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ENDOTHERMIC HEAT-SINK OF HYDROCARBON FUELS FOR SCRAMJET COOLING

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Storable liquid hydrocarbon fuels, such as JP-7, JP-8+100, and JP-10, that can undergo endothermic reactions may provide sufficient heat sink to enable hypersonic flight without having to resort to cryogenic fuels. The objective of this research is to develop and demonstrate the endothermic potential of these fuels for hypersonic scramjet cooling. A high-pressure bench-scale reactor was used to determine the overall heat sinks (including endotherm), endothermic reforming products, and coking rates for the fuels. A baseline fuel, n-octane, was also investigated for comparison. Tests were conducted in catalyst-coated tubes that simulate a single passage in a practical catalytic heat exchanger/reactor under representative flow conditions.

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Abstract

Storable liquid hydrocarbon fuels, such as JP-7, JP-8+100, and JP-10, that can undergo endothermic reactions may provide sufficient heat sink to enable hypersonic flight without having to resort to cryogenic fuels. The objective of this research is to develop and demonstrate the endothermic potential of these fuels for hypersonic scramjet cooling. A high-pressure bench-scale reactor was used to determine the overall heat sinks (including endotherm), endothermic reforming products, and coking rates for the fuels. A baseline fuel, n-octane, was also investigated for comparison. Tests were conducted in catalyst-coated tubes that simulate a single passage in a practical catalytic heat exchanger/reactor under representative flow conditions. Performance evaluations were primarily based on endotherm measurements and coke deposition. Adequate heat sink capacities have been demonstrated for JP-7 and JP-8+100 at elevated pressures using a simple, inexpensive zeolite cracking catalyst. Although the JP-10 provided an attractive heat sink, its high carbon-to-hydrogen ratio leads to significant coking/fouling problems and potential poisoning of the catalyst, even at relatively low temperatures. The results are directly applicable to the selection of fuels and the design of fuel-cooled thermal management systems for hypersonic scramjet applications.

Introduction

High heat sink fuel cooling technology can be applied to enhance engine performance over the entire spectrum of flight regimes. For hypersonic flight, it provides the only means for meeting the cooling requirements with storable fuels; for advanced fighter aircraft, it provides an identifiable path to achieving IHPTET performance goals with current materials; and, for lower-speed military and commercial aircraft, it can increase growth potential and play a key role in emissions-reduction strategies.

Although cryogenic fuels, such as liquid methane and liquid hydrogen, can provide sufficient cooling, they require large vehicles (because of their low densities) and present cost, logistics, operational and safety problems. By contrast, conventional liquid hydrocarbon fuels may offer the required cooling capacity without the problems associated with cryogenic fuels. For example, paraffinic liquid hydrocarbon fuels have significant sensible heat sink capacities for supersonic aircraft applications and may undergo endothermic chemical cracking on a catalyst for hypersonic missile applications [1,2].

The total heat sink of a hydrocarbon fuel comes from the physical heating of the fuel (raising its temperature and thereby its sensible enthalpy) and a heat-absorbing (endothermic) chemical reaction. Nixon and his co-workers [3,4] first demonstrated that the selective dehydrogenation of methylcyclohexane (MCH) on a platinum/alumina catalyst can provide a total heat sink of nearly 900 Btu/lb. MCH, the first-generation endothermic fuel, offers sufficient heat sink for cooling a Mach 4 to 6 aircraft, but is much more expensive than current aviation fuels, requires an expensive platinum catalyst, and presents significant logistics problems. On a practical path to realize the hydrocarbon fuel cooling technologies, Sobel and Spadaccini [2] first investigated the endothermic potential of liquid hydrocarbon fuels with inexpensive and readily available catalysts under operating conditions simulative of high-speed flight applications. High heat sink capacities and desirable reaction products were demonstrated in their study for pure paraffinic (e.g., n-heptane) and blended normal paraffinic (e.g., Norpar 12) fuels in coated-tube

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reactor configurations. At temperatures above approximately 1000 F, the sensible heat sink can be supplemented by a heat absorbing chemical reaction as the fuel undergoes thermal and catalytic cracking reactions that reform it into a mixture of lighter hydrocarbons and hydrogen [2], which can then be burned in the engine. The coke deposition mechanism in this high temperature regime is characterized by pyrolysis. In this process, the catalyst can serve to enhance the endothermic reaction rate and improve the selectivity of the reaction for the preferred products that may have shorter ignition delay times and more rapid burning rates and may also reduce the coke formation. The starting temperature for the endothermic reactions is on the order of 1000 F and depends primarily on the catalyst and the fuel composition. It is also a function of fuel flow rate and residence time.

Endothermic fuel cooling technology can be implemented in a practical thermal management system in two different ways: direct cooling, which refers to the incorporation of the heat exchanger into the structure of a hot component, such as a scramjet combustor, an augmentor, or a turbine exit guide vane; and indirect cooling, wherein ram air or compressor bleed air is cooled by the fuel in a nearby heat exchanger, and then used to cool the hot components. This indirect cooling, "cooled cooling air", allows a substantial increase in engine pressure ratio, with corresponding improvement in the thrust-to-weight ratio [5,6], and thermal efficiency. In both ways, the cooling capacity of conventional hydrocarbon fuels is limited by a temperature constraint necessary to limit coke deposition [7].

The principal engine operability issue that will affect hydrocarbon fuel cooling technology is coke formation. In hypersonic applications, duty cycles are short, but requirements for maximizing heat sink lead to very high fuel temperature operation (>1300 F) and the potential for accelerated coking. The extent to which the benefits of high heat sink cooling technology can be realized is directly related to our ability to mitigate against coke formation.

To assess the relative potential of various fuels for high-speed flight applications, it is important to compare directly the performance, i.e., the heat sink capacity and coking limits, in a simulation of scramjet regenerative cooling. Within this effort, several candidate fuels, namely JP-7 (baseline fuel), JP-8+100, JP-10, and n-octane (reference fuel), were tested using a single-tube reactor rig under representative flow conditions that simulate a single passage in a practical catalytic heat exchanger/reactor. The total (physical + chemical) heat sinks of these fuels were determined, and the coke deposition resulting from extended duration tests were measured. In addition, the compositions of the products from the endothermic cracking were analyzed using both GC (Gas Chromatograph) and GC/MS (Gas Chromatograph/Mass Spectrometer).

Fuel Selection

JP-7 and JP-8+100 were chosen as the primary fuels in this study. These multi-component kerosene-type fuels are defined by their physical properties and broad composition guidelines (e.g., aromatics limit) rather than specific chemical compositions. Many of the defining characteristics can be found in the CRC Handbook for aviation fuels [8]. JP-7 is a military jet fuel with low volatility and high thermal stability. The fuel specifications for JP-7 require that aromatics comprise less than 5 percent of the fuel (as determined by ASTM D-1319), the remainder of the composition being saturated species, i.e., normal-, iso-, and cyclo-paraffins. JP-8+100 is representative of a class of military and commercial aircraft gas-turbine fuels with improved thermal stability.

The design of the experiments and interpretation of the data require the ability to estimate thermodynamic and physical properties. To enable this, simple models were used to represent the complex fuel blends. Based on GC/MS analyses, 6-component and 11-component mixtures, as listed in Table 1, were selected to simulate analytically the more complex JP-7 and JP-8+100, respectively. These simulations allow computations of the physical and thermodynamic properties of the jet fuels using the NIST SUPERTRAPP program [9].

Table 1: Jet Fuel Simulations

JP-7		JP-8			
Component	Molar Fraction	Component	Molar Fraction	Component	Molar Fraction
n-undecane	0.122	methylcyclohexane	0.075	t-butylbenzene	0.055
n-dodecane	0.289	meta-xylene	0.070	n-dodecane	0.175
n-tridecane	0.368	n-octane	0.130	1-methylnaphthalene	0.052
n-tetradecane	0.031	n-decane	0.156	n-tetradecane	0.112
n-pentadecane	0.018	butylbenzene	0.055	n-hexadecane	0.065
ethylcyclohexane	0.172	isobutylbenzene	0.055		

Unlike the fuels described above, n-octane and JP-10 are single-component hydrocarbon fuels. n-Octane is a reference fuel studied for comparison. JP-10 is a missile fuel with high energy density and, therefore, is well suited to volume-limited applications. Furthermore, because of its attractive thermophysical properties (e.g., viscosity, freezing point), it is the most widely used missile fuel. However, its mission capability is limited by the extent to which it can be used as the primary coolant in a vehicle thermal management system. The benefits for expanding this mission capability through the development of the endothermic potential of JP-10 are therefore clear.

Experimental Apparatus

The high-pressure bench-scale test apparatus is shown schematically in Figure 1. Fuel is introduced into the reactor at supercritical pressure using a flow control system with a high-pressure fuel reservoir. The tests were run with or without a fuel preheater, depending on what types of heat sink data were sought. For determining the physical heat sink from ambient to 1000 F, the preheater was turned off. For all tests involving endothermic reactions (i.e., > ~1000 F), the fuel was first preheated to approximately 700 F (supercritical) in order to reduce the reactor length requirement.

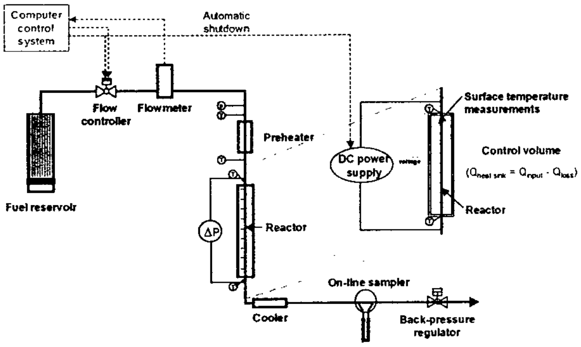

Figure 1: Bench-Scale Reactor Test Rig

Resistive heating was used to allow a direct measurement of the overall heat sink capacity of the fuels by performing an energy balance on the control volume depicted in Figure 1. With this method, heat is supplied by the imposition of an electric current through the reactor tube itself. The electrical power input, Q_{in}, is converted to heat and transferred to the fuel on the inside of the reactor and, by natural convection, to the environment on the outside. The portion of heat lost to the environment through natural convection, Q_{env}, is minimized by insulation and accounted for through multi-point calibrations without fuel flow prior to a given test. (The heat losses were in the range of 3 to 8 percent of the total power input, depending on the reactor wall temperatures and fuel flowrate.) The overall heat sink of the fuels, Q_{sink}, can be computed by

$$Q_{\text{sink}} = Q_{in} - Q_{env} \qquad (1)$$

Thermodynamically, the cooling capacity is defined as an enthalpy change of fuel between the inlet and exit. The enthalpy change can be calculated by

$$H_{exit} - H_{inlet} = \frac{Q_{\text{sink}}}{\dot{m}} \qquad (2)$$

where H_{inlet} and H_{exit} are the fuel enthalpies at the reactor inlet and exit, respectively, and $\dot{m}$ the fuel mass flowrate. The overall heat sink of fuel (Q_{sink}) can be further divided into that which results in raising the temperature of the fuel/products (sensible heating, ΔH_{sens}) and that which is absorbed in the reaction (endotherm, ΔH_{endo}). The net endotherm can then be computed as

$$\Delta H_{endo} = (H_{exit} - H_{inlet}) - \Delta H_{sens} \qquad (3)$$

and sensible heat sink computed as a function of the fuel temperatures measured at the reactor inlet (T_{inlet}) and exit (T_{exit}). For the purpose of sensible enthalpy calculation, the fuel composition is treated as constant.

All reactors were coated with an inexpensive zeolite cracking catalyst using a ceramic-like binder. In addition to the fuel temperature measurements at the reactor inlet and exit, the fuel pressures were also measured at the reactor inlet and exit to correlate reactor performance. A differential pressure gauge was used to measure and track-in-time the reactor pressure drop, which is indicative of coke deposition. Since the coated-wall reactor tubes were generally small diameter to simulate practical heat exchanger reactor passages, only tube outer wall temperatures were measured along the reactor. Downstream of the reactor, the products were quenched in a water-cooled heat exchanger and the liquid and gaseous products were collected in an on-line biphase sample collector for compositional analysis. The liquid and gaseous components were separated and analyzed using both a cryocooled Hewlett Packard Gas Chromatograph/Mass Spectrometer system and a fast-response MTI Micro Gas Chromatograph.

To determine the extent of carbon deposition, the reactor tubes were removed from the rig at the test completion, rinsed with hexane and dried in a vacuum oven. The tubes were then cut into 2-in. lengths and the carbon accumulated in each section was assessed using a LECO RC-412 Carbon Determinator which quantifies carbon deposition by measuring carbon dioxide produced in a controlled carbon burn-off.

Results And Discussion

Fuel Heat Sink

The overall heat sink (i.e., physical + chemical) and estimated endotherms (chemical only) of JP-7, JP-8+100, JP-10 and a reference fuel, n-octane, are shown in Figures 2-5. The sensible enthalpy changes of the fuels were estimated using the NIST computer program SUPERTRAPP. The SUPERTRAPP computations were carried out based on the temperature measurements at the reactor inlet and exit, and the fuel simulations in Table 1.

The test conditions are described in Table 2. As mentioned above, the wall temperatures were measured along the reactor and the data showed similar wall temperature distributions for different fuels. The peak wall temperatures were located about 1 to 2 inches from the exit (due to wall conduction), and found to be 100 to 150 F higher than exit fuel temperatures. All the tests were run to the maximum operating temperatures where the tests were limited by coking deposition. The overall heat sink data at the highest temperature for each fuel in Figures 2-5 represent a short-duration test with subsequent reactor plugging at that temperature. Therefore, these highest temperature points should not be used for design purposes.

Table 2: Test Conditions

Parameter	Condition
Catalyst coating	zeolite
Pressure	600 psia
Fuel flowrate	4.8 lbm/hr
LHSV	3000 1/hr

Comparison of the total heat sinks (on a mass basis) among these fuels at the flow conditions tested indicates that:

- There are no significant differences in physical heat sink among these fuels, except for JP-10, which has slightly lower physical heat sink on a mass basis than the other fuels.

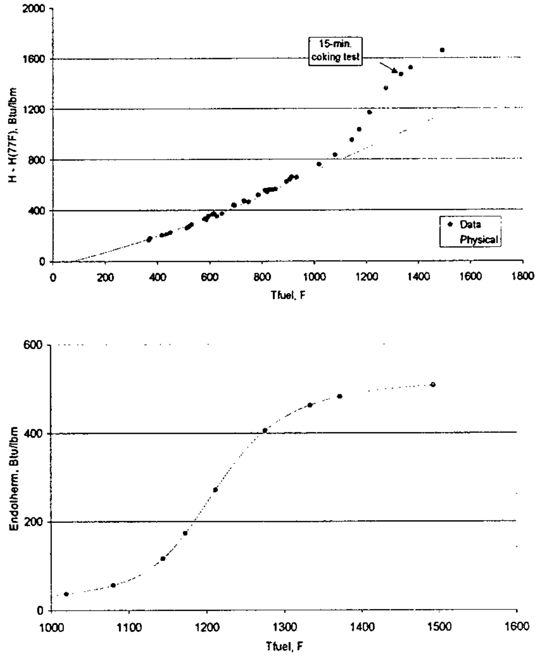

Figure 2: Heat Sink of JP-7

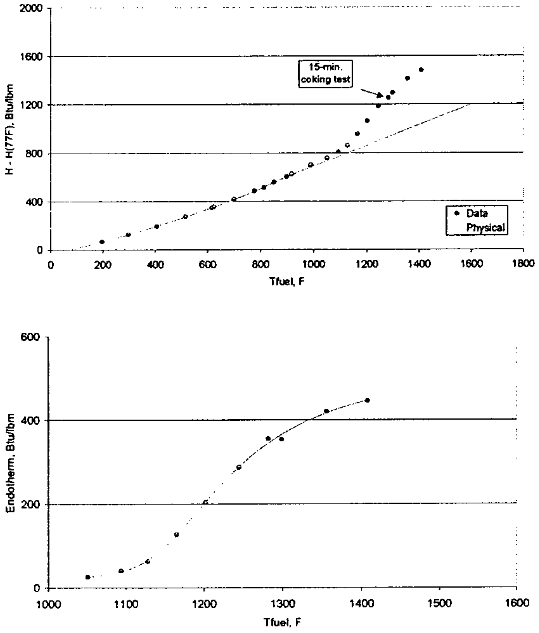

Figure 3: Heat Sink of JP-8+100

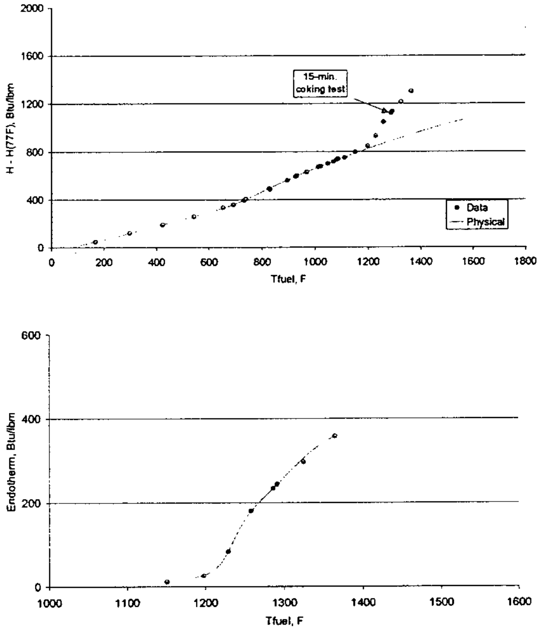

Figure 4: Heat Sink of JP-10

- At a given temperature, JP-7 has the highest overall heat sink, followed by n-octane and JP-8+100. JP-10 has the lowest heat sink.
- Compared to JP-8+100, JP-7 has the lower coke formation rate, probably due to its low olefin, low

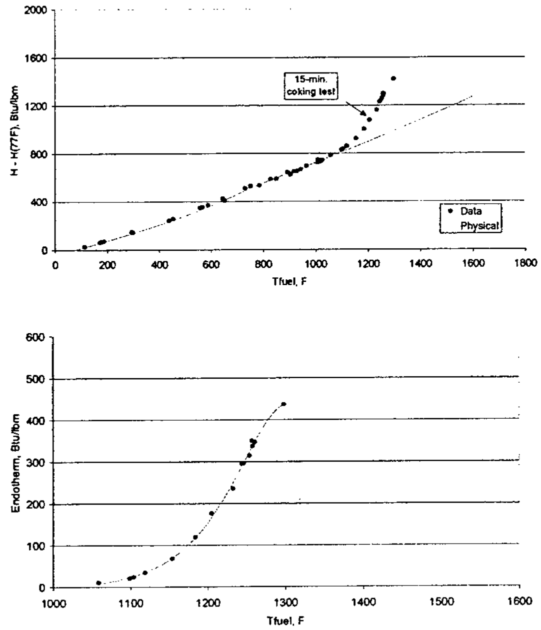

Figure 5: Heat Sink of n-Octane

aromatics, low sulfur, and/or high cyclo-paraffinic contents. Therefore, JP-7 can operate at the higher temperature and provides the higher heat sink.

- JP-8+100 has slightly lower endotherm than that of n-octane or JP-7 at the same temperatures due to its higher aromatics content. Aromatics are not cracked (thermally or catalytically) under the conditions tested.

The chemical heat sink (endotherm) and physical properties are a function of product distribution. Furthermore, the extent to which the benefits of the endothermic technology can be realized is directly related to our ability to mitigate against coke formation. Therefore, tests with durations simulative of a high-speed flight mission (15 min.) were conducted at constant temperatures for each of the fuels. During these 15-min. tests, gaseous and liquid product samples were collected at the 5-min. point for composition analysis. Also, the reactor tube was removed from the rig at the completion of each test for coke deposition assessment. The running temperatures of the extended-duration tests were selected to be approximately 100-150 F below the highest temperatures achieved in the heat sink tests to permit running the extended-duration tests without flow restriction. The test conditions and key results are summarized in Table 3. The single-point heat sinks of the fuels in the extended-duration tests for coking deposition assessment were also illustrated in Figures 2-5 and labeled as "15-min. coking test". The detailed results of these tests are discussed below.

Gaseous and Liquid Products Analysis

The GC analysis results of the gaseous product samples taken at 5 min. for JP-8+100, JP-10, and n-octane at the temperatures listed in Table 3 are shown in Figure 6. Although the primary species of gaseous products obtained are the same with all the fuels tested, differences in the species distributions among the fuels are quite significant. The GC/MS chromatographs of the JP-8+100 liquid product samples are illustrated in Figure 7. Comparisons between the unreacted and reacted fuel liquid products show substantial shifts in the composition to lower molecular weight species in all the tests. The analyses also indicate that no species with molecular weights higher than those of the unreacted fuel components were being formed as a result of the reaction. Chromatographs of the liquid product samples for the other fuels (namely, JP-7, JP-10, and n-octane) were observed and the results indicate similar substantial shifts to lower molecular weight species.

Table 3: Summary of the 15-min. Tests

Fuel	JP-7	JP-8+100	JP-10	n-Octane
Running time, min	15	15	15	15
Tfuel(exit), F	1334	1282	1286	1205
Total heat sink: H - H(77F), Btu/lbm	1468	1250	1120	1072
Endotherm, Btu/lbm	462	354	233	176
Total coke deposition, mg	14.1	9.9	13.2	6.4

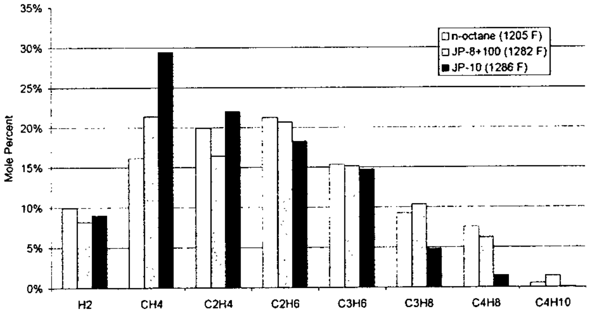

Figure 6: Gaseous Products of Reacted Fuels

Coke Deposition

The principal heat exchanger operability issue that will affect fuel cooling capacity is coke formation. The coke deposition on the surface of the heat exchanger can degrade its performance by increasing both thermal resistance and fuel pressure drop. More critically, the coke deposition may lead to system failure by blocking the fuel passages. To address these concerns, 15-min tests were conducted at a constant test condition.

The coke deposit distributions along the reactor for the fuels tested are illustrated in Figure 8. In general, the coke deposition increases with increase in fuel and wall

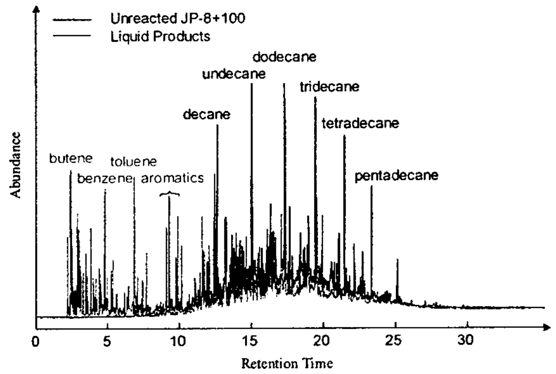

Figure 7: JP-8+100 Liquid Products

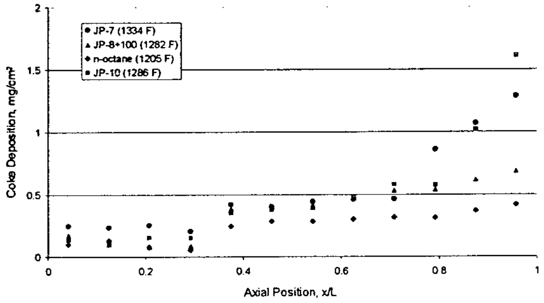

Figure 8: Coke Deposition Distribution

temperatures. As shown in Figure 8, the maximum coke depositions in the reactors for all the fuels tested are in the range of 0.4 to 1.6 mg/cm^2, equivalent to 8 to 33 μm of coke thickness (assuming coke density of 1 g/cm^3 of) on the inside wall of the tube, representing less than a 5 percent restriction of the flow cross-sectional area at the point of maximum coke build-up under the indicated test conditions.

Conclusion

Storable liquid hydrocarbon fuels, such as JP-7 and JP-8+100, that undergo endothermic reactions can provide sufficient heat sink to enable hypersonic flight without having to resort to cryogenic fuels. The endothermic heat sink capacities of the fuels (viz., JP-7, JP-8+100, and JP-10) were demonstrated under operating conditions simulative of hypersonic scramjet cooling applications. Performance evaluations were primarily based on overall heat sink (including endotherm) measurements and coke deposition. The results are directly applicable to the selection of fuels and the design of fuel-cooled thermal management systems for hypersonic vehicles.

Based on the results of the current research, the following specific conclusions may be made:

- Substantial endotherms are achievable with JP-7 and JP-8+100 using inexpensive zeolite catalysts in representative-size passages.

- Under the same temperatures, there are no significant differences in physical heat sink among the liquid hydrocarbon fuels of JP-7, JP-8+100, and n-octane. JP-10 shows a slightly lower physical heat sink on a mass basis than the other fuels.

- Although the JP-10 provided an attractive heat sink, its high carbon-to-hydrogen ratio leads to significant coking problems and potential poisoning of the catalyst, even at relatively low temperatures.

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