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Diesel auto-thermal reforming for solid oxide fuel cell systems: Anode off-gas recycle simulation

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HIGHLIGHTS

- Diesel reformation with solid oxide fuel cell anode off-gas recycle simulation.
- Thermodynamic modeling complemented experiments to optimize fuel reformation.
- Comparisons of diesel reforming with anode off-gas recycle and direct water/air.
- Single-tube reformer with Rh/CeO_2–ZrO_2 catalyst for diesel autothermal reforming.

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ABSTRACT

Diesel auto-thermal reformation (ATR) with solid oxide fuel cell (SOFC) stack anode off-gas recycle (AOGR) has a reliable steam recycling supply to the reformer and improves overall system efficiency. For the lab-scale experiments, it is crucial to develop a cost-effective technique to simulate the AOGR effects on hydrocarbon catalytic reformation due to safety and cost considerations of providing the full recycle composition in the absence of fuel cell stack hardware. The present work combined thermodynamic modeling and experiments to compare diesel ATR performance with AOGR and with direct water/air inputs as recycle simulation (RS). Variations of input water and air flow were employed to simulate the effects of recycle gas on syngas production and to analyze the contribution of recycled CO_2 dry reforming. A single-tube reformer with Rh/CeO_2–ZrO_2 catalyst was used for diesel ATR experiments with a photo-acoustic micro-soot meter to monitor carbon formation in the reformate effluent. Experimental results suggest water and air input flows are two key variables to simulate performance of diesel ATR with AOGR, whereas gas hourly space velocity and reforming temperature do not significantly affect the recycle simulation process in syngas production. The optimum AOGR ratio for an SOFC stack with 65% fuel utilization was identified as 45% for diesel ATR to achieve maximum syngas production and reforming efficiency with a given input air flow.

1. Introduction

Solid oxide fuel cell (SOFC) systems can provide high efficiency combined heat and power (CHP) for stationary power supply and vehicle onboard auxiliary power unit (APU) applications [1]. With the integration of a hydrocarbon catalytic reformer, SOFC systems enable utilizing the syngas (H_2 and CO) reformed from various types of hydrocarbon fuels ranging from methane to diesel or even biodiesel [2–4]. Common catalytic reformation techniques include steam reforming (SR), partial oxidation (POx), dry reforming (DR), and auto-thermal reforming (ATR). The mechanism of the ATR process has been investigated in many studies [1,5,6] and reported to consist of two stages, including exothermic oxidation of input hydrocarbon fuels to steam and carbon dioxide near the front end of catalyst bed, followed by successive endothermic SR and DR of light hydrocarbon to hydrogen and carbon monoxide, which result in a distinct temperature gradient along the catalyst support in the reformer. Excessive thermal stress, coke deposition, and sulfur contamination are the major degradation modes of catalytic reformers, which require well integrated reactor system/subsystem design and operating controls in the fuel reforming stage [7–9]. For example, our previous study has developed a customized nozzle integrated with a porous element to help atomize and completely vaporize heavy hydrocarbon fuel with superheated steam via micro-explosion, and this technique prevents coke formation by suppressing fuel self-pyrolysis and avoiding hot spots in the catalyst bed with a homogenous fuel/air/steam mix [10].

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For Ni-Yttria stabilized zirconia (YSZ) anode-supported SOFC systems fed with natural gas fuel, direct methane reformation occurs on the anode side of the SOFC if there is sufficient temperature and steam content available, and thus eliminates upstream fuel reforming components [2,8]. However, integration of fuel catalytic reformer with the SOFC stack is crucial for higher molecular weight hydrocarbon fuels (e.g., propane, JP8, gasoline, and diesel). For example, SOFC–APU systems with power range of 5–20 kW have been developed as power supply units for long-haul diesel trucks, utilizing the same ultra-low sulfur diesel fuel used for vehicle propulsion [7]. Fuel ATR process requires water and air as oxidants and produces a hydrogen-rich stream via catalytic reformation. For mobile applications, however, it is impractical to carry an additional tank for onboard water supply. Therefore, instead of generating steam with an external boiler, a portion of steam produced in the electrochemical reaction at the SOFC stack anode can be recycled to the reformer inlet. The anode off-gas primarily contains H_2O, CO_2, CO, H_2, and N_2. The anode off-gas recycle (AOGR) technique not only provides appreciable amounts of steam and CO_2 (at temperature of 600–800 °C) to facilitate SR and DR in fuel ATR process, but also improves waste heat recovery and overall system efficiency [11,12]. For example, an SOFC system fed with natural gas and AOGR technique helps achieve an electrical efficiency of above 46% and a CHP efficiency of 88%, which is higher than conventional SOFC systems with waste heat recovery but without AOGR (CHP efficiency of 68%) [1]. Steam and CO_2 recycled from anode off-gas mitigate coke deposition in hydrocarbon ATR above 675 °C, as a result of steam gasification (Eq. (1)) and reverse Boudouard reaction (Eq. (2)), respectively [8,13,14]. Based upon a known AOGR ratio and amounts of steam and CO_2 in the recycled stream, the required amount of input air can be determined according to Eq. (3).

$$C + H_2O \rightarrow CO + H_2, \Delta H^o_{298} = +131.3\ \text{kJ/mol}, \quad \Delta G^o_{298} = +91.4\ \text{kJ/mol} \tag{1}$$

$$C + CO_2 \rightarrow 2CO, \Delta H^o_{298} = +172.4\ \text{kJ/mol}, \quad \Delta G^o_{298} = +120.0\ \text{kJ/mol} \tag{2}$$

$$C_{15.5}H_{28} + nH_2O + mCO_2 + \frac{15.5 - n - m}{2}O_2 \rightarrow (14 + n)H_2 + (15.5 + m)CO \tag{3}$$

Shekhawat et al. [11] have investigated diesel reformation with Rh/Al_2O_3 and compared the effects of anode off-gas recycle (AOGR) and reformer off-stream recycle on syngas production. They reported that AOGR reduced carbon formation and increased hydrogen concentration in the reformate while reformer off-stream recycle with low water content resulted in poor reforming performance. By analyzing natural gas SR with a precious metal catalyst and characterizing reforming performance with AOGR and direct steam input, Halinen et al. [13] indicated that experimental data with AOGR are closer to the thermodynamic modeling result than direct SR because of the limited kinetics and high space velocities for the latter approach. Trabold et al. [7] employed a photo-acoustic micro-soot meter to monitor time-resolved carbon evolution in diesel ATR with AOGR and identified the optimum recycle ratio for syngas production within a carbon free operating condition.

Numerous studies [9,14–16] have been conducted to investigate catalytic reformation of various types of hydrocarbon fuels for syngas production. However, only a few of these studies [11–13] considered integration with an actual SOFC system and utilizing AOGR in the fuel reforming process. Therefore, it is crucial to develop techniques to cost-effectively simulate the effect of recycled gas on fuel reformation at lab scale. The present work assessed the reforming performance of diesel ATR in a single-tube reformer, which was composed of ceramic monoliths wash-coated with rhodium on ceria–zirconia catalyst. Table 1 provides fuel properties of diesel used in this study. To achieve the same production rate of syngas with a given input diesel flow, diesel ATR with direct water/air (recycling simulation, RS) and diesel ATR with AOGR/air were compared. Effects of S/C (steam to carbon from diesel), O_2/C (oxygen from air to carbon from diesel), gas hourly space velocity (GHSV), and reforming temperature were also analyzed. Our previous work integrated a single-tube reformer with a blended recycle stream based on an assumed 65% syngas fuel utilization, and analyzed the effect of various AOGR ratios on diesel ATR [7]. The present work used the same AOGR composition, which contained 16% H_2O, 10% H_2, 10% CO, 46% N_2, and 18% CO_2 by gaseous volumetric fraction. Thermodynamic modeling of diesel ATR was conducted using the method of total Gibbs free energy minimization with Aspen Plus software, to complement the experimental data and explore possible techniques for AOGR simulation.

2. Thermodynamic modeling development

The method of total Gibbs free energy minimization has been widely used to simulate hydrocarbon catalytic reformation because this approach enables determining the equilibrium products even without knowing the exact reactions involved, which would overcome the challenges of modeling the complexity of diesel fuel reformation that comprises hundreds of elementary reactions [4,17]. The total Gibbs free energy of reformate effluents can be expressed as:

$$G = \sum_{i=1}^{N} n_i (G_i^o + RT \ln \phi_i y_i P) \tag{4}$$

where n_i is the number of moles of species i; G_i^o is standard state free energy of species i; y_i is mole fraction of species i; T, P, R, and ϕ_i are temperature, pressure, gas constant, and gas fugacity coefficient, respectively. Eq. (4) is subjected to the constraint of elemental mass balance:

$$\sum_{i=1}^{N} n_i a_{ik} = b_k \tag{5}$$

where a_{ik} is the number of atoms of element k in molecule i and b_k is the total amount of element k in the effluent gases.

To simulate the thermodynamic modeling process of diesel ATR using total Gibbs free energy minimization method, several primary assumptions were made and provided as below:

(1) Diesel fuel surrogates were considered to be comprised of 50% n-decylbenzene ($C_{16}H_{26}$) with 50% pentadecane ($C_{15}H_{32}$) [18].
(2) Uniform temperature distribution within the reformer was maintained.
(3) Reformate gas mixture behaves as an ideal gas, and pressure gradients were ignored within the reactor bed (indicating fugacity coefficient ϕ_i shown in Eq. (4) is equal to 1) [19].
(4) Diesel fuel and oxidants were well mixed and fuel ATR reaches thermodynamic equilibrium condition. The considered reformate species in present work were H_2, CO, CO_2, H_2O, O_2, CH_4, C_2H_4, C_2H_6, and N_2 [4,11,17].
(5) Effect of GHSV was not included the in modeling process and the major parameters were S/C, O_2/C and reformer temperature [17,20,21].
(6) Amount of solid carbon formed in the reactor was calculated by carbon balance (deducting the total amount of carbon in CO, CO_2, CH_4, C_2H_4, and C_2H_6 from the total carbon in diesel fuel) [22].