

Effects of fuel cell anode recycle on catalytic fuel reforming

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Abstract

The presence of steam in the reactant gas of a catalytic fuel reformer decreases the formation of carbon, minimizing catalyst deactivation. However, the operation of the reformer without supplemental water reduces the size, weight, cost, and overall complexity of the system. The work presented here examines experimentally two options for adding steam to the reformer inlet: (I) recycle of a simulated fuel cell anode exit gas (comprised of mainly CO₂, H₂O, and N₂ and some H₂ and CO) and (II) recycle of the reformat from the reformer exit back to the reformer inlet (mainly comprised of H₂, CO, and N₂ and some H₂O and CO₂). As expected, anode gas recycle reduced the carbon formation and increased the hydrogen concentration in the reformat. However, reformer recycle was not as effective due principally to the lower water content in the reformat compared to the anode gas. In fact, reformat recycle showed slightly increased carbon formation compared to no recycle. In an attempt to understand the effects of individual gases in these recycle streams (H₂, CO, CO₂, N₂, and H₂O), individual gas species were independently introduced to the reformer feed.

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1. Introduction

Solid oxide fuel cells are among the most efficient energy conversion devices available [1–3]. They rely on a supply of reformat gas which can be produced by the catalytic reforming of liquid fuels [4], such as diesel fuel, in a fuel processor. Although some reforming processes are based on the addition of steam to reduce the formation of carbon, there are a number of applications where this is not feasible because a supply of water/steam is not readily available. These include mobile applications, remote power supplies in a military environment, and auxiliary power units (APUs) for long-haul diesel trucks.

In these applications, catalytic partial oxidation (CPOX) of the fuel, in which the fuel reacts with substoichiometric air to produce a gas consisting primarily of hydrogen and carbon monoxide, is the preferred reforming process. However, the lack of steam in the reactant gas stream can lead to more rapid deactivation of the catalyst than if steam is present, due primarily to carbon formation. One way to provide at least some steam to the CPOX process is to recycle a portion of the steam-containing anode off-gas, which primarily contains water, carbon dioxide, and nitrogen (Fig. 1). This also has the potential to improve the overall thermal integration of the overall process (and therefore the overall efficiency), and to inhibit the temperature rise in the CPOX reactor, which can limit deactivation due to catalyst sintering.

One of the reactions that helps limit carbon accumulation is the reaction of steam with carbon to form carbon monoxide and hydrogen (Reaction (1)):



$$\Delta H_{298}^{\circ} = +131.3 \text{ kJ/mol}$$

$$\Delta G_{298}^{\circ} = +91.4 \text{ kJ/mol}$$

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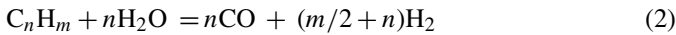
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For carbon-containing “coke” deposits that are thought to be condensed, polynuclear aromatic-type compounds, Reaction (1) can be more generally represented as:



where $n \sim m$ in most “coke” deposits. For the polynuclear aromatics of interest here, this reaction is endothermic and thermodynamically favorable at elevated temperatures (For example, anthracene $C_{14}H_{10}$, it is favorable at $>500^\circ\text{C}$ (1 atm)).

The anode off-gas also contains carbon dioxide. If the anode off-gas is to be recycled to the inlet of the fuel processor, the effect of this component of the gas must be examined as well. Carbon dioxide can be beneficial in reducing the carbon formation by the Boudouard reaction:



$$\Delta H_{298}^\circ = +172.4 \text{ kJ/mol}$$

$$\Delta G_{298}^\circ = +120.0 \text{ kJ/mol}$$

Reactions (1) and (3) become thermodynamically favorable ($\Delta G^\circ < 0$) at temperature of above 675 and 700°C , respectively. In addition to coke inhibition, carbon dioxide and water can react with the fuel directly in the steam and dry reforming reactions [Reactions (4) and (5), respectively]:



These reactions can increase the overall fuel conversion of the reformer, provided there is sufficient heat to drive these endothermic reactions. By recycling the anode off-gas, it is also possible that a lower air/fuel in the feed to the reformer can be used. Overall, water can help suppress carbon formation, allow for better thermal integration and system efficiency, and possibly inhibit temperature rise and catalyst sintering.

Another option to improve the overall efficiency of the process is to recycle a portion of the reformat produced by the fuel processor itself back to the reactor inlet (Fig. 1). This reformat contains primarily carbon monoxide and hydrogen, but also significant concentrations of steam and carbon dioxide. [The

Table 1
Composition (vol%) of simulated anode and reformat recycle streams

Recycle gas component	Composition (%) in simulated anode gas stream	Composition (%) in simulated reformat recycle stream
H ₂	3	22
CO	3	24
CO ₂	24	1
H ₂ O	18	5
N ₂	52	48

essential difference between the composition of this stream and the anode off-gas is the higher concentrations of carbon dioxide and steam in anode off-gas stream.] Among other potential benefits, the hydrogen in this gas stream may limit the dehydrogenation of the hydrocarbons in the fuel, which is one of the primary steps leading to coke formation on the catalyst.

Here, we explore two process configurations designed to provide steam and carbon dioxide to the reformer inlet: (1) recycle of the anode off-gas to the reformer inlet and (2) recycle from the reformer exit (see Fig. 1). These options are compared in terms of the yields and composition of the reformat, hydrocarbon conversion, and carbon formation over a rhodium/ γ -alumina catalyst. The effects of recycle each individual compound in these recycle gases (H₂, CO, CO₂, N₂, and H₂O) on reforming properties are also reported.

2. Experimental

2.1. Activity measurements

A mixture of 40 wt% *n*-tetradecane, 20 wt% *t*-butylbenzene, 18 wt% *t*-butylcyclohexane, and 22 wt% decalin was used as a simulated diesel fuel for this study. The compositions of the simulated anode and reformat recycle streams used here are given in Table 1. The anode recycle gas is much richer in carbon dioxide and steam than the reformat recycle gas, making it a more oxidizing gas. Note that a somewhat higher water composition than expected in actual reformer recycle stream was used for the reformer recycle stream since it was not possible to pump the water accurately at low flow rates. Gases of these compositions were blended with the oxygen-containing feed gas to the reformer to simulate the recycle of the anode off-gas and reformer outlet. When the simulated recycle gases are combined with the hydrocarbon/oxygen feed, the resulting mixture is the actual feed to the catalytic reactor. For each of the two recycle gases, five separate recycle ratios were used to calculate the simulated gas mixture; where recycle ratio is defined as the ratio of the exhaust gas flow from the reformer or anode recycled to the total exhaust flow from the reformer or anode. In addition, the effect of each individual gas (H₂, CO, CO₂, N₂, and H₂O) in the recycle streams was evaluated by adding them individually to the hydrocarbon/oxygen feed. The actual gas compositions resulting from these blends was then fed to the reactor in fifteen separate experiments, shown in Table 2 (one experiment for each of the six the anode gas recycle ratios, one for each of

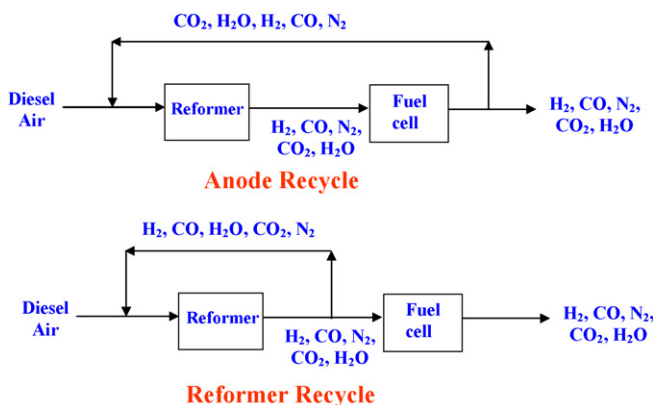


Fig. 1. Recycle configurations.

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