HYDROCARBON FUEL COOLING TECHNOLOGIES FOR ADVANCED PROPULSION

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ABSTRACT

Storable hydrocarbon fuels that undergo endothermic reaction provide an attractive heat sink for future high-speed aircraft. An investigation was conducted to explore the endothermic potential of practical fuels, with inexpensive and readily available catalysts, under operating conditions simulative of high-speed flight applications. High heat sink capacities and desirable reaction products have been demonstrated for n-heptane and Norpar 12 fuels using zeolite catalysts in coated-tube reactor configurations. The effects of fuel composition and operating condition on extent of fuel conversion, product composition and the corresponding endotherm have been examined. The results obtained in this study provide a basis for catalytic-reactor/heat-exchanger design and analysis.

INTRODUCTION

As aeropropulsion technologies advance into the twenty-first century, increasingly severe demands are being placed on structural and thermal capabilities of the engine, fuel economy, and pollutant-emissions control. At high supersonic and hypersonic flight speeds, the temperature of the ram air taken on board the vehicle is too high to cool the structure, and it is necessary to utilize the fuel as the primary coolant.

The heat sink afforded by conventional liquid hydrocarbon fuels is limited by operation at moderate temperatures to preclude deposit formation and avoid fouling the cooling or fuel injection systems. Cryogenic fuels, such as liquid methane and liquid hydrogen, can provide sufficient cooling but require large vehicles (because of their low densities) and present cost, logistics, operational and safety problems. By contrast, endothermic liquid hydrocarbon fuels offer potential for increased cooling by undergoing chemical decomposition (cracking) on a catalyst prior to injection into the combustor (Lander and Nixon, 1971). The products of the endothermic reaction are gaseous fuels with high heating values, short ignition delay times and rapid burning rates. In addition, waste heat absorbed by the fuel can be returned to the cycle, enhancing performance. Endothermic fuels have handling characteristics that are very similar to current fuels and have deposit formation rates sufficiently low for potential application in high-speed tactical aircraft and missiles.

The total heat sink available from an endothermic fuel comes both from the physical heating of the fuel (raising its temperature) and from a heat-absorbing (endothermic reforming) chemical reaction. The transfer of heat into the fuel is accomplished in a catalytic heat-exchanger reactor. Within a reactor flow passage, the rate at which fuel is reformed depends on the balance among the heat transfer through the wall, the mass transfer of fresh reactant to the catalyst and the chemical kinetics associated with the reaction. Therefore, the reactor design should provide rapid transfer of heat into the reactor, such as can be obtained with plate-fin heat exchangers: highly turbulent fuel flows for maximum heat and mass transfer; and minimum thermal resistance through the use of high-conductivity materials and very thin (micron thickness) catalyst coatings bonded to the reactor walls. A good catalyst should provide nearly complete conversion of the fuel and high selectivity to the desired products at temperatures of interest.

FUELS AND CATALYSTS

Types Of Reactions

Many types of catalytic endothermic reactions of hydrocarbon fuels are possible. Dehydrogenation of saturated ring compounds (e.g., MCH and decalin) to form aromatics has been successfully demonstrated at reasonable temperatures and pressures with relatively large endothermic heats of reaction (Nixon et al., 1964...
Dehydrogenation of normal alkanes, and ring fracture of aromatics and cycloalkenes generally require very high temperatures. **Dehydrocyclization** of normal alkanes to form saturated ring compounds is not highly endothermic and proceeds slowly on known catalysts, otherwise the saturated rings could be further dehydrogenated to form aromatics. **Dedimerization** reactions can proceed at low temperatures, but absorb little heat. **Isomerizations** do not involve molar changes, therefore entropy changes are low, and these reactions are not thermodynamically favored. **Catalytic cracking** of normal- and iso-alkanes to form olefins and hydrogen is strongly endothermic and can be performed at temperatures and pressures that are compatible with existing materials. Unlike the saturated ring (naphthenic) endothermic fuels which react to form aromatics, catalytic cracking results in the formation of olefinic and low-molecular-weight paraffinic species, which are less likely to pose problems related to soot formation and increased radiative heating of the combustor liner. In addition, normal- and iso-alkanes can be blended to meet handling, safety and other system concerns. Consequently, the aim of this investigation was to exploit the cracking reactions.

In general, thermal and catalytic cracking of normal- and iso-alkanes may follow several different reaction paths and produce hydrogen and a spectrum of saturated and unsaturated hydrocarbon products. The product compositions may be affected by the reaction pressure and temperature, and correspond to different amounts of heat being absorbed. Depending on the temperature at which the reaction begins and the products formed, the endothermicity of the decomposition can vary substantially.

As shown for \textit{n}-heptane in Fig. 1, increased unsaturation of the products results in increased heat absorption, but requires higher reaction temperatures for comparable conversions. Based on these and similar calculations, it can be concluded that formation of saturated products (such as methane, Fig. 1d) and aromatics (such as toluene, Fig. 1c) tends to decrease the endotherm, but increase the equilibrium fractional conversion at a given temperature. Production of alkenes (such as ethylene and propylene, Fig. 1b) leads to a substantial heat absorption, and formation of alkynes (such as acetylene, Fig. 1a) leads to even greater heat absorption but requires reaction temperatures above 1300 °F. In addition, a multiplicity of low molecular weight products is desirable. The formation of large numbers of products increases the entropy change during the reaction, which in turn makes the reaction more favorable thermodynamically.

Thus, the most desirable products of the endothermic fuel reaction are hydrogen and low molecular weight olefins, such as ethylene. In addition to providing high heat absorption, these products would result in a fuel with excellent combustion characteristics. Small amounts of alkanes (methane) and aromatics are acceptable to enhance the thermodynamic driving force for high conversion levels at a given temperature.

### Fuel Types And Properties

A goal of this investigation has been to identify practical endothermic fuels with a high cooling capability and performance and handling characteristics very similar to current aircraft fuels. The physical and chemical properties of two candidate endothermic fuel blends, namely \textit{n}-heptane and Exxon Norpar 12.
TABLE 1 - FUEL PROPERTIES

<table>
<thead>
<tr>
<th>Property</th>
<th>MCH</th>
<th>n-Heptane</th>
<th>Norpar 12</th>
<th>JP-7</th>
<th>JP-8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling point, F</td>
<td>213</td>
<td>209</td>
<td>370-426</td>
<td>360-484</td>
<td>284-572</td>
</tr>
<tr>
<td>Net heating value</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gravimetric, Btu/lb</td>
<td>18,649</td>
<td>19,171</td>
<td>18,980*</td>
<td>18,875</td>
<td>18,400</td>
</tr>
<tr>
<td>Volumetric, Btu/gal</td>
<td>119,746</td>
<td>109,396</td>
<td>118,793*</td>
<td>123,500</td>
<td>124,378</td>
</tr>
<tr>
<td>Viscosity @ 20 C, cSt</td>
<td>0.86</td>
<td>0.55</td>
<td>1.68</td>
<td>2.0</td>
<td>1.65</td>
</tr>
<tr>
<td>Flash point, F</td>
<td>25</td>
<td>30</td>
<td>156</td>
<td>145</td>
<td>100</td>
</tr>
<tr>
<td>Specific gravity @ 60 F</td>
<td>0.77</td>
<td>0.68</td>
<td>0.75</td>
<td>0.79</td>
<td>0.81</td>
</tr>
<tr>
<td>Vapor press. @ 100 F, psia</td>
<td>1.6</td>
<td>1.6</td>
<td>0.8</td>
<td>0.02</td>
<td>0.15</td>
</tr>
<tr>
<td>Critical pressure, psia</td>
<td>504</td>
<td>397</td>
<td>290*</td>
<td>306</td>
<td>340</td>
</tr>
<tr>
<td>Critical Temp., F</td>
<td>570</td>
<td>513</td>
<td>682*</td>
<td>746</td>
<td>772</td>
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<tr>
<td>Composition</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aromatics, percent vol</td>
<td>3</td>
<td>20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naphthenes, percent vol</td>
<td>100</td>
<td>32</td>
<td>20</td>
<td></td>
<td></td>
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<tr>
<td>Paraffins, percent vol</td>
<td>100</td>
<td>99</td>
<td>65</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>Olefins, percent vol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfur, ppmw</td>
<td>&lt;5</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>60</td>
<td>500</td>
</tr>
</tbody>
</table>

* estimated property

† varies with blend

are listed in Table 1 along with those for methylcyclohexane (MCH), and current jet fuels JP-7 and JP-8 for comparison. Norpar 12 is an inexpensive mixture of normal alkanes, principally C\textsubscript{10} to C\textsubscript{13} (i.e., decane, undecane, dodecane, and tridecane).

Characteristics that would limit the usefulness of a fuel include high freezing point, low flash point and high vapor pressure. MCH has a low flash point and high vapor pressure which may restrict its application in many aircraft systems. Norpar 12 has physical properties that are very similar to JP-7, and could be readily modified to satisfy the property requirements for current fuels. (For example, its freezing point could be lowered considerably by broadening the blend to include lighter paraffinic components, such as octane.) Previous experience with JP-7 has indicated that the presence of a low concentration of aromatic species is desirable to maintain the elasticity of seals. Addition of aromatic species (e.g., toluene) to Norpar 12 would also result in a lowering of the freezing point.

Because the efficient catalytic conversion of endothermic fuels requires high temperatures, high thermal oxidative stability is a prerequisite for such fuels to be applicable as coolants. Coke formation at elevated reaction temperatures can reduce the effectiveness of heat exchanger surfaces and cause rapid degradation of the catalyst. Fuel thermal decomposition and deposit formation can take place in fuel preheaters and reactors by both autoxidation and pyrolysis mechanisms. Deposits may also form in transfer lines and valves downstream of the heat exchanger/reactor as a result of the condensation of high-molecular-weight products of the cracking reactions. Decomposition and surface deposition is governed by several factors, including the temperature and composition of the surfaces in contact with the fuel, the bulk temperature of the fuel, the levels of oxygen or sulfur in the fuel, and the residence time at the high temperature conditions. Oxygen is known to promote the formation of coke deposits at temperatures below 700 F. and removal of oxygen dissolved in the fuel and oxides from contact surfaces prior to heating has been found to decrease deposit formation.

It is possible that a low rate of fuel deposit formation can be achieved by very rapid heating of the liquid at supercritical pressure, through the autoxidation region, followed by additional heating of the fuel beyond its critical temperature. In addition, supercritical heating in the presence of the catalyst results in a reformation reaction that upgrades the structure of the fuel by breaking the weaker chemical bonds and improves the thermal stability. Moreover, the hydrogen product can combine with free radical species (coke precursors) that are formed, providing alternative paths for reaction.

### Catalysts And Catalyst Support Techniques

The cracking of normal alkanes is similar to reforming reactions carried out in the petroleum industry, wherein molecules are stripped of hydrogen, unsaturated carbon bonds are formed, and rearrangement of molecules to both lighter and heavier species takes place. However, aircraft applications are volume and weight limited, and require specific flow rates that are more than 100 times those used in petroleum reforming. Reforming reactions are typically carried out on zeolite catalysts. These are skeletal aluminosilicate compounds that are processed from natural clays and have a narrow distribution of pore sizes that provide access to a cage-like inner structure in which the bulk of reaction occurs. The catalytic activity and selectivity of each zeolite depend upon how readily a fuel molecule can enter its internal cages, and whether products of a certain molecular geometry can pass through the pores.

Because the requisite high activity and selectivity characteristics of the catalyst itself, the implementation of the reactor design must provide several other characteristics if high endothermic
performance is to be achieved. Primary among these are the ability to provide high rates of heat transfer to the reacting surface (i.e., the fuel/catalyst interface) and high rates of mass transfer in order to provide a continual supply of fresh fuel to the catalytic surfaces. If either requirement is not satisfied, the performance capability of the reactor will be reduced. If heat transfer rates are lower than the mass transfer or the kinetics rates, the temperature of the fuel in contact with the catalyst will fall, reducing the reforming rate until the processes are again in balance. If local mass transfer rates are too low, reaction products will accumulate around the catalytically active sites, blocking the supply of fresh fuel and retarding the reaction process. The balance between the heat and mass transfer rates depends on the reactor implementation and the catalyst support configuration. In addition, incorporation of a reactor into a practical aircraft thermal management system requires that the unit impose as small a fuel flow resistance as possible (low pressure drop) and that the size and the weight of the unit be minimized.

The reactor concept can be implemented in two different ways with regard to use in the thermal management of a flight system, namely for either direct or indirect cooling (see Fig. 2). Direct cooling refers to the incorporation of the reactor into the structure of a hot component, such as an augmentor or an exhaust nozzle. With indirect cooling, a secondary fluid, such as air or a recirculating non-reacting coolant, is cooled by the fuel in a remote reactor, then used to cool the hot component structures. There are important differences between these configurations, both in the levels of local heat flux occurring and in the mechanical arrangement of the reactor. Indirect cooling implies a "conventional" heat exchanger, with relatively modest levels of heat flux. In the direct cooling configuration, the heat exchanger is part of the hot structure, and may be exposed to very hot, high velocity flow, resulting in correspondingly high heat flux levels.

**Packed-Bed and Coated-Wall Catalyst Supports.** In catalyst systems considered for aircraft applications, the catalyst is affixed to some stationary support in a manner allowing ready contact with the flowing fuel and good thermal contact with the heat source. Two methods for supporting the catalyst have been examined. The first is a packed bed in which the catalyst is formed into pellets or coated onto existing pellets, and the pellets are placed in the fuel passage. The second technique involves coating of the catalyst directly on the wall of the fuel passage.

In a packed bed, the heat must flow from the hot source, through the passage wall, and into the bulk of the fuel flow. Because the pellets form a non-continuous structure, heat must reach the interior catalytic surface by means of convection due to fluid motion. While this heating mechanism may be adequate for certain low heat load applications, it is very inefficient and leads to heavy, high-volume heat exchangers. Furthermore, in a packed bed, the temperature difference between the wall and the bulk fuel may be substantial. The fuel is the hottest at the wall where there is no catalyst, possibly leading to undesirable pyrolytic reactions with potential for coke deposit formation. Moreover, the endothermic reaction occurs at the coolest point in the fuel, i.e., the fuel/catalyst-pellet interface.

The alternative approach for supporting the catalyst is applicable for either direct or indirect cooling systems and entails coating the catalyst onto the walls of the fuel passages. Since the flow of heat is from the wall through the catalyst to the fuel, the reaction occurs where the fuel is the hottest, i.e., at the catalyst/fuel interface and undesirable thermally-driven, non-catalytic reactions can be avoided. Furthermore, although the zeolite catalysts used for thermal cracking of paraffinic hydrocarbons have relatively low thermal conductivities, similar to ceramics, the typical thickness of the coating is very small (i.e., less than 10 μm) and thus presents negligible additional thermal resistance. Another advantage associated with the coated-wall catalyst support technique is that the coating poses very little added resistance to fluid flow and therefore, minimal additional pressure loss. Packed-bed reactors, on the other hand, depending on particle size and void fraction, may impose substantial pressure loss for the required conversion efficiency.

It should be noted that additional heat transfer enhancement can be achieved if the fuel passages are of a fin-plate construction, and subsequently coated after fabrication. In this arrangement, heat flows from the hot absorption surface to the larger heat rejection surface by conduction within the metallic fins which are coated with catalyst. With a tight packing of fins, and use of staggered or interrupted fins to increase turbulence and enhance heat transfer, the effective thermal resistance from the hot source into the fuel may be significantly reduced.

**Coating Application.** The effective implementation of a coated-wall configuration requires a method for providing a very thin catalyst coating directly on the wall of the surface to be
coated-wall reactor tubes are generally small diameter (<0.10 in.) are prepared with the coating process described earlier. Since the packed-bed and coated-wall, and heat input. Coated-wall reactors apparatus, differing in both methods of catalyst support, i.e., used in the preheater to promote heat transfer, were examined while minimizing thermal cracking reactions. (Alumina spheres, temperature to 700-750 F in a preheater to reduce reactor length displacement pump. The fuel is then heated above its critical pressure through a positive-nitrogen to reduce the amount of dissolved oxygen, then metered into the system at supercritical pressure through a positive-displacement pump. The fuel is then heated above its critical temperature to 700-750 F in a preheater to reduce reactor length while minimizing thermal cracking reactions. (Alumina spheres, used in the preheater to promote heat transfer, were examined periodically and did not show signs of significant coke deposit.)

Several reactor configurations have been tested in this apparatus, differing in both methods of catalyst support. i.e., packed-bed and coated-wall, and heat input. Coated-wall reactors are prepared with the coating process described earlier. Since the coated-wall reactor tubes are generally small diameter (<0.10 in.) to simulate practical heat exchanger reactor passages, only tube outer wall temperature measurements are made along the reactor; fuel temperatures are measured at the reactor inlet and exit.

Two different methods of heat input to the reactor have been used, viz., resistive heating (shown in Fig. 3) and constant surface temperature. Resistive heating, that is, heating by an electric current, has the characteristic that the heat transfer rate is nearly uniform for a given tube cross-sectional area along the length of the reactor and the fuel and wall temperatures vary from inlet to exit. Furthermore, this mode of heating allows a direct measurement of the endotherm through a calculated energy balance. (The technique for endotherm calculation is described below.) However, aircraft-application heat exchangers are more nearly constant temperature and have substantial lengths at elevated temperatures.

### BENCH-SCALE TESTING

Tests were designed to allow screening of fuel/catalyst combinations through measurement of endotherm of reaction, extent of conversion, and identification of reaction products. Parametric studies of reactor geometry configurations were conducted to provide a design data base and the basis for validation and upgrading of analytical models. This section comprises descriptions of the bench-scale apparatus flow path and analysis procedures, and representative test results.

#### Bench-Scale Test Apparatus

The high-pressure bench-scale endothermic fuel test apparatus is shown schematically in Fig. 3. Fuel is first sparged with nitrogen to reduce the amount of dissolved oxygen, then metered into the system at supercritical pressure through a positive-displacement pump. The fuel is then heated above its critical temperature to 700-750 F in a preheater to reduce reactor length while minimizing thermal cracking reactions. (Alumina spheres, used in the preheater to promote heat transfer, were examined periodically and did not show signs of significant coke deposit.)

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A technique for providing a more uniform temperature distribution is clapping the reactor tube between isothermal copper blocks which are maintained at a desired temperature by heating strips. This mode of heating provides greatest surface temperature uniformity, however, since heat transfer rate from the block to the tube is not readily measurable, the endotherm cannot be directly calculated. In a constant-temperature reactor, a measure of the endotherm can be determined only through thermochemical calculations based on product analysis and measurement of the extent of conversion. The actual temperature distributions characteristic of individual reactor configurations are shown in Fig. 4.

#### Analysis Procedures

For resistively heated reactor tubes, the endotherm can be computed by analyzing an energy balance on the control volume depicted in Fig. 3. The power input, \( Q_{\text{in}} \), 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, $Q_{\text{env}}$, is accounted for through calibration without fuel flow prior to a given test (The reactor is well insulated to minimize this loss). The remaining energy input, i.e., that supplied to the fuel, can be further divided into that which results in raising the temperature of the fuel/products (sensible heating, $Q_{\text{sens}}$) and that which is absorbed in the reaction (endotherm, $Q_{\text{endo}}$). The sensible heating is determined by temperature measurements at the reactor inlet and exit, the fuel mass flow rate and output from the NIST computer program SUPERTRAPP (Ely and Huber, 1990) which provides the physical and thermodynamic properties of hydrocarbon mixtures as a function of composition, pressure and temperature. The net endotherm can then be computed as

$$Q_{\text{endo}} = Q_{\text{in}} - Q_{\text{sens}} - Q_{\text{env}}$$

Endotherm can also be computed from the extent of conversion and the product composition. (In the case of the constant-temperature reactor, this is the only available measure of endotherm.) Product chemical analyses were performed using a cryocooled Hewlett Packard Gas Chromatograph/Mass Spectrometer(GC/MS) system with a DB-1 megabore column. To enhance the ability to quantify low-molecular-weight species, gaseous product analysis was also performed with a thermal conductivity detector coupled with a packed column. The product chemical composition analysis allows assessment of the catalyst selectivity to be made and is used to compute the heat of reaction and thereby provide an independent measure of the endotherm.

**Test Results**

A broad range of fuels and catalysts has been tested, including simple, single-component fuels (e.g., MCH, n-heptane), and fuel blends (e.g., Norpar 12) (Spadaccini et al., 1993a and 1993b). Tests have been conducted primarily with zeolite catalysts; however, a limited number of tests have been performed without catalysts (to explore pure thermal decomposition), and with precious metal catalysts. Testing has been conducted with both packed-bed and coated-tube reactors at operating conditions that simulate those of a single passage in a practical plate-fin catalytic heat exchanger/reactor.

Early tests were conducted with the $n$-heptane using zeolite catalysts in packed-bed reactors. These tests were conducted at Liquid Hourly Space Velocities (LHSV) of up to 700 hr$^{-1}$ and pressures up to 50 atm. (LHSV is defined as the volumetric flow rate of the fuel in its liquid state divided by the volume of the reactor, and has units of hr$^{-1}$.) The results indicated very high conversion, approaching 100 percent at 1300°F (see Fig. 5), with a corresponding maximum endotherm of approximately 850 Btu/lb. The products of reaction were primarily light unsaturated hydrocarbons and no significant aromatic compounds were detected.

To explore the potential for more compact and efficient reactors, tests were also conducted with coated-foil reactors. In these tests, the catalyst pellets were replaced with a corrugated foil having a thin catalytic coating. The results of these tests compared favorably with those of the packed bed and provided the basis for coated-wall testing.

The positive results achieved with the $n$-heptane led to more extensive testing with Norpar 12, a fuel blend simulative of current jet fuels. The total heat sink determined for Norpar 12 is shown in Fig. 6, corresponding to a series of bench-scale tests covering a broad range of operating conditions for both packed-bed and coated-tube reactors. It comprises the sensible heating, manifested in an increase in temperature, and the energy that can be absorbed in reforming the fuel, i.e., the endotherm. As a point

![Figure 5. Decomposition of n-Heptane on Zeolite Catalysts](http://mechanicaldesign.asmedigitalcollection.asme.org/GT/proceedings-pdf/GT1995/78804/V003T06A041/2406244/v003t06a041-95-gt-226.pdf)
of reference, the heat sink associated with conversion of the Norpar 12 to an equilibrium composition of the products indicated is also shown. The variance between the equilibrium calculation and data can be attributed to kinetics and differences in reaction products. The correspondence between the results achievable between the packed bed and coated-tube tests indicates that, in light of the advantages of the coated tube support structure described earlier, the coated passage is clearly a preferable catalyst support technique for applications where size and weight are important.

In the following discussion, salient features of the endothermic fuels decomposition process are described using the results of Norpar 12 on zeolite catalysts in coated-tube reactors. The cooling capability is presented in terms of the endotherm (i.e., the heat absorbed in the cracking reaction) rather than the total heat sink to isolate the chemical reforming aspect of the process.

**Thermal and Catalytic Cracking.** Cracking of hydrocarbon fuels is known to occur at high temperatures even in the absence of catalyst. The effectiveness of the catalyst in the conversion of the fuel to desirable products, however, is evident in the product analysis shown in Fig. 7. This figure represents the mass spectrometer results showing the product distribution for Norpar 12 conversion with SAPO-5 zeolite catalyst compared to that without catalyst. Both of these tests were performed at approximately 325 psia, a space velocity of 1130/hr and a fuel exit temperature of approximately 1200 F. In the absence of the catalyst, the products represent the result of thermal cracking yielding high-molecular-weight species that are primarily saturated, corresponding to a low endotherm. With the zeolite catalyst, the products are substantially lower in molecular weight and are primarily unsaturated making them more desirable both from the point of view of high endotherm and favorable combustion characteristics. It was also found that the maximum temperature at which the reactor could be operated was substantially lower in the absence of catalyst due to the propensity for coking. It is concluded that any practical system will benefit from a catalytic surface to achieve adequate endotherm and produce desirable reaction products.

**Catalytic Cracking of Norpar 12.** Representative results in terms of extent of conversion and measured endotherms are presented in Fig. 8 for the catalytic cracking of Norpar 12. In this figure, results are presented for the conversion of Norpar 12 on zeolite catalysts for two of the different coated-tube reactor configurations shown in Fig. 4. The difference in the extent of conversion and endotherm between the two configurations is
attributable to the increased length of the dual-thickness tube that is at high temperature.

The product distribution for the operating condition indicated on Fig. 8 is presented in Table 2. Based on this product distribution, the measured extent of conversion and the known composition of unreacted Norpar 12, a thermodynamic calculation was performed to compute the endotherm for comparison to the measured value. The calculated value is 465 Btu/lbm, comparing favorably with the measured value of 489 Btu/lbm. Also, the hydrogen-to-carbon atom ratio for the products (H/C=2.23) compares favorably with that of the unreacted Norpar 12 (H/C=2.18), confirming the product analysis.

Space Velocity Effects. During the course of this investigation, tests were run at flow rates ranging from 500 to 1200 ml/hr. A commonly used measure of throughput is the liquid hourly space velocity. (For example, a 1-gal reactor operating at a LHSV of 1000 hr⁻¹ would process a fuel flow rate of 1000 gal/hr.) It is used for scaling reactor size for a well-characterized configuration, but does not represent the reactor physics (as would, for example, the Reynolds number) and should therefore not be used for performance estimation. For example, a coated-tube reactor element 12-in. long with an inner diameter of 0.050 in. would have the same LHSV at a given flow rate as a 3/4-in. ID tube that is 1-in. long. Clearly, the performance of the two reactors would be substantially different. For a given reactor, however, the LHSV is a measure of flow rate, or conversely, residence time. Figure 9 shows the effect of LHSV, or flow rate, on measured endotherm. For both of the tests shown, the fuel pressure was 350 psi, therefore, the residence time of the fuel vapor varies inversely with LHSV. As expected, the measured endotherm decreased with increasing LHSV (increasing flow rate, decreasing residence time). The magnitude of the space velocity that is required is application dependent and must be based on a detailed thermal management analysis, which has not been performed in this investigation. The values shown, however, are of the order believed to be required for high-speed aircraft applications.

Long-Duration Tests. A typical operating condition (viz., T_{wall}=1300 F, LHSV=1000 hr⁻¹, 0.058-in. zeolite-coated tube), was selected and maintained to permit examination of the performance of the reactor over an extended period of time. For the first 15 hours of operation, there was relatively little change in endotherm; however, the pressure began to rise slowly. The fuel flow was stopped and it was determined that deposits were building downstream of the reactor where temperature decreases below 700 F at the entrance to the water-cooled condenser. Apparently, heavy molecular weight species were condensing and forming carbon deposits in the liquid phase. This would not occur in an actual reactor since the reforming products would not be cooled before they were injected into the combustion chamber. After removing the carbon buildup downstream of the reactor, the fuel flow was restarted and the test continued. This process was repeated several times and was terminated after a cumulative run time of 60 hours had been achieved. In that time, no significant change in reactor performance or degradation of the catalyst was observed.
CONCLUSIONS

High endotherms and attractive reaction products have been achieved through the endothermic cracking of storable liquid hydrocarbon fuels using inexpensive zeolite catalysts. These results provide the basis for the continued development of high-heat-sink thermal-management systems which enable high-speed flight with practical fuels. The following specific conclusions can be drawn from the results of this study:

- High heat sinks can be realized by catalytic cracking of paraffins, including fuel blends simulative of current jet fuels.
- Efficient endothermic reactions can be achieved at high throughputs and elevated pressures using inexpensive zeolite catalysts. Substantial catalyst lifetime has been demonstrated.
- Catalyst-coated surfaces, which are essential to the practical implementation of endothermic fuels in flight-weight heat exchangers, are effective in reforming fuels at operating conditions consistent with aircraft applications.
- Catalytic cracking can be carried out with good product selectivity, providing a fuel that should have excellent combustion characteristics.

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