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Deposit Formation in Hydrocarbon Rocket Fuels — Executive Summary Report

Richard Roback
Eugene J. Szetela
Louis J. Spadaccini

UNITED TECHNOLOGIES RESEARCH CENTER
East Hartford, CT 06108

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Lewis Research Center
Cleveland, Ohio 44135

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| 16. Abstract <p>An experimental program was conducted to study deposit formation in hydrocarbon fuels under flow conditions that exist in high-pressure, rocket engine cooling systems. A high pressure fuel coking test apparatus was designed and developed and was used to evaluate thermal decomposition (coking) limits and carbon deposition rates in heated copper tubes for two hydrocarbon rocket fuels, RP-1 and commercial-grade propane. Tests were also conducted using JP-7 and chemically-pure propane as being representative of more refined cuts of the baseline fuels. A parametric evaluation of fuel thermal stability was performed at pressures of 136 atm to 340 atm, bulk fuel velocities in the range 6 to 30 m/sec, and tube wall temperatures in the range 422 to 811K. In addition, the effect of the inside wall material on deposit formation was evaluated in selected tests which were conducted using nickel-plated tubes.</p> <p>The results of the tests indicated that substantial deposit formation occurs with RP-1 fuel at wall temperatures between 600 and 800K, with peak deposit formation occurring near 700K. No improvements were obtained when de-oxygenated JP-7 fuel was substituted for RP-1. The carbon deposition rates for the propane fuels were generally higher than those obtained for either of the kerosene fuels at any given wall temperature. There appeared to be little difference between commercial-grade and chemically-pure propane with regard to type and quantity of deposit. The results of tests conducted with RP-1 indicated that the rate of deposit formation increased slightly with pressure over the range 136 atm to 340 atm. Finally, plating the inside wall of the tubes with nickel was found to significantly reduce carbon deposition rates for RP-1 fuel.</p> | | | | | |
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R. Roback
E. J. Szetela
L. J. Spadaccini

INTRODUCTION

The performance characteristics of advanced technology hydrocarbon-fueled rocket engines may be enhanced by operating at higher combustion pressures and utilizing more of the heat sink capability of the fuel to accommodate the increased heat fluxes that result from high pressure operation. 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, a progressively increasing wall temperature and, ultimately, failure. Therefore, it is desirable to establish (1) the maximum heat fluxes that can be accommodated by determining the minimum wall temperature limits for incipient deposit formation under a variety of coolant flow conditions, (2) what rates of formation will prevail, and (3) the nature of the deposit, as it affects the heat transfer limits.

Hydrocarbon fuel stability and deposit formation (coking) has been a subject of investigation for many years and the results of many of these previous studies have been summarized in Refs. 1 and 2. The rates of fuel decomposition and deposit formation have been found to be functions of the temperature, pressure, velocity, composition and physical state of the fuel. Although the exact mechanism of deposit formation has not been clearly defined, it usually results from the pyrolysis of organic molecules which make up the fuel. Free radicals are generated thermally and, because of their affinity for atoms such as nitrogen, oxygen, and sulfur which might be in the fuel, stable complex solids are formed. Studies have shown that additional processing of the fuel to remove these deposit forming precursors has improved thermal stability and decreased deposit formation.

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. However, studies of the effect of wall materials on deposit formation, Refs. 4, 5 and 6, have indicated that deposit rates on copper can be very high; although no data was available for the particular fuels and test conditions of interest. Therefore, to permit more accurate determinations of the maximum allowable wall temperatures, a fuel

coking test apparatus was designed and developed and was used in experiments directed toward (1) evaluating the thermal decomposition (coking) limits and rates of deposition in heated copper tubes for two hydrocarbon fuels, RP-1 and propane, and (2) investigating the effect of further refining of these fuels, to reduce the concentration levels of deposit-forming precursors, on improving their thermal stability (Ref. 7). Tests were conducted using RP-1 and commercial-grade propane as the standard hydrocarbon rocket fuels and deoxygenated JP-7 and chemically-pure propane as being representative of more refined cuts of these fuels. A parametric evaluation of fuel thermal stability was performed at pressures of 136 atm to 340 atm, bulk fuel velocities in the range 6 to 30 m/sec, and tube wall temperatures in the range 422 to 811K. In addition, the effect of the inside wall material on deposit formation was evaluated in selected comparative tests which were conducted using nickel-plated tubes.

TEST FACILITY AND TEST HARDWARE

The test apparatus, shown schematically in Fig. 1, consisted of: (1) a fuel supply tank, including a porous metal nitrogen sparger and a zeolite-type molecular sieve for removing dissolved oxygen and water from the JP-7 fuel; (2) a fuel delivery system consisting of two piston-type accumulators which were pressurized with nitrogen and used to drive fuel through the test section; (3) a resistance-heated test tube connected to a 40 kVA high-amperage AC power supply; (4) an in-line filter for collecting any solid particles which might form in the bulk flow or break off from the test tube wall during test; (5) a fuel cooler; (6) a turbine-type flowmeter; (7) an electrically-driven metering valve which was used to control the fuel flow through the test section; and (8) a fuel dump tank.

To permit testing at pressures up to 340 atm and tube wall temperatures up to 1000K, a duplex tube wall configuration, shown schematically in Fig. 2, was selected. In the duplex tube configuration, an inner wall of an oxygen-free, high-conductivity copper (No. 102; 99.95 percent pure; electrical conductivity = 0.0586 Megmho-cm) provided the desired test surface for studying the rates of deposit formation on copper while an outer wall of Inconel 600 provided the necessary high-temperature tensile strength. The duplex tube was manufactured by threading a 0.254-cm ID x 0.366-cm OD copper tube into an oversized Inconel outer sheath, and subsequently drawing the Inconel tube through a die to obtain a sheath thickness of 0.056 cm and an overall duplex tube OD of 0.478 cm. This configuration had the advantage that, while the structural load was carried by the outer sheath, the majority of the power (~ 95 percent) was generated in the copper and, as a result, the tube radial temperature gradient was small.

To verify the condition that no significant electrical or thermal resistance at the interface of the two metals, stemming from oxidation, contamination or local separation had developed, tube samples were subjected to various tests

which included: metallographic examination using a scanning electron microscope and microprobe, shear tests, and thermal cycling in a high-temperature oven. The results indicated that the copper closely followed the contour of the Inconel surface and the interface was free of contamination and/or air gaps. In addition, any tendency for separation at the copper/Inconel interface would be opposed during testing by the combined action of internal pressure forces and the higher rate of thermal expansion of copper relative to Inconel.

The test tube assembly is also shown schematically in Fig. 2. The test tube was silver soldered to a copper bus ring which in turn was bolted to copper ring adaptors. Ten thermocouples were spotwelded to the outer Inconel wall at equal spacings of 2.54 cm starting at a location 1.27 cm from the bus ring. The surface of the tube was coated with Sauereisen cement at the thermocouple junctions, to electrically insulate the thermocouple wire from the tube, and the wire was wrapped once around the tube and coated with additional Sauereisen cement to insure good thermal contact and minimize conduction losses. By use of an AC power supply, thermocouple errors resulting from a voltage drop across the thermocouple bead were minimized. The test tube assembly was supported on teflon lined cradles that were designed to accommodate the bus rings and to permit thermal expansion by providing a low coefficient of sliding friction. The teflon also acted as an electrical insulator and prevented grounding of the test tube. In addition, non-conductive flexible hose was installed at the entrance and exit of the test tube assembly to allow thermal expansion and to electrically isolate the tube from the other components of test apparatus.

EXPERIMENTAL RESULTS AND DISCUSSION

Prior to actual testing, the test tube inner wall temperatures were calculated from outer wall temperatures using a computerized, multi-element heat transfer analysis (TCAL) in which a finite difference representation of the heat conduction equation is solved by a relaxation technique. The calculated differences between the inner and outer wall temperatures of the duplex tube ranged from approximately 1 to 15K over the entire range of test conditions. These temperature differences were, for the most part, within the expected experimental accuracy of the temperature measurement and, therefore, the measured outer (Inconel) wall temperature was considered representative of the inner (copper) wall temperature.

The experimental program began with a sequence of calibration tests to corroborate the results of the heat transfer analysis and to verify the absence of a significant thermal resistance at the Inconel-copper interface. 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 results of these tests indicated that there was

excellent agreement between the two wall temperature distributions. The largest temperature difference measured was only 10K, thereby verifying (in a general sense) the temperature predictions as well as confirming the absence of a significant resistance at the interface between the two metals.

Kerosene Fuel Tests

Testing began with RP-1 fuel at a fluid velocity of 6.1 m/sec and a wall temperature of 422K. No significant temperature rise was observed along the tube during the ten minute test duration, suggesting the absence of significant deposit formation. Subsequent sectioning of the tube and microscopic inspection of the inner copper surface confirmed that deposits had not been formed; therefore, no additional testing was done at a wall temperature of 422K. The remaining tests with RP-1 fuel were conducted at wall temperatures between 589 and 811K, at a pressure of 136 atm, and for fluid velocities ranging from 6.1 to 30.5 m/sec. The input heat flux to the tube was varied between 173 and 1460 Watt/cm², in order to achieve the desired wall temperature. In addition, selected tests with deoxygenated JP-7 fuel were also conducted at test conditions which indicated significant deposit formation with RP-1 fuel.

Typical temperature distributions obtained with the kerosene type fuels at the maximum and minimum test velocities (i.e., 6.1 and 30.5 m/sec) are shown in Fig. 3. These results indicated that substantial changes in the heat transfer processes were incurred as the flow, power and wall temperature were varied. As can be seen in the figure, the highest wall temperatures occur near the tube entrance and the wall temperature decreases along the length of the tube. This seemingly anomalous trend stems from the variation of bulk fuel properties with temperature, and results in a local heat transfer coefficient which is lowest at the tube entrance, where the fuel is cold, and increases as the fuel is heated. At low velocity conditions, and particularly at high power, the wall temperature increased with length near the tube entrance, reached a maximum value, and thereafter decreased continuously to the end of the tube. The wall temperature distribution noted at low velocity appears to indicate laminar-like flow at the tube entrance followed by a transition to turbulent flow. This entrance effect could be expected to be minimized at the higher Reynolds numbers associated with the higher flow rates. It can also be seen that over the ten minute duration, significant wall temperature rises occurred during the RP-1 fuel tests while smaller increases in wall temperatures were observed with the JP-7 fuel. This trend was generally observed over the entire range of test conditions. The results indicated that the maximum temperature rises that were measured during the ten minute tests occurred at tube locations where the wall temperatures were initially between 700K and 750K. There appeared to be no significant effect of fluid velocity on the magnitude of the peak temperature rise.

A measure of the rate of carbon deposition which occurred during a test is the deposit thermal resistance buildup rate (R_c), which is defined as:

$$R_c = \frac{\Delta T_w}{(Q/A)(t)}$$

where ΔT_w is the wall temperature rise (deg K) observed during the test, Q/A is the heat flux (Watt/cm²) maintained during the test, and t is the test duration (min.). The thermal resistance buildup rates calculated for tube sections which exhibited temperature rises during testing with RP-1 fuel are shown in Fig. 4. It can be seen that the thermal resistance buildup rate reached a maximum at tube locations where the initial wall temperature was approximately 700K. In addition, as the fluid velocity was increased, the magnitude of the peak thermal resistance buildup rate appeared to decrease. The magnitude of the rates obtained for a fluid velocity of 30.5 m/sec are in good agreement with experimental data obtained by other investigators (Ref. 8) for RP-1 at velocities in the range 46 to 76 m/sec.

During testing, deposit formation was indicated by a significant change in the tube axial wall-temperature distribution when the system pressure, fluid velocity, and tube heating rate were held constant. After each test in which there was a positive indication of coking, the test tube was sectioned and prepared for microscopic examination and deposit analysis. Inspection of the inside surfaces of longitudinal sections of the tubes tested with RP-1 fuel revealed that the deposit coverage was generally very non-uniform and ranged from specks, to connected islands of deposits, to essentially full coverage. No particular pattern could be established with test conditions and the non-uniform deposit coverage made a determination of the point of incipient deposit formation impossible. Also, the deposits observed were multi-colored and took on various shades of red, black and sometimes gray. All three colors could sometimes be seen on samples taken from a single tube; however, it was difficult to associate color with a particular run condition or wall temperature. The deposits appeared to vary in degree of roughness but were generally hard and did not break loose from the tube surface very easily. From the general appearance of the inner surfaces of the tubes, it was concluded that the formation of deposits on copper is a very complex process, leading to various intermediate compounds which can take on various colors and textures and which will likely affect the local heat transfer processes.

The primary measure of the deposit formation rate with the various test operating conditions was made by burning off the tube deposits and measuring the quantity of CO₂ evolved. A special laboratory bench-type apparatus was employed for this task, wherein 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 CO₂ in the effluent gas. Integration of the data over the total burnoff time gave the total volume of CO₂ evolved, from which a carbon weight and deposition rate were calculated.

The rates of carbon deposition determined for RP-1 are presented in Fig. 5 as functions of the average initial wall temperatures. The open symbols represent data obtained from 3.8-cm-long tube sections while the closed symbols represent a composite of the smaller sections, or a tube average value. Although there is considerable scatter in the data, believed to result from the combined effects of experimental error and the non-uniformity of the deposits on the tubes, some general trends can be observed. The deposit rate data appear to substantiate the conclusions drawn previously from the deposit thermal resistance buildup rates (see Fig. 4); i.e., the rate of carbon deposition increases with increasing temperature, reaches a maximum at an initial wall temperature of approximately 600 to 700K, and then falls off as temperature is increased further. Also, the carbon deposition rates decrease with increasing fluid velocity.

Deposit burnoff tests were also conducted on the tube sections obtained from the deoxygenated JP-7 tests. Since only a limited number of tests were performed with JP-7, not enough test data was acquired to graphically indicate the trends with test conditions. However, the data do indicate that the deposit formation rates are generally of the same magnitude as was determined for RP-1. Since JP-7 typically has an order of magnitude lower sulfur content than RP-1 and because it must meet a stringent thermal stability specification, it was assumed that JP-7 would be a good simulator of refined quality RP-1 and demonstrate improved thermal stability. Also, since the dissolved oxygen concentration in the JP-7 was reduced to less than 5ppm by sparging with nitrogen, and because the temperature rises obtained with JP-7 were generally lower than those obtained with RP-1, it was expected that less deposit would be found with JP-7. However, when the tubes used in the JP-7 tests were sectioned, microscopic examination revealed that there was significant deposit formation and that the deposits appeared darker and more uniform than the RP-1 deposits. A diagnostic test was conducted with unsparged JP-7 fuel to determine if the presence of antioxidant and lubricity improving additives, in the absence of dissolved oxygen in the sparged JP-7 fuel, might have promoted higher rates of deposit formation. When the results of this test indicated similar deposit formation, additional testing with JP-7 was suspended because the JP-7 did not appear to offer any benefit in terms of increased thermal stability. A measurement of the actual difference in the thermal stability between the two fuels (i.e., the breakpoint temperatures) was made in a series of tests using a Jet Fuel Thermal Oxidation Tester (JFTOT). The results of this evaluation revealed that both the JP-7 and RP-1 met the thermal stability requirement for JP-7, but the RP-1 was even more stable than the nominally higher quality JP-7. Also, a comparison of certified analyses of the compositions of the two fuels indicated that the actual difference in sulfur contents was only a factor of 2.3, and not the order of magnitude expected. Therefore, it can be concluded that there is little difference in carbon deposition rates and probably no particular advantage in using JP-7.

A limited number of tests were conducted with RP-1 fuel at pressures up to 340 atm. The results indicated that there was no significant change in the tube wall temperature distributions as a consequence of increasing pressure, suggesting that the rate of deposit formation is relatively independent of pressure over the pressure range of 136 to 340 atm. Microscopic examination of the deposits obtained from these tests also revealed that there was no substantial difference in the deposit appearance. The rates of carbon deposition determined from deposit burnoff tests showed the usual data scatter; however, the overall deposition rates fell within a relatively narrow band and indicated that the deposit formation rate increased slightly with pressure.

Propane Tests

All deposit formation tests with commercial-grade and chemically-pure propane were conducted at a pressure of 136 atm. Test data was obtained at fluid velocities ranging from 6.1 to 36.6 m/sec and for tube wall temperatures ranging from 422 to 811K. Most of the tests at the higher temperatures (700 to 811K) had to be terminated prematurely; i.e., before the full ten minute test time was achieved, because the wall temperature fluctuated excessively and eventually exceeded the maximum allowable level (866K). The erratic wall temperature behavior was repeatable and was observed in tests where the initial wall temperature was set at 700 or 811K. Minor temperature fluctuations were also observed during many of the tests which were conducted at wall temperatures of 589K; however, they were not severe enough to necessitate premature shutdown. It should be noted that at the higher tube wall temperatures, the bulk temperature of the propane exceeded the critical point (366K), suggesting that the temperature fluctuations may be due to a change in character of the propane when the critical temperature is exceeded. Moreover, when severe temperature instabilities were observed, the measured bulk fluid temperature was generally between 400 and 500K, a temperature range in which the specific heat of propane at 136 atm pressure changes very rapidly and passes through a maximum (Ref. 9). Therefore, it would appear likely that other transport properties of propane (such as density, viscosity, and thermal conductivity) may also be changing very rapidly and that these properties changes could lead to the unusual heat transfer characteristics that were observed.

The wall temperature distributions obtained for both grades of propane are not appreciably different and are compared in Fig. 6. It can be seen that unlike the results obtained for the distillate fuels RP-1 and JP-7, the wall temperatures observed in the propane tests at the start of the test run exhibited a more or less monotonic increase in temperature from the inlet end to the exit end of the heated tube. This behavior is to be expected from a fluid whose local heat transfer coefficient is nearly constant over the tube length. In contrast to the test runs conducted with the kerosene fuels, a continuous drop in local wall temperature with increasing test time is shown in the figure.

This behavior was noted with the propane fuels at most of the test conditions, suggesting that deposit formation may have significantly increased the turbulence level in the flow, and thereby, increased the heat transfer rates.

Microscopic examination of the deposits obtained with both types of propane indicated heavier, blacker and more uniform deposits than those observed with the kerosene-type fuels, especially at the higher tube temperatures. The carbon deposition rates determined for propane in the burnoff tests confirmed this observation, and the deposit levels were generally higher than those obtained for either of the kerosene fuels at any given tube wall temperature. An interesting phenomenon that was observed in many of the higher wall temperature propane tests was the appearance of dendritic or tree-like formations in which the deposits appeared to grow out from the copper surface as filaments. Scanning electron microprobe analysis (discussed below) revealed that the filament composition was primarily copper, with some carbon concentrated at the base of the tree-like structure. The presence of copper in the deposit may have also contributed to the enhancement of the heat transfer with increasing test time.

Since most of the high wall temperature ($> 589\text{K}$) tests with propane were terminated prematurely, the deposit burnoff data for propane could not be used in a graphical presentation of the dependence of the rates of carbon deposition on wall temperature. The rate data for wall temperatures of 422 and 589K indicated that the deposit rates for both grades of propane fell in the range 400 to 600 $\mu\text{g}/\text{cm}^2\text{-hr}$, and generally overlapped. Although there was some scatter in the data, the carbon deposition rate for propane fuel appeared to decrease slightly with increasing fluid velocity for each tube wall temperature condition.

Nickel-Plated Tube Tests

The results of the experiments for kerosene and propane fuels appear to corroborate and extend the findings of earlier experimental studies which indicated that deposit rates on copper can be very high. Furthermore, it would appear that a copper surface probably promotes deposit formation to as great an extent as any deposit forming precursor contained in the fuels. Therefore, in order to obtain an indication of the importance of the tube wall material on deposit formation, tests were conducted using tubes in which the inside (copper) surface had been plated with nickel by means of an electroless process. All of the tests were run using RP-1 fuel at conditions which resulted in high rates of carbon deposition on copper. The tube wall temperature distributions obtained with the nickel-plated tubes were very similar to those obtained with the copper tubes; however, the temperature rises obtained with the nickel-plated tubes were significantly lower than those obtained with copper, suggesting a substantial decrease in deposit formation. A scanning electron microprobe analysis of the inner surfaces of representative tube sections revealed little

or no deposits (1600X magnification), and an elemental analysis indicated the presence of nickel and phosphorous (the major constituents in the electroless plating solution) but no copper, carbon, oxygen or sulfur. Also, the results of deposit burnoff tests indicated that very little carbonaceous material was deposited on the nickel surface during testing. The average rates of carbon deposition were approximately $50 \mu\text{g}/\text{cm}^2\text{-hr}$, an order-of-magnitude lower than corresponding rates on copper. Therefore, it can be concluded that a substantial decrease in deposit formation occurred when the copper tubes were replaced with nickel-plated tubes.

DEPOSIT MORPHOLOGY

In order to characterize the complex structure of the deposits observed, a scanning-electron microscope (SEM) was used to study the deposits. The SEM is particularly useful for examining solid specimens whose surface structures are rough, because it has a considerably greater depth of focus compared to a conventional reflected-light microscope. When viewed with a SEM, amorphous materials (such as asphalt) show no particular form, crystalline materials (such as graphite) have sharp geometric outlines, and carbonized materials (such as coke) tend to group together in tightly packed aggregates of spherical particles.

SEM analyses were performed on four deposit samples, one for each fuel, which were obtained from tests conducted with copper tubes. The photomicrographs, shown in Fig. 7, were taken at a magnification equal to 5000X and reveal the deposit microstructures. The RP-1 deposit (shown in the upper left) comprises a large number of spherically-shaped agglomerated particles which are approximately $0.5 \mu\text{m}$ diameter. It appears that the top film of deposit fractured, exposing a highly-fused substrate which has been overlaid with the tightly packed spherical agglomerates. Photomicrographs taken near the exit of the tube revealed a type of microstructure that had a more vitreous and amorphous appearance. The SEM photographs of JP-7 fuel deposits (shown in the upper right) again indicate a microstructure of tightly packed spherical agglomerates typical of coke deposits. Compared to the RP-1 deposits, the JP-7 deposits appear to be more uniform and there is not much evidence of deposit fracturing. Photographs taken at other tube locations indicated that there were areas where the deposits appeared to be more flocculent and porous, and areas where the particles appeared to have fused together, forming a knobby surface. The microstructure of commercial-grade propane deposits (shown in the lower left) reveals typical dendritic formations which were dispersed randomly along the entire length of the tube. The photograph does not show the aggregates of spherical particles that were observed with the kerosene type fuels and that are characteristic of coke formation but instead shows distinctly smooth, finger-like structures. The microstructure of deposits

obtained with chemically-pure propane is shown in the lower right side of the figure. It can be seen that the dendritic formation is not as obvious at this lower wall temperature condition (589K) and that clusters of packed particles are spread across the length of the tube. These clusters appear to overlay a fused layer of deposits and consist of packed spherical particles that are similar to those observed in the kerosene fuel deposits.

The photomicrographs shown in Fig. 7 indicate that the deposits accumulated on the tube surfaces are generally not smooth, continuous films of uniform structure and composition. Instead, they indicate that discrete particles spherical or dendritic in shape, accumulate over a fused substrate to produce a highly variable three-dimensional structure. The deposit surface appears to be sufficiently rough to significantly increase turbulence and thereby affect heat transfer. However, there also appears to be areas on the tube where the surface appears smoother after deposit formation. From the SEM photomicrographs, it is obvious that surface roughness and deposit homogeneity can be expected to change along the length of a test tube and may significantly affect the local heat transfer characteristics.

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 which are present in the deposit, and a selective wavelength spectrometer, for x-ray mapping of selected elements. The presence of the selected element is indicated by clusters of white dots on a dark background that matches the standard photomicrograph of the sample and allows easy identification of the areas of local concentration of the particular element. The results of the selected-wave-length analysis made with the SEMP are shown in Fig. 8. In the figure, the upper series of photographs correspond to a tube deposit obtained with JP-7 fuel. The first photograph shows a SEM photomicrograph of the deposit sample. This region was selectively scanned for the presence of copper, carbon, oxygen and sulfur and, if present, these elements would be indicated by an agglomeration of white dots against the dark background. It can be seen that the copper surface of the tube is clearly outlined but that no significant copper is contained in the area occupied by the deposit. The deposit, however, contains a heavy concentration of carbon and a smaller concentration of sulfur. The SEMP analysis of RP-1 fuel deposits gave essentially the same result as the JP-7 analysis, except that a small concentration of oxygen was also present.

The bottom set of photographs represent a SEMP analysis of the microstructure of deposits obtained with propane at a high tube wall temperature (~700K) condition and show a typical dendritic formation. It can be seen that the dendrite contains a high concentration of copper, suggesting that tube material was forced up and away from the surface. Most of the carbon image results from the composition of the potting material, but some carbon is also evident at the base of the tree-like deposit structure. A very small concentration of sulfur

is also indicated in the deposit but no oxygen was observed. Analysis of a tube deposit obtained with chemically-pure propane at a lower wall temperature (~589K) revealed no obvious dendritic formations; however, the deposit material contained significant amounts of copper and substantially more carbon than was found in the dendritic structure.

CONCLUDING REMARKS

The thermal decomposition (coking) limits and rates of carbon deposition in heated copper tubes were investigated for two standard hydrocarbon rocket fuels, RP-1 and commercial-grade propane. In addition, tests were conducted using deoxygenated JP-7 and chemically-pure propane as being representative of more refined cuts of the standard rocket fuels. The apparatus developed for these tests permitted independent variation and control of tube wall temperature, fluid pressure, and fluid velocity in order that the effects of each parameter could be investigated independently.

The results of the experiments with RP-1 fuel were as expected, in that there was previous evidence that copper promotes deposit formation in kerosene-type fuels. However, the relatively high deposition rates of between 400 and 600 $\mu\text{g}/\text{cm}^2\text{-hr}$ at wall temperatures of 500 and 800K for only a ten minute test duration were not anticipated. Peak deposit formation occurred at tube wall temperatures near 700K, which is consistent with results obtained with kerosene-type aviation fuels. The deposit coverage was generally non-uniform and ranged from specks, to connected islands of deposits, to essentially full coverage. No particular pattern could be established with test conditions, and the non-uniformity of deposit coverage made a determination of the point of incipient deposit formation impossible. Plating the inside wall of the tubes with nickel was found to significantly reduce carbon deposition rates for RP-1 fuel.

It was believed that JP-7, which has a lower sulfur content (typically an order of magnitude lower) and meets a stringent thermal stability specification, would be a good simulator of refined quality RP-1 and demonstrate improved thermal stability. However, no benefit in terms of increased stability was realized with JP-7.

Deposits obtained with propane fuels were heavier, blacker and more uniform than those observed with the kerosene-type fuels and there appeared to be little difference between commercial-grade and chemically-pure propane with regard to type and quantity of deposit. The carbon deposition rates for the propane fuels were generally higher than those obtained for either of the kerosene fuels at any given wall temperature. An interesting phenomenon observed in the deposits formed from propane was the appearance of dendritic or

tree-like formations which seemed to grow out from the copper surface as filaments. The filament composition was primarily copper, with some carbon concentrated at the base of the tree-like structure.

Post-test photomicrographic examination of the tube surfaces indicated that the deposits were generally not formed as smooth, continuous films of uniform structure and composition. Instead, discrete particles, spherical or dendritic in shape, accumulated over a fused substrate to produce a highly variable three-dimensional microstructure. The deposit surface appeared to be sufficiently rough to significantly increase turbulence and thereby affect heat transfer. However, there were instances where the surface became smoother during deposit formation. It was obvious from the photomicrographic analysis of the deposits that surface roughness and deposit homogeneity can be expected to change along the length of a test tube and may significantly affect the local heat transfer characteristics. Finally, deposition rate appeared to change with time and, therefore, test duration is an important factor to consider in deposit rate correlations.

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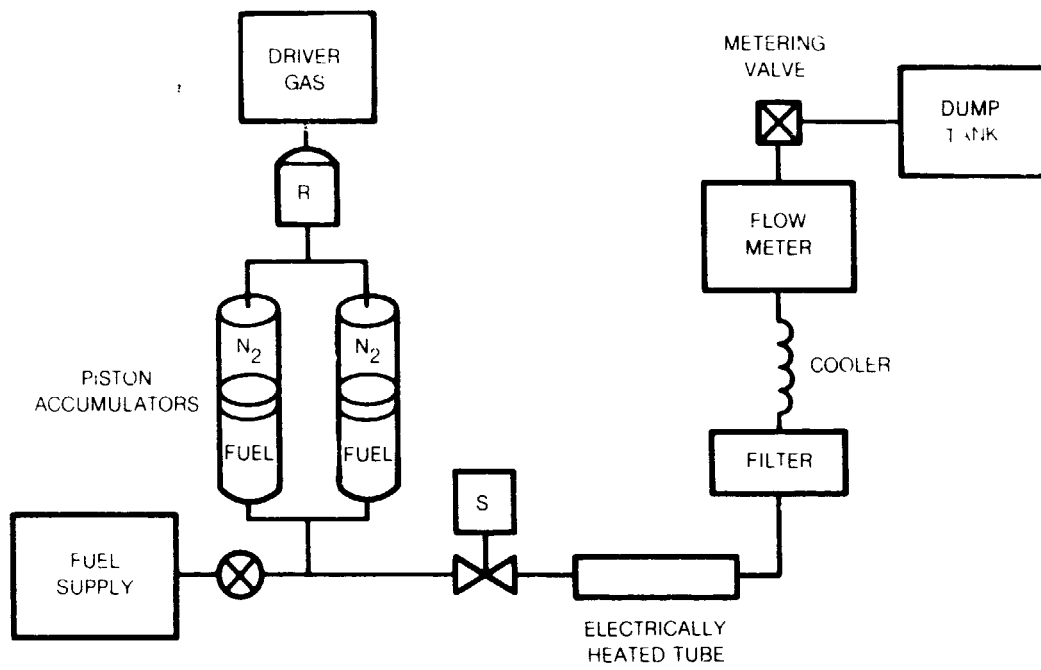


Figure 1. Fuel Deposit Test Apparatus

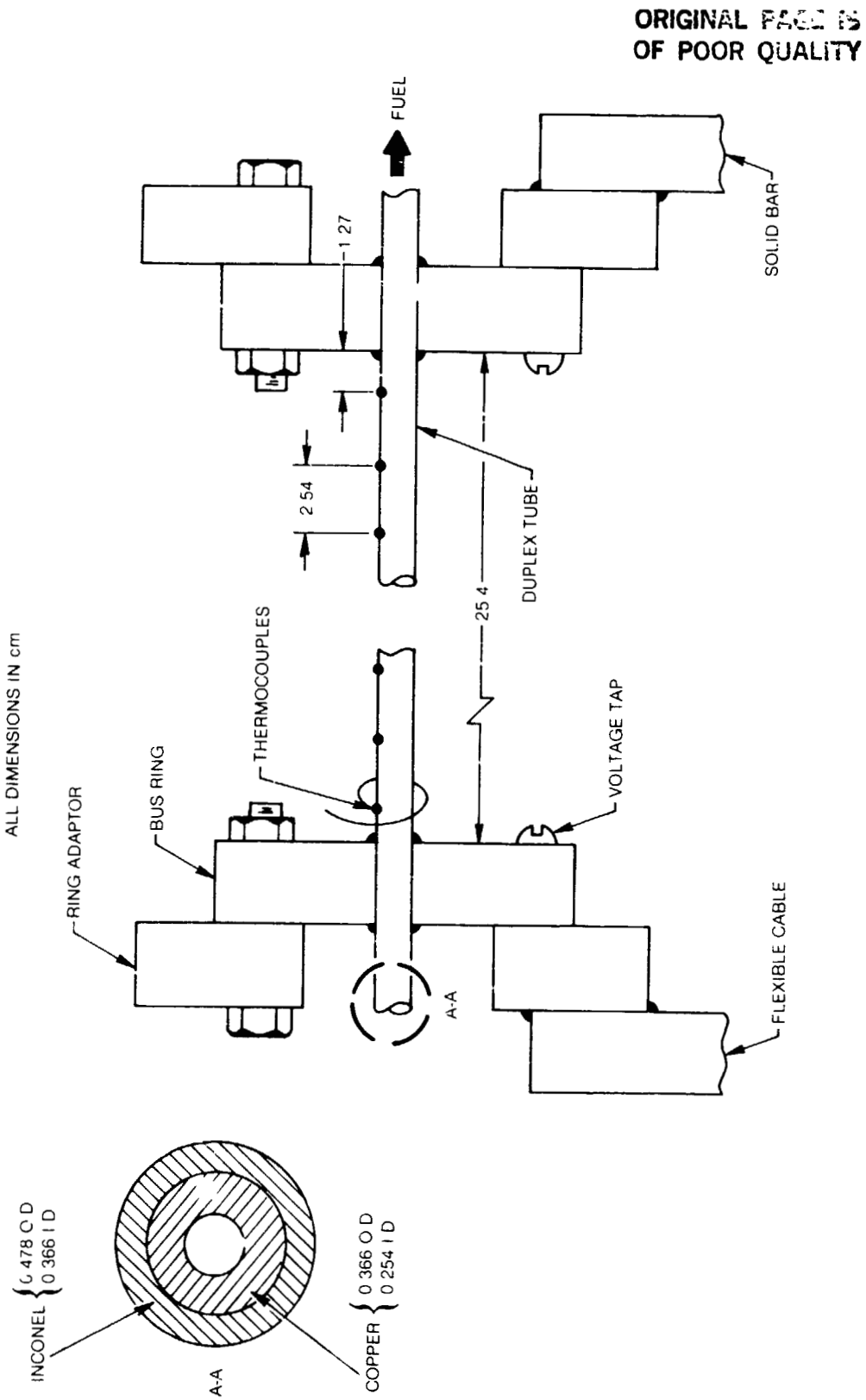


Figure 2 1st Tube Assembly

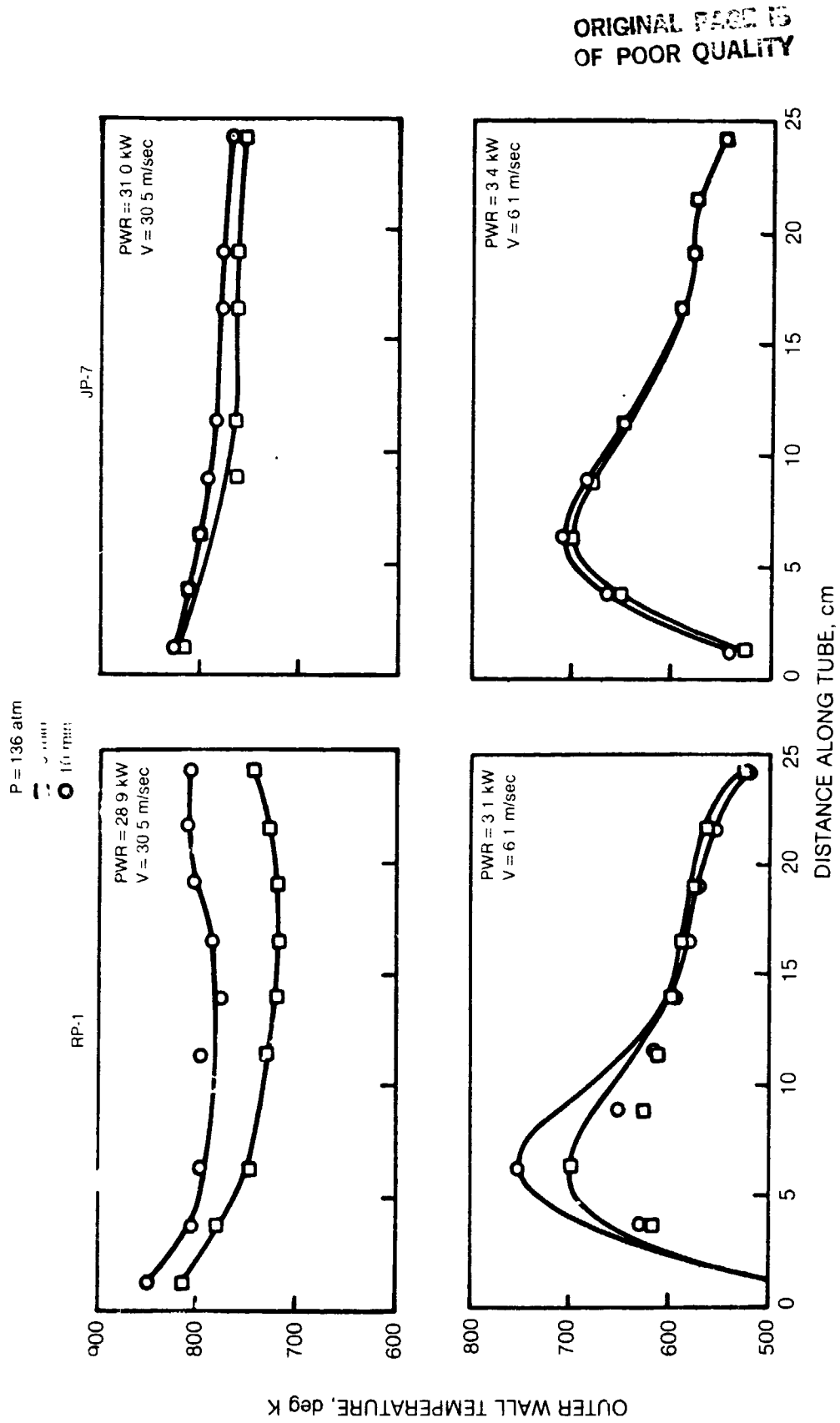
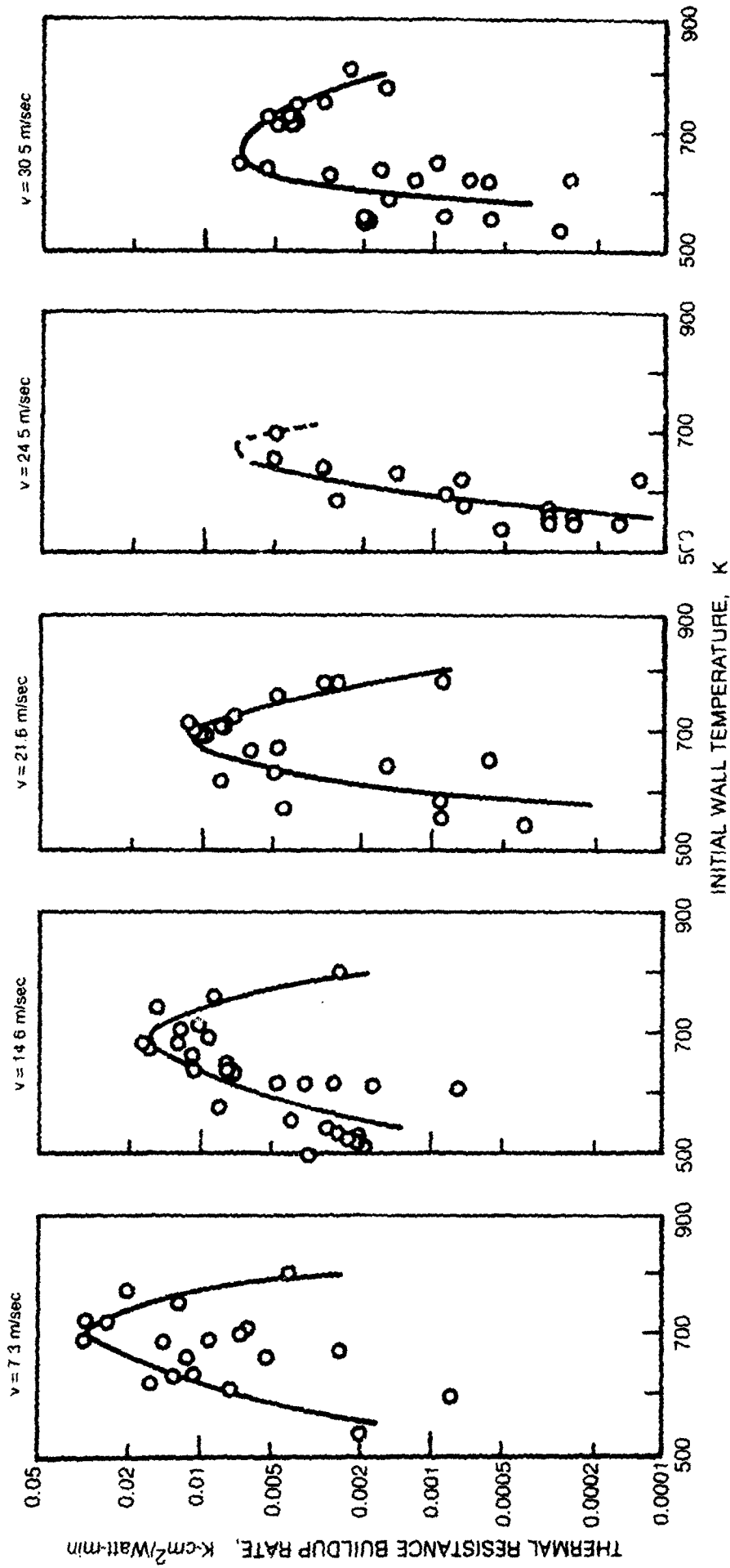


Figure 3. Comparison of Temperature Distribution for RP-1 and JP-7

RP-1 FUEL
P = 136 atm



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Figure 4. Variation of Thermal Resistance Buildup Rate with Wall Temperature

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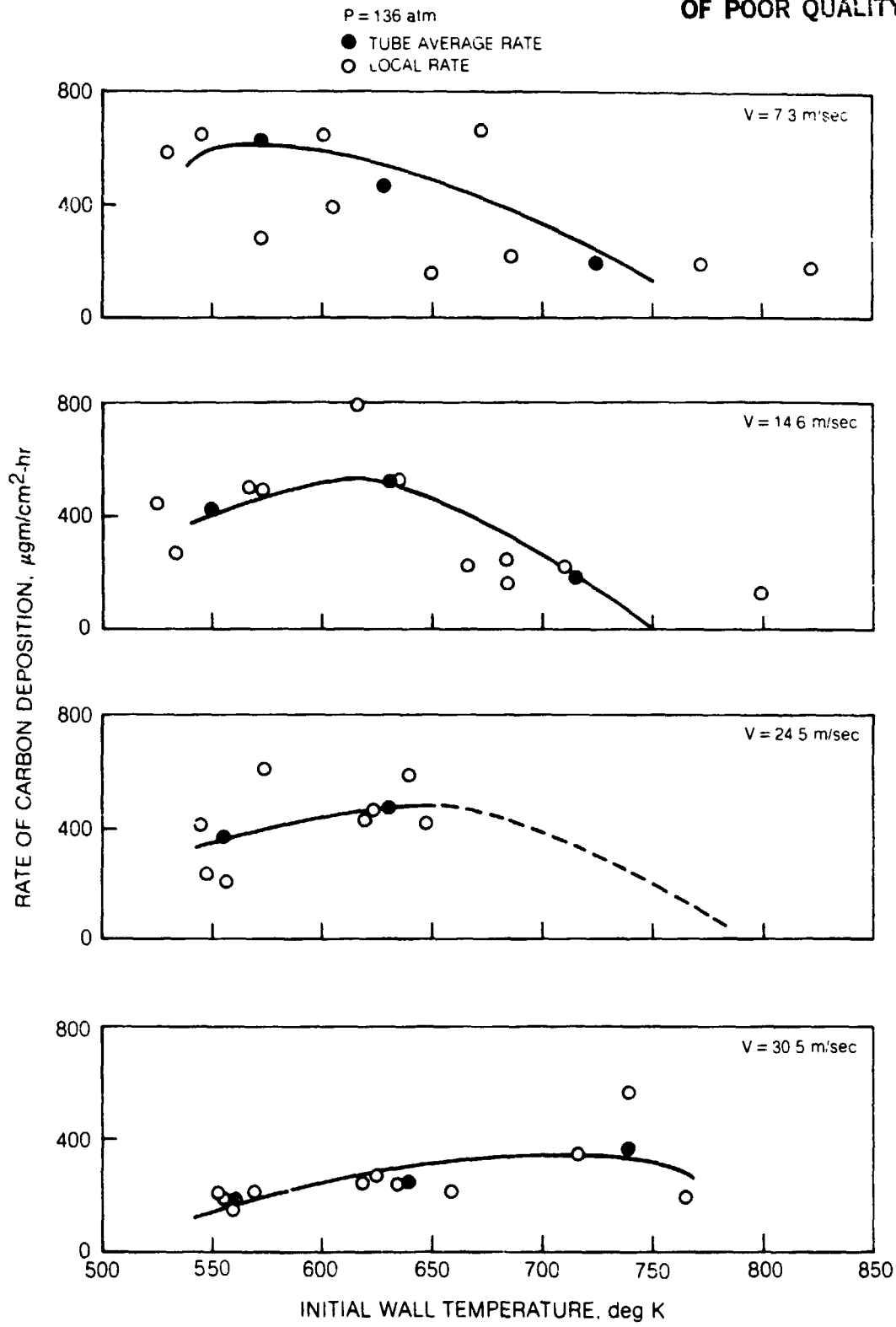


Figure 5. Rate of Carbon Deposition for RP-1 Fuel

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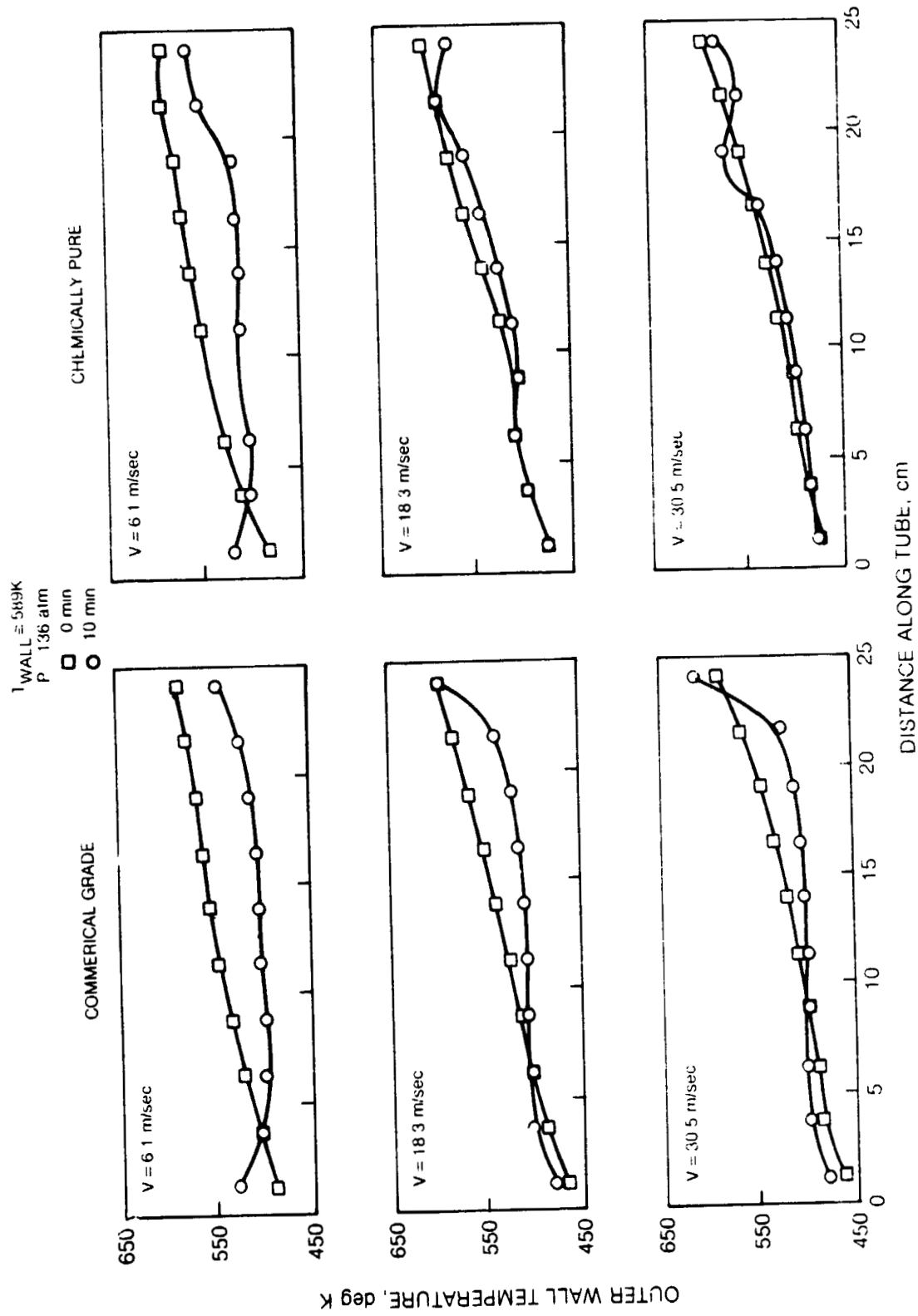


Fig. 6. Comparison of Temperature Distributions for Propane

CHARACTERIZATION
OF POOR QUALITY

P = 136 atm

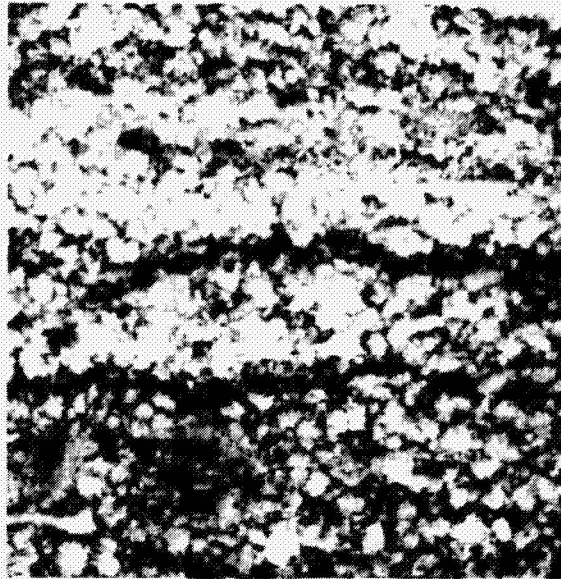
MAG = 5000 x



RP-1

V = 7.2 m/sec

T_{WALL} = 700 K



JP-7

V = 30.5 m/sec

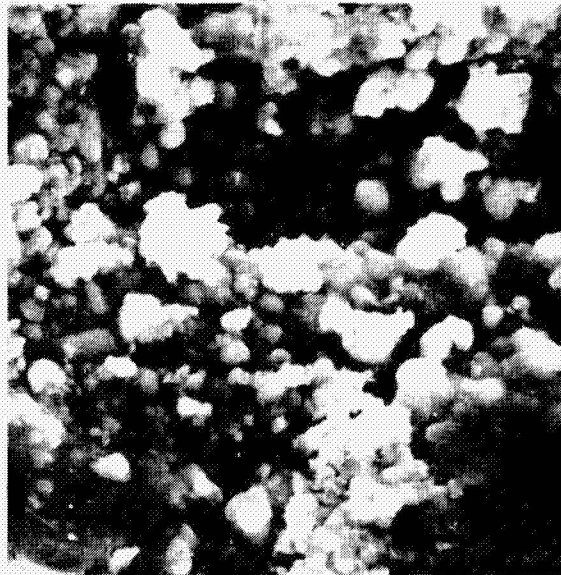
T_{WALL} = 700 K



COMMERCIAL PROPANE

V = 30.5 m/sec

T_{WALL} = 644 K



C.P. PROPANE

V = 18.3 m/sec

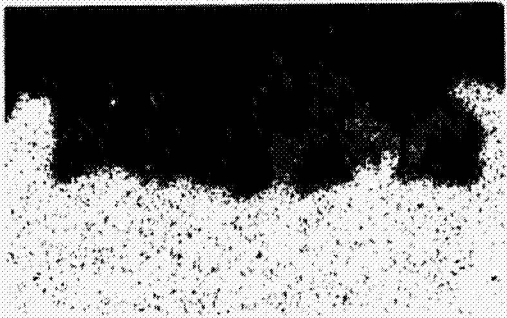
T_{WALL} = 589 K

Figure 7. Microstructure of Fuel Deposits on Copper

PRESSURE = 136 atm T_{WALL} ≈ 700K VELOCITY = 30.5 m/sec



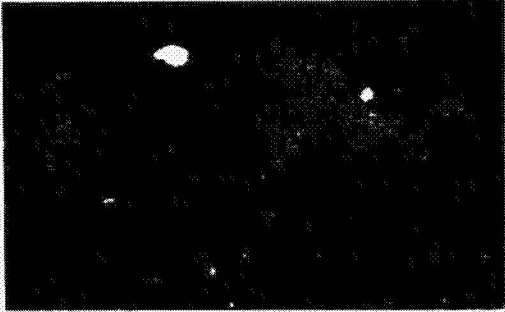
JP-7
MAG. = 800 X



COPPER



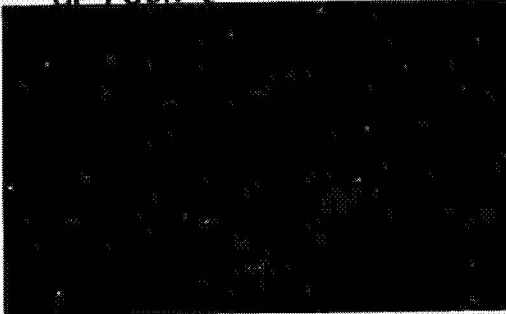
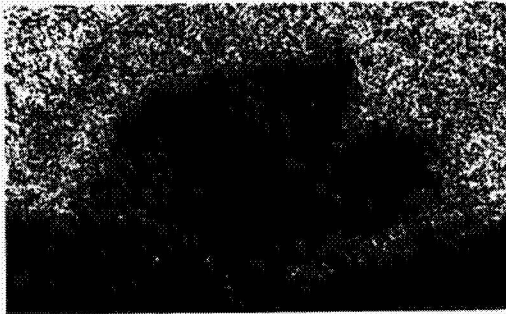
CARBON



SULFUR



COMMERCIAL
PROPANE
MAG. = 1600 X



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Figure 8. Scanning Electron Microprobe Analysis of Deposits