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Fuel effects on start-up energy and efficiency for automotive PEM fuel cell systems

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Abstract

This paper investigates the effects of various fuels on hydrogen production for automotive PEM fuel cell systems. Gasoline, methanol, ethanol, dimethyl ether and methane are compared for their effects on fuel processor size, start-up energy and overall efficiencies for 50 kW_e fuel processors. The start-up energy is the energy required to raise the temperature of the fuel processor from ambient temperature (20 °C) to that of the steady-state operating temperatures. The fuel processor modeled consisted of an equilibrium-ATR (autothermal), high-temperature water gas shift (HTS), low-temperature water gas shift (LTS) and preferential oxidation (PrOx) reactors. The individual reactor volumes with methane, dimethyl ether, methanol and ethanol were scaled relative to a gasoline-fueled fuel processor meeting the 2010 DOE technical targets. The modeled fuel processor volumes were, 25.9 L for methane, 30.8 L for dimethyl ether, 42.5 L for gasoline, 43.7 L for ethanol and 45.8 L for methane. The calculated fuel processor start-up energies for the modeled fuels were, 2712 kJ for methanol, 3423 kJ for dimethyl ether, 6632 kJ for ethanol, 7068 kJ for gasoline and 7592 kJ for methane. The modeled overall efficiencies, correcting for the fuel processor start-up energy using a drive cycle of 33 miles driven per day, were, 38.5% for dimethyl ether, 38.3% for methanol, 37% for gasoline, 34.5% for ethanol and 33.2% for methane assuming a steady-state efficiency of 44% for each fuel.

Keywords: Fuel cell feeds; Dimethyl ether; Gasoline; Natural gas; Ethanol; Methanol; Start-up energy; Fuel processor efficiency; Fuel processor volumes; Autothermal systems

1. Introduction

An integrated fuel cell power system for automotive applications is a topic that has generated widespread interest because of its potential for increasing fuel efficiency. Primary issues for the development and commercialization of integrated fuel cell power systems for automotive applications are both political and environmental. Political issues include the need to remove or relax the US' dependence on foreign oil which is accomplished by increasing efficiency, while environmental issues include reduction in vehicle emissions such as pollutants; e.g., NO_x, CO, hydrocarbons and SO_x, and greenhouse gases (i.e., CO_2).

Many developers have concentrated research efforts on gasoline- and diesel-reformate fuel cells since gasoline and diesel are the readily available transportation fuels. However, fuel cell systems for automotive applications with gasoline as the hydrogen source are a technically challenging endeavor. A gasoline-fueled fuel processor is potentially the most technically challenging issue delaying the commercialization of fuel cell powered passenger vehicles due to the complexities of gasoline fuel processing. Technical issues include, but are not limited to, start-up energy and time, carbon formation, high operating temperatures, sulfur poisoning and large fuel processor mass and volume [1–10].

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Nomenclature

C_p^{SS}	heat capacity of stainless steel, 500 J/kg K
F	vapor molar flow rate, mol/s
H	enthalpy, J/mol
Q	heat energy, J
T_{amb}	ambient temperature, 293 K
T_{op}	operating temperature, K
V	volume, L
v	influent volumetric flow rate in the vapor state, L/s
X	conversion, dimensionless
y	mole fraction, dimensionless

Greek symbols

Δ	change in property or state
ρ_{FP}	density of fuel processor meeting 2010 technical targets, 1 kg/L

Subscripts

$P_e{=}50\,kW_e$	quantity evaluated for a fuel processor with a power rating of 50 kW
k	quantity referenced to chemical species, hydrogen, carbon dioxide, water or nitrogen
n	quantity referenced to the processed fuel
j	quantity referenced to the processed fuel

Acronyms and abbreviations

ATR	autothermal reactor
DME	dimethyl ether
DOE	Department of Energy
HTS	high-temperature shift reactor
LTS	low-temperature shift reactor
PrOx	preferential oxidation reactor
eff	effluent
inf	influent
Eq	equilibrium

Steady-state modeling of fuel cell systems with on-board hydrogen generation from hydrocarbon fuels predicts efficiencies of 44–48%, with reformer efficiencies of 80% [11,12]. However, the efficiency of a fuel processor involves both the transient and steady-state operations of the fuel cell system. The start-up energy, which is needed to initiate operation of the fuel processor, is a major concern, although limited research or emphasis has been called to it. The energy requirement for the start-up of a fuel processor reduces the overall efficiency of the integrated fuel cell power system, and needs consideration as commercial systems are developed. Successful start-up of the fuel cell system is vital in terms of durability, time and efficiency.

This study focuses on the start-up energy required for automotive on-board fuel processors for PEM fuel cell systems and correlates the overall efficiency penalties incurred when the start-up energy is quantified and incorporated into an overall steady-state efficiency target of 44%. The start-up energy requirement is associated as a function of the chemical nature of various fuels, namely, methane, methanol, ethanol, dimethyl ether and gasoline. More complete details of this study can be found in LA-14153 at http://www.osti.gov/bridge/.

2. Modeling methodology

The start-up energy is defined as the energy required to increase the fuel processor from ambient temperature (e.g., 20 °C) to the desired operating temperature. The fuel processor start-up energy requirement using various fuels is calculated relative to a gasoline fuel processor meeting the 2010 DOE targets in size (62.5 L), weight (62.5 kg) and efficiency (44%). The fuel processor for this study was modeled as an ATR (autothermal partial oxidation coupled with steam reforming), high-temperature water gas shift (HTS), low-temperature water gas shift (LTS) and preferential oxidation (PrOx) of CO reactors as depicted in Fig. 1. Any sulfur removal or sulfur adsorption steps are ignored in this modeling study. The reactor units, as modeled, are drawn to scale, illustrating the relative sizes that one might expect to see in a current state of the art gasoline-fueled fuel processor.

The ATR reactor (estimated at 12.4% of the total fuel processor volume) is responsible for partial oxidation and steam reforming of fuel to produce a hydrogen-rich fuel cell feed stream. Although the ATR produces a hydrogen-rich fuel cell feed stream, the stream cannot be fed into a PEM fuel cell stack due to the presence of CO [13–21]. Carbon monoxide is converted into hydrogen via the water gas shift reaction; thus producing additional hydrogen for the fuel cell. The HTS reactor (estimated at 25.9% of the fuel processor volume) is responsible for CO removal from the ATR effluent to a CO concentration level of ∼ 4%. The LTS reactor (estimated at 49.4% of the fuel processor volume) is responsible for further CO reduction, whereby the LTS effluent CO concentration is ∼ 0.9%. The PrOx reactor (estimated at 12.4% of the fuel processor volume) is the final stage of the fuel processor system and reduces the CO concentration to approximately 10 ppm. A CO concentration level of 10 ppm is a common target for efficient operation of a PEM fuel cell stack.

In order to properly design catalytic reactors, the flow rates, operating temperatures and concentration dependencies must be defined for the system under consideration. The operating temperature for the ATR reactor was chosen based on the fuel being processed. In contrast, the operating temperatures of the HTS, LTS and PrOx reactors are independent of the processed fuel and therefore constant. Based