Hydrogen production via catalytic autothermal reforming of desulfurized Jet-A fuel

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ABSTRACT

On-board hydrogen production via catalytic autothermal reforming is beneficial to vehicles using fuel cells as auxiliary power unit because it eliminates the challenges of hydrogen storage. As the primary fuel for both civilian and military air flight application, Jet-A fuel (after desulfurization) was reformed for making hydrogen-rich fuels in this study using an in-house-made $Rh/NiO/K-La-Ce-Al-O_X$ catalyst under various operating conditions. Based on the preliminary thermodynamic analysis of reaction equilibrium, important parameters such as ratios of H_2O/C and O_2/C were selected, in the range of 1.1—2.5 and 0.5—1.0, respectively. The optimal operating conditions were experimentally obtained at the reactor's temperature of 696 °C, which gave $H_2O/C = 2.5$ and $O_2/C = 0.5$, and the obtained fuel conversion percentage, hydrogen yield, and energy efficiency were 0.89, 1.44, and 0.65, respectively. In addition, a discussion of the molar fraction variation of CO and CO_2 at different H_2O/C, as well as the analysis of fuel conversion profile, leads to the finding of effective approaches for suppression of coke formation.

Introduction

Hydrogen has been considered for use as an alternative fuel [1] due to its potential for low-greenhouse gas emission [2], abundance in domestic sources [3], and crucial role in fuel cell systems [4]. As an energy carrier [5], hydrogen can be used to store and deliver energy or be converted into other types of energy, such as heat, electrical energy or mechanical work. These properties have made hydrogen a fuel promising for stationary power plant, transportation, or household portable power sources [5,6]. Hydrogen is required as the main fuel [7—10] for fuel cells working as the APUs (auxiliary power units) on board of vessels and vehicles. One of the most feasible and effective ways to produce hydrogen onboard is known as autothermal reforming of Jet-A fuel which is the logistic fuel for both civilian and military vessels [11]. An Autothermal Reforming (ATR) is a combination process of exothermic POX (partial oxidation) and endothermic SR (steam reforming), and generally remains as slightly exothermic or thermally neutral, resulting in no need for external heating or cooling source. The advantages of ATR, such as rapid thermal response, relatively high hydrogen yields, and remarkable coke-suppression capability, make it the most suitable technique for on-site hydrogen production using heavy hydrocarbon fuels [12].

Research has been focused on autothermal reforming of heavy hydrocarbons for hydrogen production in recent years. Krumpelt et al. (2002) [13] developed a 10 kW integrated gasoline fuel processor for a PEMFC (proton exchange membrane fuel cell) and studied the issues including startup time

minimization and reduction of heat loss. The processor is capable of producing 40 mol% H_2 at steady state and 25% H_2 at 25% of full power during startup. Villegas and his co-workers (2014) [14] conducted some tests to study the activities of Ni, Ru and Ni-Ru/Al_2O_3 monolith catalyst for ATR of isooctane. Their results showed that bimetallic catalysts had better performance than the monometallic catalysts. The rate of production of the reformate exhibited stable behavior after 140 h of tests at 700 °C. Qi et al. (2005) [15] evaluated the performance of ATR of n-octane on Ru/K_2O-CeO_2/γ-Al_2O_3 catalysts based on the thermodynamic analysis. The optimal operating conditions were obtained through experiments with the operating temperature around 750–800 °C, O_2/C and H_2O/C ratios of 0.35–0.45 and 1.5–2.2, respectively. ATR of dimethyl ether (DME) was investigated by Nilsson et al. (2007) [16] over Pd-based catalysts. CO_2 selectivity, DME conversion, and H_2 concentration were analyzed with consideration of various parameters such as the catalysts composition, inlet temperature, ratios of O_2/DME and H_2O/DME. Other studies have been performed on the ATR of acetic acid [17], diesel [18] as well as Jet fuel. As a common surrogate for Jet-A fuel, n-dodecane has been used in the studies for autothermal reforming over the past few years [2,19–22]. Our previous research [23] has exhibited outstanding results with the energy conversion efficiency of 84% as well as the CO_x selectivity over 90%. However, concerns may arise when dealing with the commercial fuels which could have a sulfur concentration as high as 1000 ppmw. Research [24,25] showed that sulfur facilitated poisoning and deactivation of catalysts, which dramatically inhibited syngas production. Therefore, results obtained from ATR of dodecane may not be fully applicable to the Jet fuel case.

In order to reduce the impact of sulfur, various types of catalysts have been developed and systematically characterized. Precious-metal-coated metallic oxide catalysts were extensively studied because of the unique sulfur-resistance capability of the precious metals (Pt, Pd, Rh, Ru, etc.). Strohm et al. (2006) [26] prepared bimetallic Rh-Ni/CeO_2-Al_2O_3 catalyst by wet-impregnated method and sieved the catalyst to 0.5–1 mm before experiment. The catalyst was able to tolerant 22 ppm sulfur contained in JP-8 for 72 h with fuel conversion >95%. Sulfur-tolerance was also discovered over Pt-based catalysts [27]. Xue and his co-workers prepared Pt/Gd_2O_3-CeO_2-Al_2O_3 catalysts by stepwise incipient wetness impregnation (IWI) method and performed activity tests on the ATR of retail gasoline containing 158–500 ppm sulfur. The optimal conditions were found at 800 °C with gasoline WHSV (weight hourly space velocity) of 0.9 h^{-1}, and a H_2O/O_2/C molar ratio of 5/0.35/1. Microlith™ technology developed by PCI [28] had been used for reforming of E85 fuel to improve the catalyst sulfur tolerance. The catalyst substrates were built on catalytically coated metal meshes with very small channel diameters. With this technology, the catalysts were able to achieve >95% fuel conversion and over 70% reforming efficiency (LHV based) in the presence of 20 ppm sulfur, and also reached >95% fuel conversion and >66% reforming efficiency in the presence of 100 ppm sulfur. Perovskite catalysts ($La_{0.6}Ce_{0.4}Fe_{0.8-z}Ni_{0.2}Me_zO_{3-\delta}$) were synthesized by Dinka et al. (2007) [10] and tested using real JP-8 with 228 ppm sulfur content. Results showed that with 1 wt.% of Ru doping in the catalyst, the fuel conversion decreased significantly from 85 to

95% at sulfur content $\leq$10 ppm to 77% at 228 ppm. Commercial catalysts with precious metals were adopted by several other researchers [25,29–33]. At low sulfur concentration conditions all catalysts exhibited considerable sulfur-tolerance capability. However, when the sulfur content increased to 200 ppm [8], the fuel efficiency dropped dramatically from 100% to 75% with H_2 concentration decreasing from 28% to 19%.

In the present study, Jet-A fuel obtained from a local fuel company has a sulfur concentration as high as 1140 ppmw. A preliminary selective adsorptive desulfurization process [34] has been carried out before it can be used for the ATR experiment. The ATR catalyst (Rh/NiO/K-La-Ce-Al-O_X) developed in our previous work [23] shows excellent performance on the ATR of different types of fuels, thus it is promising to extend it to the ATR of desulfurized Jet fuel. This paper is aimed at testing the ATR performance of our in-house developed new catalyst on the desulfurized Jet fuel and investigating the effect of operating conditions (feeding temperature, H_2O/C and O_2/C) on the performance of the reaction system with respect to reformate composition, fuel conversion, H_2 yield, and energy efficiency.

Catalyst materials and experimental methods

Feedstock and catalyst preparation

The desulfurized Jet-A fuel with sulfur concentration below 20 ppmw was obtained through selective adsorption by the novel adsorbent prepared in-house. Table 1 shows the average properties of Jet-A fuel. A total sulfur analyzer Thermo TS 3000 in resolution of 1 ppm was used to detect the sulfur concentration in the Jet-A fuel.

The ATR catalyst designed in our previous work [23] was used in the present work. K-La-Ce-Al-O_x, NiO and Rh were washcoated onto the cordierite monolith substrate, layer by layer through wet-impregnation approach. Calcination was carried out after each washcoating process, during which the loading weight and compositional ratio were carefully controlled. Different from the previous work [23], the cordierite monolith substrate used in this work was the honeycomb with 100 cells per square inch (cpsi), which is selected allowing insertion of thermocouples into the channels of honeycomb reaction section.

Experimental setup

Several modifications including preheating, setting of thermocouples in the reaction zone, and post-cooling device have been made on the basis of the previous ATR testing system [7]. Fig. 1 shows the previous ATR reactor and the modified new

Table 1 – Basic properties of Jet-A fuel.	
	Jet-A fuel
Average chemical formula	$C_{11.6}H_{22.3}$
Molecular weight (g/mol)	161.5
Liquid density (g/cm^3)	0.81
Lower heating value (LHV, MJ/kg)	43.26