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Additives to Improve Fuel Heat Sink Capacity in Air/Fuel Heat Exchangers

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Hypersonic air-breathing vehicles travel at high speeds and generate heat loads that are greater than can be met from sensible heating of the fuel. However, the fuel can provide about 50% more heat sink capacity if it undergoes endothermic thermal cracking reactions before combustion. Unfortunately, thermal cracking reactions require high temperatures, in excess of 1100°F, to obtain useful reaction rates. However, a fuel additive has been identified that increases the rate of thermal cracking reactions, allowing the same chemical endotherm to be obtained at lower fuel temperatures. This paper describes work in which we conducted extensive laboratory bench-scale calorimetric tests to directly measure the effectiveness of the cracking initiator compound with several prospective fuels, including JP-7 and normal decane. We then used the data obtained from the laboratory experiments to generate rate models, which we then used in the design of a pilot scale fuel/air heat exchanger. Finally, we tested the pilot scale unit at heat fluxes approaching 100, 000 $\mathrm{Btu/ft^2 \cdot h}$ with JP-7 and *n*-decane with and without the initiator. At each test point, the data clearly indicated that the initiator produced significant increases in the rate of cracking and fuel heat sink capacity.

I. Introduction

IMPROVING commercial access to space will require substantial reductions in the cost of reaching low Earth orbit. Studies have suggested that the cost must be reduced from the value of 10, 000/lb to about 1000/lb to have a measurable effect [1]. In addition, these studies have concluded that significant reductions in cost likely will require the development of reusable launch vehicles, and these vehicles will need to use air-breathing propulsion modes such as the rocket-based combined cycle (RBCC). In an RBCC system, the propulsion is divided into four phases depending on the speed and altitude of the vehicle [2]. In the first phase, from liftoff and low speed to Mach 2.5, power is provided by a combination of the rocket and ramjet engines. As the vehicle gains speed and the ramjet cycle becomes more effective, the rocket thrust is reduced. When the vehicle reaches the second phase, at about Mach 2.5, the rocket is shut down and thrust is provided by the ramjet engine alone. By the time the vehicle reaches Mach 5, the high duct pressure and cooling needs require that the engine make a transition into supersonic combustion, or scramjet mode, which is the third phase of the launch progression. Finally, at Mach 10, where supersonic combustion is not effective, the vehicle makes the transition to pure rocket power for entrance into orbit.

Previous work has indicated that air-breathing vehicles traveling at high speeds need to use the fuel to meet the high heat loads generated [3]. Moreover, the fuel heat sink requirement is a strong function of Mach number, increasing from about 800 Btu/lbm at Mach 4 up to about 2000 Btu/lbm at Mach 10. However, the maximum heat sink that can be obtained from the sensible heating of most hydrocarbon fuels from ambient to about 1025°F is approximately 800 Btu/lbm. Thus, additional fuel heat sink capacity is needed for air-breathing vehicles that travel at speeds greater than Mach 4, including those in the third stage of the aforementioned RBCC system. Fortunately, the fuel heat sink capacity can be improved substantially if it undergoes an endothermic chemical reaction before being combusted.

The use of endothermic reactions to augment fuel heat sink capacity is an area that has been well studied previously [3–7]. Some endothermic reactions require solid catalysts to achieve the necessary rates and product distributions, whereas other reactions may occur in the gas phase without catalytic assistance. For example, the dehydrogenation of methyl cyclohexane (MCH) to hydrogen and toluene, which has a chemical endotherm of +930 Btu/lbm, requires a catalyst consisting of platinum or palladium dispersed on a high surface area support [4]. In tests of a catalytically coated heat exchanger with fuel flows of up to 0.81 lb/ min, 78.5% of the MCH flow was converted to products when the fuel temperature was 1060°F. In addition, the total heat sink capacity (including sensible heating) at this temperature was found to be about 1500 Btu/lbm.

Unfortunately, there are two problems with using MCH as an endothermic fuel. First, heterogeneous catalysts are composed primarily of high surface area materials such as alumina or silica, which have low thermal conductivities. Therefore, catalyst layers coated on the heat exchanger surface will increase the resistance to heat transfer and reduce the unit's efficiency. In addition, catalysts can become less active as they are used, potentially slowing the rate of the endothermic reaction and thereby reducing the effective fuel heat sink capacity. Deactivation can be caused by coke deposition on the catalyst surface or from attrition as the catalyst becomes detached from the walls of the heat exchanger. Unfortunately, reducing the effective fuel heat sink capacity by either of these mechanisms could have serious consequences on the vehicle. Second, MCH is a specialty chemical and is not currently used as an aircraft fuel. Thus, to employ MCH on a widespread basis, separate fuel distribution and storage systems would have to be constructed.

A more desirable solution would be to identify an endothermic process that existing jet fuels, such as JP-7 or JP-8, could undergo. One such reaction is cracking, where C_{12}, C_{13}, and C_{14} paraffins, which comprise a high percentage of typical jet fuels, are cracked into mixtures of lower molecular weight olefins and paraffins. In this case, product distributions containing higher concentrations of

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olefins produce larger endotherms. However, the paraffins typically found in fuel are rather stable, and therefore the reaction either requires a catalyst or high temperatures to occur at a useful rate. In recent work, zeolite catalysts were reported to increase the cracking rates for normal paraffin fuels such as *n*-heptane and Norpar-12 [5]. In tests with thin layers of catalyst coated on the inside of an electrically heated tube, conversions of over 80% were obtained at temperatures of approximately 1200°F. In addition, the product distribution included high concentrations of low molecular weight compounds such as methane, ethane, and ethylene. Finally, chemical endotherms of over 600 Btu/lbm were reported. However, as pointed out, coating a catalyst on the surface of a heat exchanger reduces its efficiency; in addition, when catalysts are employed, deactivation is a constant concern.

However, at high temperatures (about 1100°F), cracking can also occur in the gas phase without a catalyst. This reaction is referred to as thermal cracking. Unfortunately, high temperatures are undesirable because they reduce the allowable stress in the heat exchanger materials, requiring increased wall thickness to avoid mechanical failure. In addition, high temperatures also reduce the efficiency of the unit. In recent work, however, an additive has been identified that, when added to model fuels consisting of single component normal paraffins, increased the rate of thermal cracking, thus reducing the required operating temperature of the heat exchanger [6,7]. Perhaps more important, the additive eliminates the complications and risks associated with the use of a heterogeneous catalyst.

Thermal cracking is a free radical reaction that occurs in the gas phase. A detailed discussion of the thermal cracking process, along with an explanation of how the additive functions, has been presented previously [7,8]. Briefly, the additive generates reactive free radicals at temperatures lower than those that are required to produce radicals from fuel molecules. Because radical generation is the slow step in thermal cracking processes, the addition of the initiator produces a substantial increase in the rate of the endothermic cracking reaction. The most effective additive identified in the previous work consists of carbon, hydrogen, and oxygen; is stable under ambient conditions; is not highly toxic; and did not add significantly to the cost of the fuel [7,8]. Although the previous studies were encouraging, they were done with single component “model” fuels, such as *n*-heptane, instead of real aviation fuels, which are mixtures of hydrocarbons. In addition, calculations of cracking rates were based on gas chromatograph (GC) analyses and not direct calorimetric measurements of the fuel heat sink capacity.

Thus, the goal of this work was to measure the effect of the additive on the fuel heat sink capacity of a real hydrocarbon fuel, such as JP-7. To characterize the heat sink capacities of complex mixtures such as JP-7, a test section was constructed that made direct measurements of power to calculate fuel heat sink capacity instead of relying on GC analyses of the product stream. Kinetic models for both initiated and uninitiated cracking of JP-7 and *n*-decane were then developed. Finally, a pilot scale heat exchanger was constructed and tests were carried out with the unit to demonstrate the effect of the initiator in a fuel/air heat exchanger under realistic operating conditions with both initiated and uninitiated fuel.

II. Experimental Procedures

A. Laboratory-Scale Apparatus

A fully automated test apparatus was used for the laboratory-scale measurements. The hydrocarbon feed was introduced at the desired pressure and flow rate with one or two high-pressure liquid chromatography pumps (ISCO 2350). One pump was used to deliver the primary fuel flow, whereas a second pump was used to deliver the initiator at the desired concentration. After the two streams were combined, the fuel flow passed through a 10-ft-length of tube wrapped with heat tape to preheat the fuel to 752°F (400°C), then entered the test section. The flow exiting the reactor was combined with a flow of ambient temperature nitrogen, quenching the fuel cracking reaction and reducing the coke deposition in the lines downstream of the test section. After passing through the test section pressure control valve, a small portion of the process flow was split off and directed into a gas chromatograph (SRI 8610) equipped with a thermal conductivity detector and a 3-ft-length of a 1/8-in. outer diameter (OD) column packed with silica gel (provided by SRI).

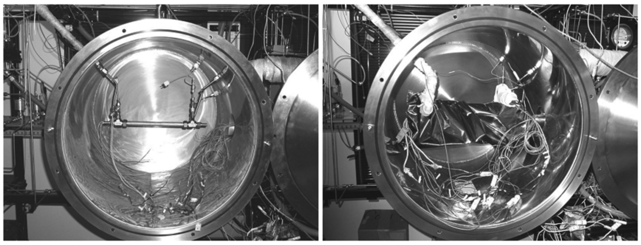

Fig. 1 Photograph of the calorimetry test section installed in the vacuum chamber.

JP-7 was obtained from Wright Patterson Air Force Base (batch no. POSF 3327), whereas *n*-heptane, *n*-decane, cyclohexane, and 2-2-4-trimethyl pentane (isooctane) were obtained from Chevron Phillips Chemical Co., Woodlands, Texas. Finally, Norpar-12, made by Exxon-Mobil, was purchased from a local distributor, Univar USA.

The test section consisted of an annular flow path, 0.005-in in height, formed by inserting a 1/2-in. OD custom-made 500 W cartridge heater (Chromalux) inside a 3/4-in.-in OD × 0.120 in. wall stainless steel tube. The small annular dimension allowed us to achieve a relatively small radial temperature gradient from the wall of the heater outward. Thermocouples were located in the fuel flow paths at the reactor inlet and exit to measure the change in fuel temperature, resulting from the application of test section heater power. In all tests, a preheater was used to maintain a fuel temperature of 752°F (400°C) at the reactor inlet, whereas the internal cartridge heater in the test section provided the power to raise the fuel temperature to the desired value at the reactor exit. The power required by the cartridge heater to achieve the desired temperature increase was used along with the fuel flow rate to calculate fuel heat sink capacity.

During the heat sink measurements, the test section was installed in a vacuum chamber evacuated to about 25 mtorr to reduce convective heat losses. Photographs of the reactor installed in the vacuum chamber are shown in Fig. 1. The photograph on the left shows the test section before an outer insulation layer was added. The photo on the right shows the test section after it was wrapped with several layers of aluminized mylar (Spectrum Astro) to minimize radiative losses.

The method used to measure power has been described in detail previously [6]. Briefly, a high-speed oscilloscope simultaneously records the current and voltage drop through the heater at a rate of 1000 Hz. A high sample rate was required because the heater was powered by ac current, and a proportional controller, which varied the percentage of time that full power was applied to the heater, was used to control the heater.

One issue that complicates cracking experiments is the formation of coke inside the test section. In previous testing, we have found that we could prevent the formation of filamentous coke on iron- and nickel-based materials with the addition of low concentrations of selenium [9]. Thus, 10 ppm selenium in the form of diphenyl selenide was added to all fuels before testing. Tests were also conducted to show that the addition of this coke mitigation additive had no measurable effect upon the rate of endothermic cracking reactions [10].

B. Experimental Procedures

To carry out the laboratory measurements, fuel was first flowed through the reactor a rate of 1000 cm^3 of liquid fuel per cm^3 of reactor per hour, which is equivalent to a liquid hourly space velocity (LHSV) of 1000 h^{-1}. The system pressure was then increased to 550 psig, which is representative of that expected on board a vehicle, and the preheater power output was adjusted so that a temperature of 752°F (400°C) was obtained at the reactor inlet. We preheated the fuel to minimize the power required in the test section; at 752°F, none of the fuel components undergo thermal cracking and so preheating does not affect the heat sink measurements. The power in the main heater was then adjusted so that the fuel temperature increased to 887°F (475°C) as it exited the reactor. After the system temperatures stabilized, the main heater power was measured over a period of 8 min to obtain a baseline measurement of the fuel heat sink capacity. At this point, the injection of the chemical initiator was started, and the fuel flow rate was reduced to maintain an overall constant mass flow. Typically, the increased level of cracking experienced when the initiator was injected caused the temperature at the reactor exit to drop, which in turn required the control system to increase heater power to bring the exit temperature back to its original set point. After steady-state conditions were achieved, the heater power was again monitored for 8 min to obtain a direct measure of the effect of the chemical initiator. When the initiated power measurement was complete, the initiator flow was stopped and the test section temperature was increased to the next set point, where the process was repeated. At each test point, the fuel inlet and outlet temperatures, the heater powers, and the fuel flow rates were used to calculate the fuel heat sink capacity. In addition, in tests with the single component fuels, the cracking data obtained from the GC, along with the Peng–Robinson thermodynamic properties, were used to calculate a theoretical heat sink capacity. The theoretical and measured heat sink capacities generally agreed to within 10% of each other.

To estimate the amount of power that was lost to the surroundings, cyclohexane was run through the test section (without the initiator) at temperatures up to 1112°F (600°C) and GC measurements were used to monitor how much cracking had occurred at each condition. Cyclohexane is very resistant to thermal cracking, and less-than-detectable levels of cracking products were observed at temperatures up to 1067°F (575°C) and only minimal levels at 1112°F. Thus, for temperatures through 1067°F, the external heat losses at each temperature were simply the difference between the measured power output and the power required to satisfy the sensible heating requirements. At 1112°F, the additional endotherm from the small level of cracking that occurred was added to the power required for sensible heating; this total was subtracted from the total measured power to estimate losses. Typically, the external heat losses were about 20–25% of the total input power when the test section was installed in the vacuum chamber under vacuum and enclosed by the radiation shield.

III. Results of Laboratory-Scale Testing

A. Results of Tests with *n*-Decane at 550 psig and SV = 1000 h^{-1}

The results obtained with a model fuel, *n*-decane, are shown in Fig. 2. This figure shows the heat sink capacity for the fuel from 77°F to the measured temperature under three different conditions: from sensible heating only (calculated with NIST Supertrapp), where no cracking occurs (open squares); the measured heat sink capacity with no initiator (filled squares); and finally the measured heat sink capacity with the initiator (open circles). At temperatures up to 975°F, very little thermal cracking occurs without the initiator, as evidenced by heat sink capacities that fall very close to the values calculated for sensible heating. However, above this temperature, the measured heat sink lies significantly above the sensible heating line. At 1067°F, the measured value is 851 Btu/lbm, or 71 Btu/lbm greater than the sensible heating value of 780 Btu/lbm. At 1112°F, the measured heat sink is 953 Btu/lbm, 134 Btu/lbm greater than the sensible heating value of 819 Btu/lbm. These results show that thermal cracking reactions are adding a substantial amount to the overall heat sink capacity of *n*-decane.

Figure 2 also shows that the addition of the initiator can produce even larger increases in heat sink capacity at all temperatures, though the effect of the initiator is more pronounced at the higher temperatures. At 1022°F, for example, the initiator increases the heat sink capacity from 766 to 849 Btu/lbm, a gain of 83 Btu/lbm, whereas at 1067°F, the initiator produces an increase of 104 Btu/lbm (from 851 to 955 Btu/lbm). Finally, at 1112°F, where substantial cracking is occurring without the initiator, the initiator still causes a significant improvement. A heat sink capacity of 953 Btu/lbm was measured without the initiator, whereas a value of 1055 Btu/lbm was obtained with the initiator. In addition, the value of 1055 Btu/lbm represents an increase of 28% (236 Btu/lbm) over the heat sink of 819 Btu/lbm available from sensible heating only.

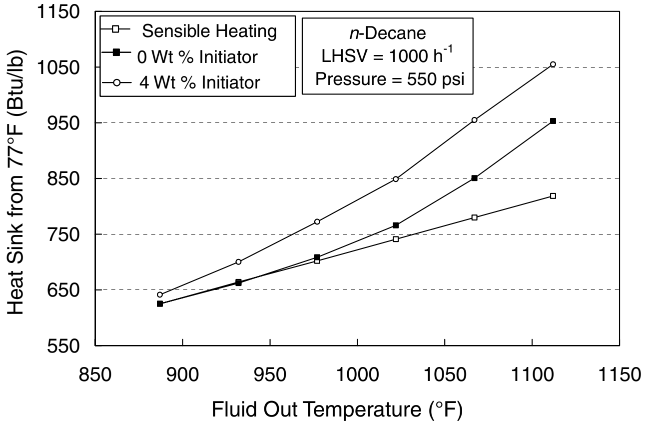

Fig. 2 Heat sink capacity of *n*-decane measured at a space velocity of 1000 h^{-1}.

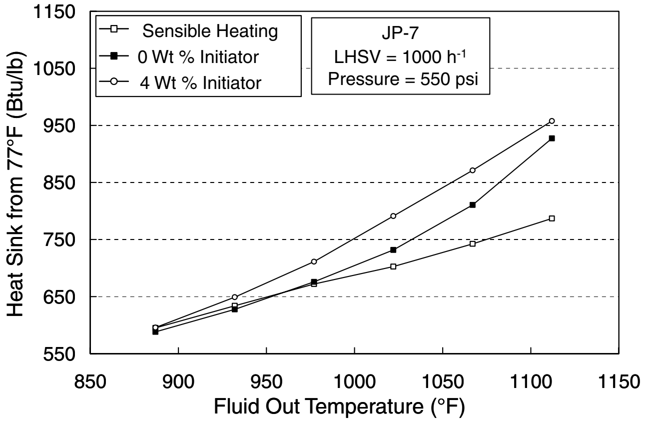

Fig. 3 JP-7 heat sink capacity measured at a space velocity of 1000 h^{-1}.

B. Results of Tests with JP-7

Heat sink measurements were also carried out on JP-7, which is a potentially attractive fuel because of its thermal stability. It consists of paraffins (65%) and cycloparaffins or naphthenes (32%) and has a low concentration of aromatics (3%). The fuel has an average molecular formula of $C_{12}H_{25}$, and a molecular weight of 169 g/mol [11].

The results of heat sink measurements made at fluid out temperatures ranging from 887°F to 1112°F with initiator concentrations of 0 and 4 wt % are presented in Fig. 3. In addition, the figure includes the calculated heat sink capacity available only from sensible heating of the fuel. At temperatures up to 975°F, the measured heat sink capacities without the initiator are all very close to the calculated values from sensible heating only.

These results show that under these conditions without the initiator, the individual hydrocarbon components of JP-7 are not undergoing endothermic cracking reactions. At higher temperatures, Fig. 3 shows that the measured heat sink capacities without the initiator are all greater than the calculated sensible heating values, indicating that endothermic thermal cracking reactions are occurring. At 1067°F, the measured heat sink without the initiator is 811 Btu/lbm, which is 69 Btu/lbm higher than the value of 742 Btu/lbm from sensible heating only. At 1112°F the measured value of 927 Btu/lbm is 140 Btu/lbm higher than the value

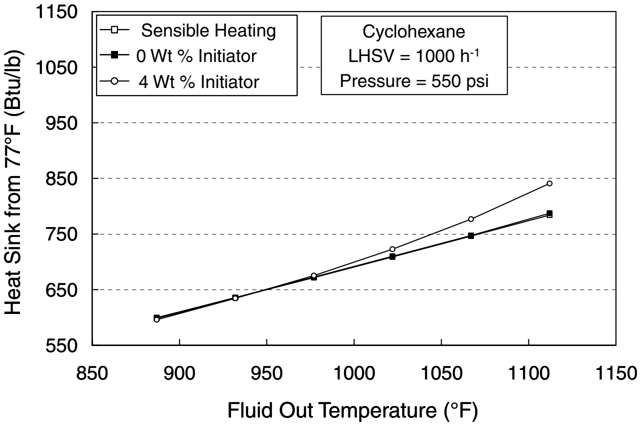

Fig. 4 Heat sink capacity of cyclohexane; sensible heating only, measured without the initiator and measured with the initiator.

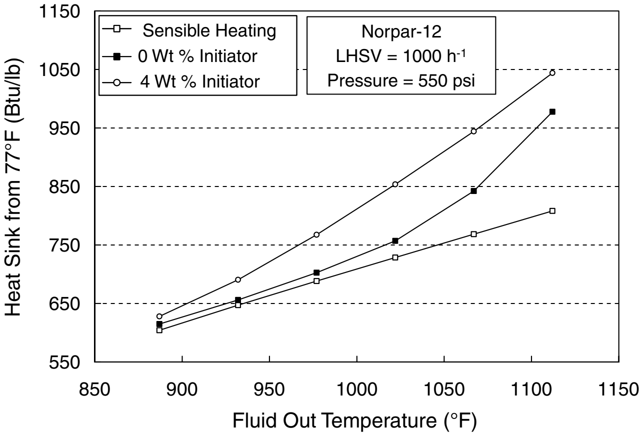

Fig. 5 Heat sink capacity measurements with Norpar-12.

available from sensible heating. Finally, Fig. 3 shows that the addition of the initiator produces significant increases in heat sink capacity over those measured when no initiator is present. For example, at 1022°F, the addition of initiator increases the heat sink from 732 to 791 Btu/lbm and, at 1067°F, the increase is from 811 to 871 Btu/lbm. Finally, at the highest temperature, 1112°F, the initiator had a less significant effect on the heat sink capacity. Without the initiator, the fuel heat sink capacity is 927 Btu/lbm; on the other hand, with the initiator, the heat sink is 958 Btu/lbm. However, the latter value is still 172 Btu/lbm higher than the heat sink from sensible heating only.

Comparison of the maximum heat sink capacities from *n*-decane to JP-7 shows that the values available from the single component normal paraffin exceed those of JP-7. For example, with the initiator, the maximum heat sink capacities for *n*-decane were 955 and 1055 Btu/lbm at 1067 and 1112°F, respectively, (Fig. 2). On the other hand, for JP-7, the values with the initiator at these temperatures were 871 and 958 Btu/lbm, about 100 Btu/lbm lower than those obtained with *n*-decane.

C. Results of Tests with Cyclohexane

The results obtained for cyclohexane at LHSV = 1000 h^{-1} are shown in Fig. 4. This figure shows heat sinks from 77°F for three cases: sensible heating only, measured heat sink with no initiator, and the measured heat sinks when 4 wt % initiator was added to the fuel. The figure shows that, without the initiator, the measured heat sink is very near (within 1 Btu/lbm) the values obtained from pure sensible heating of the fuel up to about 1075°F. This indicates that this compound undergoes very little thermal cracking at these temperatures, an observation that was confirmed with GC analyses. Even at 1112°F, the measured heat sink of 787 Btu/lbm is only 3 Btu/lbm greater than the quantity for sensible heating alone. These results indicate that very little cracking occurs with cyclohexane under these conditions when the initiator is not present in the fuel. This demonstrates why this material is an excellent compound to use to calculate energy losses in the test section.

Finally, Fig. 4 shows the measured heat sink capacities when 4 wt % initiator is added to the fuel flow. Beginning at 1022°F, the addition of the initiator increases the heat sink capacity from 710 to 723 Btu/lbm. Additionally, at the higher temperatures, the figure shows that improvements in heat sink capacity continued to increase. At 1067°F, the initiator increased the heat sink from 746 to 777 Btu/lbm, whereas at 1112°F, its addition improved the fuel heat sink from 787 to 841 Btu/lbm, or by 7%.

D. Results of Tests with Norpar-12

Previous results have shown that the heat sink capacity for *n*-decane is greater than that of JP-7, which contains compounds that are naturally more resistant to thermal cracking reactions. Unfortunately, single component fuels such as *n*-decane are much more expensive than mixtures. Some selected mixtures of normal paraffins are available at a relatively low cost, however, and therefore tests were conducted with Norpar-12. Norpar-12 is a mixture of normal paraffins centered around C_{12} and consists of approximately 50% $C_{12}H_{26}$, along with 25% each of $C_{11}H_{24}$ and $C_{13}H_{28}$. It is available from Exxon-Mobil at a cost of about 4.41/gal or 0.70/lb (2003 prices) when purchased in 54 gal drums quantities, which is significantly lower than the cost of pure *n*-decane.

The results of these tests are shown in Fig. 5. The figure shows that, without the initiator, the heat sink capacities are similar to the sensible heating values at the lower temperatures, up to 975°F, indicating that there is relatively little cracking that is occurring at these temperatures. Beginning at 1022°F, however, the measured heat sink capacity begins to increase rapidly, reaching a value of 978 Btu/lbm at 1112°F, which is 170 Btu/lbm greater than the value of 808 Btu/lbm from sensible heating of the compound.

As shown in Fig. 5, the initiator produces measurable increases in heat sink capacity at all temperatures. For example, at 1022°F, the initiator increases the measured heat sink from 757 Btu/lbm to 854 Btu/lbm and, at 1067°F, the initiator improves the heat sink from 842 to 944 Btu/lbm, or by 102 Btu/lbm. Finally, at 1112°F, the initiator increases the heat sink capacity from 978 to 1044 Btu/lbm. The latter value is just below 1054 Btu/lbm, which was measured for *n*-decane at this temperature. This is the highest heat sink capacity that was obtained for any of the compounds tested in this study.

E. Results of Tests with a Fuel Blend

We also conducted a test with a mixture of equal parts *n*-decane, 2,2,4-trimethylpentane (isooctane), and cyclohexane. These components are representative of those contained in a jet fuel such as JP-7 [11]. In Fig. 6, we show the results obtained with the mixture, along with values calculated for the mixture from the data obtained with the individual components. The maximum heat sink capacity obtained with this mixture is about 900 Btu/lbm at 1112°F when the initiator is present. This value is about 150 Btu/lbm lower than the highest heat sinks measured with either *n*-decane or Norpar-12, and it is also about 50 Btu/lbm lower than the maximum value we obtained with JP-7.

Figure 6 also shows that the calculated and measured heat sink capacities for both uninitiated and initiated cracking are within about 10 Btu/lbm. At 1067°F, without the initiator, the calculated heat sink capacity was 791 Btu/lbm, whereas the measured value was 781 Btu/lbm, a difference of 10 Btu/lbm. At all other conditions the differences between the calculated and measured values are less than this value. Thus, we conclude that the error in the heat sink capacity measurements presented in this study is less than 10 Btu/lbm.

F. Summary of Laboratory-Scale Testing

In summary, the laboratory-scale results have shown that thermal cracking reactions can provide significant increases in heat sink

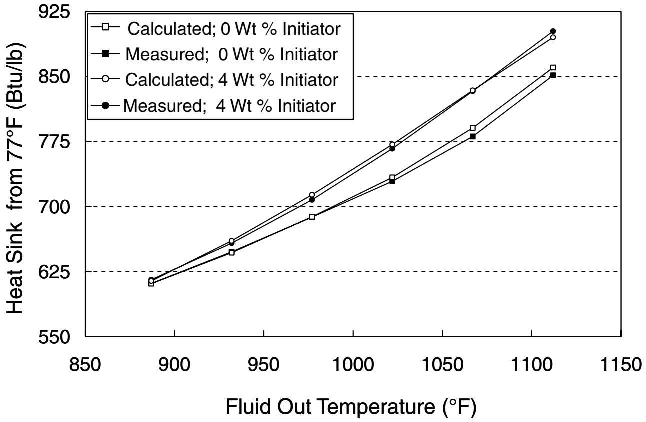

Fig. 6 Calculated and measured heat sink capacity values with a fuel blend.

capacity over those available from sensible heating, and that the addition of the chemical initiator can produce further improvements. In addition, the data show that higher heat sink capacities can be obtained from normal paraffins such as Norpar-12 and n-decane than from JP-7 or cyclohexane.

IV. Kinetic Rate Expressions

After conducting the laboratory measurements of cracking rates, the data were used to generate rate expressions for n-decane and JP-7 cracking with and without the initiator. A general form of a first order rate expression is shown as

$$\text{rate} = \nu^* \exp(-E_a/RT)^* P_{\text{fuel}} \tag{1}$$

where ν is the preexponential factor in units of moles fuel $\text{s}^{-1} \cdot \text{atm}^{-1}$, E_a is the activation energy of the cracking reaction, R is the gas constant, T is the reaction temperature in K, and P_{fuel} is the partial pressure of the fuel. Once we have solved for ν and E_a, the rate expressions can be used to calculate the conversion of each compound as it proceeds through the pilot scale heat exchanger.

To solve for these variables, a kinetic model of the laboratory-scale reactor was generated and the rate parameters that best fit the laboratory data were identified. Analyses for JP-7 and n-decane with and without the initiator were conducted. To model the reactor, the fluid compositions that would be generated as a function of cracking level were calculated based on product distributions that have been measured previously for n-dodecane. Supertrapp was then used to calculate transport properties as a function of cracking level and temperature assuming a constant pressure of 550 psig. With these properties, it was possible to calculate residence time, overall heat transfer coefficient, temperature change, and finally cracking rate as a function of length down the reactor as the fuel temperature increased to 1100°F. In all cases, the Reynolds numbers were below 1000, indicating laminar flow in the test section; therefore, the Nusselt number was set to 4.36, which is the value derived for fully developed laminar flow with a constant wall heat flux [12]. To fit the data, the activation energy was adjusted to match the changes in cracking level that were observed as a function of temperature and the preexponential factor was then set to match the measured cracking level.

Because JP-7 is a mixture of many different individual hydrocarbon compounds, GC analyses of the product stream could not be used to measure the percentage of fuel that was cracked in the laboratory experiments. Instead, this parameter was estimated from the increase in heat sink capacity over sensible heating, assuming a chemical endotherm of 388 Btu/lbm of fuel reacted. This value is the average of chemical endotherms that were previously measured for normal and isoparaffins [7]. To calculate the cracking level for n-decane, a chemical endotherm of 476 Btu/lbm, which was previously measured for n-heptane, was used [7].

In Tables 1 and 2, measured cracking levels for JP-7 and n-decane, respectively, are listed with and without the initiator. The tables also include the values calculated with our reactor model, along with the rate parameters used. The tables show that, in most cases, the calculated conversions are relatively close to the measured values. In addition, the tables show that the activation energies for cracking without the initiator are 60 and 65 kcal/mol for JP-7 and n-decane, respectively.

The value of 65 kcal/mol obtained for n-decane agrees well with previous measurements of thermal cracking of normal paraffins. For example, in a previous work, Rosen obtained an activation energy of

Table 1 Modeling results for JP-7 in the laboratory-scale reactor

	JP-7 without initiator		JP-7 with initiator	
		$E_a = 60$ kcal/mol, $\nu = 2.0\text{E}-9$ mol/s $\cdot$ cm^3 $\cdot$ atm		$E_a = 40$ kcal/mol, $\nu = 3.7\text{E}-4$ mol/s $\cdot$ cm^3 $\cdot$ atm
Temperature, °F	Measured cracking, %	Calculated cracking, %	Measured cracking, %	Calculated cracking, %
887	0	0.2	0.2	2.6
932	0	0.7	3.9	5.5
977	1.0	2.1	10.1	10.9
1022	7.5	6.1	22.8	19.6
1067	17.6	15.0	33.2	31.8
1112	36.2	30.9	44.0	46.9

Table 2 Modeling results for *n*-decane in the laboratory-scale reactor

	n-decane without initiator		n-decane with 4% initiator	
		$E_a = 65$ kcal/mol, $\nu = 3.2\text{E}-10$ mol/s $\cdot$ cm^3 $\cdot$ atm		$E_a = 39$ kcal/mol, $\nu = 2.4\text{E}-4$ mol/s $\cdot$ cm^3 $\cdot$ atm
Temperature, °F	Measured cracking, %	Calculated cracking, %	Measured cracking, %	Calculated cracking, %
887	0	0.1	3.4	3.2
932	0	0.4	7.5	6.7
977	1.4	1.5	14.8	12.9
1022	3.8	4.6	22.9	22.4
1067	12.2	12.7	34.1	35.2
1112	28.3	28.4	49.7	50.7

65 kcal/mol with *n*-decane [13]. In addition, Voge and Good generated correlations for cracking of normal paraffins based on carbon number and concluded that a value of 60 kcal/mol was representative of the activation energies for these reactions [14]. In a more recent work, the measured activation energies for *n*-decane and *n*-dodecane were 60 and 62 kcal/mol, respectively [15].

Finally, the tables show that, with the initiator, the activation energies for both JP-7 and *n*-decane are reduced by a substantial amount. Values of 40 and 39 kcal/mol were obtained for JP-7 and *n*-decane, respectively, which are about 25 kcal/mol lower than the uninitiated values. The substantial reduction in the activation energy produced by the initiator is consistent with the mechanism by which the initiator is thought to function. Without the initiator, the rate-determining step in the thermal cracking reaction is the generation of free radicals from the compounds contained in the fuel through the homolytic cleavage of either a carbon–carbon or carbon–hydrogen bond. Because both of these bonds are strong, the activation energy is relatively high. On the other hand, the initiator contains other bonds that are significantly weaker than carbon–carbon or carbon–hydrogen bonds. Thus, less energy is required to create free radicals and therefore the activation energy of the process is reduced.

The data also show that the initiator has a larger effect at lower temperatures than it does at the highest temperatures. This observation is also consistent with the reduction in activation energy caused by the initiator. Rates of reactions with higher activation energies increase more rapidly with temperature than rates of reactions with lower activation energies. Thus, as the reaction temperature increases, the rate of uninitiated cracking reaction increases more rapidly than initiated cracking, which lessens the effect of the initiator at high temperatures.

V. Pilot Scale Tests

A. Fabrication of the Fuel/Air Heat Exchanger

An additional goal of this project was to demonstrate that the chemical initiator was effective under the high heat flux conditions expected in an endothermic fuel/air heat exchanger. Therefore, a fuel/air heat exchanger/reactor was constructed to operate at a heat flux close to $100,000\ \mathrm{Btu/ft^2 \cdot h}$. The heat exchanger was then installed in a fully automated rig for testing. In the following sections, descriptions of the test rig, along with the specific design of the heat exchanger, are presented.

Liquid hydrocarbon fuels such as JP-7 and model fuels such as *n*-decane were stored in 55 gal drums. A small drum pump was used to draw the fuel out of the drum and provide a pressure of 100 psi for the main fuel pump. A Maximator air-driven pump generated fuel flows up to 60 gal/h at pressures up to 1500 psi. Immediately downstream of the fuel pump, the flow passed through a 1-liter pulsation dampener followed by a coriolis mass flow meter, a Badger pressure control valve, and a preheater before entering the heat exchanger housing. After exiting the heat exchanger, the heated fuel and cracked products passed through a second Badger valve and two heat exchangers, then into a scrap tank where the condensable portion of the products was collected. The Badger valves controlled the fuel pressure and flow. The valve upstream of the heat exchanger controlled pressure and the valve downstream of the heat exchanger controlled the fuel flow.

The noncondensable components that were not collected in the scrap tank were directed through a volumetric gas flow meter, then mixed with an airstream generated with an 1100 $\mathrm{ft^3/min}$ blower, and finally vented. The volumetric flow meter was used to estimate the level of cracking as a function of reaction condition, assuming that the product distribution measured previously in the laboratory-scale reactor also formed in these tests.

The heat for the air side of the heat exchanger was generated by burning ethylene in air in a swirl-stabilized diffusion flame burner. Ethylene was delivered from a compressed gas cylinder. A 780-W heater prevented the in-line regulator from freezing due to the heat absorbed from ethylene vaporization. The hot burner exhaust gas was then directed through the air side of the unit over the finned fuel tube in an overall counter flow configuration. A diesel-powered compressor generated airflows up to 375 standard cubic feet per minute at a pressure of 100 psi.

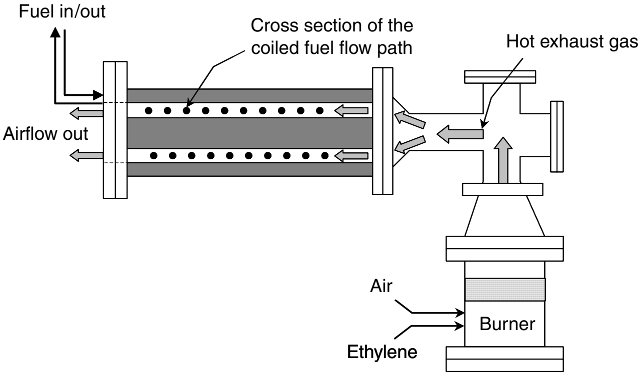

Fig. 7 Schematic of the heat exchanger installed in the reactor housing.

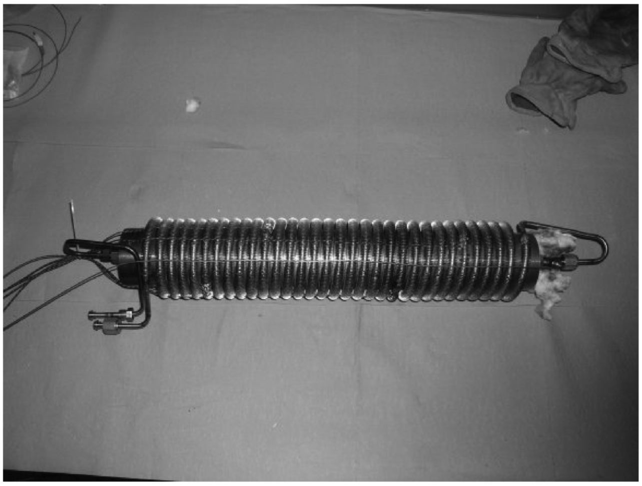

Fig. 8 Photograph of the finned heat exchanger tubing coiled over the inner annulus wall.

A schematic of the heat exchanger interfaced with the ethylene burner is shown in Fig. 7. The exhaust gases exiting the ethylene burner were directed through an annulus that housed the heat exchanger coil, which consisted of a coiled 30-ft-length of 1/4-in. OD Inconel tube fit with fins 1/8-in. in height and spaced about 12/in. (fabricated by Cain Industries, Germantown, Wisconsin). The figure shows cross sections of the heat exchanger tubing in the annulus with the fuel flow in a direction normal to the page. The unit was rolled into a coil 3 in. in diameter by 25 in. in total length.

A photograph of the finned heat tubing wrapped around the inner core of the annulus is shown in Fig. 8. Both the inner core and the outer pressure shell were fabricated by a commercial machinist from 0.036-in stainless steel sheet metal. The figure also shows the thermocouples installed in the fuel inlet and the exit fittings that bring the fuel in (through the center of the core), then back out, of the heat exchanger.

B. Test Procedure

A fuel flow of about 100 lbm/h was started, and then the fuel pressure was raised to 550 psig. The ethylene burner was then ignited and the computer controlled the ethylene flow to maintain the desired air set point temperature measured by a thermocouple at the entrance to the heat exchanger. Typically, the mass flow of air was approximately 10 times that of the fuel to keep the maximum air temperature as low as possible. Once steady state conditions were reached, the fuel source was switched from the drum of pure fuel to one that contained the initiator at a concentration of 2 wt %. Because each fuel drum was equipped with a pump that provided 100 psi to the main fuel pump, switching between initiated and noninitiated

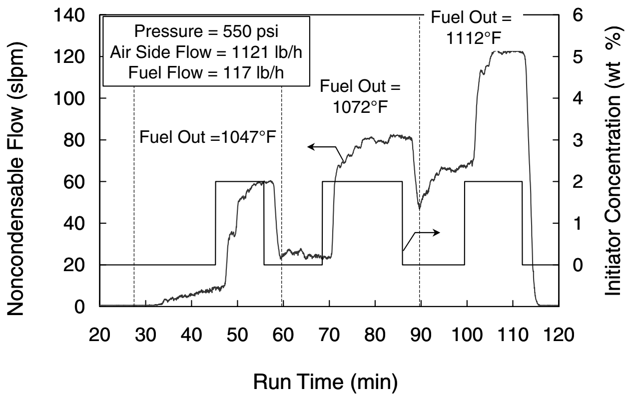

Fig. 9 Noncondensable flow with and without the initiator for JP-7. Fuel temperatures exiting the reactor are shown.

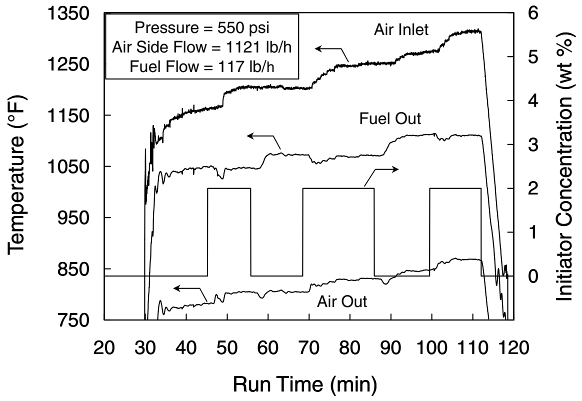

Fig. 10 Air and fuel temperatures achieved during the test of JP-7.

fuel was simply a matter of deactivating one drum pump and activating the other. As was the case in the laboratory reactor, when the initiated fuel reached the heat exchanger, the level of cracking increased, causing the fuel exit temperature to decrease and in turn requiring that the ethylene fuel flow rate be increased so that the fuel temperature could be brought back up to the temperature measured before the initiator addition. After steady state conditions were achieved, the fuel was switched back to the uninitiated fuel and the fuel outlet temperature was set to the next temperature.

C. Results of the Pilot Scale Testing

The results obtained for JP-7 are shown in Figs. 9 and 10. In Fig. 9, the measured flow of noncondensable gases is shown as a function of initiator concentration and fuel out temperature. Noncondensable gases are the result of thermal cracking reactions and include the lighter compounds, such as methane, ethane, ethene, propane, propene, butane, and butene. Thus, the flow rate of these gases can be used to estimate changes in cracking rate as the concentration of initiator or fuel temperature is changed. The figure shows that at the first condition, where the fuel out temperature is 1047°F and there is no initiator flow (between the times of 35 and 45 min), the rate of noncondensable gas flow is about 8 standard liters per minute (slpm) and is increasing slowly (because the flow rates of fuel and ethylene consumption were so high, the run times were limited to about 90 min and therefore sometimes parameters had to be changed before completely steady state conditions had been achieved). Eight slpm corresponds to about 1.5% cracking at this fuel flow rate.

At a time of 45 min, the fuel flow was switched from pure JP-7 to the drum that contained JP-7 with 2 wt % initiator. The figure shows that, 2 min after the initiator was switched on, there is a sharp rise in the flow rate of noncondensable gases, indicating a significant rise in the amount of thermal cracking that is occurring. At 59 min, the noncondensable flow leveled out at 60 slpm, corresponding to a cracking level of approximately 10%. The initiator flow was then stopped and the fuel outlet temperature increased to 1072°F. Even at the higher temperature, the flow of noncondensable gases levels out at about 24 slpm, a factor of 2.5 lower than observed at 1047°F with the initiator. At 69 min, the initiator flow was started and once again the flow of noncondensable gases increased significantly, reaching a steady state value of about 82 slpm. Finally, at 1112°F, the figure shows that the addition of the initiator increased the noncondensable flow from 67 to about 122 slpm, or by almost a factor of 2.

Figure 10 shows the air temperature entering the annulus, the air temperature exiting the annulus, and the fuel temperature exiting the heat exchanger. At the first test condition, from 40 to 45 min, the air temperature entering the annulus was 1157°F, the air temperature exiting the heat exchange was 783°F, and the fuel temperature exiting the heat exchanger was 1047°F (the fuel temperature entering the test section was near ambient, about 60°F). Initiator flow was started at 45 min, and the figure shows that at 47 min the fuel temperature drops rapidly, reaching a minimum 1026°F at 49 min. This drop is due to the increase in the rate of endothermic thermal cracking reactions caused by the initiator. At this point, the inlet air temperature was increased from 1157°F to 1204°F to bring the fuel exit temperature back to 1047°F, the value measured before initiated fuel was used.

In these tests, the difference between the air inlet and air exit temperatures can be used to determine the fuel heat sink capacity. At the first condition, without the initiator, the air temperature entering the heat exchanger was 1162°F and the air temperature exiting the heat exchanger was 783°F, for a difference of 379°F. On the other hand, with the initiator, the air inlet temperature was increased to 1203°F to maintain the same fuel out temperature. Moreover, at this condition, the air temperature exiting the heat exchanger was 804°F, resulting in a difference of 400°F. Because the mass flow rates of air and fuel were constant and the fuel temperature exiting the heat exchanger was the same with the initiator as without, we conclude that the increase in the temperature difference across the air side of the heat exchanger corresponds directly to an increase in fuel heat sink capacity, which was caused by the addition of the initiator.

Similar results were obtained at higher test temperatures. For example, at 65 min, when the fuel temperature was 1072°F, Fig. 10 shows that the air temperatures were 1202°F and 804°F entering and exiting the heat exchanger, respectively. However, after the initiator was added, the air temperature required to maintain a constant fuel out temperature of 1072°F was increased to 1251°F. In addition, the air outlet temperature with the initiator was 831°F, resulting in a temperature difference of 420°F, compared to a difference of 397°F before initiator was added. Finally, at a fuel out temperature of 1112°F, the air temperature difference without the initiator was 423°F versus a difference of 445°F with the initiator.

In Fig. 11, the heat sink capacities that were obtained during this test (the individual symbols) are shown along with the values generated with the kinetic model (lines). To estimate the energy losses, the measured flow of noncondensable gases was used to

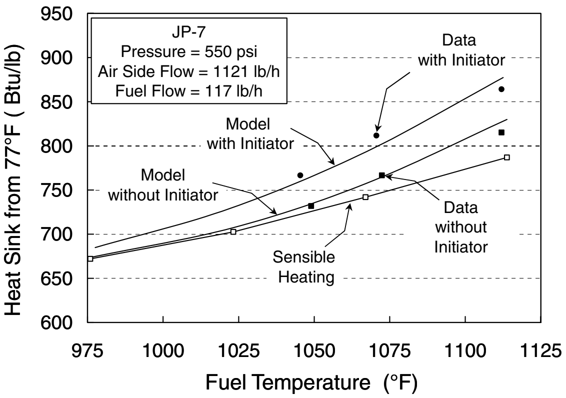

Fig. 11 Measured and predicted heat sink capacities for JP-7 with and without the initiator.

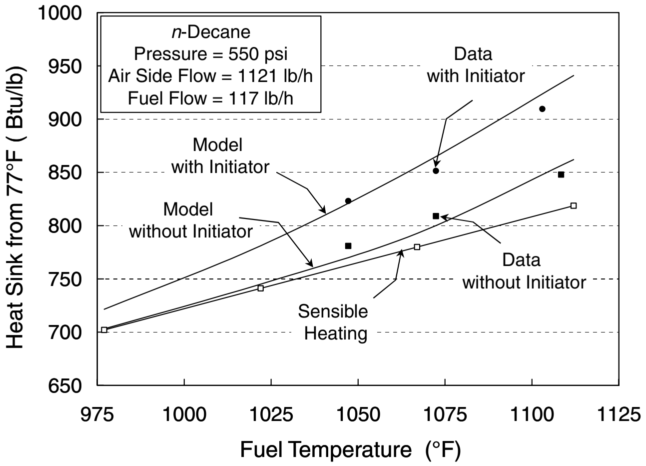

Fig. 12 Measured and predicted heat sink capacities for *n*-decane with and without the initiator.

estimate the level of cracking at the lowest temperature, noninitiated point. The energy losses were then adjusted so that the heat sink capacity based on air temperature difference agreed with that calculated from sensible heating of the fuel in addition to the small amount of additional heat sink obtained from the thermal cracking reaction. Using this method, the energy losses at 1049°F were 24% of the total input thermal power. The same percentages were assumed at the higher temperatures, which allows the energy losses to scale with the air temperature.

Figure 11 shows that, at a fuel out temperature of 1049°F, the heat sink capacity obtained for JP-7 in the pilot scale test was 732 Btu/lbm without the initiator, whereas the heat sink capacity increased to 767 Btu/lbm when we added the initiator. At a fuel outlet temperature of 1072°F, the measured heat sink was 767 Btu/lbm without the initiator, increasing to 812 Btu/lbm with the initiator. Finally, at 1112°F, a value of 815 Btu/lbm was measured without the initiator, whereas with the initiator the total heat sink capacity was 864 Btu/lbm. The latter value represents an improvement of 49 Btu/lbm over the heat sink obtained without initiator and an increase of 77 Btu/lbm over that available from sensible heating alone.

Figure 11 also shows the values predicted with the kinetic model listed in Eq. (1). The model for uninitiated cracking fits very well over the range of temperatures measured and shows that relatively little chemical endotherm is being obtained under these conditions. On the other hand, the initiated cracking model predicts that a significant improvement in endotherm can be obtained, which is in agreement with the measured points. Considering the kinetic model was developed from laboratory data obtained with an electric heater on a much smaller scale, we believe the agreement obtained in these pilot scale tests, under much more realistic conditions, is quite good.

Figure 12 presents a summary of the data obtained with n-decane at fuel out temperatures of 1047, 1072, and 1112°F, along with the values predicted with the kinetic model. Overall there is relatively good agreement between the predicted heat sink capacities and the values obtained in the pilot scale testing. Moreover, the results show that the initiator has a significant impact on the heat sink available from n-decane. For example, at 1047°F, the measured heat sink without the initiator was 781 Btu/lbm, whereas the value with the initiator is 823 Btu/lbm, an improvement of 42 Btu/lbm. At 1072°F, the initiator increases the heat sink from 809 to 851 Btu/lbm. Finally, when the fuel temperature is 1108°F, the heat sink measured without the initiator is 848 Btu/lbm. With the initiator, the heat sink has increased to 910 Btu/lbm, at a slightly lower fuel temperature of 1103°F. Based on the slope of the line, the heat sink would be about 915 Btu/lbm at 1108°F, and therefore we conclude that the initiator increased the heat sink capacity by 67 Btu/lbm over the measured value without the initiator. Finally, the value 915 Btu/lbm is about 95 Btu/lbm greater than the heat sink from sensible heating, and if the slopes of the lines are extrapolated to higher temperatures, the data suggest that the differences in the heat sink values will increase further. Figure 12 shows that the values predicted by the kinetic model agree very well (within 5–7 Btu/lbm) with the measured values at all test conditions. In addition, the slopes of the model lines match the data well, indicating that the activation energies identified for both initiated and uninitiated cracking are reasonably accurate.

Finally, the highest heat sink capacity was obtained with n-decane at a fuel out temperature of 1103°F with the initiator. At this condition, a value of 910 Btu/lbm was obtained and the fuel flow rate was 117 lb/h, resulting in a heat flow of 106,500 Btu/h or 31.1 kW. The internal surface of the heat exchanger is 1.19 ft^2, resulting in a heat flux of 89,400 $\mathrm{Btu/ft^2 \cdot h}$. In addition, the overall heat transfer coefficient was 185 $\mathrm{Btu/ft^2 \cdot h \cdot {}^\circ F}$ with an air side pressure drop of 8 psid. This value is equivalent to 0.9 psid at the expected operating pressure of 180 psia, which is less than 2.5% of the inlet total pressure. Finally, the weight of the finned heat exchanger was 7.5 lbs, resulting in a thermal power to weight ratio of 4.15 kW/lb. These performance parameters could be used in the preliminary design of a full scale heat exchanger.

VI. Conclusions

The laboratory-scale results show that substantial improvements in heat sink capacity can be obtained if the fuel undergoes endothermic, thermal cracking reactions, and that the use of a chemical additive allows the cracking reactions to occur more rapidly. Thermal cracking provides larger improvements in the heat sink capacities of fuels that consist primarily of normal paraffins, such as n-decane, compared to fuels, like JP-7, which contain a substantial fraction of less reactive compounds such as isoparaffins and naphthenes. Finally, in tests with a pilot scale fuel/air heat exchanger, we demonstrated that the addition of our initiator produced measurable improvements in the heat sink capacity of JP-7 and n-decane under realistic heat flux and temperature conditions.

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