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# Bio-fuel reforming for solid oxide fuel cell applications. Part 2: Biodiesel

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## ARTICLE INFO

### Article history:

Received 2 April 2013

Received in revised form

8 October 2013

Accepted 11 October 2013

Available online 9 November 2013

### Keywords:

Autothermal reforming

Solid oxide fuel cells

Diesel

Biodiesel

Thermodynamic analysis

Carbon formation

## ABSTRACT

Biodiesel is considered as a renewable hydrogen source for solid oxide fuel cells (SOFCs). This study contributes to a fundamental understanding of biodiesel autothermal reforming (ATR), which has not yet been widely explored in the open literature. Ultra-low sulfur diesel (ULSD) ATR is established as a baseline for this analysis. This work applies a micro-soot meter based on a photo-acoustic method to quantify the condensed carbon from a single-tube reactor, and uses a mass spectrometer to measure the effluent gas composition under different operating conditions (reformer temperature, steam/carbon ratio, oxygen/carbon ratio, and gas hourly space velocity). The key objective is to identify the optimum operating environment for biodiesel ATR with carbon-free deposition and peak hydrogen yield. Thermodynamic analysis based on the method of total Gibbs free energy minimization is used to evaluate the equilibrium composition of effluent from the reformer. The experimental investigations complimented with this theoretical analysis of biodiesel ATR enable effectively optimizing the onboard reforming conditions. This study is one component of a three-part investigation of bio-fuel reforming, also including fuel vaporization and reactant mixing (Part 1) and biodiesel–diesel blends (Part 3).

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## 1. Introduction

Fuel cell technologies are increasingly deployed in residential and transportation applications due to their high efficiency for conversion of fuel to electricity with less environmental impact. For example, the onboard solid oxide fuel cell (SOFC) system serves as an auxiliary power unit (APU) for long-haul diesel trucks to supply cabin electrical needs (heating, cooling, and electronic devices) and mitigate the emission of particulate matter during truck idling [1]. Hydrocarbon catalytic reformation has been widely developed to generate hydrogen as part of an integrated fuel cell system. A typical reforming system is comprised of a pretreatment process, a

reformate reactor, a shift reactor, and a gas purification step [2]. Unlike proton exchange membrane fuel cells (PEMFCs), SOFCs operate at high temperatures (773–1273 K) and have the advantage of using carbon monoxide along with hydrogen as input fuels. Different methods of fuel reforming have been investigated previously, including steam reforming (SR) [3], partial oxidation (POx) [4], autothermal reforming (ATR) [5], and dry reforming (DR) [6]. SR is an endothermic reaction with high H<sub>2</sub>/CO yield whereas POx is an exothermic reaction with relatively low H<sub>2</sub>/CO. For transportation applications in particular, ATR is the most promising approach because it combines SR and POx to reach an internal thermal balance and therefore external power supplies are not required [7].

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<http://dx.doi.org/10.1016/j.ijhydene.2013.10.058>

Three common performance degradation modes of catalysts in fuel reformation are sulfur poisoning, high temperature sintering, and solid carbon formation. Most of the sulfur contained in hydrocarbon fuels converts to hydrogen sulfide at low temperatures (573–673 K) in non-oxidizing atmosphere and sulfur dioxide at high temperature (>873 K) in an oxidizing condition [8]. Cheekatamarla et al. suggest that the hydrogen yield from diesel ATR with 1% Pt/ceria-based catalyst at 673 K and would drop from 75% to 40% with a 200 ppm increase of SO<sub>2</sub> [8]. The sulfur poisoning issue can be prevented if sulfur compounds are removed from the fuel before entering the reformer. The typical autothermal reformer is an adiabatic reactor, and if the exothermic reaction (POx) dominates, excess heat will be generated. The catalyst in the test bed would be sintered due to high temperature and its lifetime reduced. Borup et al. indicate the oxidation reactions of hydrocarbon fuels without fine mix with steam tend to create local hotspots and sinters the catalyst at the reactor inlet [9]. The mechanism of carbon formation in the reactor is so complex because the solid carbon evolves dynamically and is simultaneously affected by many parameters (including active catalyst, input hydrocarbon fuel, operating reactor temperature, pressure, water-to-carbon ratio (H<sub>2</sub>O/C), oxygen from air-to-carbon ratio (O<sub>2</sub>/C), gas hourly space velocity (GHSV), and fuel pretreatment process), thus thermodynamic analysis is applied in many studies to identify the optimum conditions for carbon-free operation and provide valuable information to guide the experimental design [3,7,10]. Carbon formation during system startup and operation would lead to catalyst deactivation and potentially contaminate downstream components [9]. However, fundamental understanding of carbon formation under different operating conditions still needs to be explored. For example, our previous work demonstrates there is a strong correlation between ethylene and solid carbon, and that solid carbon formation is proportionally increased with increased ethylene concentration [11,12]. Many studies suggest conventional nickel-based reforming catalysts easily form carbon deposition on Ni surface and degrade dramatically under high temperature sintering, especially for reforming heavy hydrocarbons [6,8,13]. Noble metals (e.g., rhodium, platinum) are widely used to reform petro-diesel surrogate, gasoline, and JP 8 [14]. Several reports have demonstrated that CeO<sub>2</sub>-ZrO<sub>2</sub> supported Rh catalyst enables achieving high reforming activity and hydrogen selectivity for sulfur-content fuels reformation with low carbon formation [15].

Many hydrocarbon fuels have been reported as viable hydrogen precursors, such as methane [6], ethanol [16], dimethyl ether [3], butanol [10], gasoline [17], diesel [7], and even vegetable-oil [18]. But from the perspective of developing a sustainable and feasible pathway for fuel cell applications in the transportation sector, hydrocarbon fuels need to be derived from clean energy sources that are compatible with the existing fuel delivery infrastructure. Our previous work has evaluated the environmental impacts of different bio-fuels derived from waste biomass for SOFC-based APU applications through life cycle assessment (LCA) techniques and it has been shown that biodiesel obtained from transesterification of waste cooking oil has a relatively low carbon footprint [19]. Biodiesel is an

oxygenated fuel and possesses physical and chemical properties that are similar to petroleum diesel, which suggests biodiesel could potentially replace conventional diesel with no significant modifications of the truck fuel system. However, there are few reports in the open literature related to the investigations of biodiesel catalytic reformation from combined experimental and thermodynamic analysis. Therefore, it is important to explore the optimum operating conditions of biodiesel reformation and its potential technical challenges.

In this study, biodiesel was used as the primary fuel feedstock to a single-tube reactor with ATR under various operating conditions (reformer operating temperature, H<sub>2</sub>O/C, GHSV, and O<sub>2</sub>/C). Ultra-lower sulfur diesel was used to establish a baseline. A vapor pretreatment process was designed with a customized spray nozzle integrated with a 2 μm filter that helps the fuel completely vaporize with less hydrocarbon self-pyrolysis before entering the reactor [20]. A direct photo-acoustic based micro-soot meter was used to analyze carbon dynamic evolution under different conditions while a mass spectrometer was applied to measure the gas composition in the effluent from the reformer. Thermodynamic analysis based on total Gibbs free energy minimization was applied to evaluate the equilibrium compositions of effluents from biodiesel as well as ULSD ATR. The main objective of this work was to identify the optimum operating conditions with high hydrogen yield and no carbon formation for biodiesel ATR, using both thermodynamic modeling and experimental measurements. Combinations of H<sub>2</sub>O/C and O<sub>2</sub>/C to reach a carbon-free boundary at certain temperatures were also investigated.

## 2. Thermodynamic analysis

Generally, two approaches were used to predict the equilibrium compositions of hydrocarbon reformation: equilibrium constant (stoichiometric) and Gibbs free total energy minimization (non-stoichiometric) [7,21]. The latter method was applied in this work to simulate the equilibrium species effluent from the reformer with diesel ATR and biodiesel ATR under various operating conditions, because this method has the advantage of quantifying the presence of condensed species in the reaction products without necessarily knowing the exact chemical reactions involved [11].

The total Gibbs energy with two phases can be expressed as:

$$G = G_{\text{gas}} + G_{\text{condensed}} = \sum_{i=1}^N n_i (G_i^{\circ} + RT \ln \phi_i y_i P) + \sum_{i=N+1}^{N_s} n_i G_{c(s),i} \quad (1)$$

where  $n_i$  is the number of moles of species  $i$ ;  $G_i^{\circ}$  is standard state free energy of species  $i$ ;  $y_i$  mole fraction of species  $i$ ;  $N$  is the number of gas species and  $N_s$  is the number of condensed species;  $T$ ,  $P$ ,  $R$  are temperature, pressure, and gas constant, respectively. When solid carbon is considered in the system, its Gibbs free energy  $G_{c(s),i}$  equalizes to zero [7,10]. The gas phase species were assumed to behave ideally because of the high operating temperature and low pressure (slightly above atmospheric) in the reactor, so the fugacity coefficient  $\phi_i = 1$ .

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