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Deposit Formation in Hydrocarbon Rocket Fuels with an Evaluation of a Propane Heat Transfer Correlation

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DEPOSIT FORMATION IN HYDROCARBON ROCKET FUELS WITH AN EVALUATION

OF A PROPANE HEAT TRANSFER CORRELATION

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ABSTRACT

A high pressure fuel coking test apparatus was designed and developed to evaluate thermal decomposition limits and carbon decomposition rates in heated copper tubes for hydrocarbon fuels. A commercial propane (90 percent grade) and chemically pure (CP) propane were tested. Heat transfer to supercritical propane was evaluated at 13.7 MPa, bulk fluid velocities of 6 to 30 m/s, and tube wall temperatures in the range of 422 to 811° K. A forced convection heat transfer correlation developed in a previous test effort verified the prediction of most of the experimental data within a ±30 percent range. No significant differences were apparent in the predictions derived from the correlation when the carbon resistance was included with the film resistance. A post-test scanning electron microprobe analysis indicated occurrences of migration and interdiffusion of copper into the carbon deposition.

INTRODUCTION

Renewed interest in hydrocarbon fueled rocket propulsion systems has stimulated cooling studies covering the thermodynamic range of interest for selective hydrocarbons in regenerative cooling applications[1,2]. A requirement in support of these studies is an evaluation of the cooling capability of the fuel along with the conditions influencing its thermal stability.

The advantages of a hydrocarbon as a potential fuel are its low cost, relative safety, and high density. An inherent disadvantage is the tendency for hydrocarbons when used as regenerative coolants to undergo decomposition and to form carbon deposits. When thermal decomposition occurs, the released carbon deposits on the passage walls and can form a barrier surface coating, thus reducing the effectiveness of the cooling. This condition results in a wall temperature limit when using hydrocarbon fuels as coolants and has restricted their utility to relatively low chamber pressures, e.g., below 10.34 MPa (1500 psi) in the case of RP-1. To enhance thermal stability in kerosene-type fuels, some benefit has been reported by reducing the impurities, primarily the concentration levels of dissolved oxygen and sulfur and by the removal of certain sulfur compounds.

The requirement for high engine performance necessitated by the imposition of more demanding mission roles has pushed the propulsion system design to greater chamber pressures, with the ensuing problem of dissipating extremely high thermal loads. OFHC (oxygen-free, high conductivity) copper and its alloys are required as chamber wall materials. Most of the reported data show that copper causes high deposit formation rates while deposition on nickel and stainless steels are usually low. The lighter hydrocarbons, although lower in

density have better heat transfer characteristics, are potentially more energetic and thus provide the opportunity for favorable overall propellant density and specific impulse tradeoffs. However, the problem of thermal stress decomposition is not eliminated by selecting the lower molecular weight hydrocarbon. Verification of heat transfer characteristics, temperature limits, and measurement of deposit rates are still necessary for assured cooling performance capability of hydrocarbons in advanced propulsion systems.

A fuel coking test apparatus was designed, developed, and used in experiments directed toward the following technologies: (1) evaluating the thermal decomposition (coking) limits, (2) determination of deposition rates in heated copper tubes for propane, (3) evaluating the validity of a propane heat transfer empirical equation, and (4) investigating the effect of further refining to reduce deposition[3,4].

The test program was conducted and reported by the United Technologies Research Center, L. J. Spadaccini, Program Manager.

TESTING AND APPARATUS

A test consisted of flowing the fuel through the heated tube (Figure 1) for ten minutes at a constant regulated supply pressure, fluid velocity, and heat input. The fuel flow was initiated by opening a solenoid valve. A metering valve was used to trim the fuel flow to the final setting. A 40 KVA power supply required for tube heating was controlled by powerstats that were set to respond to the temperature measurements in the test tube. Wall temperatures and local temperature differential measurements were recorded at one minute intervals. The thermocouple output signals were displayed on a video bar-graph generator for time sequence monitoring by the test conductor. An automatic data acquisition system recorded and stored information on magnetic tape for computer processing.

Figure 2 shows a high pressure test tube design assembly. The dual wall configuration consisting of an inner wall of OFHC copper (99.95 percent Cu.) with an Inconel 600 sheath permits testing at pressures to 34.5 MPa (5000 psi) and tube wall temperatures to 866K (1100° F).

Duplex tubing was fabricated by threading a 0.254-cm ID x 0.366-cm OD copper tube into an oversized Inconel outer sheath and drawing the Inconel-copper composite tube through a die to obtain an overall duplex tube OD of 0.478 cm.

The test tube assembly had the advantage that, while the high fluid pressure was sustained by the Inconel sheath, the majority of the power (approximately 95 percent) was generated in the copper. As a result, the tube radial temperature gradient was small.

To assure satisfactory fabrication of the duplex tubing, metallographic examination of samples, shear tests, and thermal cycling in a high-temperature oven were conducted. Although the copper closely followed the contour of the Inconel surface, any tendency for interfacial separation would be opposed during testing by the combined action of the internal pressure and the higher rate of thermal expansion of copper relative to Inconel.

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Prior to actual testing, a computerized, multi-element heat transfer analysis of the duplex test tube and bus rings evaluated inner wall temperatures from outer wall values. In the analysis a finite difference representation of the heat conduction equation was solved by a relaxation technique. The calculated differences between the inner and outer wall temperatures were equivalent to the experimental accuracy of the temperature measurements along the tube, when no interfacial resistance between wall metals was assumed. Tests were performed with a specially instrumented test tube which allowed direct measurement of the temperature at the Inconel-copper interface as well as at the Inconel outer wall. The tests confirmed the assumption that no significant thermal resistance in the conduction model evaluation was reasonable.

During testing, coking was detected by a change in the tube axial wall temperature distribution when the supply pressure, fluid velocity, and tube heat rate were held constant. After each test in which there was an indication of coking, the test tube was sectioned and the surface scanned using an electron microprobe to evaluate the structure and composition of the deposit.

The carbon deposition rate determinations were made by burning off the tube deposits and measuring the quantity of CO_2 evolved. A metered flow of air was passed at a constant rate through heated sections of the test tube. The product gases resulting from the burnoff were subsequently passed through a nondispersive infrared analyzer which provided a continuous measurement and record of the concentration of CO_2 in the effluent gas. Integration of the data over the total burnoff time gave the total volume of CO_2 evolved, from which a carbon weight and deposition rate were calculated.[3]

TEST RESULTS

All deposit formation tests with commercial-grade (90 percent) and chemically-pure (CP-) propane were conducted at a pressure of 13.7 MPa (approximately 2000 psi). Test data was obtained for wall temperatures ranging from 422 to 811K (300-1000° F) and velocities from 6.1 to 30.0 M/s (20-100 ft/sec).

The results of the carbon evaluation indicated that carbon deposition rates for propane fuels were generally higher than those obtained for kerosene fuels at any given wall temperature. Rates ranged from 300 to 750 micrograms per sq cm-hr at 400-650K (260-710° F) temperatures. There appeared to be little difference between 90-percent and CP-propane with regard to type and quantity of deposit.

Figure 3 shows a graph of wall temperature versus test duration with the temperature history at selected wall locations beginning near the fluid inlet to a position at the discharge end of the test tube.

An anomaly in the propane tests was the manifestation of sharp temperature variations. An example of this behavior near the tube exit appears in Figure 3. Even though test conditions were essentially constant, the wall temperature fluctuated over a 200K temperature range. The temperature variations occurred consistently, but to varying degrees along the entire length of the tube. When the wall temperature was set at 700 or 811K (800 or 1000° F), most of the tests had to be terminated prematurely because the

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excessive temperature fluctuations eventually exceeded the maximum wall temperature limitation (866K). Although the test pressure of 13.7 MPa (approximately 2000 psi) is well above the propane critical pressure of 4.3 MPa (617 psia), the temperature of the propane near the wall can exceed the propane critical temperature of 370K (206° F). In this region the character of the propane changes and there are large variations in physical properties such as density and specific heat for relatively small temperature changes. These changes would affect the heat transfer characteristics and influence the temperature swings.

DATA CORRELATION

Forced convection heat transfer data were correlated by using the following equation:

$$\frac{h_{calc}D}{k_b} = Nu_b = (K)\,(Re_b)^a\,(Pr)^c\left(\frac{\rho_b}{\rho_w}\right)^d\left(\frac{\mu_b}{\mu_w}\right)^e\left(\frac{k_b}{k_w}\right)^f\left(\frac{\overline{C}_p}{C_{p_b}}\right)^g\left(\frac{P}{P_{crit}}\right)^h\left(1+\frac{2}{L/D}\right) \quad (1)$$

where

Nu   Nusselt number

Re   Reynolds number

Pr   Prandtl number

ρ Density

μ Viscosity

k   Thermal conductivity

C_p Specific heat

$\overline{C}_p$ Integrated average specific heat from T_w to T_b

K   Experimental determined constant

P   Pressure

P_{crit} Critical pressure

L/D   Length/diameter from initiation of heating

h   Heat transfer coefficient

and subscripts

b   denotes property evaluated at bulk temperature

calc   calculated parameter

w   denotes property evaluated at wall temperature

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The constants K, a, c, d, e, f, g, and h were determined in Reference 5 from the forced convection data by using a multiple regression analysis computer program. Transport property data were obtained from NBS and API sources[6],[7]. The constants were derived from tests with 96 percent purity propane[5].

The last case delineated in Table I provides the exponents employed in this evaluation (Figures 4-8).

The initial tube wall temperatures were recorded immediately after achieving overall system steady-state (usually less than 6 seconds) and the correlations derived from these data are represented in Figures 4 and 5 as 'pristine' data. These figures compare experimental data to a correlation in a logarithmic plot with the imposed bandwidth defining the spread or departure[5]. The ordinate is derived from the experimental heat transfer coefficient, and the calculated Nusselt parameter on the abscissa is obtained from the right side of equation (1). The equation is satisfactory for the data with 99.4 percent (CP-) propane (Figure 4).

Figure 5 shows the data for both grades of propane. The 90-percent propane grade included 5 volume percent propylene with the remainder essentially butane hydrocarbons and 0.015 weight percent sulfur. This sulfur content exceeded the trace amount in the CP- grade by a factor of 3. Approximately 1/3 of the data fall outside the +30 percent band in Figure 5. These data cover the entire velocity range although the scatter is greater for velocities of 21-30 m/s.

In Figures 6 and 7, the experimental Nusselt number is obtained from the propane experimental tests after accounting for the additional carbon resistance.

Since the heat flux (Q/A) is maintained constant for the test duration, the propane receives the same heat regardless of the carbon deposit which may build up. With this occurrence, the temperature at the tube wall must rise to account for the temperature difference across the carbon layer.

For the same flow condition, the experimental propane coefficient after deposit formation is:

$$h_{exp} = \frac{(Q/A)}{(Tc - Tb)} \tag{2}$$

where Tc is the temperature of the carbon surface, and Tb is the fuel (coolant) temperature. The thermal resistance of the carbon layer which resulted from the deposit is defined as:

$$Rc = \Delta Tw/(Q/A) \tag{3}$$

where ΔTw is the measured wall temperature rise for the time period. It is equivalent to (Tcw-Tc), and Tcw is the coolant wall temperature. The property ratios required for the calculated Nusselt number would remain unchanged for the same Tb.

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Figure 6 shows the good agreement of the calculated propane Nusselt number as compared to the experimental value by the small amount of scatter from the diagonal, and like Figure 4 supports the prediction capability of the equation (1) correlation for the CP- propane grade.

Figure 7 shows a greater tendency for the data to depart from the correlation with the inclusion of the 90 percent grade data, although most of the data is confined to the ±30 percent bandwidth. The recorded pressure drop across the tube length varied slightly from run to run with no significant difference over the test period. Therefore, film coefficient enhancement due to surface roughness was not considered significant for these test conditions.

With the occurrence of carbon deposits, most of the tests at 700 and 811K (1000° F) wall temperatures had to be terminated before the full ten minutes for test time was achieved because the wall temperatures fluctuated excessively. Even with wall temperatures below 700K (800° F), the fluctuations resulted in some wall temperatures lower than the first test measurements. These irregularities in wall measurements were excluded from the data in Figures 6 and 7.

Finally, the correlation was employed for all the propane data, but with the carbon layer resistance R_c, and propane film resistance combined as follows:

$$R = \frac{1}{h'_{exp}} = R_c + \frac{1}{h_{exp}} = \frac{\Delta T_w}{Q/A} + \frac{(T_c - T_b)}{Q/A} = \frac{(T_{cw} - T_c) + (T_c - T_b)}{Q/A} \tag{4}$$

This correlation is presented in Figure 8. Upon close examination of the data displayed in Figures 7 and 8, it becomes evident that there is no essential effect of a carbon layer resistance.

The deposits observed from photomicrographs taken at different sections of the tube indicate an average thickness of approximately 0.001 cm.

The conclusion from these results is that the resistance attributed to the deposit is negligible compared to the resistance of the fluid film for the circumstances involved with these deposits.

DEPOSIT MORPHOLOGY

A limited qualitative elemental analysis of the deposits was made utilizing a Scanning Electron Microprobe (SEMP). The SEMP incorporates an x-ray energy-dispersive spectrometer to identify elements present in the deposit, and a selective wavelength spectrometer for x-ray mapping of selected elements.

Filament deposits viewed in Figure 9 have been observed in various studies of carbon deposition on metal surfaces and several mechanisms have been proposed to explain filamentary carbon growth[3]. Copper does not dissolve carbon, but instances of filamentary deposit with dendritic growth have been recorded. In the SEMP analysis, the presence of the selected element is indicated by clusters of white dots on a dark background that matches a standard photomicrograph of the sample and allows easy identification of the areas of local concentration of the particular element.

The results of the SEMP analysis in Figure 10 indicate that the dendritic mass contains a high concentration of copper, suggesting that the tube material was forced up and away from the surface[4]. Surface chemistry may suggest a process for protecting the material and/or reducing the effects of the deposition.

SUMMARY OF RESULTS

Deposit formation tests with commercial-grade (90-percent) and chemically-pure (99.4 percent) propane were conducted at a pressure of 13.7 MPa (approximately 2000 psi). Test data was obtained for wall temperatures ranging from 422 to 811K (300-1000° F) and velocities from 6.1 to 30.0 m/s (20-100 ft/sec).

1. Photomicrographic examination of the deposited tube surfaces using propane under forced-convection heat transfer conditions indicated that the deposits were not formed as smooth, continuous films of uniform structure and composition. Spherical discrete particles, and random dendritic clumps, accumulated over a fused substrate to produce a highly variable, three-dimensional microstructure[3,4].

2. Deposition of carbon on copper walls appeared to build up at a rate of 300-750 micrograms per sq. cm-hr.

3. The Nusselt correlation shows all data to lie within a bandwidth of ±30 percent for chemically pure propane prior to deposition.

4. The Nusselt correlation with the included 90-percent propane grade shows agreement within the ±30 percent bandwidth for approximately 70 percent of the data prior to deposition indicating a slight variation in thermal character due to impurities.

5. The Nusselt correlation for all the carbon deposit data, with carbon layer resistance in the correlation shows a bandwidth of ±30 percent for approximately 80 percent of the data.

6. Scanning Electron Microprobe (SEMP) analysis indicates that carbon deposits in copper tubes actually caused a migration of one element into the other.

REFERENCES

1. Cook, R. T., "Advanced Cooling Techniques for High-pressure Hydrocarbon-Fueled Engines," Rocketdyne, Canoga Park, CA., RI/RD79-310, Oct. 1979. (NASA CR-159790).

2. Luscher, W. P. and Mellish, J. A., "Advanced High Pressure Engine Study for Mixed Mode Vehicle Applications," Aerojet Liquid Rocket Co., Sacramento, CA., Jan. 1977. (NASA CR-135141).

3. Roback, R., Szetela, E., and Spadaccini, L., "Deposit Formation in Hydrocarbon Rocket Fuels," United Technologies Research Center, East Hartford, Conn., R81-915216-1, Aug. 1981. (NASA CR-165405).

4. Roback, R., Szetela, E., and Spadaccini, L., "Deposit Formation in Hydrocarbon Fuels," ASME Paper No. 82-GT-49, Apr. 1982.

5. Gross, R. S., "Combustion Performance and Heat Transfer Characterization of LOX/Hydrocarbon Type Propellants," Aerojet Liquid Rocket Company, Sacramento, CA., Aug. 1980.   (NASA CR-160874).

6. Goodwin, R. D., "Provisional Thermodynamic Functions of Propane, from 85 to 700K at Pressures to 700 BAR," National Bureau of Standards, Report NBSIR 77-860, July 1972

7. Technical Data Book, 3rd ed., American Petroleum Institute, Washington, D.C., 1976.

TABLE I

PROPANE FORCED CONVECTION CORRELATION SUMMARY**

Correlation Form: $Nu = (1 + \frac{2}{L/D})(K)(Re_b)^a (Pr_b)^c (\rho_b/\rho_w)^d (\mu_b/\mu_w)^e (k_b/k_w)^f (\overline{C}p/Cp_b)^g (P/P_{crit})^h$

Case number	Coefficients/Exponents								STD deviation	Comments
	K	a	c	d	e	f	g	h		
1	0.00538	0.90	0.4*	−0.125	0.242	0.193	−0.395	−0.024	0.130	All forced convection data
2	.00145	1.0*	.4*	−.227	.357	.069	−.299	−.037	.136	All forced convection data Reynolds number fixed
3	.00545	.898	.4*	−.114	.228	.268	−.526	0*	.130	All forced convection data (P/P_{crit}) removed
4	.00532	.889	.4*	−.129	.351	.0995	−.432	0*	.127	Supercritical data (P/P_{crit}) removed
5	.00568	.876	.4*	.120	−.142	.828	−.368	.254	.121	Supercritical data with (P/P_{crit}) term

* Denotes exponent held constant in analysis
** Reference 5
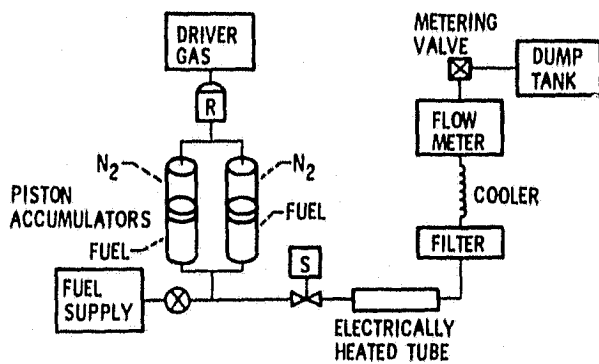
Figure 1. - Fuel deposit test apparatus.
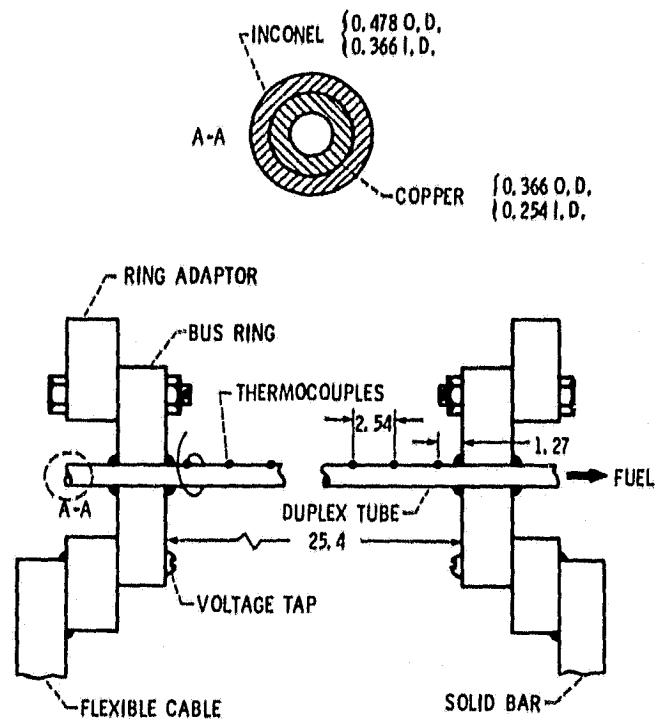
Figure 2. - Test tube assembly. (All dimensions in cm).
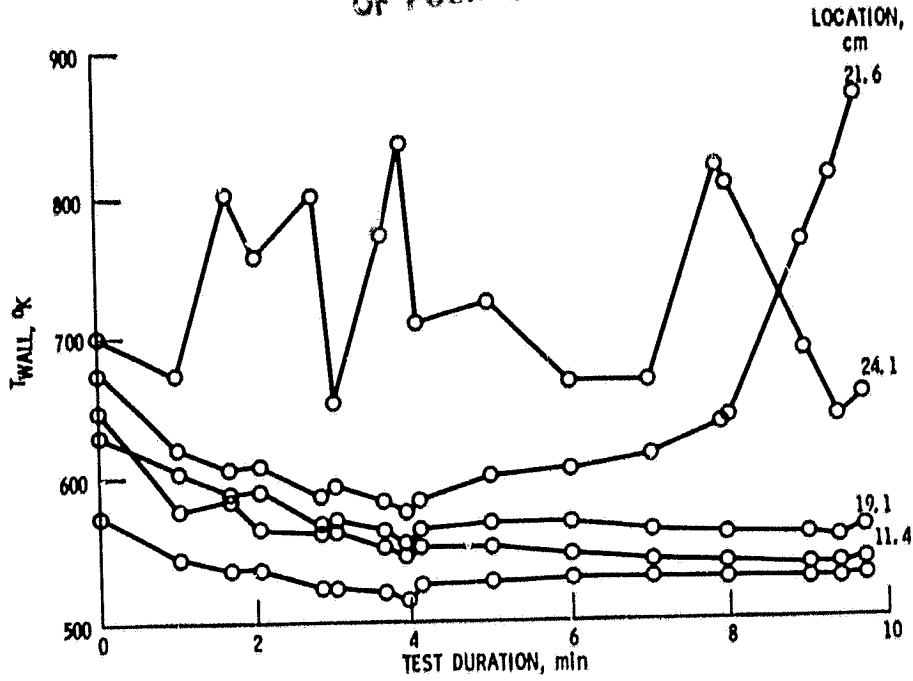
Figure 3. – Variation of propane wall temperature with time.
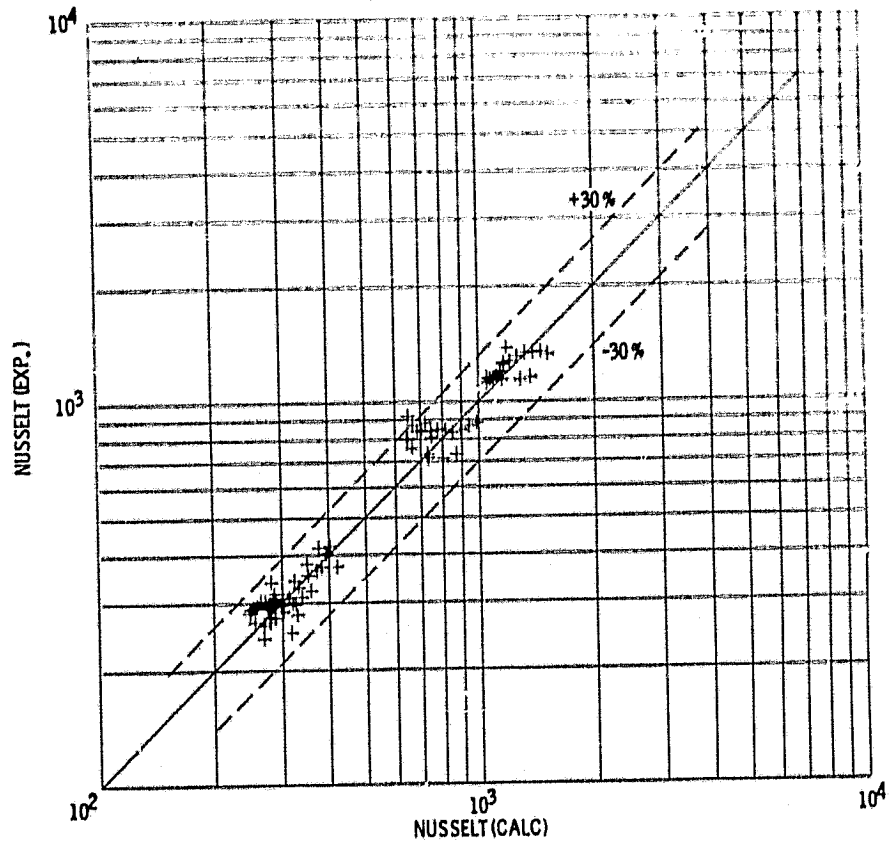
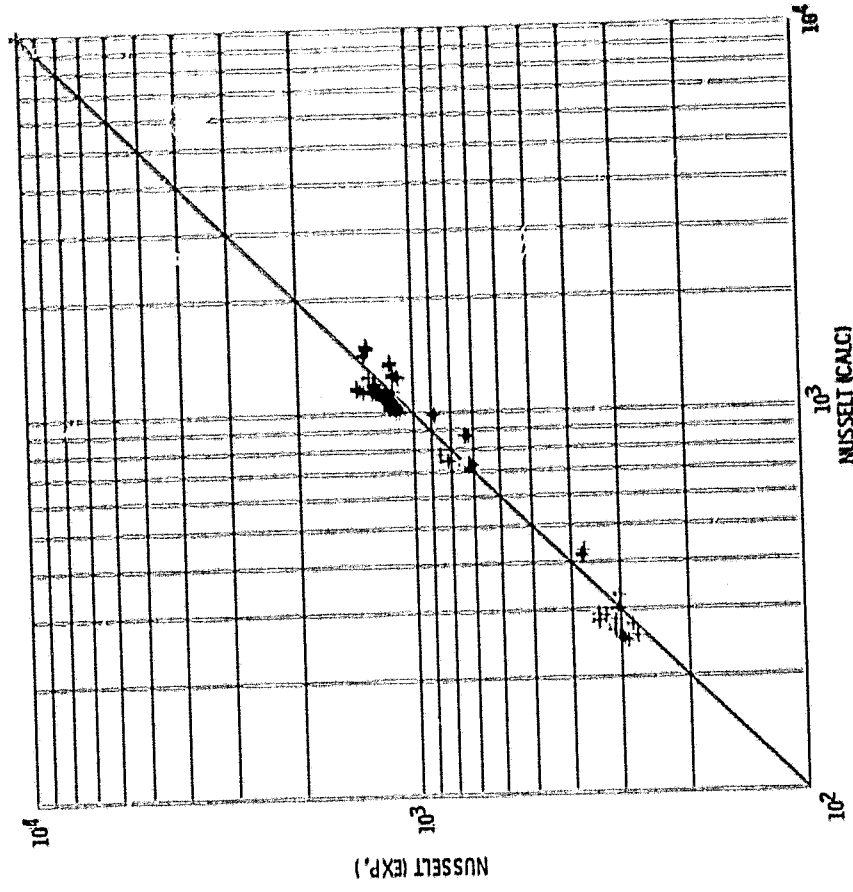Figure 4. – Propane Nusselt evaluation. Pristine data, CP propane.

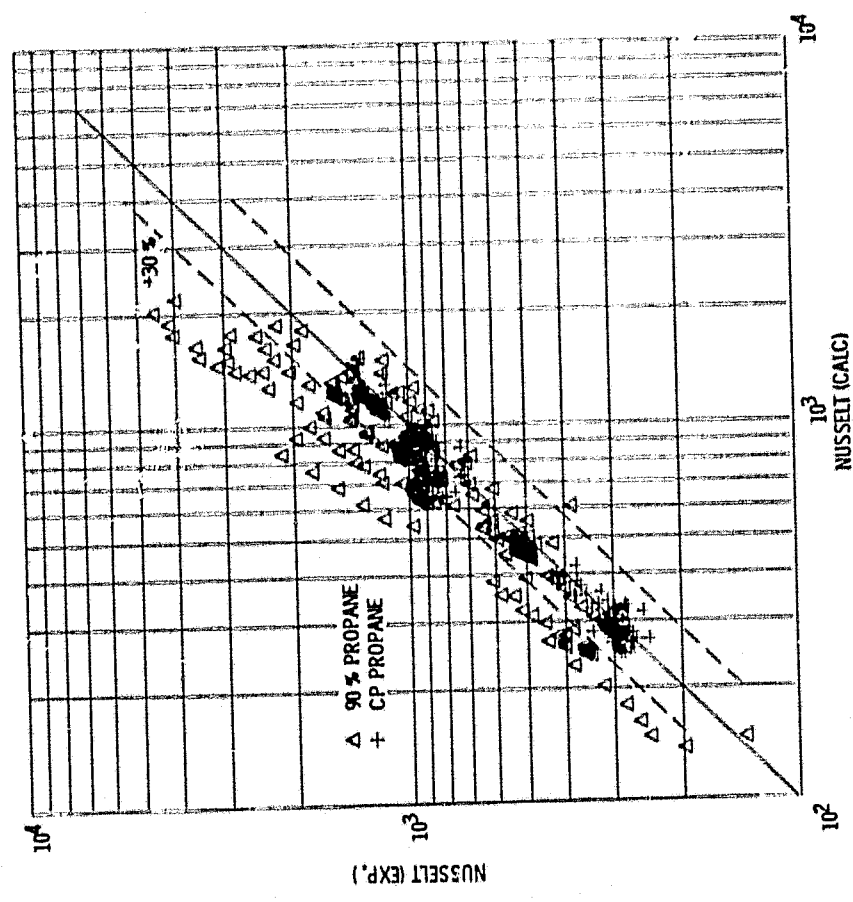Figure 6. – Propane Nusselt evaluation. Carbon present, CP propane.

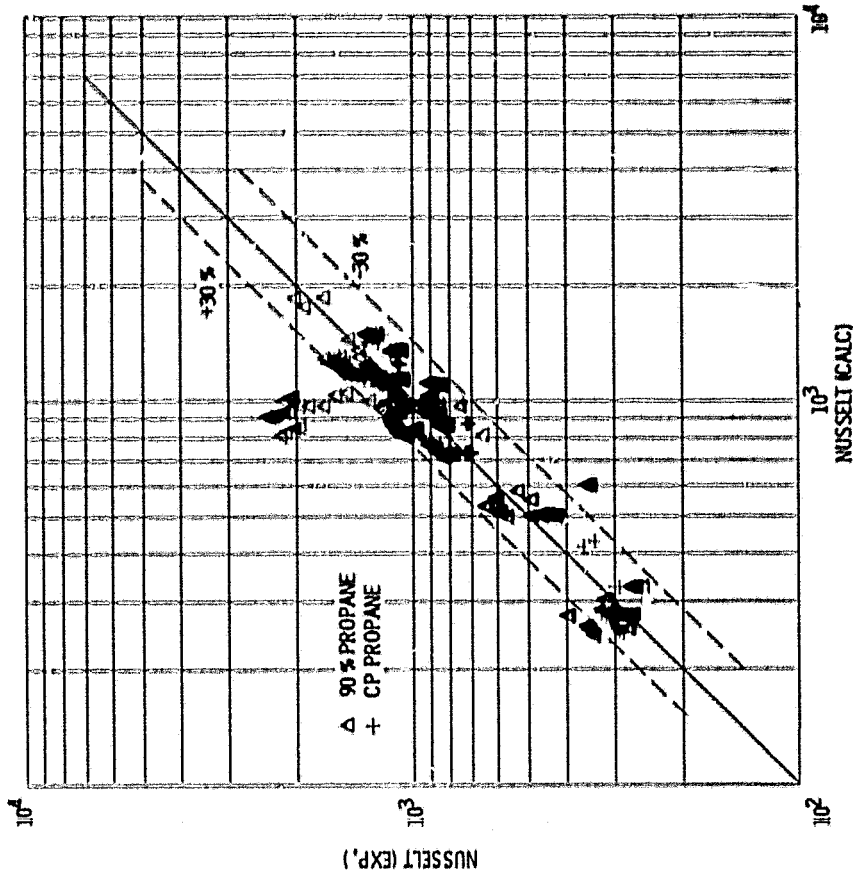Figure 5. – Propane Nusselt evaluation. Pristine data, CP and 90 percent propane.

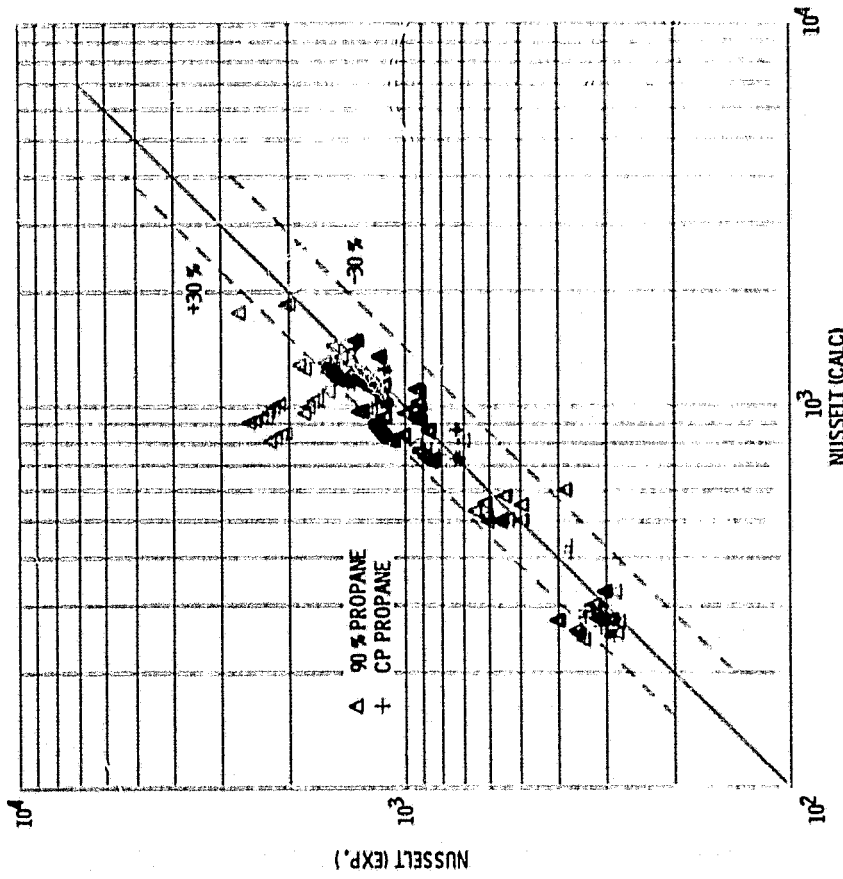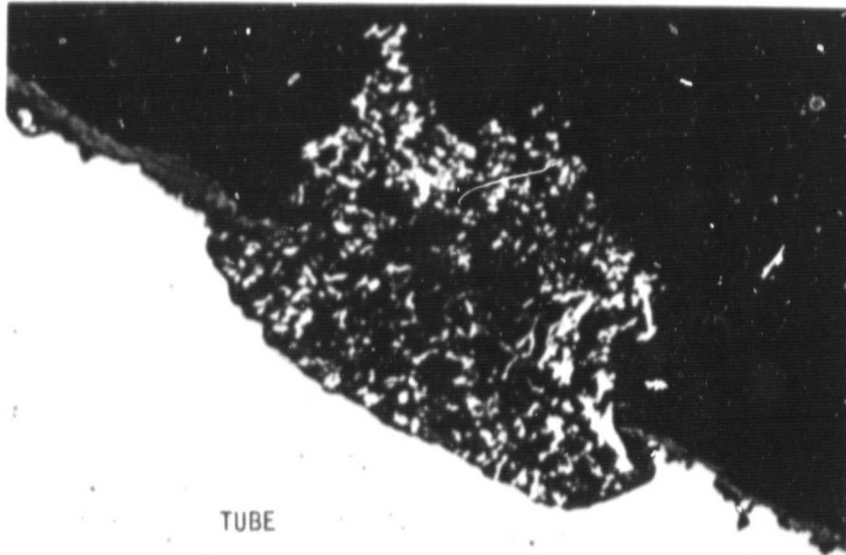Figure 8. – Propane Nusselt evaluation. Carbon present in correlation, CP and 90 percent propane.
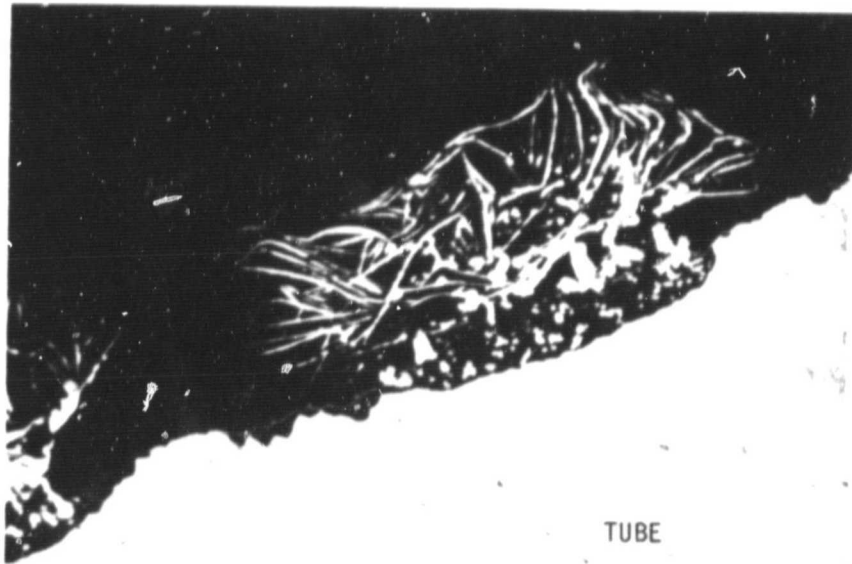

Figure 7. – Propane Nusselt evaluation. Carbon present, CP and 90 percent propane.

TUBE

TUBE

Figure 9. - Propane Fuel Deposits. 500X MAGNIFICATION T_{WALL} = 700K

COPPER   CARBON
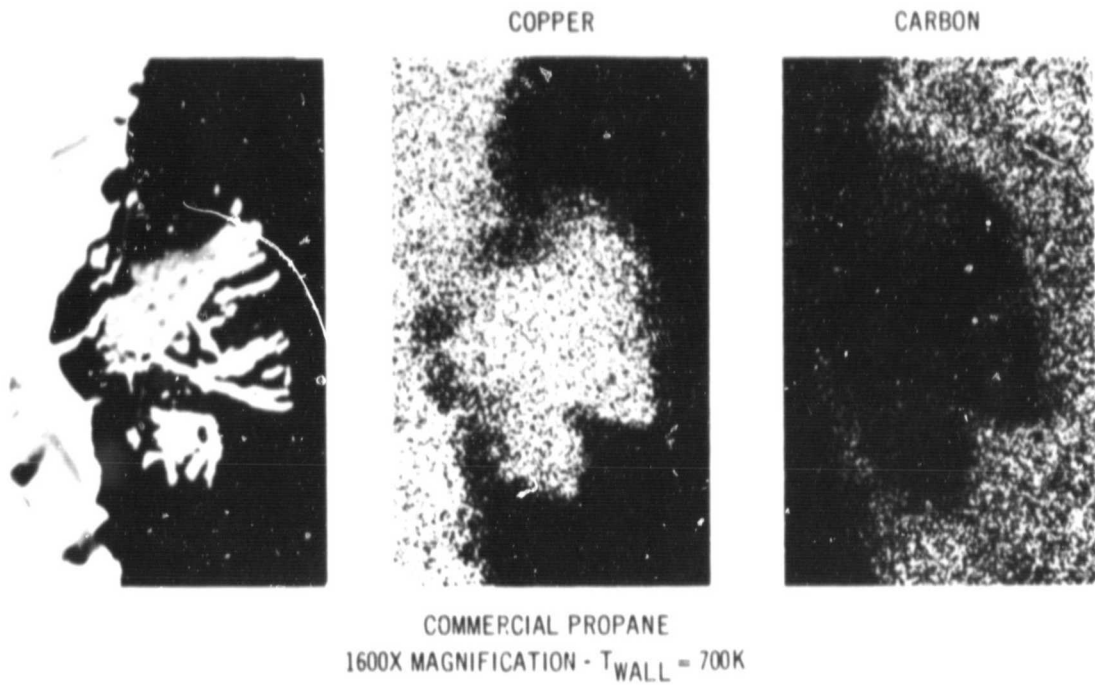

COMMERCIAL PROPANE
1600X MAGNIFICATION - $T_{WALL} = 700K$

Figure 10. - Scanning Electron Microprobe Analysis of Deposits.