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Water neutrality and waste heat management in ethanol reformer - HTPEMFC integrated system for on-board hydrogen generation

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HIGHLIGHTS

• High temperature dual reforming of ethanol for on-board hydrogen production.

ASPEN simulation of fuel processor-fuel cell integrated system.

• High overall efficiency system with low complexity.

• Water neutrality condition derived and analyzed for the system.

• Suitability assessed for use as auxiliary power unit in vehicular applications.

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1. Introduction

ABSTRACT

On-board power generation for vehicular applications requires a compact, simplified and well-integrated fuel processor-fuel cell system. In the present paper, the integration of an ethanol reformer unit with a 50 kWe high temperature polymer electrolyte membrane (PEM) fuel cell is studied for potential automotive applications. A high-efficiency dual reformer system is used for on-board production of hydrogen from ethanol. Heat transfer equipment for recovery of water and effective utilization of waste heat has been incorporated into the integrated system. Detailed analysis using ASPEN simulations shows that gross system efficiencies of up to 39% can be achieved. Estimates of size, weight of the integrated system have been made to assess its suitability for application as auxiliary power units in automotive systems.

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Hydrogen is an excellent fuel for power generation through fuel cells because of its high gravimetric energy density, good electrochemical properties and pollution-free power generation. There is increasing interest in using fuel cells in conjunction with batteries for vehicular applications [1–3] including for flights [4] and industrial applications [5]. For vehicular applications, hydrogen storage is a major disadvantage, and on-board hydrogen generation is more attractive from the view point of safety. A number of studies have been reported in recent literature on the development of fuel processors and integrated systems for on-demand hydrogen production for stationary applications and auxiliary power units [3,6–13]. Specchia [14] presented a European level review of fuel processing activities and listed a number of commer-

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http://dx.doi.org/10.1016/j.apenergy.2017.04.069 0306-2619/© 2017 Elsevier Ltd. All rights reserved. cial systems manufactured in various European countries with systems details including power output, fuel consumption, hydrogen generation, operating temperature range, dimensions, weight, etc. Sharaf and Orhan [15] listed various companies, some of which include vehicle manufacturing companies, developing these integrated systems for several onboard applications in different countries all over the world. The state-of-the-art has reached such a level that the company Serenergy offers a compact 30 kWe power unit system based on high temperature PEM fuel cell and using steam reforming of methanol-water feed that weighs only 140 kg and occupies a volume of only 1.54 m³ [16].

Catalytic steam reforming of liquid fuels for hydrogen generation has been studied extensively, and useful reviews can be found [17–19]. Kolb [20] discusses micro-structured reactors for fuel processing and power generation using fuel cell. The issues and challenges related to microfuel processors and integration with fuel cells have been discussed recently by Moharana et al. [21], Samsun et al. [22] and Kalmula et al. [23]. Of late, ethanol is attracting







attention as a fuel for hydrogen production for fuel cell applications [24–26] and system-level simulations have shown these to be of high efficiency. In a previous study by the present authors [27] the possibility of a two-step reforming of ethanol has been explored to increase hydrogen generation efficiency for a low temperature PEM fuel cell. The ethanol-water feed is vapourized and reformed at 500 °C in the presence of Co-Zn/FeO catalyst [28] as per the following overall stoichiometric equation [24] to generate hydrogen and other gases:

$$\begin{split} C_2H_5OH + 2.2H_2O &\rightarrow 4.66H_2 + 1.47CO_2 + 0.26CO \\ &\quad + 0.27CH_4, \ \Delta H^\circ = 139.5 \text{kJ/mol} \end{split} \tag{1}$$

The exhaust gases from the ethanol reformer are then heated to 800 °C and sent to a methane reformer operating at 800 °C in the presence of Ni/K₂Ti_xT_y-Al₂O₃ catalyst [29] to generate further hydrogen as per the following reactions:

 $CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H^\circ = 206 kJ/mol \tag{2}$

 $CO+H_2O\rightarrow CO_2+H_2 \quad \Delta H^\circ=-41 kJ/mol \tag{3}$

$$CH_4 + 2H_2O \rightarrow CO + 4H_2 \quad \Delta H^\circ = 165 kJ/mol \tag{4}$$

Detailed analysis of the dual reformer coupled to a low temperature polymer electrolyte membrane (PEM) fuel cell [27] showed that high efficiencies could be obtained for the overall system.

The objective of the present work is to extend the analysis to the case where the integrated system is applied for on-board generation in heavy duty fuel cell powered electric vehicles such as buses, trucks and locomotives. For such applications, additional requirements of the integrated system are (i) fast response, (ii) high efficiency under off-design conditions reflecting the variable load on the engine during driving cycles, (iii) water recovery, and (iv) overall compactness in terms of size and weight of the fuel processor unit. To a large extent, rapid ramp-up of power in electric vehicles is provided through rechargeable batteries [30]. Fuel cells too have rapid response capacity [31] and fuel processors employing catalytic reformers are claimed to have sufficiently fast response characteristics to serve as auxiliary power units (APU) [16]. The focus of the present work is on the other three aspects. To this end, we consider two configurations of a fuel processorfuel cell integrated system: one having a single catalytic ethanol reformer and another having an additional catalytic methane reformer to increase hydrogen production. Since catalytic reforming requires considerable amount of water or steam, the issue of recovery of water produced on-board is studied in detail. ASPEN Plus simulations of both configurations have been used to assess the part-load efficiencies of the integrated system. Estimates of sizes and weights of the fuel processor unit system have also been made. Details of these calculations and estimations are given below.

2. Brief description of the integrated system and modelling approach

The configurations studied in the present work draw from our previous studies of fuel cells and fuel processors, in particular from [24,27,32]. The first configuration consists of a single ethanol reformer feeding hydrogen to a high temperature PEM fuel cell and is shown schematically in Fig. 1. Ethanol and water are drawn from their individual tanks in the molar proportion of 1:3 and are vapourized in heat exchangers HE1 and HE2. The vapours are mixed and are heated in heat exchangers HE3 and HE4 to reach a temperature of 500 °C at which point they are sent to the ethanol reformer (ER) containing Co-Zn/FeO catalyst where the vapour mixture is cracked to form mostly hydrogen and other products, including carbon monoxide. The mole concentration of CO, however, is small enough (<2.5%) for a high temperature PEM fuel cell to operate at 200 °C without significant deterioration of performance [33]. Therefore the products of the ethanol reformer can be cooled, dried and sent directly to a high temperature PEM fuel cell. The unused hydrogen and the other combustible components of the ER product gas can be burnt in a combustor to generate heat for the various heat exchangers and the ethanol reformer.



Fig. 1. Schematic diagram of a high temperature PEM fuel cell integrated with an ethanol reformer for on-board application.

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