Cooling and coke deposition of hydrocarbon fuel with catalytic steam reforming

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ABSTRACT

The strong endothermic reaction of hydrocarbon-fuel catalytic steam highlights its potential for use in high-temperature wall cooling. The cooling capacity and cracking-controlled coke of hydrocarbon fuel have been compared experimentally with and without a catalytic steam reforming reaction under supercritical pressure conditions, and the interaction effects between the thermal cracking and catalytic reforming reactions were analyzed. The results show that the hydrocarbon fuel catalytic steam reforming reaction can not only significantly improve the total heat sink and fuel conversion, but also reduce the coke deposition arising from the thermal cracking process. The chemical heat sink of the catalytic steam reforming reaction is higher than that of thermal cracking, especially in the high-temperature range. At temperatures below 500 °C, catalytic steam reforming provides a boost to the fuel compounds and turns them into small-molecular gas-phase products such as hydrogen and carbon monoxide. The catalytic reforming and thermal cracking reactions occur simultaneously at temperatures above 500 °C. The catalytic reforming reaction can lower the degree of thermal cracking and inhibit the polymerization of small molecules produced by cracking to aromatics, consequently resulting in less coke deposition.

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1. Introduction

The heat load on the surface of an engine increases sharply with an increased flight Mach number, and hydrocarbon fuel regenerative cooling has been considered as an effective form of thermal protection to solve the aerodynamic heating problems associated with hypersonic flight conditions. The lack of sufficient endothermic heat sink capability from aviation kerosene, however, has limited the development of regenerative cooling systems. Thermal protection systems would require 4 MJ/kg of total heat sink at Mach number 8, which represents a heat sink capability that surpasses the maximum value of most jet fuels [1].

A number of studies have been conducted with the aim of improving the heat sink capability of hydrocarbon fuels, including (1) enhancing the upper limit of the available operating temperature range using a hydrocarbon hydrogenation process or an additive package [2–4]; (2) developing endothermic fuels by making changes to the fuel compositions that control the properties of the hydrocarbon fuel [5–7]; and (3) generating endothermic reactions in the hydrocarbon fuel under catalytic dehydrogenation and cracking conditions [8,9].

Although the above measures, especially catalytic dehydrogenation and cracking methods, can generate a higher heat sink from fuel, the high cost of the platinum catalyst as well as the formation of a large amount of coke deposition has limited the use of these techniques.

Further development is needed to enhance the fuel heat sink capacity of jet fuels while at the same time to mitigate the carbon deposition from thermal cracking.

As one of endothermic catalytic reactions that can increase the cooling capacity, achieve high levels of hydrogen production and minimal coke deposition, the catalytic steam reforming of hydrocarbon fuel has recently drawn significant attention [10–12]. Catalytic steam reforming technology, originating in the chemical industry [13], is used to produce hydrogen and ammonia, and subsequently has been developed in the fields of fuel cell [14,15], internal combustion engines [16], and gas generators [17]. In recent years, this technique has been investigated for thermal protection of hypersonic flight vehicle. Korabelnikov et al. [18–20] studied the catalytic conversion and output characteristics of steam reforming for methane, heptane, and decane. It is found that the reaction system with catalytic reforming could lead to a fuel having a longer working life even in a thermal cracking regime. Hou et al. [21] investigated the heat sink capacity and conversion of a catalytic steam reforming reaction for aviation kerosene. However, the quantitative measurement of coke deposition under the catalytic reforming condition and the interaction between thermal cracking and catalytic steam reforming reactions have not been studied previously.

The objective of this work is to provide new insights into the cooling capacity and coke deposition behaviors under the coupling interaction between thermal cracking and steam reforming reactions. To do so, we have conducted a series of experimental studies of the catalytic steam reforming based on a specific hydrocarbon fuel. The thermal

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cracking and coke deposition behaviors as well as the heat sink performances of the fuel with and without the catalytic steam reforming reaction have been compared and analyzed. Results on the coupling interactions between the thermal cracking and steam reforming reactions were obtained.

2. Principle and experimental systems

The heat sink capacity of a hydrocarbon fuel can be improved by the catalytic steam reforming reaction. In essence, the C–H bonds in the fuel and the H–O bonds in steam are broken and reformed into hydrogen, carbon monoxide, and low molecular weight hydrocarbons on the surface of the catalyst:

$$aC_nH_m + bH_2O \rightarrow \{H_2, \ CH_4, \ CO...\}. \tag{1}$$
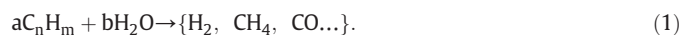
This reaction serves as a thermal protection component since it is an endothermic process. It also generates flammable gaseous species, such as hydrogen, carbon monoxide, and low-molecular-weight hydrocarbon compounds, which effectively shorten the ignition delay of the fuel in the kerosene-fueled supersonic combustor.

The test apparatus that was used under supercritical pressure conditions is shown in Fig. 1. High purity nitrogen gas was used to remove the residuals before and after the test process. Chinese kerosene was used as hydrocarbon fuel. The critical pressure and temperature are 2.459 MPa and 404 °C, respectively. Cycloalkanes are major components of kerosene and constitute up to 49% of the fuel in mass. Water and kerosene, together with 0.3% emulsifier, were fed into the fuel tank in advance of the test process and then mixed to form an emulsion fuel using a static in-pipe mixer. The fuel itself was pressurized into a pre-heater and the reactor using a metering pump following a filtration treatment process. A Coriolis mass flowmeter was used to measure and control the flow rate of the liquid fuel. The capacity of the flowmeter is 10 MPa, and the flow rate limit is 3 g/s. Its measurement resolution is ±0.2%. As a result, the fuel supply can be delivered in a stable and uniform way to the subsequent heating and sampling sections.

The fuel was then heated using electric power in a pre-heater and a plate reactor. The fuel at the outlet can be heated to the maximum temperature of 700 °C, surpassing the critical temperature 404 °C. In the preheater, a pipe coil with an inner diameter of 2 mm and a 1 mm wall was coiled around the electric-heating rod and inserted into the small-scale heating furnace. The plate reactor was used to verify the cooling capacity of the high-temperature plane surface via the endothermic reaction, as shown in Fig. 2. The plate reactor was made of high-temperature alloy stainless steel and consisted of five loops with a total length of 2883 mm and a rectangular cross-sectional dimension of 4 × 2 mm. In addition to the fuel temperature measurements at the
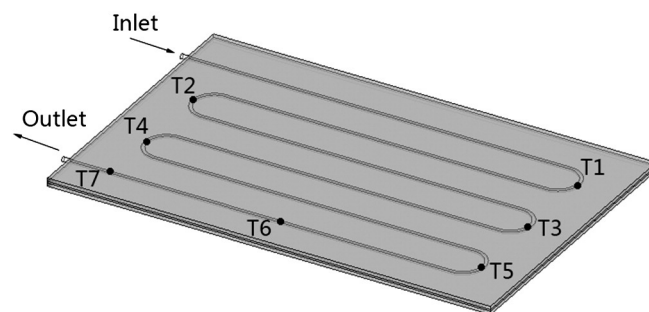

Fig. 2. Schematic diagram of the reactor.

reactor inlet and exit, seven thermocouples were used to measure the outer-wall temperatures along the flow path of the reactor. An inexpensive nickel-based reforming catalyst from Sinopec Qilu Company was coated onto the inner wall of the reactor by means of plasma spraying using a ceramiclike binder, and the thickness of the catalytic layer was controlled within 0.2 mm. Nickel element as an active component is added in the carrier of calcium aluminate using an impregnation method. Potash is used as an additive in the reforming catalyst for the resistance to carbon formation. The two sides of the reactor were covered with electric-heating boards. The heating flux was simulated by gradually regulating the output voltage of the power.

The plate reactor was heated electrically and most of the heat was absorbed by fuel. A small portion of the heat, however, was dissipated to the environment by means of heat loss. The energy equation of the experimental system could be expressed as follows:

$$P_{in} = q_m \Delta h_T + P_{loss}, \tag{2}$$

where P_{in} is the input power of the electrical heater, q_m is the mass flow rate of the fuel, Δh_T is the total heat sink per unit fuel of mass, and P_{loss} is the system heat loss to the environment that could be minimized through insulation and be obtained through calibration without a fuel flow. Using the current setup, the heat loss was measured to be in the range of 13.4–16.5% of the total power input, depending on the reactor's wall temperature and the environment.

The total heat sink represents the endothermic ability of the fuel and takes both the physical heat sink (Δh_p) and the chemical heat sink (Δh_c) into account. The physical heat sink can be calculated as a function of the fuel temperature measured at the reactor inlet (T_{in}) and exit (T_{out}). The fuel composition is assumed unchanged for the calculation of the sensible enthalpy. The constant-pressure specific heat can be computed according to the procedure described by Hu [22]. The chemical heat sink Δh_c is the endothermic heat sink of the fuel thermal cracking
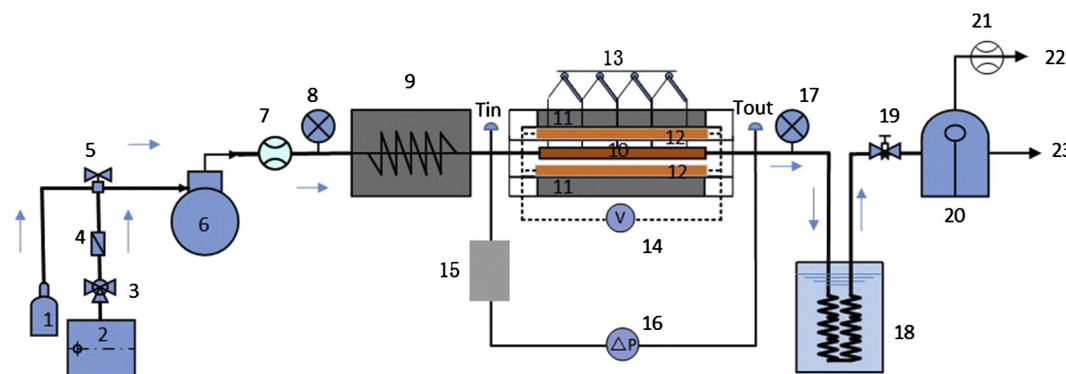

Fig. 1. Experimental setup. 1. High purity nitrogen; 2. fuel tank; 3. online static mixer; 4. filter; 5. switch valves; 6. metering pump; 7. mass flow meter; 8. pressure gauge; 9. pre-heater; 10. reactor; 11. insulating layer; 12. heating plates; 13. temperature measurement; 14. voltage regulators; 15. overheat protection; 16. differential pressure transmitter; 17. pressure gauge; 18. condenser; 19. backpressure regulator; 20. gas–liquid separator; 21. gas flow meter; 22. Gaseous products; 23. liquid products.