Thermal Stability of RP-2 for Hydrocarbon Boost Regenerative Cooling

Julie Kleinhenz[1], Matthew Deans[1], Benjamin Stiegemeier[2], and Peter Psaras[1].
[1]NASA Glenn Research Center, Cleveland, OH 44135
[2]Aviometix, Cleveland, OH 44135

ABSTRACT

A series of tests were performed in the NASA Glenn Research Center's Heated Tube Facility to study the heat transfer and thermal stability behavior of RP-2 under conditions similar to those found in rocket engine cooling channels. It has long been known that hydrocarbon fuels, such as RP-2, can decompose at high temperature to form deposits (coke) which can adversely impact rocket engine cooling channel performance. The heated tube facility provides a simple means to study these effects. Using resistively heated copper tubes in a vacuum chamber, flowing RP-2 was heated to explore thermal effects at a range of test conditions. Wall temperature (850-1050°F) and bulk fluid temperature (300-500°F) were varied to define thermal decomposition and stability at each condition. Flow velocity and pressure were fixed at 75 ft/s and 1000 psia, respectively. Additionally, five different batches of RP-2 were tested at identical conditions to examine any thermal stability differences resulting from batch to batch compositional variation. Among these tests was one with a potential coke reducing additive known as 1,2,3,4-Tetrahydroquinoline (THQ). While copper tubes were used for the majority of tests, two exploratory tests were performed with a copper alloy known as GRCop-42. Each tube was instrumented with 15 thermocouples to examine the temperature profile, and carbon deposition at each thermocouple location was determined post-test in an oxidation furnace. In many tests, intermittent local temperature increases were observed visually and in the thermocouple data. These hot spots did not appear to correspond with a higher carbon deposition.

INTRODUCTION

NASA has set economical access to space as one of its Space Technology Grand Challenges[1]. For next generation launch vehicles, RP/LOX engines are appealing for booster stage application due to the relatively high density and ease of handling of the fuel. But, higher performance required by future mission architectures[2] will necessitate more extreme engine operating conditions than those of past designs. Increasing the operating pressures of engines is one way to meet these requirements, though this comes with an increased heat load. While some design parameters (mass flow, configuration) can be altered to accommodate this, increasing the operating temperature of the fuel is one simple way to regulate the additional heat load.

One risk posed by hydrocarbon fuels is the potential for fuel decomposition at elevated temperatures including auto-oxidation and pyrolysis reactions, the former dominating below 900 °F.[3] The different reaction pathways can change how the propellant decomposes, resulting in different thermal reaction behaviors and different fluid properties such as viscosity, density, and specific heat. The decomposition can also yield residue, or coke, which collects along the walls of the cooling channels and hinders heat transfer to the cooling propellant.

The likelihood, and quantity, of this type of residue deposition is affected by many factors such as heat flux, fuel composition, pressure, and tube material. While many of these factors can be independently designed and controlled, their mutual interaction is not well understood, especially at extreme conditions such as those found in rocket engine coolant channels. To enable the efficient and informed design of advanced engines, further insight into these interactions is critical.

Although RP-1 has long been the standard hydrocarbon rocket propellant for US engines, a newer blend, designated RP-2, has been developed with a lower sulfur and olefin content (military

specification (or mil-spec) MIL-DTL-25576E). RP-2 is currently the leading candidate for next generation hydrocarbon boost engines due to previous heated tube tests showing an improved thermal stability at high temperature operation[4]. (MIL-DTL-25576E specifies a lower sulfur and olefin content for RP-2). One outcome of these previous investigations was the observation that the thermal stability of within specification ("inspec") RP-2 was dependent on the batch of fuel. The purpose of this current study is to further investigate the heat transfer and thermal stability of RP-2, while also gaining insight into the role played by differences in fuel composition stemming from batch-to-batch variation. In addition, one fuel batch was altered with the hydrogen donating compound 1,2,3,4-Tetrahydroquinoline (THQ) that has been identified by the Air Force Research Laboratory (AFRL) as a potential coke reducing additive. While it showed promise in small scale, stagnant tests[5], this heated tube test was the first trial in a larger scale, flowing environment.

Another set of tests explored excursions in coolant channel wall temperatures and bulk fluid temperatures to help better define limits of operation for RP-2 fuels. While the majority of tests were performed with copper channels, two tests utilized a new copper alloy called GRCop-42. This is a lower alloy variant of GRCop-84 which showed increased carbon deposition (coke) in previous studies[6]. GRCop-42 retains the strength, manufacturing, and stability benefits offered by GRCop-84, but the reduction in alloy may decrease the deposition.

Included in this document are preliminary results of all test variables (fuel batch, operating temperatures, tube material). Full analysis is still underway.

FACILITIES AND HARDWARE

The NASA Glenn Research Center Heated Tube Facility (HTF) was developed to simulate heat flux conditions in a liquid rocket engine for evaluation of regenerative cooling channels. The facility, shown schematically in Fig.1, is designed to flow propellant through resistively heated tube sections of various configurations. Electrical current from up to four 80VDC, 1500A welding power supplies is passed directly through the tube section to achieve a constant heat flux over the length (Fig.2). The flow rate and pressure of the coolant (propellant) in the tube is regulated by nitrogen pressurization of the supply tank. Mass flow is measured with a Coriolis flow meter and is used to control inlet and outlet valves (flow control and backpressure) to maintain test conditions. The heated fuel then passes through heat exchangers before entering the return tank, which is vented to atmosphere.

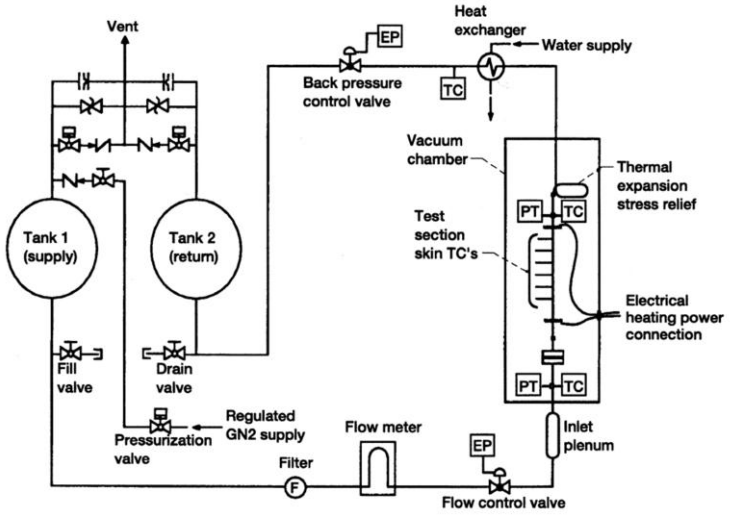

Figure 1: Flow schematic of the NASA Glenn Research Center's Heated Tube Facility.

All the test sections in this study were drawn tubing with 0.125 in OD and 0.061 in ID. Figure 2 shows a schematic of a test section. Pure copper and copper alloy GRCop-42 were used. Wall temperatures along the tube were measured with type K thermocouples. The majority were torch brazed onto the tube surface, but laser welding and an alternative higher temperature braze were used for two high wall temperature condition test pieces. Rectangular bus bars were also brazed to the tube to provide electrical connections.

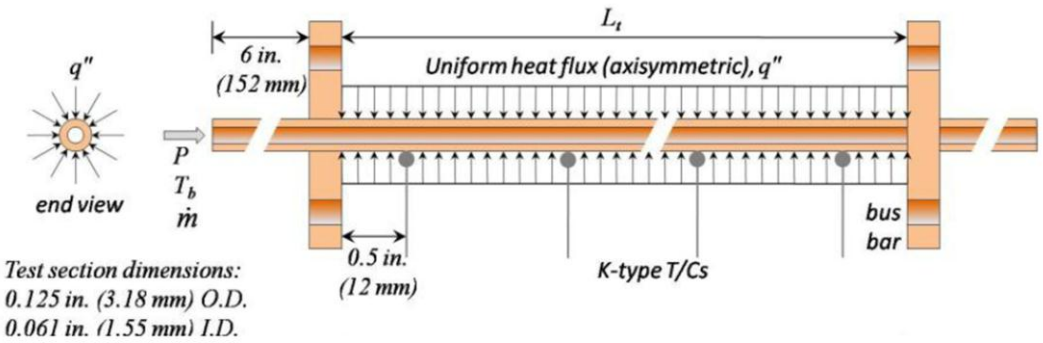

Figure 2: Schematic of a heated tube test piece.

Because the thermocouples were directly attached to a resistively heated tube, there could be an induced error from the voltage on the tube. To correct for this, a short calibration run was performed prior to each test. Using the flow conditions of that test, the test section was brought to operating temperature using reverse polarity on the power supplies. The calibration run ended as soon as temperature was reached, with power ramp up only lasting a few minutes. The flow was halted and the polarity was switched back to normal for the actual test. The calibration run, along with the power ramp up of actual test, were used in post processing to determine the voltage bias and correct the thermocouple temperatures.[7]

All tests were done using fixed mass flow of 0.063 lb/s (corresponding to a 75ft/s flow velocity) and pressure of 1000psi. Heat and flow were maintained for 1 hour to allow time for carbon deposits to form. This duration follows the standard set in previous tests[3,6,7] for data compatibility. The primary variables were wall temperature, bulk fluid temperature at the exit, and fuel batch. The length of the tubes and heat flux were varied to achieve the target temperature conditions. The unheated entrance length of the tube was at least 4.75in for all tests to allow flow development.

In addition to the thermocouple and flow data for each test, video was recorded for all tests. Due to the restricted optical access on the chamber, the CCD camera viewed the downstream portion of test section (usually midpoint and beyond). This data was used to interpret heating patterns. Carbon deposition (coking) data was determined using destructive analysis of the test sections. Each tube was cut into 1 in sections surrounding each thermocouple. These were then cleaned and analyzed using an oxidizing induction furnace. The downstream flow filters were also replaced after each test and examined for residue.

RESULTS AND DISCUSSION

A preliminary evaluation of the test data is presented in the following sections, which address the three primary variables: fuel batch, temperature, and tube material.

Fuel batch variations

To further explore the effect that fuel compositional changes play in the thermal stability of RP-2, tests were performed under similar conditions for several fuel batches provided by the AFRL. These batches were 2008 (WC0721HW01), 2010 (YA2921HW10), 2011 (Option A), and 2011 (UltraLow (UL) replicate). The UltraLow designation referring to the lower sulfur RP-1 variant used to set the RP-2 military specification ("milspec"). Test numbers 5 to 10 encompass this fuel batch study and are summarized in Table 1. The heated length of the copper tubes used in all tests was 18.9in, with a 4.75in unheated entrance length. The target wall temperature was 850°F with a target bulk fluid exit temperature of 500°F. Mass flow was fixed at 0.063 lb/s, corresponding to a 75ft/s flow.

Carbon deposition data for these tests are shown in Fig. 3. Deposition analysis was also performed on a blank tube, which was a baseline tube section that was never exposed to fuel or heat. Test 8, which

utilized the 2008 fuel batch, experienced a failure during shut down, so no carbon deposition is available. In lieu of this, test 10 was performed with a replicated fuel batch. This fuel batch had the least deposition. The average carbon deposition in the remaining fuel batches was at least one standard deviation greater than the blank, but the scatter in the deposition data was great enough that the fuel blends were largely indistinguishable from each other. More tests would be needed to determine statistical significance.

Table 1: The test matrix for the fuel batch study. Actual test average values are listed for operating conditions.

Test number	Fuel	Fuel Lot #	Duration, hr	T_{wall} avg, °F	T_{in} avg, °F	T_{exit} Avg, °F	Mdot_avg, lb/s	Q avg, BTU/in^{2}s
5	2011	UL - Replicate	1	815	69	512	0.0622	4.4
6	2010	YA2921HW10	1	850	78	501	0.0629	4.32
7	2011	Option A	1	895	69	502	0.0628	4.31
8	2008	WC0721HW01	1	852	77	516	0.0587	4.16
9	2010	YA2921HW10	0.5	838	70	520	0.0628	4.53
10	2011	2008 - Replicate	1	907	87	501	0.0591	3.92
4	2010 + THQ	YA2921HW10 + 5% THQ	1	845	81	510	0.0629	4.32

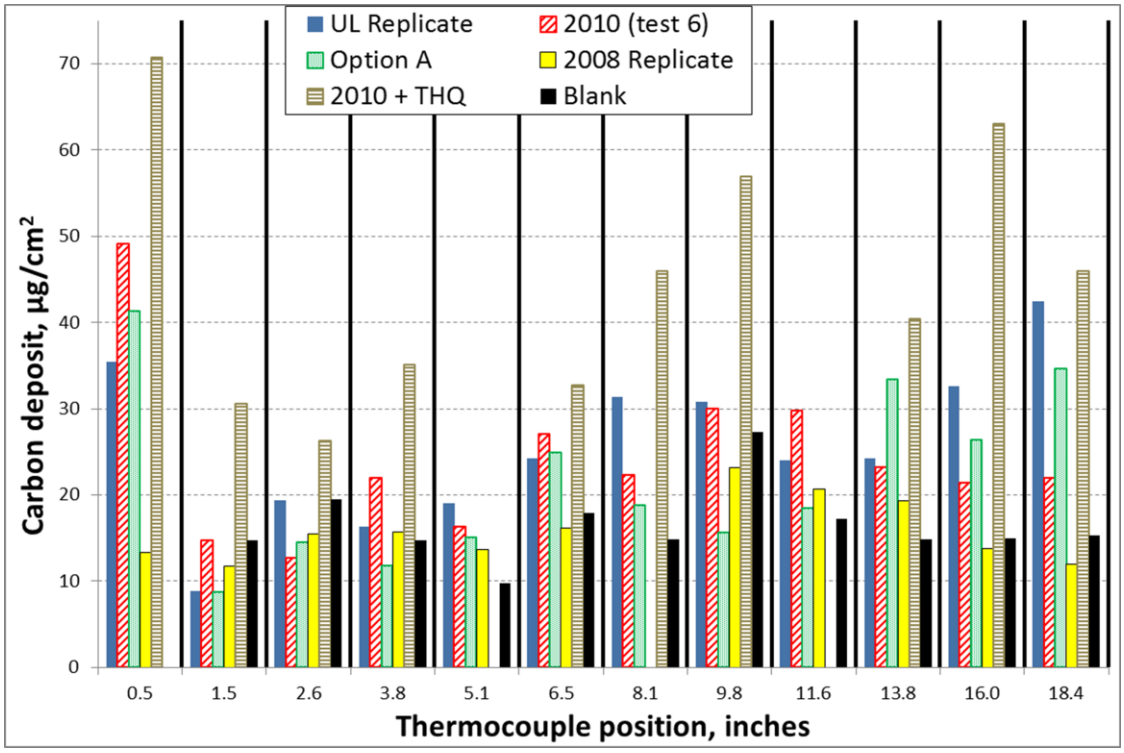

Figure 3: Carbon deposition was measured for 1in tube sections, centered on each thermocouple. The results are shown for each fuel batch, including a batch with fuel additive THQ. The results from a reference, or blank, tube is also shown.

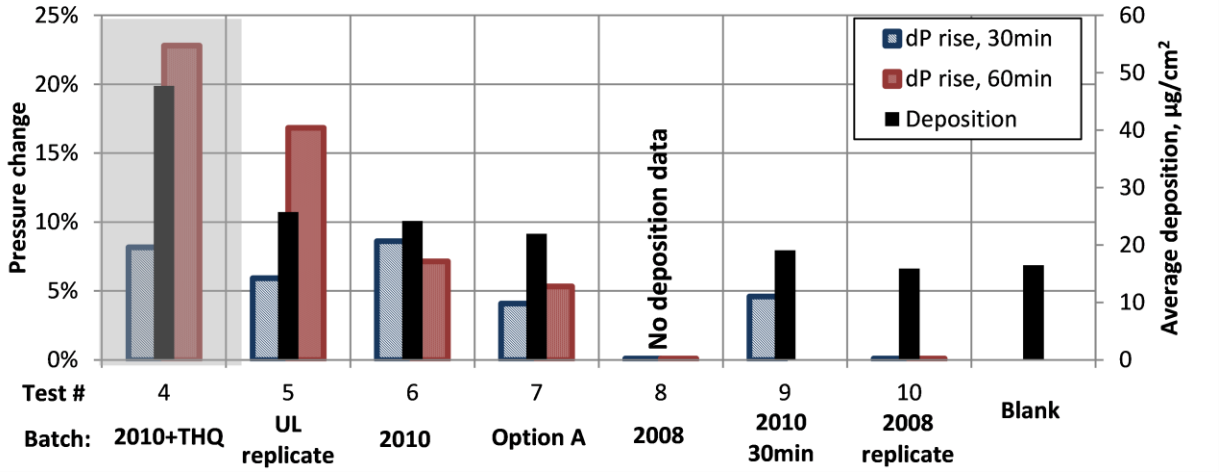

Figure 4: The change in pressure drop across the tube (relative to unheated conditions) at the middle (30min) and end (60min) of the heated test. Average carbon deposition in the tube is also shown for each test.

Another indication of coking is the pressure drop (dP) through the tube. Carbon deposition along the walls will restrict the flow and cause an increase in the pressure drop during the test. Figure 4 shows the change in the pressure drop from the beginning of the test (0min) to 30min and 60min into the test. Test 9 only lasted 30min, while all the other tests ran a full hour. Previous studies[6] indicated that most of the deposition took place within 30min. Indeed, test 9 seems to support this, since the measured carbon deposition (averaged over the tube) is 75% of the hour test with the same fuel batch (test 6).

In addition to the deposition data, the thermal behavior of the tubes was monitored during the tests. As in Ref. 7, hot spots were observed on the tube during tests both visually and in the thermocouple data. Figure 5 shows representative thermocouple data from each fuel batch test. Temperature spikes are indicative of these hot spots. These temperature spikes tended to occur in the downstream locations (mid tube and beyond). The first 3 tests shown (tests 5, 6, and 7) had similar average deposition results, yet test 5 showed no evidence of hot spot activity while test 6 and 7 did. Test 10 (2008 replicate fuel) had the least amount of carbon deposition but still showed considerable hot spot activity. Also, while in most other tests the hot spots occurred randomly, fading in and out, in test 10 it was a propagating feature. This is illustrated in Fig.6, where the hot spot started around 11in from the tube entrance and gradually propagated 3 in upstream.

In previous studies[7] the hot spot observations were attributed to the formation and shedding of localized carbon deposits. However, the discrepancy between the hot spot activity and the low deposition data in test 10, as well as the reverse in test 5, seem to contradict this. Looking at the length dependent deposition data in Fig. 3, the positions with higher deposition values do not correlate with the temperature spikes (Fig. 5). Additionally the fuel line filters downstream of the heated section showed no visible evidence of carbon residue that would be indicative of shedding. The hot spots could instead represent local fuel decomposition and/or surface roughness changes, short of coking, that change the fuel properties enough to affect the local heat transfer.

Test 4 was a unique test condition whereby a coke-reducing additive was used with the 2010 fuel batch. The additive, known as 1,2,3,4-Tetrahydroquinoline (THQ), had been shown to reduce decomposition rate of RP-2 in small-scale studies[5]. Using it in this test series was an attempt to assess its effectiveness in larger scale, flowing conditions. Since only one test was possible, the most extreme, and effective, case from Ref. 5 was chosen: 5% THQ additive by mass. The test was run at the same baseline condition as the other fuel batch tests. While no hot spot activity was observed in this test, the

deposition results were surprising. The average carbon deposition of the additive test was nearly double that of the neat test (Figs. 3 & 4).

Though more trials are required to establish certainty, these results suggest that the THQ does not reduce carbon deposition in this application. This trial also gives support to the theory that hot spot behavior corresponds to localized fuel breakdown but not coking; with the THQ, no hot spot activity was seen despite a large amount of coking. With the addition of this chemical, it may have altered the breakdown mechanism such that carbon deposition was increased without the species that significantly changed the heat transfer in the trials with observable hot spots.

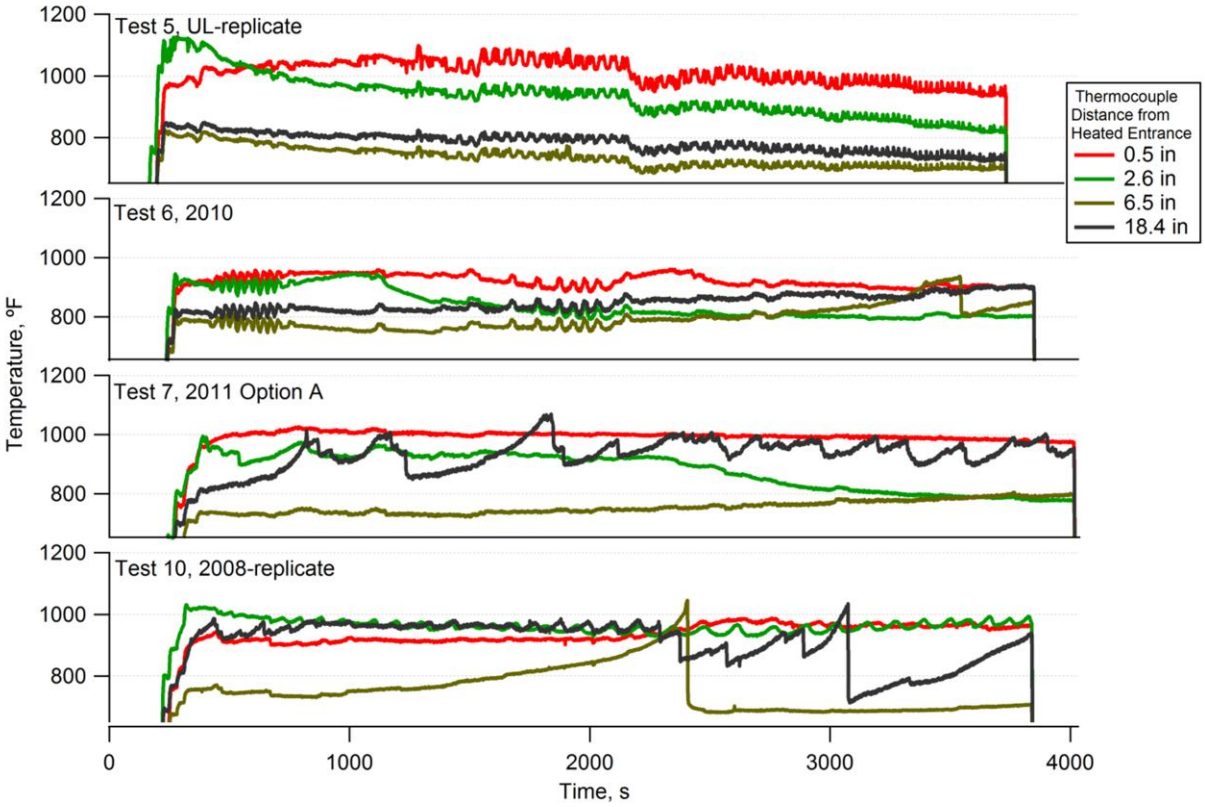

Figure 5: Time dependent temperatures are shown for representative thermocouples along the tube. Spikes in temperature indicate localized hot spots. (small fluctuations, like test 5, are due to an issue with the back pressure regulator).

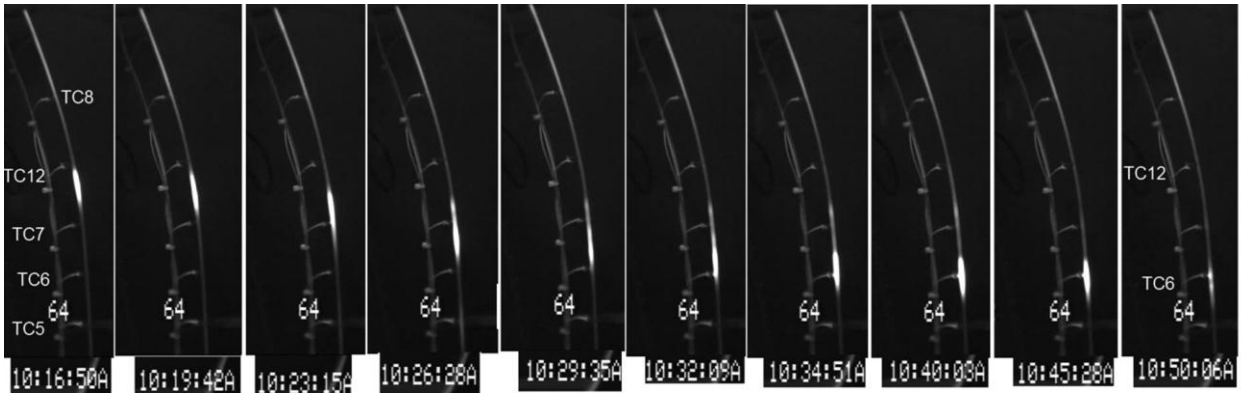

Figure 6: Visible hot spot activity during test 10. In this test the hot spot propagated slowly upstream. The tube in on the right, with thermocouple leads coming off horizontally to the left.

Temperature Excursions

Another goal of these tests was to explore the effect of temperature operating conditions. The coking and stability of the fuel at these different conditions will drive decisions for actual engine operations. The majority of these tests were performed with fuel bulk fluid exit temperature fixed at 500°F. The tube temperature, along with heat flux into the fuel, was varied. A few tests were also performed at a fixed wall temperature of 850°F with lower bulk fluid temperatures. This test set is listed in Table 2. The variables, as they differ from the baseline condition, are bolded.

Table 2: The test matrix for the temperature condition study.

Test number	Fuel	Fuel Lot #	Tube	T_{wall} avg, °F	T_{wall} target, °F	T_{in} avg, °F	T_{exit} avg, °F	Mass flow avg, lb/s	Heat flux, BTU/in^{2}s
1	2010	YA2921HW10	copper	871	850	51	**325**	0.0678	5.14
2	2010	YA2921HW10	copper	880	850	58	**400**	0.0644	4.41
3	2010	YA2921HW10	copper	892	850	61	509	0.0629	4.47
11	2010	YA2921HW10	copper	647	850	33	493	0.0628	4.49
12	2010	YA2921HW10	copper	895	**950**	48	501	0.0628	5.23
14	2010	YA2921HW10	copper	911	**950**	27	**301**	0.0628	5.26
15	2013	BB0821HW10	copper	924	**1050**	37	501	0.0628	6.05
13	2010	YA2921HW10	**GRCop42**	903	**850**	36	501	0.0628	4.54
16	2013	BB0821HW10	**GRCop42**	929	**1050**	37	500	0.0620	5.98

The first thing of note in Table 2 is the difference between the wall temperature target conditions and the actual test averages. Tests 3 and 11 were identical in terms of operating conditions (tube length, heat flux, mass flow), yet the average wall temperature on test 11 was nearly 200°F lower than test 3 with the same bulk fluid exit temperature. Tests 11 through 16, which were performed a year after the first ten, were also generally below their target conditions. This could be due in part to the much lower initial temperature of the fuel (T_{in}) in the later tests. The fuel run tank is subject to weather variations, and the latter test set was performed in the winter.

The average carbon deposition and pressure drop results are shown in Fig. 7. The position dependent deposition results are shown in Fig. 8. The largest increase in pressure drops occurred during the baseline condition (850°F wall, 500°F exit) in test 3 and the low temperature condition in test 11. As wall temperature was increased past 900°F (tests 14, 15) the change in pressure drop lessened. The carbon deposition apparently decreased as well (test 15,16), but Fig. 8 indicates the variability of the deposition results. At temperatures below approximately 900°F, autoxidation reactions are expected to dominate, while above this the dominant mechanism is pyrolysis. The apparent lower pressure rise at elevated temperatures may be evidence of this transition. The change in bulk exit temperature did not appear to have a significant effect in this regime.

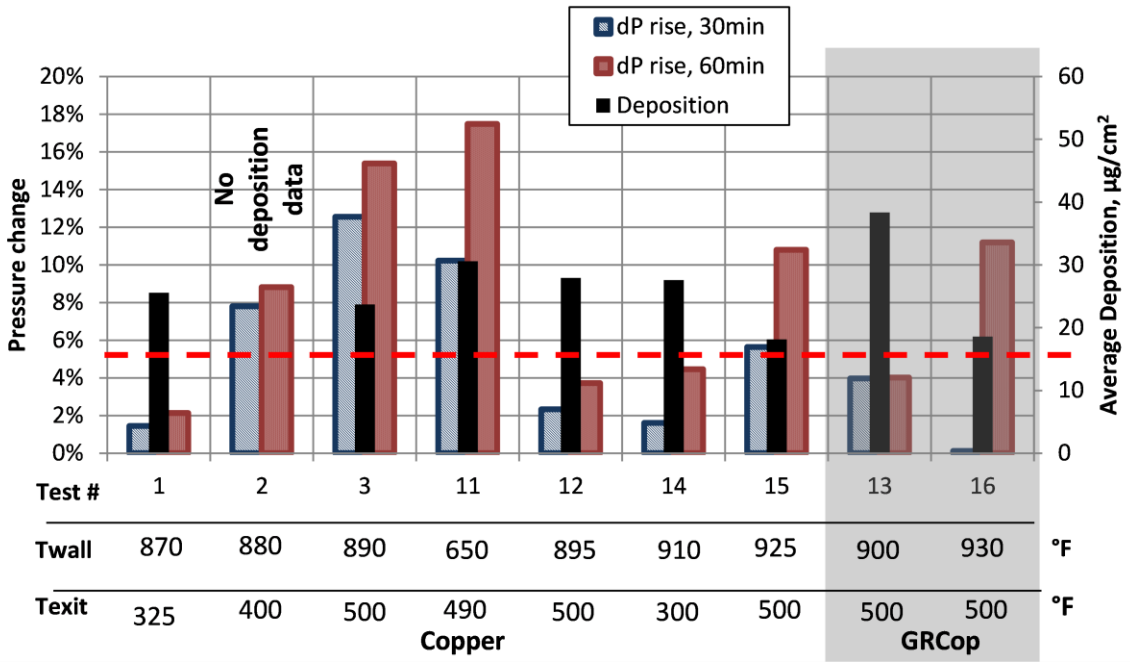

Figure 7: The change in pressure drop across the tube (relative to unheated conditions) at the middle (30min) and end (60min) of tests with different temperature set point conditions. The dashed line shows the average carbon deposition of the blank (reference) test piece.

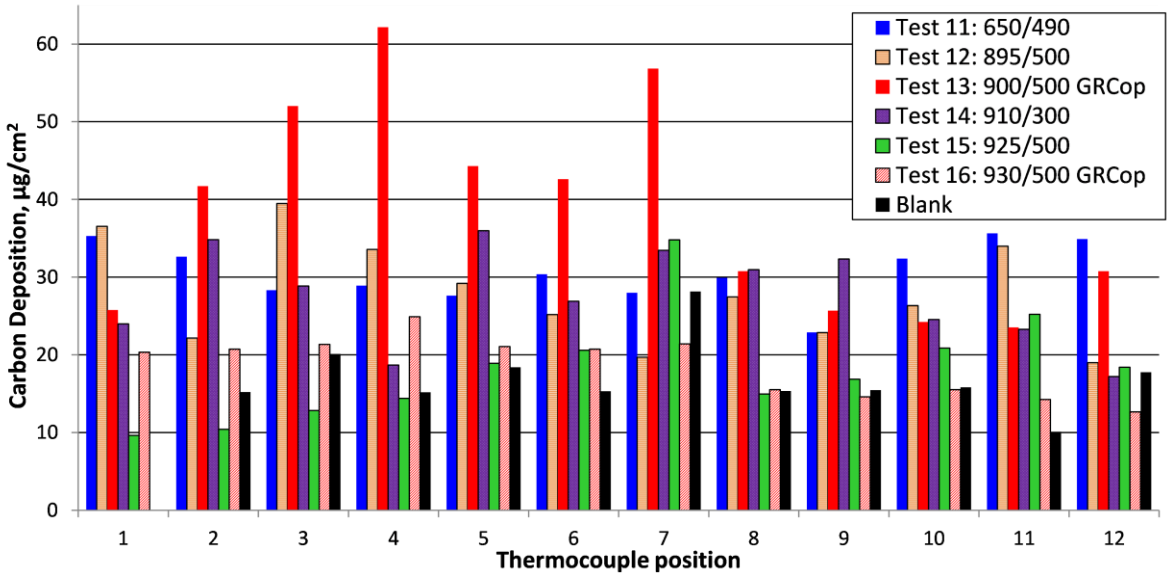

Figure 8: The position dependent deposition data is shown for the temperature excursion tests. The two tests using the GRCop material are included. Thermocouple position 1 near the inlet with the numbers sequentially downstream.

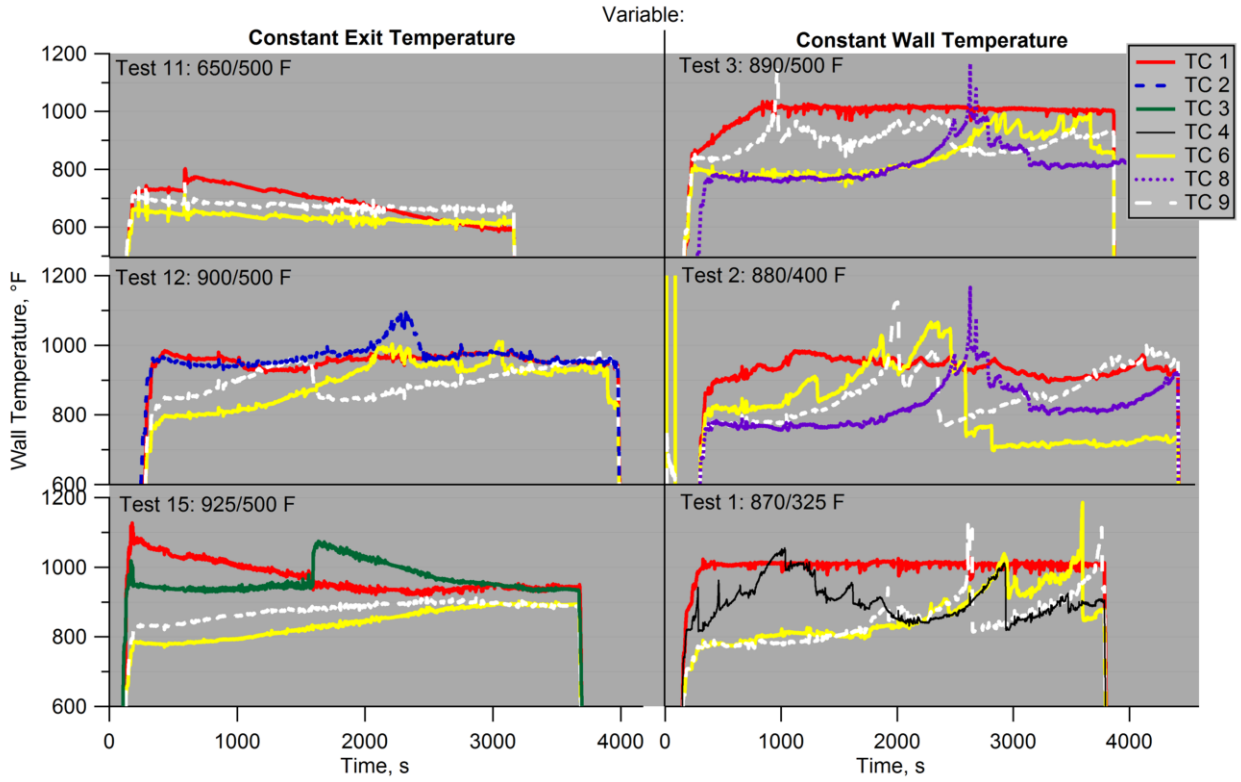

Figure 9: Time dependent temperatures are shown for representative thermocouples along the tube for tests with different setpoint temperature conditions. The test designation is shown along with average wall and exit temperatures (wall/exit).

The left side of Fig. 9 shows the effect of wall temperature variation on hot spot activity while the right side looks at hot spot activity for constant wall temperature and varying exit temperatures. Test 3 at the baseline condition (upper right of figure) showed significant temperature spikes. The thermal changes at the higher wall temperatures of tests 12 and 15 were slower, with few temperature spikes. While the tube did glow, it was more uniform with any localized spots fading in and out gradually. The lower wall temperature condition of test 11 also showed limited hot spot activity in spite of a significant pressure rise and carbon deposition.

Excursions of bulk fluid temperatures were also performed to temperatures lower than the baseline condition. Deposition results are available for the baseline case (test 3) and one excursion (test 1). Figure 10 shows that more deposition is present in the lower bulk fluid temperature case of

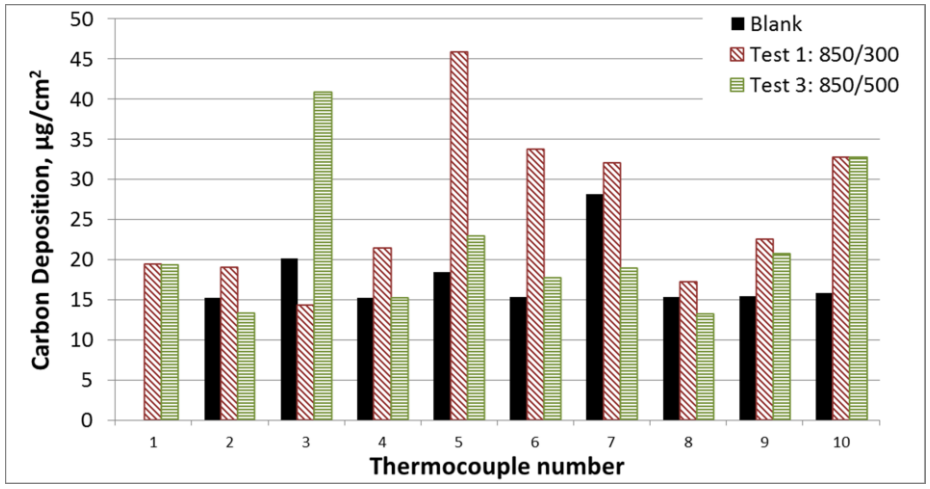

Figure 10: Carbon deposition was measured for 1in tube sections, centered on each thermocouple. Thermocouples are numbered sequentially downstream.

test 1, though this is not reflected in the dP values in Fig. 7. The temperature data on the right of Fig. 9 indicates a similar amount of localized hot spot activity for tests 1, 2, and 3. Thus, wall temperature seems to be the more substantial driver of hot spot activity (decomposition).

Tube material

The final test variable was the tube material. A high strength copper alloy, known as GRCop, has been developed at NASA Glenn Research Center for application in engine liners. Previous testing[6] was performed with GRCop-84, but showed elevated deposition with respect to pure copper. The current testing was performed with a new alloy blend, GRCop-42. This blend has half the alloying additions of GRCop-84, giving it a more similar conductivity to pure copper while still retaining the strength, manufacturing, and stability benefits offered by GRCop-84.

Two tests were performed with GRCop-42. Other than the material, the tests were identical to the pure copper tests. Both tests use the baseline bulk fluid temperature conditions of 500°F, with wall temperature set points of 850°F and 1050°F (Table 2). The pressure drop and deposition data are shown in Fig.7, where tests 3 and 15 are the copper tests and tests 13 and 16 are the corresponding GRCop tests. The pressure drop for the GRCop is lower than pure copper at the 850°F wall condition and there was less hot spot activity in the GRCop test at this condition (Fig.11). However the carbon deposition was noticeably higher in the GRCop test. At the higher wall temperature condition the Copper and GRCop tests show similar deposition results. The pressure drop data for the GRCop (test 16) is misleading because the mass flow was low at the beginning of the test due to a regulator issue. (The higher pressure drop at 60min is due to the increased back pressure). Hot spot activity in both the copper and GRCop test was limited at the 1050°F setpoint. Temperature fluctuations were gradual, as shown in Fig.11 with Test 14, TC 8 and Test 16, TC4.

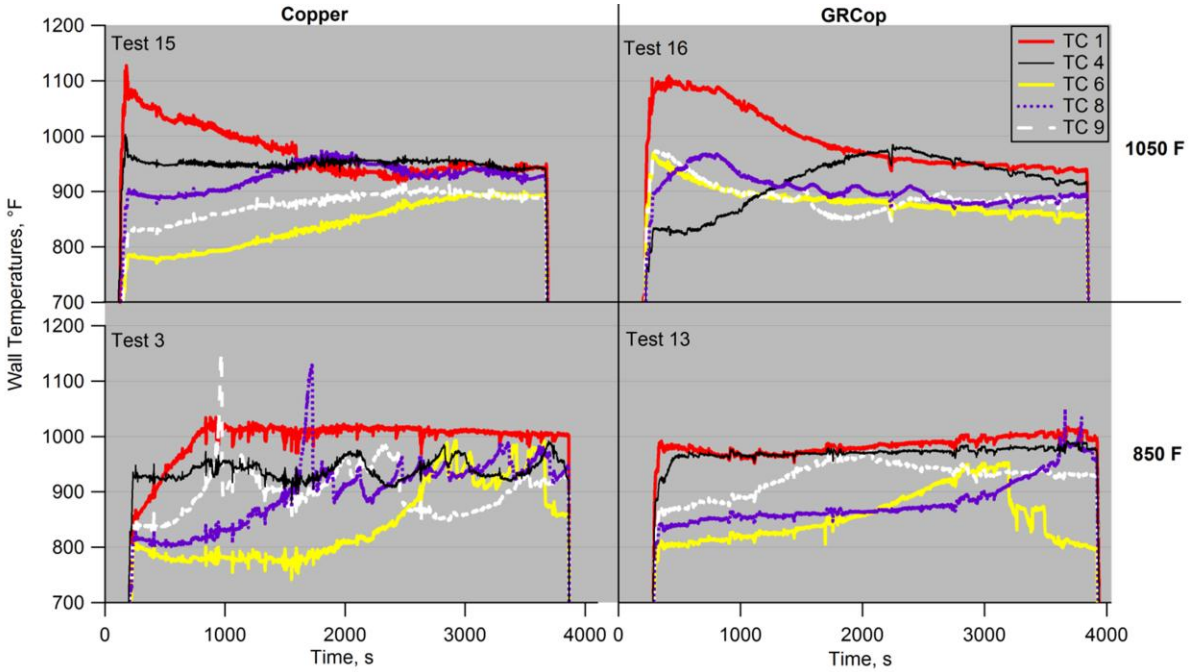

Figure 11: Time dependent temperatures are shown for representative thermocouples along the tube for tests with different tube material. All tests had a 500°F bulk fluid temperature, wall temperature targets are shown at the right.

SUMMARY AND CONCLUSIONS

RP-2 was developed as an improved hydrocarbon fuel in order to reduce coking and obtain improved performance over RP-1. This study continued to characterize RP-2 propellant in a regenerative cooling application to enable better design of advanced engines. Using a resistively heated tube to mimic a cooling channel, flowing RP-2 was heated to a range of temperature conditions. Thermocouples on the tube wall indicated local thermal behaviors during the test, and carbon deposition was measured post-test in an oxidizing furnace.

Localized temperature increases, or hot spots, were observed throughout testing. These did not correlate with regions of elevated carbon deposition. Rather, they may be a result of local chemical changes that reduce the local heat transfer. Though coking has been a historical concern for these types of regenerative engines, the magnitudes of the temperature spikes should also be considered in engine design especially when considering materials temperature thresholds.

These hot spots did appear to be correlated to wall temperature. Much of the activity was observed at 850°F wall temperature, regardless of the bulk fluid temperature conditions. This may be associated with a transition regime between auto-oxidation reaction, which dominates at lower temperature, and pyrolysis at the higher temperatures. Hot spot activity appears to be less active at lower (625°F) and higher (925°F) wall temperatures. Changes in the bulk fluid temperature did not have an apparent impact on hot spot activity, but may have impacted the pressure drop through the tube. Increasing bulk fluid temperature resulted in increased pressure drop over the course of the test, suggesting a flow restriction or viscosity change with time.

The within-specification variations of the different batches of RP-2 resulted in slightly different heat transfer and deposition results. The 2008 batch had the least amount of deposition, and least pressure rise, but all the others showed similar results. However, the hot spot activity was varied, with no activity with the UL-replicate batch. The 1,2,3,4-Tetrahydroquinoline additive, which was theorized to reduce coke, showed significantly higher carbon deposition than neat fuel, though the hot spot activity was eliminated. While coking is still not desired, the changes in chemistry bear further study to confirm this behavior.

While the results of this study are still preliminary, they contribute to a relevant body of work regarding the use of hydrocarbon propellants in advanced propulsion systems. The higher performance requirements on the engines result in more extreme regenerative fuel temperatures. While some unique thermal behaviors were observed at these conditions, the variations are relatively minor and none have presented hazardous conditions. Further study and more complete analysis can help optimize operating conditions and enable a better understanding of the concerns in current engines.

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