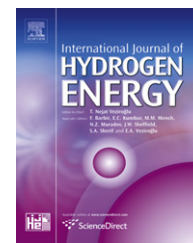


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# Measurement and analysis of carbon formation during diesel reforming for solid oxide fuel cells

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## ARTICLE INFO

### Article history:

Received 18 July 2011

Received in revised form

3 December 2011

Accepted 6 December 2011

Available online 31 December 2011

### Keywords:

Auxiliary power unit

Solid oxide fuel cell

Auto-thermal reformer

Carbon measurement

Diesel reforming

Equilibrium analysis

## ABSTRACT

Experiments and equilibrium analysis were conducted to study carbon formation during diesel reforming for a solid oxide fuel cell-based auxiliary power unit (APU) application. A photo-acoustic instrument provided direct measurements of solid carbon concentration in the reformer effluent stream, which could be correlated to reformat gas composition (as determined via mass spectrometer) and reformer temperature. These measurements were complimented by equilibrium calculations based upon minimization of total Gibbs free energy. It was determined that oxygen-to-carbon ratio (O/C), fuel utilization fraction and anode recycle fraction all influence the degree of carbon formation, and that once significant carbon concentration is measured, the reformer performance begins to show marked degradation. At a fixed operating point, lowering the reformer temperature produced by far the largest change in effluent carbon concentration. Systematic variation in O/C, fuel utilization and anode recycle revealed the interdependence among reformer temperature, effluent gas composition and carbon concentration, with a strong correlation between carbon and ethylene concentrations observed for  $[C_2H_4] > 0.8\%$ . After each experiment, baseline reformer performance could be recovered by operation under methane partial oxidation (POx) conditions, indicating that reformer degradation results at least in part from carbon deposition on the reformer catalyst.

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## 1. Introduction

Heavy-duty trucks which transport goods long distances often have a cabin to accommodate the sleeping, cooking, lighting and environmental comfort needs of the driver. Traditionally these needs have been satisfied by idling the engine used for propulsion to provide the necessary electrical power. However, because of the low engine efficiency at idle and resulting high greenhouse gas (GHG) emissions, recent anti-idling legislation has now made this practice illegal in some regions [1]. Auxiliary power units (APUs) sized in the range of

2–10 kW are under active development to provide a secondary system to deliver cabin electrical power, independent of the primary internal combustion engine. Of the APU technologies which are closest to commercialization, fuel cells offer among the highest efficiency and lowest GHG emissions, as well as the advantage of utilizing available on-board liquid fuel as feedstock [2–7]. It would appear that fuel cells also offer potential performance and environmental benefits when coupled with various bio-fuels that are now entering the marketplace [8].

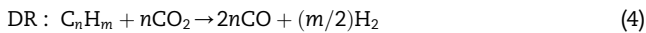
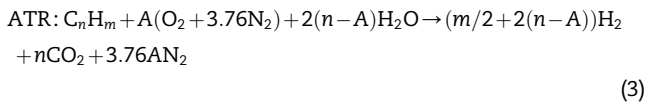
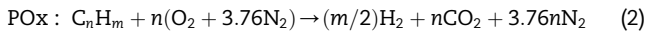
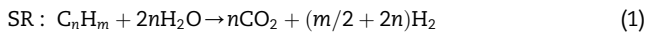
Fuel cell APUs for heavy-duty truck applications usually include a diesel reformer subsystem to convert the available

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Nomenclature		R	universal gas constant
$a$	activity	$T$	temperature
$G$	Gibbs free energy	$y$	mole fraction
LHV	lower heating value	$\Phi$	fugacity coefficient
$P$	pressure	$\lambda$	Lagrange multiplier

fuel supply into a hydrogen-rich effluent that can be directed to the anode side of the fuel cell stack. High temperature solid oxide fuel cell (SOFC)-based APUs have the advantage of accepting feed gas containing carbon monoxide, and thus their reformers do not require additional reactors for achieving  $[\text{CO}] < 20$  ppm, as is the case for proton exchange membrane fuel cell (PEMFC)-based systems. Different methods of fuel reforming have been investigated previously, including steam reforming (SR, Eq. (1)) [9], partial oxidation (POx, Eq. (2)) [10], autothermal reforming (ATR, Eq. (3)) [11], and dry reforming (DR, Eq. (4)) [12].



ATR is the thermally-balanced combination of SR (endothermic reaction) and POx (exothermic reaction), and has a number of advantages in terms of system mechanization. However, for transportation applications in particular, APUs using the ATR reforming method are inherently complicated because of the lack of an on-board water source, which must instead be supplied by recycling part of the exhaust from the anode side of the fuel cell stack [13]. This exhaust contains an appreciable quantity of water as a result of the hydrogen oxidation reaction within the stack.

The complex interaction of the fuel reformer and electrochemical stack demands dynamic control of temperature, pressure and reactant flows to deliver the commanded electrical power, while avoiding known system degradation modes. It is difficult to achieve acceptable long-term performance of the diesel reformer due to degradation of the catalyst and solid carbon (coke) formation [14,15]. Parmar et al. [16] have described a thermodynamic analysis of the diesel ATR process under different operating conditions, including temperature, pressure, oxygen-to-carbon ratio (O/C), steam-to-carbon ratio (S/C), and product molar fraction. But diesel ATR with SOFC anode gas recycle (AGR) has not been described in detail previously, nor has there been a systematic study combining analysis with supporting experimental data. Part of the difficulty in executing small-scale fuel reformer experiments is that there has not been a readily available method for *in-situ* measurement of carbon concentration in the reformer effluent stream, which can then be linked directly to gas composition, reactor temperature and pressure, etc. Thus, most researchers are forced to infer the presence of solid-phase carbon by the degree of deviation in the

measured carbon balance, or to determine the time-averaged carbon deposition rate at the completion of the experiments by thermally programmed oxidation (TPO) [17,18].

In this study, we report results of single-tube fuel reforming experiments with ultra-low sulfur diesel (ULSD). The reformer effluent was characterized by simultaneous measurements of gas composition via mass spectrometer and direct, *in-situ* measurement of carbon concentration using a photo-acoustic sampling device. The objective was to characterize the reforming conditions in term of temperature, oxygen-(from air and AGR)-to-carbon ratio (O/C), AGR fraction and fuel utilization fraction to eliminate carbon formation with high hydrogen yield. Also, thermodynamic analysis of equilibrium compositions was modeled through minimization of Gibbs free energy, as calculated by the Solver function contained in the Microsoft Excel spreadsheet package [19,20].

## 2. Equilibrium analysis

The method of minimizing the Gibbs free energy (non-stoichiometric) was applied to analyze the equilibrium compositions in the reformer. This method has been widely applied and reported in the literature because one can readily test for the presence of condensed species in the reaction products without necessarily knowing the exact chemical reactions involved [10,11,15,16,23].

The total Gibbs energy can be expressed as:

$$G = \sum_{i=1}^N n_i (G_i^{\circ} + RT \ln \Phi_i y_i P) \quad (5)$$

In light of the high operating temperature and low pressure (generally slightly above atmospheric) considered in the fuel reforming process studied here, the gas phase species were assumed to behave ideally, so the fugacity coefficient  $\Phi_i = 1$ . Also, Eq. (5) is subject to the constraint of elemental mass balance:

$$\sum_{i=1}^N n_i a_{ik} = b_k \quad k = 1, \dots, M \quad (6)$$

To minimize the objective function provided by Eq. (5), the Solver function contained in Microsoft Excel was applied based on the method of the Generalized Reduced Gradient (GRG) [19,20].

By introducing the Lagrange multipliers, Eq. (6) can be rewritten as:

$$\lambda_k \left( b_k - \sum_{i=1}^N n_i a_{ik} \right) = 0 \quad k = 1, \dots, M \quad (7)$$

In an ATR-based system with anode recycle, there are four elements present (C, H, O, N), and thus  $M = 4$  in Eqs. (6) and (7).

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