced as part of an overall power generation system. Small-scale fuel processing systems generate reformate using catalytic reforming with additional reactors to reduce the CO concentration to acceptable levels for the fuel cell. Since each reactor in a fuel processor must be operated at specified temperatures and require reactants to be pre-heated, thermal integration is critical for maintaining high thermal efficiency. Effective thermal integration strategies for fuel processing systems must balance the heat requirements of each reactor with the attainment of high thermal efficiency, low cost, and reduction in system size and complexity.
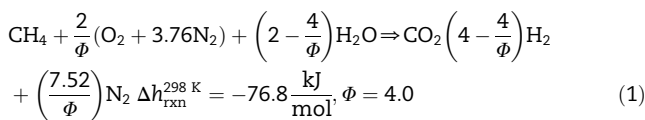
---

* Corresponding author. Department of Chemical Engineering, University of Michigan, 3030 H.H. Dow Building, 2300 Hayward Street, Ann Arbor, MI 48109-2136, USA. Tel.: +1 734 763 5748; fax: +1 734 763 0459.
    E-mail address: ltt@umich.edu (L.T. Thompson).

Fuel processor thermal integration for PEM fuel cell applications has been reviewed by Qi et al. [2]. Numerous reactor and heat exchanger configurations have been proposed for stationary systems operating on natural gas and liquefied petroleum gas (LPG) [3–11], automotive systems operating on gasoline, diesel and kerosene [12–16], and portable systems using methanol or ethanol [17–22]. Although many different fuels and potential applications have been proposed, most fuel processing systems for PEM fuel cell use the same basic series of catalytic reactors. These include reforming, water gas shift (WGS) and CO cleanup sections.

Autothermal reforming (ATR), a combination of steam reforming and partial oxidation has advantages for compact fuel processing systems due to its simpler design, high conversion efficiency and ability to startup quickly [23]. The reaction can be described for methane as

$$CH_4 + \frac{2}{\Phi}(O_2 + 3.76N_2) + \left(2 - \frac{4}{\Phi}\right)H_2O \Rightarrow CO_2\left(4 - \frac{4}{\Phi}\right)H_2$$
$$+ \left(\frac{7.52}{\Phi}\right)N_2 \ \Delta h_{rxn}^{298 \ K} = -76.8\frac{kJ}{mol}, \Phi = 4.0 \qquad (1)$$

where $(2-4/\Phi)$ is the ideal molar steam to carbon ratio (S/C) and the equivalence ratio (Φ) is defined as the ratio of the stoichiometric molar oxygen to fuel ratio to the actual ratio. For methane, Φ is given as

$$\Phi = \frac{2}{\left(\dfrac{O_2}{CH_4}\right)_{actual}} \qquad (2)$$

The ATR also includes the WGS reaction which usually favors higher CO based on thermodynamic equilibrium at high exit temperatures.

$$CO + H_2O \Leftrightarrow CO_2 + H_2$$
$$\Delta h_{rxn}^{298 \ K} = -41.2 \ kJ/mol \qquad (3)$$

The combination of eq. (1) and the reverse of eq. (3) (WGS reaction) can result in a net zero heat of reaction depending on stoichiometry which is the point of highest hydrogen conversion efficiency [23]. Traditionally, nickel-based catalysts have been used for ATR reactors in industrial applications [24] but precious metal catalysts have advantages for compact fuel processing systems since they attain high activities at higher space velocities and lower inlet temperatures [25].

Catalytic WGS reactors are commonly used in fuel processing systems to decrease CO concentration and to increase the hydrogen concentration in the reformate. For compact fuel processors, precious metal-based WGS catalysts have excellent activity over a large temperature range from 275 to 350 °C [26] and avoid the pyrophoricity of copper-zinc oxide and iron oxide catalysts. It is typical to operate WGS reactors with a decreasing temperature gradient favoring lower equilibrium CO concentrations while maintaining a high inlet temperature to enhance reaction kinetics.

Preferential oxidation (PROX) is a commonly used method to further reduce the concentration of CO, a known poison for most fuel cell anode catalysts. In the PROX, CO is oxidized with air that is introduced just prior to the catalyst bed according to the following reaction

$$CO + \frac{1}{2}(O_2 + 3.76N_2) \Rightarrow CO_2 + \frac{3.76}{2}N_2$$
$$\Delta h_{rxn}^{298 \ K} = -283.0 \ kJ/mol \qquad (4)$$
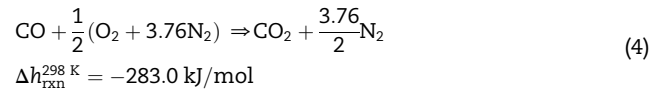
H_2 oxidation also occurs in competition with the reaction in eq. (4) though platinum catalysts have demonstrated excellent selectivities to adsorb CO over H_2 for temperatures below 180 °C [27]. As the CO selectivity decreases with increasing reactor temperature, active heat removal is necessary in practical PROX reactors to absorb the heat generated by the strongly exothermic oxidation reactions.

Steam is a key reactant for the ATR and WGS reactions and also helps to prohibit carbon formation [28]. Therefore S/C ratios used in practice are higher than the ideal value indicated in eq. (1). As such, the amount of H_2O added to the system impacts the reaction kinetics and size of catalyst beds [12]. The latent heat of H_2O is often used to control the reactor temperatures for compact, thermally integrated fuel processors. Where it is vaporized, however, varies widely. Most designs use the vaporization of H_2O to cool the reformate stream between the exit of the reforming section and the inlet of the WGS with some systems employing heat exchangers [17] and others directly injecting liquid H_2O into the reformate [9]. Liquid H_2O can be injected between reactors to cool the stream directly [14] reducing the heat transfer area and thus the system weight and volume.

In work described in this paper, a novel fuel processor thermal integration strategy is explored that uses the latent heat of H_2O to control the temperature profile through the entire series of catalytic reactors. The fuel processor included ATR, WGS, and PROX reactors along with interstitial heat exchangers between the catalysts. A counter-flow heat exchange configuration is demonstrated that uses a minimal number of control parameters to both manage the temperatures of the catalytic reactors and preheat the reactants prior to the ATR. Experimental results from a prototype fuel processor operated on methane over a range of thermal inputs and external heat inputs demonstrate that the design can provide reformate with a low concentration of CO for use with a PEM fuel cell system.

2. Design

2.1. Fuel processor design

The objective for the fuel processor design described in this paper was to use heat generated by the exothermic catalytic reactions to directly heat premixed reactants in a compact and simple manner. A schematic of the system is given in Fig. 1. Since an energy deficit exists between the heat required to preheat the reactants to the desired temperature for the ATR inlet and the heat available from the fuel processing reactions, additional heat must be supplied to the reactants from a source external to the system. In the design, this heat is added to H_2O required for the fuel processor along with a small stream of carrier air in a pre-boiler. If integrated into a complete PEM fuel cell system, the heat added to the pre-boiler would be supplied by combustion of unutilized reformate from the anode. However, since this work focuses on the