

Deposit Formation and Heat-Transfer Characteristics of Hydrocarbon Rocket Fuels

Anthony J. Giovanetti,* Louis J. Spadaccini,† and Eugene J. Szelc†
United Technologies Research Center, East Hartford, Connecticut

An experimental research program was undertaken to investigate the thermal stability and heat-transfer characteristics of several hydrocarbon fuels under conditions that simulate high-pressure cooling systems of rocket engines. The rates of carbon deposition in heated copper and nickel-plated copper tubes were determined for RP-1, propane, and natural gas using a continuous flow test apparatus that permitted independent variation and evaluation of the effect on deposit formation of wall temperature, fuel pressure, and fuel velocity. In addition, the effects of fuel additives and contaminants, cryogenic fuel temperatures, and extended-duration testing with intermittent operation were examined. Corrosion of the copper tube surface was detected for all fuels tested; however, plating the insides of the tubes with nickel reduced deposit formation and eliminated corrosion in most cases. The lowest rates of carbon deposition were obtained for natural gas and the highest rates for propane. Forced-convection heat-transfer film coefficients were satisfactorily correlated using a Nusselt-Reynolds-Prandtl number equation for several of the fuels tested.

Nomenclature

A	= empirically determined constant
C_p	= specific heat at constant pressure
\bar{C}_p	= average C_p between T_w and T_f
D	= tube inside diameter
h	= clean tube heat transfer film coefficient
k	= thermal conductivity
Nu	= Nusselt number, hD/k
P	= pressure
Pr	= Prandtl number, $C_p\mu/k$
Q/A	= heat flux applied to tube
R_c	= thermal resistance buildup rate
Re	= Reynolds number, $\rho VD/\mu$
T	= temperature
V	= velocity
X/D	= axial distance-to-diameter ratio
Δt	= elapsed heating time
ΔT_w	= observed rise in wall temperature
μ	= absolute viscosity
ρ	= density

Superscripts

b, c, d, e, f, g = empirically determined exponents

Subscripts

c	= critical
f	= fuel
i	= initial condition
w	= inside tube wall

Introduction

IN an effort to increase the performance of hydrocarbon/liquid oxygen rocket engines for space booster or orbit transportation systems (i.e., to reduce weight and increase specific impulse), combustion pressures as high as practical are desirable. However, increased combustion pressure leads to a nearly proportionate increase in wall heat

flux in the thrust chamber and, therefore, greater stress is placed on the design of the regenerative cooling system. Regenerative cooling with hydrocarbon fuels is feasible up to a point where the coolant wall temperature reaches a limit defined by a thermal decomposition or "coking" temperature. Deposit formation on the coolant wall surface, which usually occurs when the thermal decomposition temperature is reached, causes an increased thermal resistance, leading to a progressively increasing wall temperature and, ultimately, failure.

Although there is presently only a limited understanding of the chemical mechanisms responsible for fuel thermal degradation, it is believed that the deposit formation process involves oxidation and pyrolysis of the hydrocarbon molecules that make up the fuel and formation of free-radical species. These intermediates undergo further reaction to form materials with higher molecular weights that usually contain carbon, hydrogen, oxygen, sulfur, and nitrogen. Additional processing of the fuel to remove impurities (e.g., oxygen, sulfur, or nitrogen) has improved thermal stability and reduced deposit formation.¹ In contrast to this, the thermal decomposition reactions may be accelerated if a catalytic metal surface such as copper is present.²

Because of its superior thermal conductivity, copper has been the preferred material for forming the regenerative cooling passages in the high-heat-flux regions of high-pressure rocket thrust chambers. In previous related research,³ experiments were conducted to evaluate the carbon deposition rates in heated copper tubes for two hydrocarbon rocket fuels, RP-1 and commercial-grade propane. Also, tests were conducted using JP-7 and chemically pure propane to represent more refined cuts of the baseline fuels. The results indicated that substantial deposit formation occurred in 10 min tests with RP-1 at wall temperatures between 600 and 800 K, with peak deposit formation rates of $600 \mu\text{g}/\text{cm}^2 \cdot \text{h}$ occurring at wall temperatures near 700 K. No improvements were obtained when deoxygenated JP-7 fuel was substituted for RP-1, but plating the inside wall of the tubes with nickel significantly reduced carbon deposition for RP-1. At a given wall temperature, the carbon deposition rates for the propane fuels were generally higher than those for the kerosene fuels. In addition, tube corrosion in the form of dendritic formations that appeared to grow from the copper surface were typical. There was little difference between commercial-grade and chemically pure propane with regard to the type or quantity of the deposit for wall temperatures between 400 and 600 K.

Submitted Dec. 19, 1983; presented as Paper 84-0512 at the AIAA 22nd Aerospace Sciences Meeting, Reno, NV, Jan. 9-12, 1984; revision received Nov. 8, 1984. Copyright © 1984 by United Technologies Corporation. Published by the American Institute of Aeronautics and Astronautics, Inc., with permission.

*Associate Research Engineer, Propulsion Technology Section.

†Supervisor, Propulsion Technology Section.

‡Senior Research Engineer, Propulsion Technology Section.

In the present investigation, additional experiments were conducted to extend the available data base and to evaluate the rates of carbon deposition in electrically heated tubes for RP-1, commercial-grade propane, and natural gas (97% methane) for a range of fuel pressures, flow velocities, and tube wall temperatures.⁴ In addition, the effects on fuel thermal stability of variations in the tube material, fuel additives and contaminants, cryogenic fuel temperatures, and extended duration testing with intermittent operation were examined.

Experimental Apparatus and Instrumentation

The experimental apparatus, shown schematically in Fig. 1, consisted of: fuel supply tanks; a zeolite-type molecule sieve used to remove water, carbon dioxide, and sulfur from the natural gas; a fuel delivery system consisting of four piston-type accumulators to drive the fuel through the test section; a cryogenic heat exchanger to cool the propane and natural gas for selected tests; a resistance-heated test tube connected to a 40 kV·A ac high-amperage power supply; an in-line nylon membrane filter for collecting any solid particles that might form in the bulk flow or break off from the tube wall during a test; a fuel cooler; an electrically driven metering valve to control the fuel flow through the test section; turbine and venturi flowmeters; a fuel dump tank; and an air-driven ejector and exhaust stack used when testing with natural gas.

The heated tube assembly and a cross-sectional view of the tube configuration are shown in Fig. 2. The test tube comprised a duplex arrangement formed by an inner 99.99% pure copper tube and an outer Inconel 600 tube. The Inconel sheath provided the necessary high-temperature tensile strength, while the inner copper tube provided the desired test material and surface condition for studying fuel deposit formation in rocket engine cooling systems (i.e., wall temperatures up to 866 K and fuel pressures up to 13.8 MPa). While the structural load was carried by the outer Inconel sheath, the major electrical power fraction (approximately 95%) was carried by the higher-conductivity copper tube. Therefore, the induced radial temperature gradient was small.

Metallographic examinations of a sample of duplex tubing were conducted to insure against the existence of any significant electrical or thermal resistance that could stem from oxidation or contamination of the Inconel/copper interface. Also, the roughness height of the interior surface (i.e., the average deviation from the mean surface) was in the range of 0.25–0.30 μm as determined by a profilometer. In an effort to passivate the normally reactive copper surface, several test tubes were plated with nickel (6 μm thick) using an electroless process.

As shown in Fig. 2, the test tube was silver soldered to copper bus rings that in turn were bolted to copper ring adaptors. Ten thermocouples were spot welded to the outer Inconel wall at equal spacings of 2.54 cm and the thermocouple junctions were coated with Sauerisen cement to insure good thermal contact and to minimize conduction losses. By use of an ac power supply to heat the tube, thermocouple errors resulting from a voltage drop across the thermocouple bead were minimized. The test tube assembly was electrically isolated from other components of the test apparatus using a special support fixture and nonconductive fuel lines.

All test data were recorded with a calculating data-logger microprocessor and were subsequently reduced on a high-speed digital computer. The inner tube wall temperatures were computed from the measured outer wall temperatures using results from a numerical heat-transfer simulation. The temperature at the interface between the fuel and the deposit layer that forms inside the tube equals the initial inner wall temperature, provided the convective heat-transfer coefficient remains constant (i.e., constant heat flux and flow rate).

After testing, the quantity of carbon on the test tube surface was determined by burning off the deposit in a metered flow of oxygen and passing the product gases through a nondispersive infrared analyzer, which continuously recorded the con-

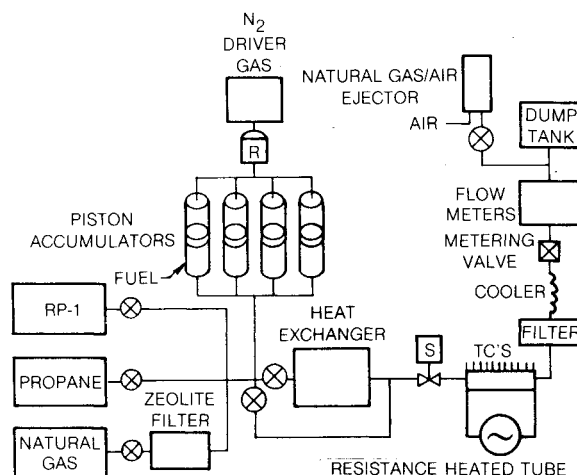


Fig. 1 Deposit formation test apparatus.

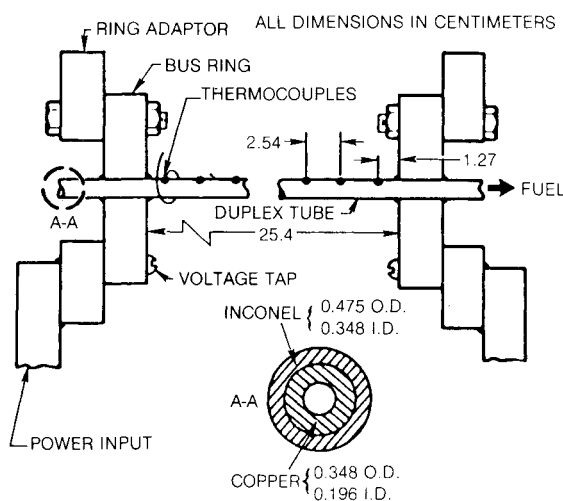


Fig. 2 Test tube assembly.

centrations of carbon dioxide and carbon monoxide. Integration of the concentrations of these species over the total burn-off time permitted computation of a carbon mass and carbon deposition rate. The carbon deposition rate is defined as the mass of carbon deduced from the burnoff analysis divided by the product of the inside lateral surface area of the tube and the total test time, and is expressed in units of $\mu\text{g}/\text{cm}^2 \cdot \text{h}$. Four equally spaced sections (each approximately 3.81 cm long) were cut from each test tube and used in the burnoff analyses; the remainder of the tube was cut into sections that were examined microscopically. Local carbon deposition rates were computed for each 3.81 cm long tube section and the tube-averaged rates were based on the arithmetic mean of four 3.81-cm long sections.

In selected cases, a scanning electron microscope (SEM) was used to elucidate the morphology of the deposit; limited elemental analysis of the deposit was performed using a scanning electron microprobe (SEMP). This procedure involved a qualitative scan of elements present in the deposit (e.g., carbon, copper, sulfur, oxygen, and nitrogen) within a detectability limit of approximately 200 ppm. X-ray emission imagery of the selected element (indicated by clusters of white dots on a black background) was matched to standard photomicrographs of the sample deposits.

Experimental Results and Discussion

RP-Tests

A series of tests was conducted using RP-1 to explore the effects of fuel velocity, tube material, and fuel additives and

contaminants on carbon deposition. Baseline test conditions consisted of a fuel inlet pressure of 13.8 MPa, a velocity of 30 m/s, a temperature of 290 K, a maximum initial inner wall temperature of 700 K, and a test duration of 10 min.

In Fig. 3a, the rate of carbon deposition for RP-1 in copper tubes is plotted as a function of initial inner wall temperature for several fuel inlet velocities.³ The data are based on tube-averaged quantities, that is, an average temperature and an average carbon deposition rate have been computed for each tube. As shown in Fig. 3a, the rate of carbon deposition initially increases, reaches a maximum value at an intermediate value of the wall temperature, and decreases thereafter with further increases in the tube wall temperature. As the fuel velocity increases, the maximum rates of carbon deposition shift to higher wall temperatures.

In Fig. 3b, the data are replotted as a function of fuel inlet velocity and grouped into two bands, enclosing wall temperature data below and above 640 K, as suggested by the trends indicated in Fig. 3a. An additional data point at a fuel inlet velocity of 58 m/s from an experiment conducted in the present investigation is also shown. In Fig. 3b, it is seen that the rates of carbon deposition decrease as the fuel velocity increases for wall temperatures below 640 K. For wall temperatures above 640 K (because of the shift of the maximum rates of carbon deposition to higher wall temperatures), the rates of carbon deposition exhibit a reverse trend and increase as fuel velocity increases. Also, for wall temperatures below 640 K and for fuel velocities between 7 and 15 m/s, the rates of carbon deposition exceed those for wall temperatures above 640 K.

The opposing trends observed for the effect of fuel velocity on carbon deposition for wall temperatures above and below 640 K may be explained as follows. At low wall temperatures (i.e., below 640 K), the rate of deposit formation may be limited by the kinetics of the carbon deposition processes, so that the additional fuel supplied to the hot wall (corresponding to an increase in fuel velocity) is not reacted. Because coverage of the tube surface by deposit for RP-1 is not uniform, the slight decrease in the rate of carbon deposition associated with

an increase in fuel velocity at these temperatures may be due to the increased flaking of deposit from the tube surface. However, at high wall temperatures (i.e., above 640 K), the carbon deposition kinetics are accelerated so that in the limit, the rate at which deposit forms is governed only by the rate at which fuel is supplied to the hot tube surface. Thus, at the higher temperatures, the increase in fuel mass flow rate associated with an increase in fuel velocity promotes further deposit formation.

Similarly, for nickel-plated tubes (data not shown), the rate of carbon deposition increases with fuel velocity. Also, for fuel velocities between 6 and 18 m/s, the rates of carbon deposition for nickel tubes are approximately one-fifth of those for copper.

A measure of the effect of carbon formation on heat transfer is the thermal resistance buildup rate, defined as

$$\dot{R}_c = \frac{\Delta T_w}{(Q/A)\Delta t} \quad (1)$$

The effect of fuel velocity on the thermal resistance buildup rate was explored for copper tubes. Previously, it was determined that, for fuel velocities between 7 and 30 m/s, the thermal resistance buildup rate reached a maximum at an initial wall temperature in the range 650-700 K and decreased thereafter for further increases in wall temperature.³ In addition, the thermal resistance buildup rates decreased as fuel velocity increased. In order to summarize this trend, a plot of the maximum thermal resistance buildup rate as a function of the fuel inlet velocity is shown in Fig. 4. In Fig. 4, which includes data from the previous study³ and the present investigation, the thermal resistance buildup rate is shown to decrease by a factor of five with an increase in the fuel velocity from 8 to 58 m/s, a trend that cannot be explained by a reduction in the level of deposit produced (cf., Fig. 3b). Therefore, the reduction in the thermal resistance buildup rate is attributed to enhancement of the local heat-transfer coefficient due to increased velocity and/or roughening of the tube wall during the carbon deposition process. Also, it is postulated that, as the mass of deposit increases, its porosity decreases and its thermal conductivity increases from a value representative of the fuel to a value typical of amorphous carbon. Consequently, the higher deposit loadings observed for an increase in fuel velocity could improve the heat transfer and reduce the thermal resistance buildup rate.

Separate tests were conducted to explore the effects of 1) doping RP-1 base fuel with DuPont metal deactivator to mitigate the catalytic effect of the copper surface and 2) contaminating the fuel with the sulfur compounds thianaphthene and benzyl disulfide (in proportions recommended by the refiner for simulating the real fuel) to increase the total sulfur concentration to the specification maximum of 0.05% by weight. Although there was scatter in the data, there appeared to be a reduction in the rate of carbon deposition when RP-1

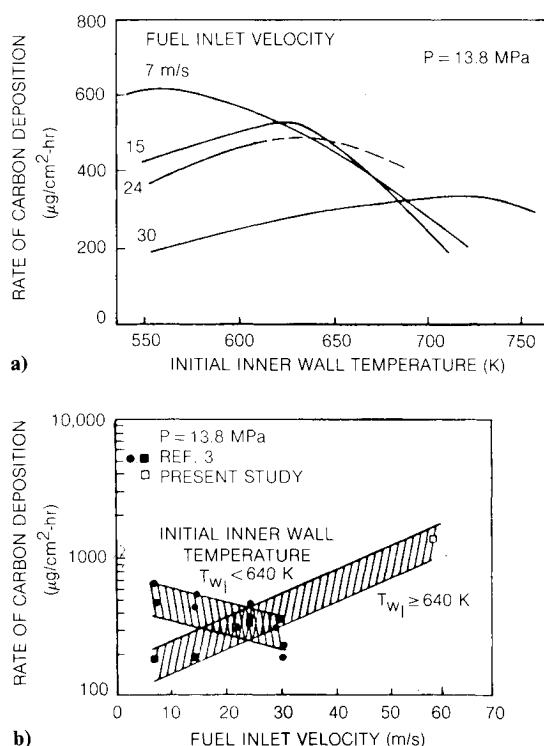


Fig. 3 Rate of carbon deposition for RP-1 in copper tubes: a) as function of initial inner wall temperature; b) as function of fuel inlet velocity.

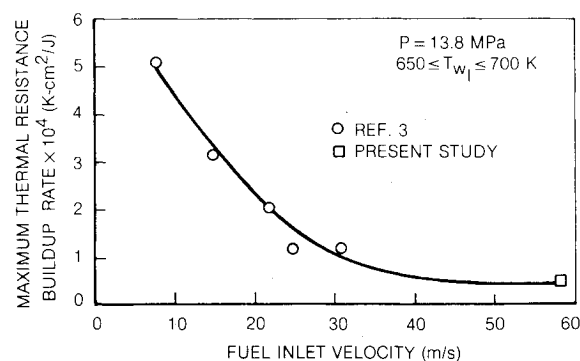


Fig. 4 Effect of fuel velocity on thermal resistance buildup rate for RP-1 in copper tubes.

was doped with metal deactivator (up to a factor of two) with respect to the RP-1 base fuel. With regard to the data obtained for the sulfur-doped fuel, a significant loss of deposit caused by flaking from the tube surface because of corrosion of the copper was characteristic for most of this tube. In general, the deposit appeared thicker than that obtained for RP-1 base fuel (0.014 wt. % S); also, a threefold increase in the peak deposit rate relative to the base fuel was observed for tube sections where flaking did not occur. The results of the sulfur-doped fuel test indicate that high concentrations of fuel-bound sulfur (i.e., 0.05 wt. % S) accelerate deposit formation and tube corrosion. However, further work utilizing fuels with naturally occurring high sulfur concentrations is necessary before a definitive conclusion can be reached.

Propane Tests

The deposit formation characteristics of commercial-grade propane (94% pure) were also investigated and the effects of fuel velocity, tube material, fuel chilling, and intermittent operation were evaluated.

As is the case for RP-1, an increase in the tube initial wall temperature accelerates the fuel thermal decomposition and generally produces an increase in deposit formation. However, unlike RP-1, the rate of carbon deposition for propane decreases as the fuel velocity increases, suggesting that the process is limited by the reaction kinetics. Also, in contrast to what was observed for RP-1, coverage of the tube surface by deposit is uniform and local flaking of the deposit is not apparent.

Tests were conducted using nickel-plated tubes and ambient temperature propane (290 K) to explore the effects of tube material on carbon deposition. The SEMP photograph³ (Fig. 5) shows extensive degradation of the tube wall manifested in the form of dendrite structures to be characteristic for propane flowing through a copper tube. The dendrite contains a high concentration of copper, suggesting that tube material is forced up and away from the surface. Some carbon is evident at the base of the tree-like deposit structure. A very low concentration of sulfur is present, but no oxygen is detected. The objective of the nickel tube experiments was to determine if this phenomenon could be mitigated.

The carbon deposition data for the copper tubes, reported previously,³ and the data for the nickel tubes tested in this program are plotted in Fig. 6, with all data corresponding to a nominal fuel inlet velocity of 30 m/s and a 10 min test duration. In the figure, the rate of carbon deposition is plotted as a function of the initial inner wall temperature. Lines are drawn through the two groups of tube data to indicate the trends. The plot shows that at relatively low wall temperatures (e.g., 400 K) the rates of carbon deposition for copper and nickel tubes are similar. However, as the wall temperature increases, the rate of carbon deposition for copper tubes increases, while that for nickel tubes remains nearly constant. At 580 K (the highest common value of wall temperature tested) the rate of carbon deposition on copper tubes exceeds that on nickel by a factor of four. In addition, as noted in Fig. 6, the tube surface degradation that is characteristic of copper tubes does not occur on nickel tubes in the range of conditions explored.

The differing trends exhibited by the rates of deposition for copper as compared with nickel tubes may be related to the tube surface degradation process. Microscopic examination of several tube sections revealed that at higher wall temperatures, dendrite size is visibly larger than that found at lower temperatures. Therefore, at higher wall temperatures, more copper metal is pushed out from the tube and the surface area exposed to fuel is increased. Consequently, additional carbon deposits are formed around the base of a dendrite; the SEMP analyses shown in Fig. 5 support this conclusion. This mechanism is not present in nickel tubes, as witnessed by the absence of visible dendrites. Also, at wall temperatures below 400 K, dendrite formation (i.e., corrosive attack) on copper is

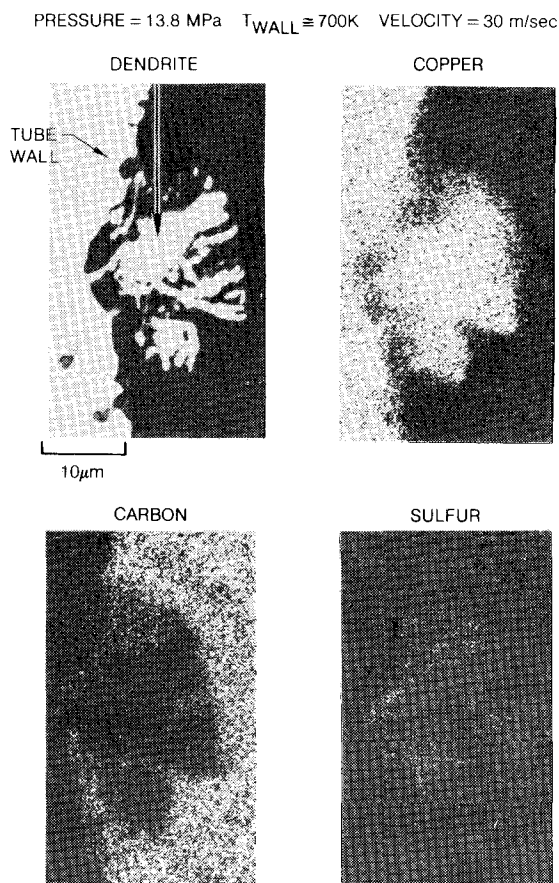


Fig. 5 Propane deposition and tube corrosion.

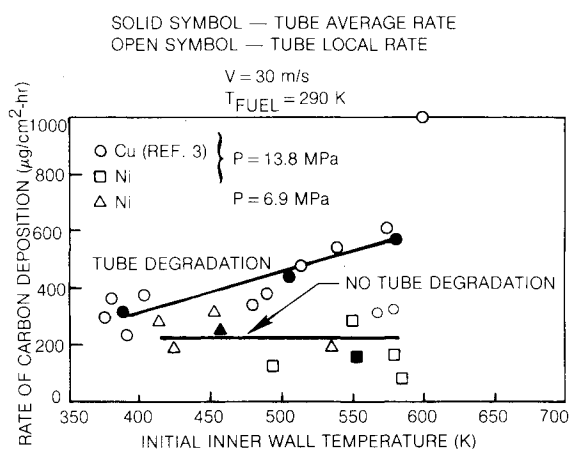


Fig. 6 Rate of carbon deposition for commercial-grade propane in copper and nickel tubes.

not as prevalent and the rates of carbon deposition for copper and nickel tubes are similar, as the data of Fig. 6 indicate.

A series of tests was performed to study the effects on carbon deposition in copper and nickel tubes of prechilling the propane to 233 K. The motivation for fuel prechilling was an attempt to reduce fuel temperatures and thereby avoid the wall temperature instabilities that limited previous experiments.³ The carbon deposition rates determined from the chilled fuel tests are plotted in Fig. 7 together with the results obtained for the ambient temperature fuel that were previously presented in Fig. 6. As indicated in Fig. 7, chilling the propane to 233 K reduces deposit formation by a factor of three for nickel tubes and by over two orders of magnitude for copper tubes. Although the rates of carbon deposition for chilled propane

on copper tubes appear to be lower than those on nickel tubes, the differences may not be significant due to the inherent scatter in the data at these low deposit rates.

The reduction in the rates of carbon deposition observed for chilled commercial-grade propane may be due to the freezing and removal of trace sulfur impurities present in the fuel. Chemical analysis of the propane showed a total sulfur concentration of 25 ppm. This sulfur is usually in the form of corrosive compounds such as methyl mercaptan (CH_3SH), hydrogen sulfide (H_2S), and carbonyl sulfide (COS). Absorption of these compounds on the heated tube wall could provide a mechanism for carbon deposit formation. It is likely that some fraction of these impurities was frozen and retained inside the cryogenic heat exchanger upstream of the heated tube. Consequently, the chilled propane entering the heated test tube probably contained lower concentrations of sulfur impurities that, in turn, should have resulted in a reduced amount of adsorption onto the tube wall and a lower rate of carbon deposition. It is unlikely that the slight reduction in the fuel bulk temperatures for the chilled propane tests had a significant effect on the carbon deposition processes.

Using ambient temperature propane, a test in which a nickel tube was heated intermittently for eight 3 min cycles was performed to determine the effects of intermittent operation and extended test duration on carbon deposition. The motivation for intermittent testing derives from a desire to simulate a number of operating cycles for a reusable rocket engine application. When compared to a continuous 10 min test at comparable conditions, the average rate of carbon deposition for the 24 min intermittent test was reduced by a factor of five. The reduction in the deposit formation rate with increasing test time may be due to deposit breaking away from the tube surface (this effect would be intensified by intermittent operation) or to a suppression of the deposit formation rate owing to passivation of the tube surface resulting from the buildup of deposit over the longer operating period.

Natural Gas Tests

A series of tests was conducted using natural gas as a simulant for methane. Ambient temperature (290 K) and cryogenic natural gas (160 K) were tested in copper and nickel-plated copper tubes. Nominal inlet conditions were a pressure of 13.8 MPa and a velocity of 30 m/s. Higher velocity tests and a test in which the tube was operated intermittently were also conducted.

Figures 8a and 9a summarize the carbon deposition rate data for natural gas on copper and nickel tubes, respectively. In each figure, the rate of carbon deposition is plotted as a function of initial inner wall temperature. Data for both ambient temperature (gaseous) and cryogenic (compressed liquid) natural gas are displayed. Contrary to the previous results for RP-1 and propane, on average, the carbon deposition rates for nickel tubes exceed those for copper tubes. Research done for light hydrocarbon gases⁵ and methane⁶ has shown that the rate of deposit formation on nickel is often greater than that on copper.

In Figs. 8a and 9a, a trend of decreasing rates of carbon deposition with increasing wall temperature is evident. The highest rates of carbon deposition occur at wall temperatures in the range of 300–500 K and correspond to those tests using cryogenic fuel. Because of the possibility that this trend is due to the difference in fuel flow rates (density) between ambient temperature and cryogenic fuels (a factor of four), the rates of carbon deposition were normalized relative to the total mass of fuel passed through the test tube. These normalized results are summarized as Figs. 8b and 9b. A trend of decreasing rates of carbon deposition with increasing wall temperature may still exist, but the relative magnitude of this decrease is obviously not nearly as great as it first appeared when comparisons were made on an absolute basis. Of course, differences due to surface material are unaffected by normalizing the data.

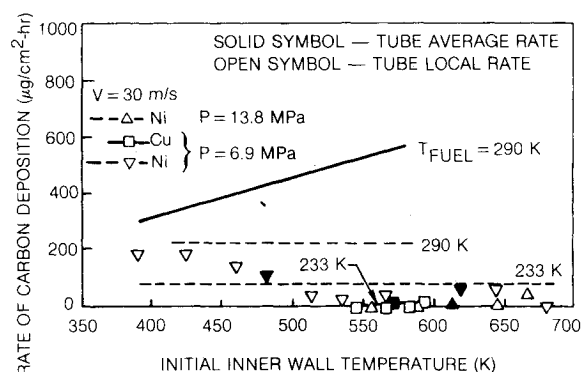


Fig. 7 Effect of fuel chilling on carbon deposition for propane in copper and nickel tubes.

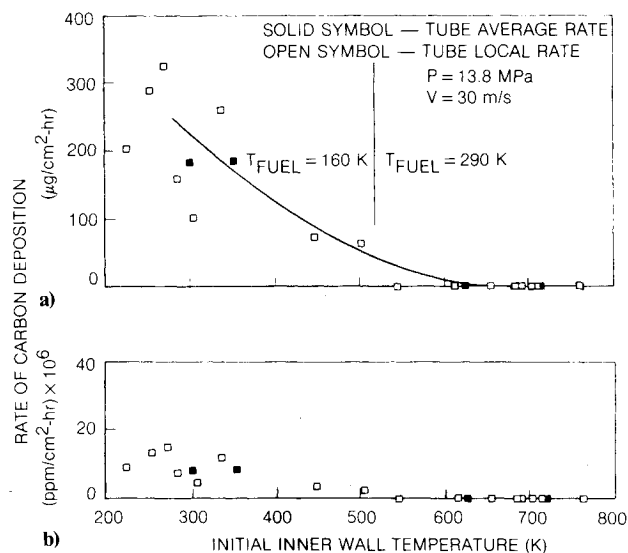


Fig. 8 Absolute and normalized rates of carbon deposition for natural gas in copper tubes. a) absolute, b) normalized.

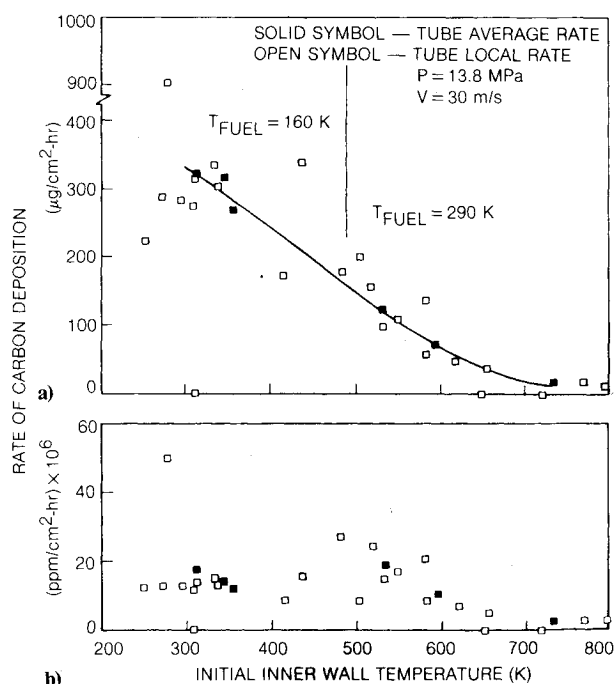


Fig. 9 Absolute and normalized rates of carbon deposition for natural gas in nickel tubes. a) absolute, b) normalized.

Similar to observations with propane, most natural gas tests using copper tubes show a uniform deposit layer and deterioration of the surface manifested in the form of copper dendrites. However, the size and number of these dendrites appear to be significantly less than observed for a typical propane test. Dendrite formation is greatest on tube sections with initial inner wall temperatures between 500 and 700 K. At wall temperatures above 700 K, dendrite and carbon deposit formation are significantly reduced. This observation is consistent with the hypothesis that carbon deposition in natural gas may be due to adsorption of the corrosive hydrocarbon-sulfur compound tertiary-butyl mercaptan $[(CH_3)_3CSH]$ added to the natural gas as an odorant at a level of about 4 ppm. As the wall temperature increases, the rate at which the adsorption mechanism proceeds decreases, thereby decreasing deposit formation and tube corrosion. Also, deposit formation owing to pyrolysis reactions (i.e., cracking of the hydrocarbon fuel molecule), which normally occur at high temperature for fuel molecules having more than a single carbon atom, are nonexistent for methane. Thus, it may be possible to minimize deposit formation in natural gas by operation at high wall temperatures.

In order to explore the effects of fuel velocity on carbon deposition for natural gas, copper tube tests were performed at two additional fuel inlet velocities (65 and 98 m/s) above the baseline value (30 m/s). Unlike either RP-1 or propane, the rate of carbon deposition for natural gas did not show a velocity dependence, suggesting that deposit formation in natural gas may be limited by the kinetics of the deposition processes. Also, a longer duration test in which a nickel tube was intermittently heated for eight 3 min cycles showed no significant change in the rates of carbon deposition when compared to continuous 10 min tests at comparable wall temperatures.

Heat Transfer Correlation Analyses

Analyses were performed to correlate the experimentally derived heat-transfer film coefficients in clean tubes for each of the fuels tested in this program and the previous investigation. In addition, data from several of the fuels were commingled and generalized correlations were developed. The film coefficient is defined as

$$h = \frac{Q/A}{T_w - T_f} \quad (2)$$

where all temperatures correspond to those at the start of the test. The film coefficient can be nondimensionalized to form the Nusselt number, which may be correlated as⁷

$$\frac{Nu}{Pr^c [1 + 2/(x/D)]} = AR e^b \left(\frac{\rho}{\rho_w} \right)^d \left(\frac{\mu}{\mu_w} \right)^e \left(\frac{k}{k_w} \right)^f \left(\frac{\bar{C}_p}{C_p} \right)^g \left(\frac{P}{P_c} \right)^h \quad (3)$$

where subscript w denotes the evaluation of the fuel property at the inside wall temperature. All other properties are evaluated at the fuel bulk temperature. The unknown coefficient A and exponents b , d , e , f , g , and h were determined using a multiple linear regression and correlation analysis computer program. In this analysis, the exponent c was fixed at 0.4.

The results of the heat-transfer correlation analyses are summarized in Table 1. As shown, an attempt is made to simplify the correlating equations by eliminating some of the fuel properties terms. For RP-1 and propane (chemically pure and commercial grades), the simple Dittus-Boelter form of the equation is satisfactory for correlating the data; that is, there is no significant reduction in the correlation coefficient when the fuel properties ratios are deleted. There is very good agreement between the Dittus-Boelter type of correlation for RP-1 in Table 1 and an expression for RP-1 generated at Rocketdyne.⁸ Also, the commingled correlation for RP-1 and propane from Table 1 is plotted as Fig. 10. Correlations were developed for natural gas and are reported elsewhere,⁴ but because of the narrow range of Reynolds number tested, they are sensitive to input accuracy and may have limited usefulness.

Summary of Results

A plot summarizing the variation of the rates of carbon deposition for RP-1, commercial-grade propane, and natural gas as a function of wall temperature is shown in Fig. 11. Carbon deposition rates for propane in copper tubes were highest and ranged 300-580 $\mu\text{g}/\text{cm}^2 \cdot \text{h}$ at wall temperatures between 400 and 580 K. The lowest rates of carbon deposition were obtained for natural gas in copper tubes and did not exceed 80 $\mu\text{g}/\text{cm}^2 \cdot \text{h}$ at wall temperatures between 500 and 650 K. Carbon deposition rates of 200-320 $\mu\text{g}/\text{cm}^2 \cdot \text{h}$ were typical for RP-1 in copper tubes at wall temperatures between 560 and 750 K. For natural gas, the unexpected trend of increasing carbon deposition rates (approaching those of RP-1) with decreasing wall temperature was explained as being possibly due to wall adsorption of mercaptans present in the fuel in trace concentrations. It was postulated that at higher fuel temperatures, this mechanism did not exist.

Table 1 Forced-convection heat-transfer correlations for hydrocarbon rocket fuels

$$\text{Correlation equation: } Nu = AR e^b Pr^c \left(\frac{\rho}{\rho_w} \right)^d \left(\frac{\mu}{\mu_w} \right)^e \left(\frac{k}{k_w} \right)^f \left(\frac{\bar{C}_p}{C_p} \right)^g \left(\frac{P}{P_c} \right)^h \left(1 + \frac{2}{x/D} \right)$$

Fuel	Coefficient/exponent								No. of points	Correl. coeff.
	A	b	c	d	e	f	g	h		
RP-1	0.0095	0.99	0.4 ^a	0.37	0.60	-0.20	-6.0	-0.36	274	0.97
	0.0068	0.94	0.4 ^a	0 ^a	0 ^a	0 ^a	0 ^a	0 ^a	274	0.96
Chem. pure propane	0.011	0.87	0.4 ^a	-9.6	2.4	-0.57	0.26	-0.23	79	0.99
	0.020	0.81	0.4 ^a	0 ^a	0 ^a	0 ^a	0 ^a	0 ^a	79	0.97
Commercial propane	0.034	0.80	0.4 ^a	-0.24	0.098	-0.48	2.1	-0.38	285	0.94
	0.028	0.80	0.4 ^a	0 ^a	0 ^a	0 ^a	0 ^a	0 ^a	285	0.93
RP-1/Propane ^b	0.044	0.76	0.4 ^a	0 ^a	0 ^a	0 ^a	0 ^a	0 ^a	638	0.98

^adenotes exponent held constant in analysis. ^bCommingled correlation for RP-1, chemically pure propane, and commercial-grade propane.

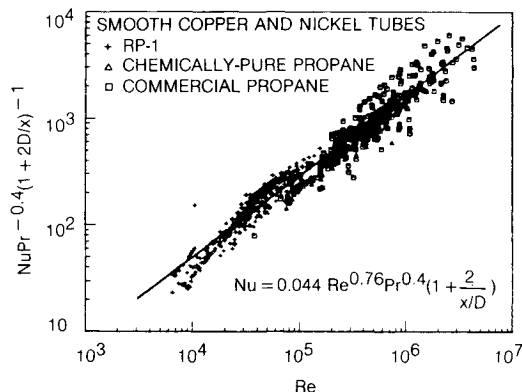


Fig. 10 Forced-convection heat transfer for liquid hydrocarbons in clean tubes.

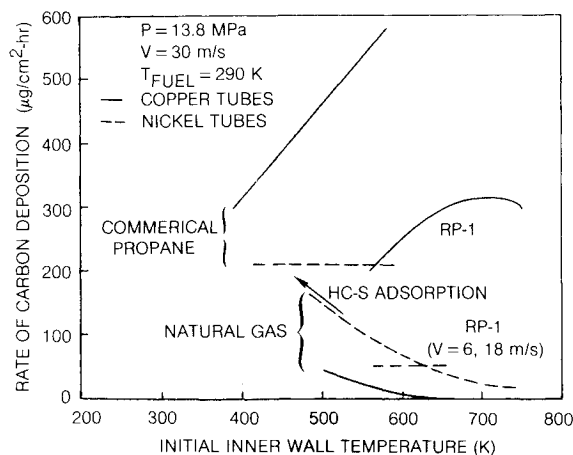


Fig. 11 Rates of carbon deposition for three hydrocarbon fuels.

Conclusions

Based on the results of this program, the following conclusions can be made:

- 1) Natural gas is an attractive rocket fuel with regard to thermal stability.
- 2) Metallic coatings on the insides of the copper cooling tubes are an effective way to reduce deposit formation and tube corrosion.
- 3) Cryogenic cooling of the fuel may be a means to remove some of the impurities detrimental to thermal stability.

4) Doping RP-1 fuel with metal deactivator can significantly reduce the level of deposit formed.

The key benefit derived from this program is the quantitative assessment of the carbon deposition and the associated thermal resistance rate as a function of wall temperature for several fuels. Measurable deposits occur for all the candidate hydrocarbon fuels over the temperature range tested and the data generated serve as a basis for the specification of cooling system design criteria.

Acknowledgment

This work was performed with the support of the NASA Lewis Research Center under Contract NAS3-23344, Mr. Philip A. Masters, Project Manager. Additional support for heat-transfer correlation analyses was provided by United Technologies Research Center as part of a corporate-sponsored IR&D program.

References

- ¹Taylor, W. F., "Deposit Formation from Deoxygenated Hydrocarbons, Part I—General Features," *Industrial and Engineering Chemistry, Product Research and Development*, Vol. 13, No. 2, 1974, pp. 133-138.
- ²Anonymous, "CRC Literature Survey on the Thermal Oxidation Stability of Jet Fuel," Coordinating Research Council, Inc., Atlanta, CRC Rept. 509, April 1979.
- ³Roback, R., Szetela, E. J., and Spadaccini, L. J., "Deposit Formation in Hydrocarbon Rocket Fuels," *Journal of Engineering for Power, Transactions of ASME*, Vol. 105, Jan. 1983, pp. 59-65.
- ⁴Giovanetti, A. J., Spadaccini, L. J., and Szetela, E. J., "Deposit Formation and Heat Transfer in Hydrocarbon Rocket Fuels," NASA CR-168277, Oct. 1983.
- ⁵Baker, R. T. K. and Harris, P. S., "The Formation of Filamentous Carbon," *Chemistry and Physics of Carbon*, Vol. 14, edited by P. L. Walker and P. A. Thrower, Marcel Dekker, Inc., New York, 1978.
- ⁶Nishiyama, Y. and Tamai, Y., "Wall Effects During Thermal Reactions," *Chemtech Journal*, Nov. 1980.
- ⁷Masters, P. A. and Aukerman, C. A., "Deposit Formation in Hydrocarbon Rocket Fuels with an Evaluation of a Propane Heat Transfer Correlation," NASA TM-82911, June 1982.
- ⁸Hines, W. S., "Turbulent Forced Convection Heat Transfer to Liquids at Very High Heat Fluxes and Flowrates," Rocketdyne Div., Rockwell International, Canoga Park, CA, Rept. 61-41, 1961.