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Autothermal steam reforming of higher hydrocarbons: *n*-Decane, *n*-hexadecane, and JP-8

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Abstract

Steam addition to the catalytic partial oxidation of *n*-decane and *n*-hexadecane with air over Rh-coated monoliths at millisecond contact times produces considerably higher H_2 and CO_2 and lower olefin and CO selectivities than without steam addition. For steam to carbon feed ratios from 0.0 to 4.0, the reactor operated autothermally, and the H_2 to CO product ratio increased from ~1.0 to ~4.0, which is essentially the equilibrium product composition near synthesis gas stoichiometry (C/O ~1) at contact times of ~7 ms. In fuel-rich feeds exceeding the synthesis gas ratio (C/O > 1), steam addition suppressed olefins and promoted synthesis gas and water–gas shift products. Steam addition also reduced catalyst surface carbon. Furthermore, steam addition to the catalytic partial oxidation of the military fuel JP-8 was performed successfully, also increasing H_2 and suppressing olefins.

Keywords: Autothermal reforming; JP-8; Higher hydrocarbons; Millisecond reactors; Rhodium reactor

1. Introduction

Reformation of heavy hydrocarbons and logistic fuels, such as diesel and JP-8 (similar to kerosene, used as a military fuel), to synthesis gas (H_2 and CO) is attractive for mobile applications, because synthesis gas can be used to generate electricity in solid oxide fuel cells and to abate pollutants in internal combustion engines [1–5]. Also, automotive onboard reforming of these liquid fuels is desirable, since it eliminates gaseous H_2 storage issues and avoids the need for H_2 refueling stations [1–3].

Higher hydrocarbons, such as isooctane, *n*-decane, *n*-hexadecane, and diesel fuel, have been successfully catalytically partially oxidized over Rh-coated monoliths, producing high yields of H_2 and CO (~80%) in autothermal millisecond reactors [6–10]. The catalytic partial oxidation (CPOx) reactor is attractive for mobile applications, primarily due to its autothermal operation, high fuel and O_2 conversion, short contact times, fast lightoff, and easily scalable design.

Some applications require less CO and more H_2 than are currently produced by autothermal CPOx. To increase H_2 and reduce CO concentrations, steam could be added to the inlet feed. Steam addition to the CPOx of methane and ethanol over Rh- and Rh–Ce-coated monoliths in millisecond reactors has been successfully demonstrated [11–13]. The results propose that CO reacts with steam to form CO_2 and H_2 through the water–gas shift reaction

$$CO + H_2O \leftrightarrow CO_2 + H_2, \quad \Delta H^0 = -41\,\text{kJ/mol}, \tag{1.1}$$

and the fuel also reacts with steam to form H_2 and CO through the steam reforming reaction, as shown for the hydrocarbon fuel *n*-decane

$$C_{10}H_{22} + 10H_2O \rightarrow 10CO + 21H_2, \quad \Delta H^0 = 1563\,\text{kJ/mol}. \tag{1.2}$$

In addition, steam addition to the catalytic partial oxidation of diesel and gasoline fuel and their surrogates over various precious and transition metal catalysts at contact times typically

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greater than milliseconds was found to increase H_2 and CO_2 and reduce CO levels when compared to dry conditions [1,3,14–21]. These results further suggest that water–gas shift and steam reforming occur with the addition of steam to the reactor feed.

Dry CPOx could produce a maximum of 11 mol of H_2 per mole of *n*-decane

$$C_{10}H_{22} + 5O_2 \rightarrow 10CO + 11H_2, \quad \Delta H^0 = -855\,\mathrm{kJ/mol} \tag{1.3}$$

while CPOx with steam addition could perform water–gas shift on the CO to potentially increase the H_2 yield to a maximum of 21 mol per mole of *n*-decane

$$C_{10}H_{22} + 5O_2 + 10H_2O \rightarrow 10CO_2 + 21H_2, \quad \Delta H^0 = -1267\,\mathrm{kJ/mol}. \tag{1.4}$$

Even though these reactions are exothermic, the addition of steam dilutes the reactants, lowering the adiabatic reactor temperature. With lower operating temperatures, the possibility of autothermal operation with steam addition in millisecond reactors is unclear. These species are also limited by equilibrium, and thus, the maximum level of H_2 produced is less than stoichiometrically indicated.

This paper investigates the effect of steam addition on autothermal CPOx of liquid alkanes in millisecond contact times, specifically the pure major components of liquid logistic fuels, *n*-decane and *n*-hexadecane, and the logistic fuel JP-8. Also, olefin production, an undesirable competing reaction to partial oxidation, will be investigated. These results can be used to assess the potential application of this technology in mobile fuel-reforming of liquid logistic fuels.

2. Experimental

2.1. Reactor and procedure

The reactor consisted of a Y-shape 19 mm inner diameter (i.d.) quartz tube as sketched in Fig. 1. The fuel, *n*-decane, *n*-hexadecane (HPLC-grade >99.9% purity), or United States Army East Coast JP-8 (Fort Belvoir Military Base), and steam were delivered into the reactor through two automotive fuel injectors from 5 psig pressurized liquid tanks. The injectors sprayed liquid fuel on the heated reactor walls. High pressure cylinders of high purity (>99.9%) gases fed the system with O_2 and N_2, and the flow rates were adjusted to air stoichiometry using mass flow controllers. Air entered the reactor through a small port located below the fuel injector. As the liquids evaporated on the walls of the reactor, the air convectively fed the steam and vaporized fuel toward the catalyst, preventing the reflux of reactants.

An uncoated 80 pores per linear inch (ppi), 17 mm outer diameter (o.d.), and 10 mm length α-alumina (91% α-Al_2O_3, 9% SiO_2) foam monolith was wrapped in approximately 1 mm thick ceramic fiber paper around the perimeter surface of the catalyst. This uncoated monolith provided a static, tortuous path for the uniform mixing of the fuel and air, and the paper prevented bypassing of gases. A thermocouple was placed below the static mixer to measure the temperature of the reactants upstream of the catalyst. Under steady-state operation, the upstream feed temperature was maintained at ~250 °C. The upstream feed temperature of ~250 °C is below the normal boiling point of *n*-hexadecane, 287 °C. Since the autoignition temperature of *n*-hexadecane is below its normal boiling point, the upstream temperature had to be maintained at ~250 °C to prevent a cool

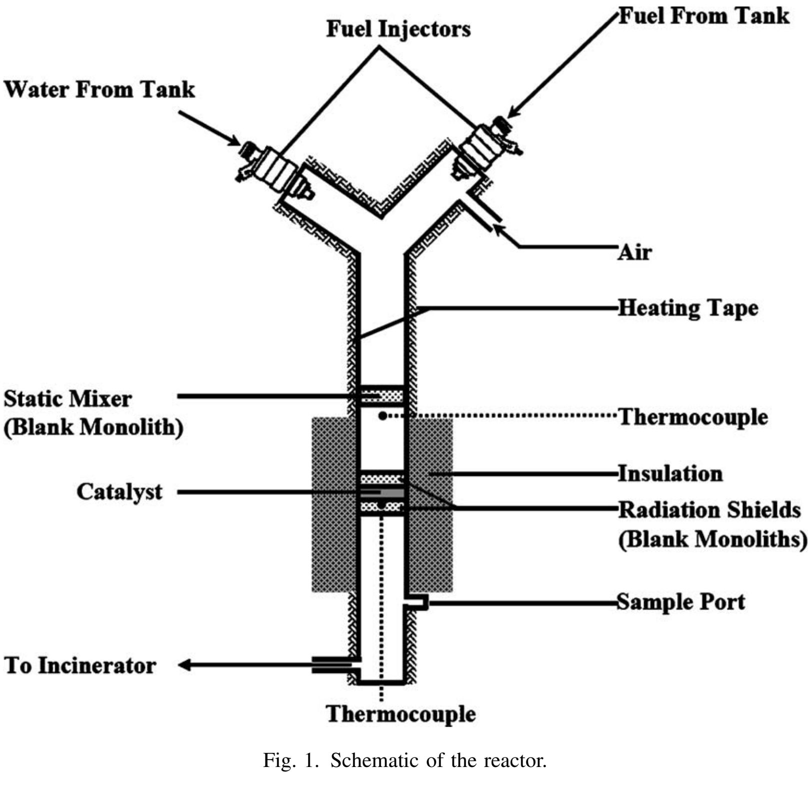

Fig. 1. Schematic of the reactor.