# Evaluation of a Jet Fuel Thermal Stability Rig

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## ABSTRACT

Current and planned gas turbine engines use fuel as their primary heat sink. When jet fuel is thermally stressed it will form gums and deposits. These deposits can block engine fuel nozzles, causing damage to the engine hot sections, especially the combustor region. The fuel's thermal stability is a critical fuel property with respect to optimum performance of modern military gas turbine engines. The current standard method to rate fuel thermal stability, the Jet Fuel Thermal Oxidation Tester (JFTOT), is a subjective, pass-fail type test and is not adequate as a tool to quantitatively investigate fuel thermal stability. This report describes a program to design, construct and commission a rig capable of quantifying fuel's thermal stability based on carbon and sulphur deposit formation in a heated metal test tube. A fuel known to be unstable both chemically and thermally, sourced from RAAF Townsville, was used as a test fuel for commissioning the rig. The rig was found capable of discriminating between differing test conditions and was successful in rating fuels' thermal stabilities based on quantification of the fuels' deposit-forming capacities. A significant finding of commissioning procedures was the high levels of sulphur deposit formed in the test fuel.

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## Executive Summary

Jet fuel under normal operating conditions is heated by the hot components of gas turbine engines. The hot regions include the fuel nozzles, fuel nozzle support assemblies and heat exchangers. The fuel is also used as the primary heat sink in all modern aircraft. As jet fuel is subjected to high heat loads, it undergoes thermal stress and will degrade. This degradation will lead to the formation of solid deposits in the aircraft fuel system and specifically in fuel nozzles. Thermally generated deposits are detrimental to efficient operation of aircraft engines and may cause damage in the engine's hot section due to distorted fuel spray patterns. The current standard test method for evaluating a fuel's thermal stability, ASTM 3241, Thermal Oxidation Stability of Aviation Turbine Fuels (JFTOT Procedure) is a subjective and qualitative method that offers no quantitative assessment of fuel's thermal stability. A test to quantitatively rate a fuel's thermal stability was required to assist the Royal Australian Air Force (RAAF) in evaluating current fuels relative thermal stabilities and to assist in the assessment of the proposed fuel thermal stability additives, commonly known as JP8+100.

A rig has been designed, constructed and commissioned by AVD to rate jet fuel thermal stability. The thermal stability rating is based on quantifying the mass of carbon and sulphur deposits formed under controlled conditions. The test fuels used to assess the capabilities of the rig were a standard dodecane and a fuel from RAAF storage that was known to have a low thermal stability.

The rig was successful in measuring fuel thermal deposit formation over a range of test conditions, including temperature, flow rate and test duration. The central heating element of the rig is a fluidised sand-bath capable of heating the test specimens up to 600°C. While no fuel testing was done above 400°C, this high temperature capability was considered essential to extend the functionally of the rig to enable further investigation into JP-225 and higher temperature fuel programs. A significant outcome of the testing was the discovery of high levels of sulphur deposit formation. The AVD rig is unique in that no other rigs are capable of quantifying the sulphur compound deposit formation from thermally stressed jet fuels.

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# 1. Introduction

A key property that limits the use of conventional fuels in modern military aircraft applications is thermal stability. Thermal instability of aviation fuel can result in several effects that are detrimental to the operation of the aircraft. The most frequently cited effects are reduced efficiency of fuel-oil heat exchangers, due to deposition on the heat exchange surfaces, fouling of fuel control units and fuel injector blocking (1).

With worldwide increased awareness of declining fuel quality and associated concerns of the thermal stability of current and future fuels from Australia and the Asian-Pacific region, including the recent introduction of shale naphtha-blended military jet fuel, the RAAF have become increasingly more concerned with the problem of fuel nozzle blocking.. Fouled nozzles will result in an uneven flame pattern with some regions much hotter than the flame pattern produced by a nozzle in pristine condition. This is commonly referred to as "streaking" which can decrease the life of all stationary components downstream of the nozzle such as the combustor liner and nozzle guide vanes. In extreme cases the expected life of turbine blades may be compromised if the burner outlet temperature profile is changed in any significant manner.

If an engine has multiple fuel nozzles, and one or two become partially blocked, then the remaining unblocked nozzles will have to make up the short-fall in fuel distribution. This effect can result in thermal distress to stationary components downstream of the fuel nozzles. In addition, a forced vibration can occur as rotating components are exposed to different densities and gas velocities around the engine.

Many nozzles have internal valves to schedule fuel to different orifices in the nozzle. If the shuttle valve seizes due to the formation of fuel deposits, then the effect is similar to a partially blocked nozzle, unless the valve seizes in the open position. In this case, severe damage will occur to all stationary components downstream from that nozzle, possibly resulting in combustor can burn-through.

The current specification requirement for measuring the thermal stability of jet fuel is the Jet Fuel Thermal Oxidation Tester (JFTOT) ASTM D1655. This method was introduced in the US in 1972 and the UK in 1973. The method passes pre-conditioned fuel over a heated tube and then through a filter to trap any filterable insolubles formed during the test. The fuel is rated partly by the extent of filter plugging, as indicated by a pressure drop across it, and by the visual appearance of the deposition on the heated tube. The major deficiency of the JFTOT method is that it is qualitative and requires a subjective visual rating of thermal deposition. In order to improve the qualitative rating method and establish a quantitative method based on the JFTOT equipment, a number of instrumental rating techniques have been evaluated, including optical reflectance changes, interferometry, ellipsometry and dielectric breakdown measurements of deposit film thickness (2).

Commercial and military jet aircraft use fuel as a heat sink for cooling avionic and hydraulic systems and, after absorbing heat from these systems, only a fraction of the fuel is burnt, and the rest is recycled back into the fuel tanks, to undergo the heat exchange processes

repetitively. High Mach number flight of advanced aircraft also imparts aerodynamic heating into the fuel *via* wing tank skins. Trace chemical components in the fuel react to the thermal stress placed on them by the heat exchange and other usage, and form deposits on heat exchange elements within the aircraft, significantly reducing the efficiency of the heat exchangers.

In order to overcome the shortcomings of the JFTOT technique and to develop an in-house method for evaluating and quantifying jet fuel thermal deposition, this report describes the design, construction and results from a laboratory rig to quantify fuel thermal stability.

A flowing, single pass heat exchange system has been developed to evaluate thermal stability of jet fuel. The primary purpose of the rig is to quantitatively evaluate the relative thermal stabilities of Australian-refined aviation fuels. The secondary purpose of the rig is to study molecular chemical mechanisms responsible for inherent thermal instability of some fuels, so that it might be possible to identify trace fuel chemical species responsible for thermal deposition in aircraft fuel systems.

# 2. Rig Design

The central component of the test rig is a low fuel flow rate, single pass heat exchanger. The rig is constructed from 3.18 mm O.D. x 2.2mm I.D. annealed type 304 chromatography stainless steel tubing. Fuel flows of 0.1 - 9.9 mL/min are maintained by a Waters Model 510 HPLC pump. The pump is capable of developing and maintaining high system pressures, (up to 41 MPa), and is fitted with a surge suppressor to dampen the effect of pump piston pulsations. The system pressure is maintained at greater than 3.45 MPa via a NUPRO series R3A 2400-5150 kPa pressure release valve. Heating up to 600°C is provided by a Techne SBL-2 fluidised sand bath.

The rig can be operated in two modes described as the Gravimetric JFTOT mode, Figure 2, and U-Tube test section mode. A post filter system was incorporated to enable collection and analysis of filterable fuel-insoluble material formed during thermal stress and deposition rates. A high precision Constametric III metering pump provided flow through a 0.5 µm pre-filter. The filter differential pressure is monitored via a pressure transducer, and is fitted with a needle valve to regulate the backpressure across the filter.

This system was designed to be independent of the thermal stressing system and to allow independent flow and pressure conditions. Heat-stressed fuel that has passed through the heated test section is collected in a small reservoir as a feed to the Constametric III pump.

*Figure 1. DSTO Jet Fuel Thermal Stability Rig*

## 2.1 Gravimetric JFTOT

The test vessel is constructed from a 304 stainless steel cylinder 120 mm long X 12 mm I.D. The test specimen is a stainless steel shim strip 0.025 mm x 8 mm x 92 mm. The shim is pre-cleaned in trisolvent (Acetone:Propanol:Toluene) and dried in a 100ºC oven for 30 mins. The vessel is arranged vertically in the sand bath so the fuel flows along the length of the test piece. When operated in this mode the fuel flow is maintained at 2.5 mL/min. This low-laminar flow rate ensures effective heat transfer from the vessel wall to the bulk fuel and increases the residence time of thermally stressed fuel in contact with the test strip. A turbulent flow would enable more effective heat transfer and distribution throughout the fuel in the vessel, but the relativity large diameter of the vessel prohibits this. The test specimen is weighed on a CAHN C-30 microbalance to the nearest microgram.

A secondary function of the rig in this mode is to produce thermal deposits for chemical investigation. A 100 x 40 mm strip of shim is shaped into a cylinder and fitted into the vessel. At the end of the test this shim can be removed for analysis of the deposits.

*Figure 2. Gravimetric JFTOT vessel. Note the discolouration of the stainless steel which has been caused by exposure of the vessel to high temperatures in the sand bath.*

## 2.2 U-Tube Test Section

The second and most common mode of operation of the rig replaces the gravimetric JFTOT vessel with a 660 mm length of 304 stainless steel tubing 3.18 mm O.D. x 2.2 mm I.D. formed into a U-tube. The tube is pre-cleaned with a rinse of tri-solvent, then dried in a vacuum oven at 100°C for 30 min. The fuel flow rate is kept low to maintain near isothermal conditions in the test section (3). The combination of low flow rates and small tubing diameter creates long fuel residence times and thus heat transfer and chemical reaction conditions that are largely free from axial and radial temperature gradients. However, due to the nature of the fluidised sand bath, the fuel is exposed to a thermal gradient in the vertical sections of the tube. This is unavoidable, but variations can be minimised with controlled fluidisation of the sand bath. Moisture in the fluidisation air can cause surging in the sand as the moisture meets the high temperature sand and expands rapidly as steam. To minimise the surging an air and moisture trap combined with an air pressure regulator were installed in-line to the air inlet for the fluidised sand bath. Three thermocouples are attached to the U-tube wall during each test run and the temperature at each was monitored to ensure reproducible positioning of the test section and to minimise the effects of the thermal gradient within the bath. The thermal gradient intrinsic to the sand bath was used favourably to investigate the test fuels reaction to differing temperature conditions in one test run, that is, the fuel is exposed to a cool - hot -

cool temperature gradient and useful analytical data can be obtained from this temperature profile.

### 2.2.1  Deposits

The post-test tubing was rinsed with hexane, dried in a vacuum oven at 100ºC and then cut into 3 cm long sections for deposit analysis. The sections were analysed in a LECO CS-244 carbon and sulphur analyser using lecocel-II combustion accelerator. This method combusts the test piece and measures total carbon and sulphur content, thus requiring a blank of clean tubing to be subtracted from the test section values. This method assumes that all carbon and sulphur determined is acquired from the thermal deposits and relies on a single point calibration against high precision combined carbon and sulphur standards.

### 2.2.2  Filterable Insolubles

To monitor the rate of formation of filterable insolubles an interchangeable 0.5 - 2 µm titanium frit in-line post filter was installed. Alternately, fuel can bypass the post filter assembly and the total heat stressed fuel can be filtered to determine a total mass of filterable insolubles formed. Theses insolubles were collected on a 0.8 µm glass fibre filter and determined gravimetrically, making them available for further chemical investigation.
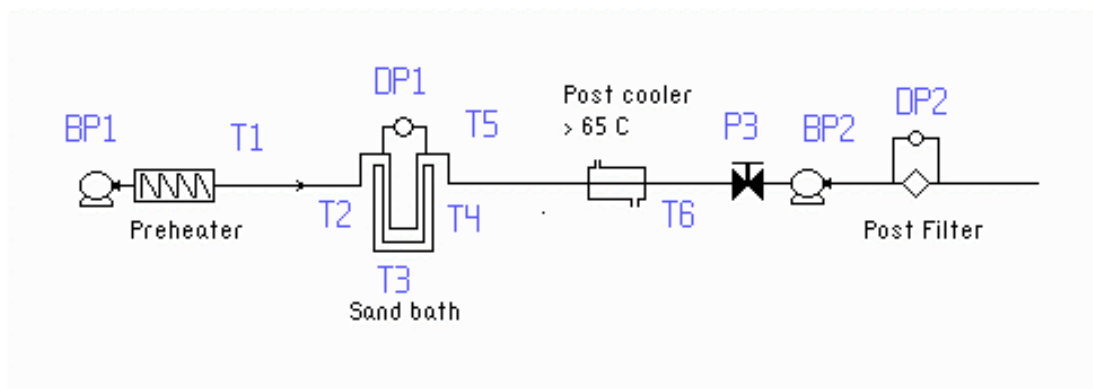
### 2.2.3  Schematic of the Rig



*Figure 3. Line drawing of thermal stability rig.*

### 2.2.4 Thermal Stability Rig Instrumentation

Process values are monitored at the locations described in Figure 3.

| Sensor Label | Sensor Description | Sensor Function |
|---|---|---|
| BP1 | Back pressure from pump 1 | Monitoring this pressure increase gives information on the rate of blockage of an inline filter located prior to the pre-heater, this filter is to ensure no particulate matter is introduced into the test section. |
| T1 | Outlet temperature of fuel from preheater | This thermocouple measures the temperature of the fuel leaving the pre-heater. |
| T2 | Tube vertical section wall temperature | Thermocouples T2 & T4 are located 100 mm from the horizontal section of the U-tube. They are used to ensure consistent positioning of the tube in the sand bath. |
| T3 | Tube horizontal section wall temperature | This thermocouple is placed at the midpoint of the horizontal U-tube section and is used to ensure the tube is consistently located in the sand bath and that the wall temperature of the tube is consistent with the sand bath set point. |
| T4 | Tube vertical section wall temperature | See T2 description. |
| T5 | Fuel temperature | This thermocouple is used to monitor the fuel temperature exiting the test section. |
| DP1 | Pressure increase across tube section | Not used for large $^1/_8''$ o.d. tubing, but intended for use with smaller diameter tubing (1/16) to monitor the rate of pressure drop across the tube as deposits form and restrict fuel flow. |
| T6 | Fuel temperature post cooler | Monitors the fuel temperature post fuel filter to ensure the fuel is below its flash point. |
| P3 | System pressure | Used to monitor the system pressure of the fuel in the test section. |
| BP2 | Back pressure post filter pump | Used in combination with DP2 used to monitor the rate of formation of filterable insolubles in the heat-stressed fuel. |
| DP2 | Pressure increase across post filter | as described in BP2 |

Note: Figure 4 displays the thermocouple outputs for a typical 400ºC run. This information is essential for calculating the actual time at temperature for each test. The long 'heat-up' period can be determined and subtracted from the test stressing time.
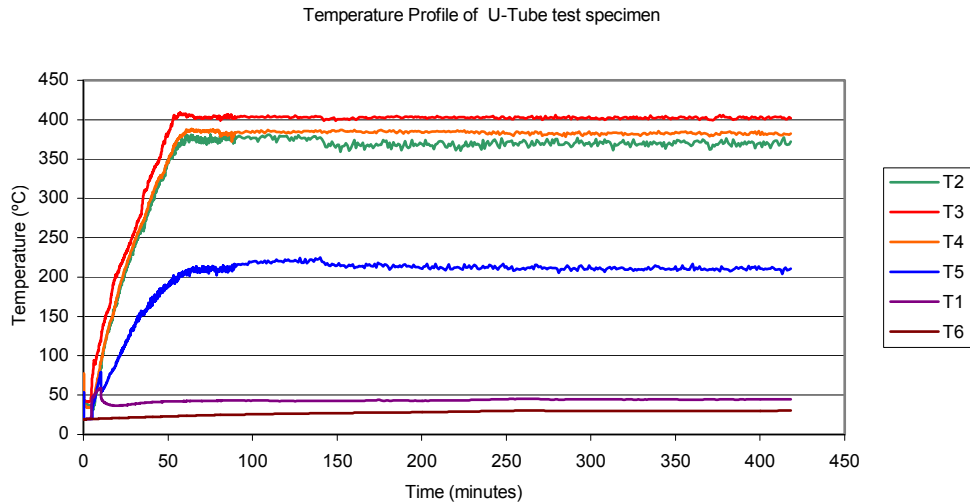
Temperature Profile of U-Tube test specimen



*Figure 4. Average thermocouple readings for standard 400ºC run*

Thermocouples T2, T3 and T4 are monitored to ensure the U-Tube is located in a consistent heat region in the sand bath. T2 and T4 are placed 100 mm from the bottom of the U-Tube on the 1st and 3rd stages of the tube and by matching their temperature outputs the correct orientation of the tube can be maintained throughout the test run. At higher fuel flow rate, there is a notable difference in T2 and T4 due to the cooler fuel taking time to heat to the external wall temperature. This can be noted in Figure 4 as the tube wall temperature at T2 is lower than T4.

## 2.2.5 Software Design

The rig is controlled manually, with data acquisition and rig condition monitoring carried out by a specifically designed program. The program was written in Visual Basic and data acquisition was taken from a National Instruments MIO-16E-10 data acquisition card. The software was designed to monitor and display, in real time, rig temperatures and pressures. Initially, six thermocouples were monitored, plus one differential pressure transducer plus three pressure transducers, with six free data acquisition channels.

The program display is divided into two main areas, the first area is a line drawing of the rig with each process value displayed in real time next to its corresponding physical location on the rig, as per Figure 3. The second is a configurable graphical display screen, consisting of up to three graphs plus their derivatives, thus a display of six graphs on the screen is possible. This area can be used to zoom in on a specific area of a graph of interest and a single graph can then replace the normal six, for example, if desired the thermocouple log only can be graphically displayed. This single graph will fill the entire graphical display area. All graphs have a back scroll capability and fully configurable scales. The program has a configurable

alarm function built in, and an alarm flag will prompt the rig operator that an alarm has been tripped. The operator then has to examine a line diagram of the rig and the appended process values to determine which value is out of the desired range.

The program also has a replay and analyse data capacity, in which collected data files can be reviewed in detail in both a graphical and tabular format. This function of the program is very useful for graphically investigating suspect areas in the data. The Rig data is then downloaded into Excel for further analysis.

# 3.  Thermal Stability Analysis

## 3.1  Experimental Procedure

To examine the thermal stability rigs' capabilities and thermally stressed fuel's response to various experimental conditions, a set of experiments were conducted at varying fuel flow rates (0.5 - 2.0 millilitres per minute), thermal stressing temperatures (300ºC to 400ºC) and total thermal stressing times (6 to 18 hours). The fuels used were a sample of "Black AVTUR". The "Black AVTUR" was a F-34 sourced from a South East Asian refinery and supplied to RAAF base Townsville. This fuel was known to have poor storage stability, and analytical grade dodecane.

### 3.1.1  Variable Flow Ability - Significance

It is known that fuel stress duration influences the formation of thermal deposits (4). A minimum fuel stress duration is required to complete the fuel-oxygen-metal surface reactions within the test section. Changes in fuel flow rate have a direct impact on fuel thermal stressing times, quantity of fuel stressed in a fixed time period and flow velocity. Fuel thermal deposition is maximised under laminar flow conditions (5,6), suggesting that the deposition reaction may be governed by the rate of transport of reactants to the test section wall rather than by chemical kinetics. The high precision, low flow rate pump used in this experimental rig was not capable of providing turbulent flow conditions in the 2.2 mm i.d. tubing, limiting all tests to laminar flow conditions.

### 3.1.2  Reaction Thermal Stress Duration and Experimental Test Time

Under dynamic test conditions, two distinct time frames are important. The first, stress duration, is the time during which the test fuel experiences the test stressing temperature and can be altered by altering the fuel flow rate within the fixed tube length. From a chemical standpoint, this time relates to the average time allowed for thermal-oxidative fuel degradation. Under steady flow conditions, the fuel stress duration '$t$' may be readily determined by the relation $t=s/v$. The average linear velocity '$v$' is directly proportional to the fuel flow. The distance along the tube '$s$' is fixed for each length of tube section (7). The second time frame is the test duration, that is the total length of time the test specimen, with fuel flowing through it, is subject to the test stress temperature. A minimum test duration of six

hours was found to be suitable to generate sufficient thermal deposit for accurate carbon/sulphur analysis by the LECO analyser.

The sand bath has a time lag before it reaches the test temperature. The total test duration was determined at the end of the test by analysing the data acquisition results for the tube wall and fuel temperatures to determine the actual test start time and the total test duration. The 12 and 18 hour test durations were not a continuous run, but the addition of multiple six hour runs.

### 3.1.3  Deposit Formation Analysis

Combustion of 3 cm lengths of the test tubing in a LECO CS-244 carbon sulphur analyser provided information on carbon and sulphur compounds formed in segments of the tube over the test duration. Carbon and sulphur deposit data was analysed in two ways, first, as total deposit and the second as a deposition rate.

Total deposit formation under the specified test conditions was monitored *via* the mass of deposit formed per area of tube section. This can be normalised for test time variations by dividing the deposit mass by the total test time to produce a deposition rate.

A deposition rate is calculated by dividing the total mass of deposit in the tube section by the residence time of fuel in the tube section and the surface area of the tube section. The deposition rate is equivalent to micrograms of carbon per time per unit area of tube section.

The deposition profile in the U-Tube is divided into three very distinct regions each being approximately 22 cm in length. The fuel is exposed to a vertical down section, experiencing a thermal gradient. The next region of the tube is the horizontal section closest to the bottom of the sand bath. In this region the fuel is exposed to very near isothermal heating and little or no thermal gradient exists. The third region of the tube is the vertical flow up section in which the fuel is travelling from the horizontal section upwards and out of the bath. This deposition profile phenomena was apparent at all fuel-stressing temperatures. The profile pattern varies with temperature as the fuel is undergoing different deposition mechanism at different thermal stress temperatures.

The CS-244 Carbon/Sulphur Determinator is a microprocessor-based instrument for measurement of carbon and sulphur content in metals, ores, ceramics and other inorganic materials. A pre-weighed sample of ~ 1 gram is combusted in a stream of high purity oxygen. The carbon in the sample is oxidised primarily to carbon dioxide with some carbon monoxide possibly being produced. The sulphur is oxidised to sulphur dioxide. These gases are swept, along with oxygen, through a dust filter and drying reagent into an infrared cell where sulphur is detected as sulphur dioxide. The gases are then routed through a heated catalyst which converts CO to $CO_2$ and $SO_2$ to sulphur trioxide. The $SO_3$ is removed by a filter and $CO_2$ is measured in a separate IR cell. Molecular $CO_2$ and $SO_2$ absorb IR energy at precise wavelengths within the IR spectrum. Energy at these wavelengths is absorbed as the gases pass through respective IR absorption cells. Changes in energy are attributed to only $CO_2$ or $SO_2$ and their concentrations are then determined.

# 4.  Experimental Results and Discussion

## 4.1  Filterable Insolubles

When a fuel is subjected to thermal stress, the fuel will tend to form gums, these gums can agglomerate and adhere to fuel wetted metal components or remain in the bulk fuel as filterable insoluble material. To rate a fuel's relative thermal stability any definition of fuel thermal stability must incorporate both types of deposit formation, that is filterable insolubles plus surface deposits.

The dependence of filterable insoluble deposit formation on fuel stressing temperature has been examined by other researchers (8,9,10). It was concluded by these researchers that filterable insoluble deposit mass generally decreases with increasing temperature and that filterable insoluble weight increases with increasing temperature. However, the relationship of filterable insoluble formation with temperature is fuel dependent and it is recognised that the effect of temperature on insolubles formation is not universal for all fuels (8).

The AVD test rig, with the single test fuel, was found to give an increasing mass of filterable insolubles with increasing fuel stressing temperature, Figure 5, suggesting that the stressing temperature range, rig configuration and refinery finishing process of the test fuel play a important role in the formation of the filterable insolubles. This inverse relationship was also found by other researchers (11) where an inverse dependence with temperature occurs. This inverse relationship was most apparent with test fuels of poor thermal stability, as determined by the JFTOT and is attributed to reduced concentrations of hydroperoxides and increased deposit solubility in the bulk fuel at higher temperatures.

The filterable insoluble material formation occurs rapidly in the thermally stressed fuel. Figure 6 shows the formation of filterable insolubles with fuel flow rate, the highest flow rate corresponds to the shortest fuel residence time in the rig hot zone.
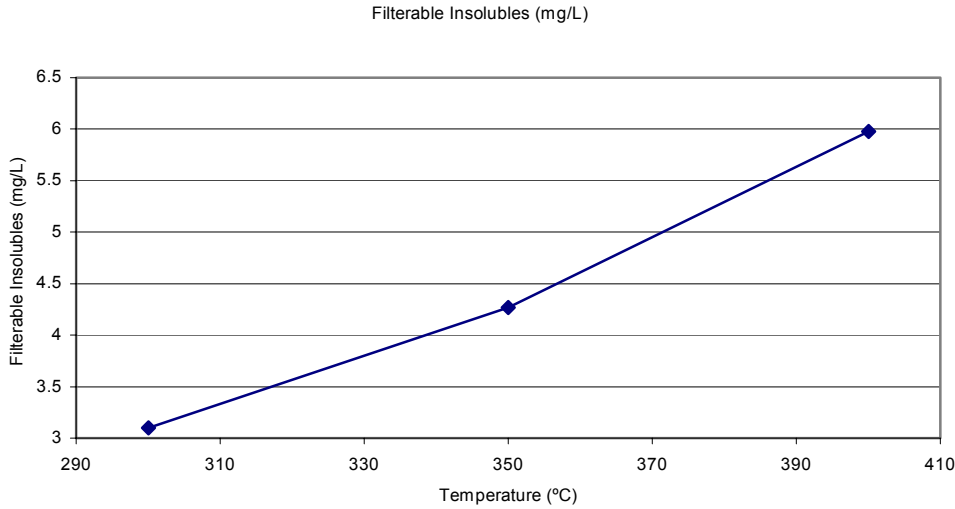
Filterable Insolubles (mg/L)



*Figure 5 Filterable insolubles formation with increasing fuel-stressing temperature. Fuel Flow Rate 1 mL/minute*

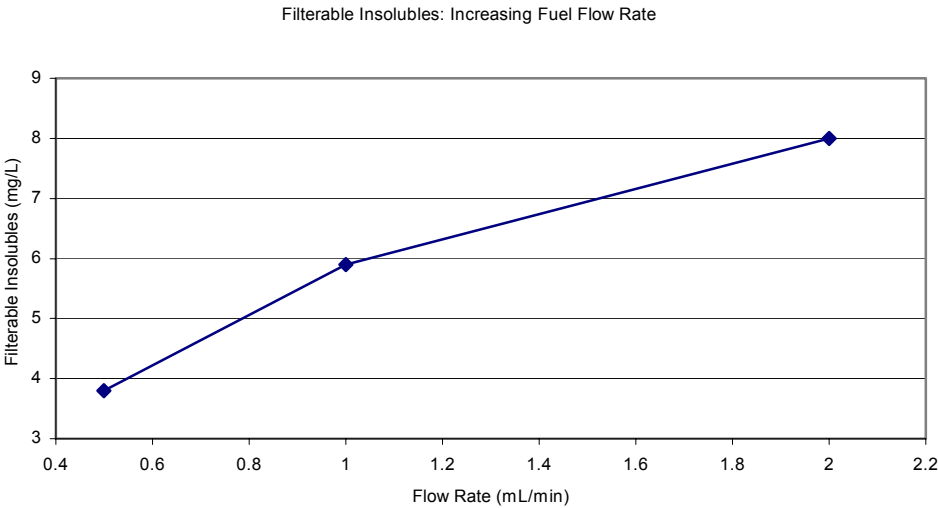Filterable Insolubles: Increasing Fuel Flow Rate



*Figure 6 Filterable insolubles formation with increasing fuel flow rate. Fuel Temperature 400ºC*

### 4.1.1 Thermal Stability of Dodecane

Dodecane was used as a standard fuel as it is a significant component of all straight run aviation fuels. Thermally-stressed, air-saturated dodecane will undergo autoxidation reactions to form solid and insoluble deposits (11,12,13). The deposit formation mechanism of dodecane by autoxidation and pyrolysis is well defined (14). The average carbon deposition profile of two runs for dodecane stressed at 400ºC for 12 hours is displayed in Figure 7. This deposition profile was used as a baseline to determine changes in deposit formation due to the test fuel.
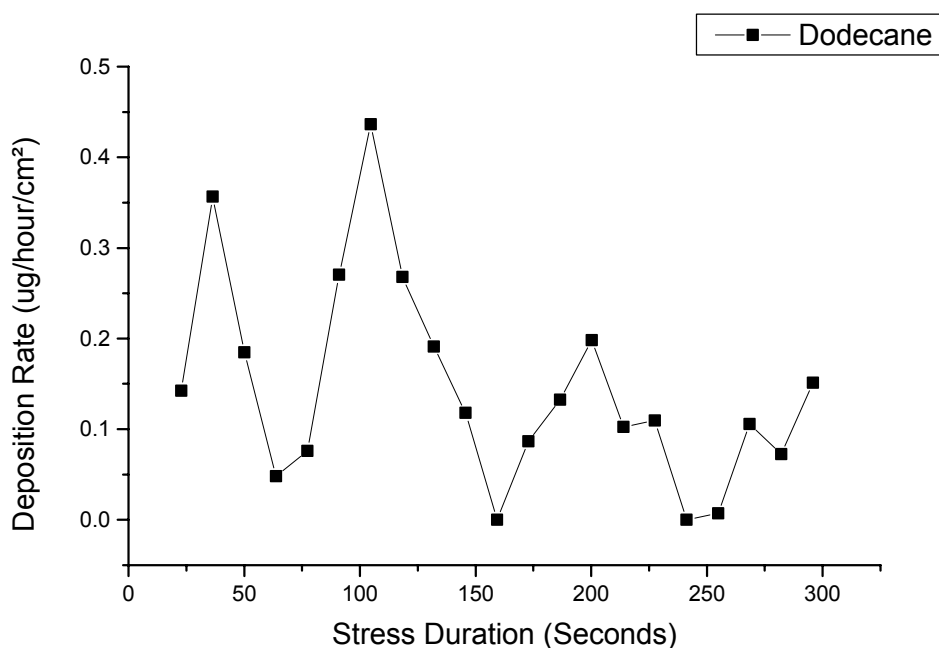
*Figure 5 Deposition profile for dodecane standard*

## 4.2 Deposit Formation: Fuel Stress Temperature

To investigate the rig's capabilities and the test fuel's response to increasing fuel stress temperature, the test fuel was stressed at 300, 350 and 400ºC wall temperatures for 12 hours at a flow rate of 1.0 mL/minute.

Carbon and sulphur compound deposition profiles are given in Figures 8, and 9. and are analyses of the same test specimen.

### 4.2.1 Fuel Temperature Effect on Carbon Compound Deposition

Carbon deposits form predominantly in the early, cooler stages of the stainless steel test piece. This early high rate of carbon deposition also corresponds to the fuel being air saturated and thus oxygen rich. Carbon deposition in the air saturated region dominated by autoxidative mechanisms (14,15).

A significant proportion of deposit formed within the first sixty seconds of fuel heat stressing, Figure 8. This sixty-second stress duration marks the boundary between autoxidative and pyrolytic mechanisms of thermal deposition and is an intermediate region incorporating deposition reactions from free radical decomposition and free radical initiated pyrolysis. Lower rates of deposition are noted at longer stress times, Figure 9. The deposition rates are

comparable for all three stress temperatures, closely following the deposition profile for the dodecane standard.

The carbon deposition rate is highest for the 400°C stress temperature and decreases with decreasing fuel stress temperature. As the fuel stress temperature increases the time for maximum deposition rate decreases indicating rapid reaction mechanisms dominate the deposit formation.
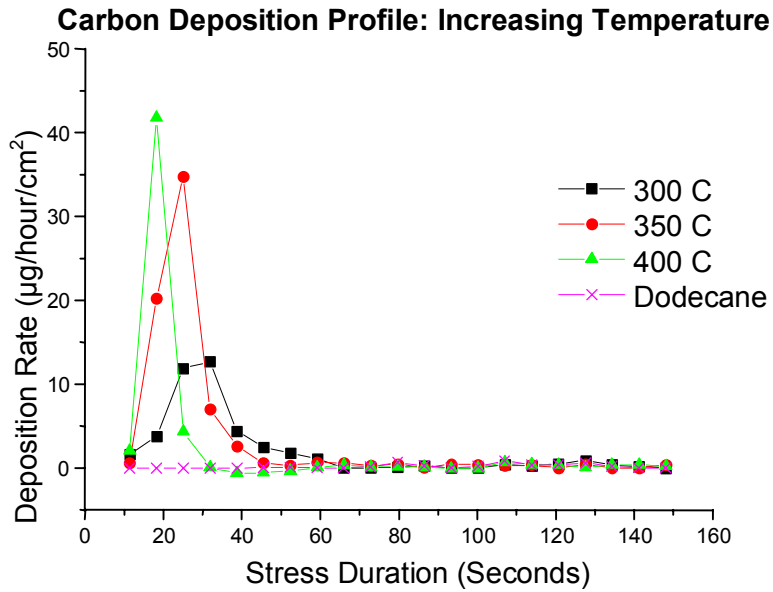


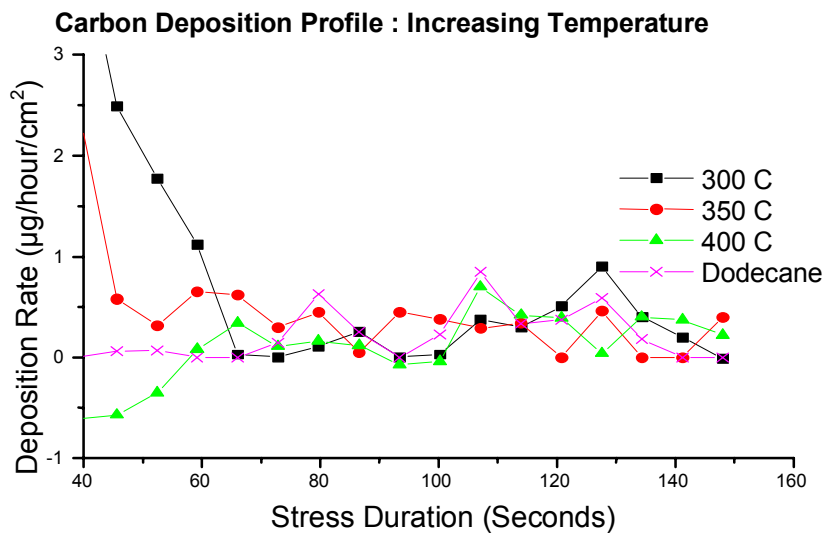*Figure 6 Carbon deposition profile with increasing fuel temperature for entire test specimen*



*Figure 7 Carbon deposition profile with increasing fuel temperature 40-160 cm section of the test specimen. Note the differing scales in Figures 8 and 9*

### 4.2.2  Fuel Temperature Effect on Sulphur Compound Deposition

The deposition of sulphur compounds occurs at longer fuel stress periods and was highest at 400ºC. There was an initial high rate of deposition in the early, cooler stages of the test piece. This initial deposition (Figure 10) follows the same profiles as for carbon deposition. For all fuels a high rate of deposition was found in the later, hotter stages of the tube where the fuel has undergone longer thermal stress. The appearance of an early high deposition rate and then another maximum suggest two differing reaction mechanisms, possibly dependant on the levels of dissolved oxygen in the fuel. The rate was maximum for the 400ºC test at ~ 2.25 µg/hour/cm² (Figure 10), dropping to a lower maximum of 0.5µg/hour/cm² for the 350ºC run, then to less than 0.25 µg/hour/cm² for the 300ºC fuel stress temperature, suggesting a strong dependence on high temperatures and longer reaction times for sulphur compound deposition.
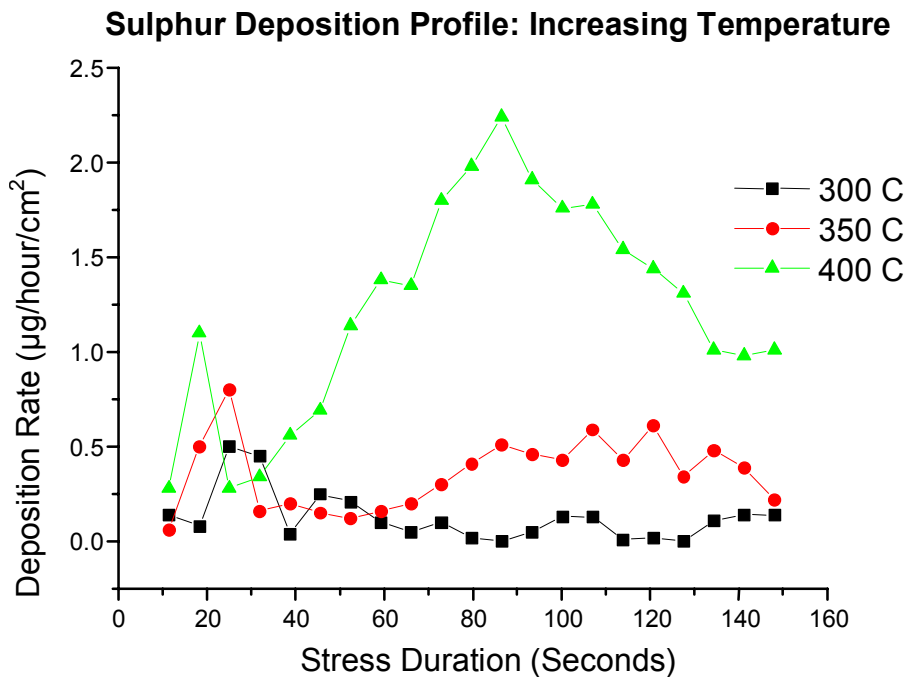


*Figure 8 Sulphur deposition profile with increasing fuel temperature*

### 4.2.3  Total Carbon and Sulphur Compound Formation

A plot of total carbon deposit formed per litre of fuel vs. stress temperature revealed a maximum deposit formation at 350ºC, indicating total carbon deposit formation has a strong dependence on the fuel stressing temperature. The higher stress temperature forces the deposition reaction toward the pyrolysis mechanism, however, the mass of filterable insolubles increased at 400ºC, Figure 6. The cause of this change of deposit formation from the test piece wall back into the bulk fuel is unknown.

Total sulphur compound deposition follows an increase with increasing temperature, reinforcing its strong temperature dependence at high reaction temperature. This increasing trend suggests that future high temperature hydrocarbon type fuels will need to have thermal stability defined by both carbon and sulphur deposition. The total carbon and sulphur compound deposition rates are given in Figure 11.
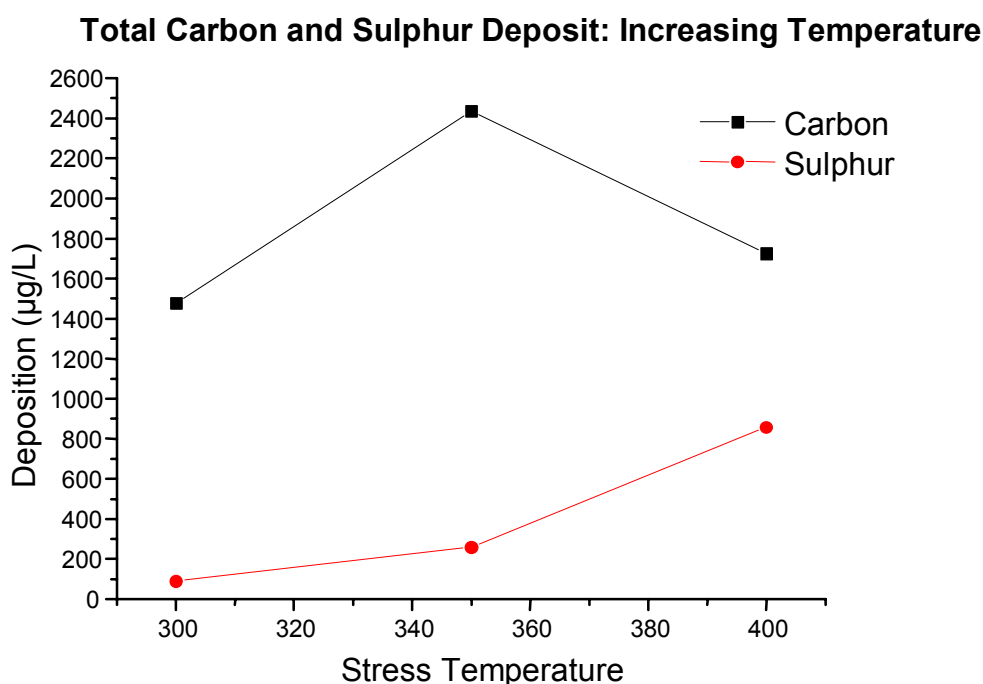
**Total Carbon and Sulphur Deposit: Increasing Temperature**



Figure 9 Total Carbon and Sulphur deposit formation with fuel temperature

## 4.3 Deposit Formation: Increasing Fuel Flow Rate/Decreasing Fuel Stress Time.

The influence of variations in fuel flow velocity and thus residence time and volume of fuel thermally stressed was determined by conducting tests at three different flow rates while maintaining the tube length, test duration and discharge temperature as constant. The three flow rates chosen were 0.5, 1.0 and 2 mL/min. of fuel.

An increase in the fuel flow rate through the test section corresponds to a decrease in the time the fuel is subject to heat stress and an increase in the volume of fuel stressed (i.e. 360, 720 and 1440 mL, respectively, at each flow rate).

4.3.1 Carbon Deposit Formation: Increasing Fuel Flow Rate/Decreasing Fuel Stress Time.

In the first stages of the test section the rate of carbon deposition is high for the highest fuel flow, dropping as the flow rate decreases. This trend suggests that fuel subjected to autoxidation-dominated deposit mechanisms has a strong dependence on bulk fuel flow rate,

Figure 12. The rate of deposition for bulk fuel flow increases with decreasing fuel flow. These results are given in Figure 14.
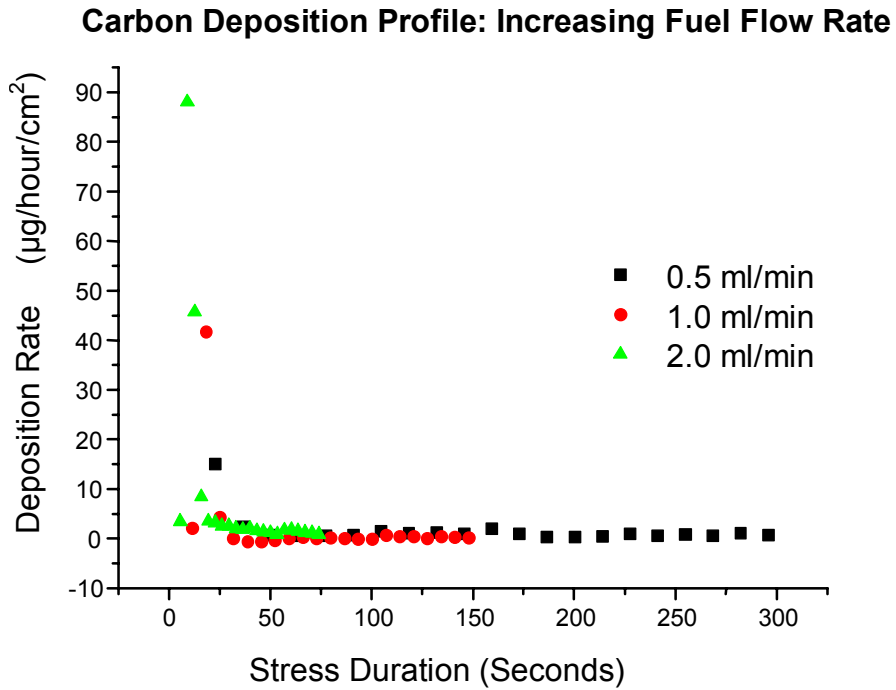
**Carbon Deposition Profile: Increasing Fuel Flow Rate**



*Figure 10 Carbon deposition profile with fuel flow rate*

### 4.3.2  Sulphur Compound Deposit Formation: Increasing Fuel Flow Rate.

A significant increase in sulphur compound deposition was apparent for the lowest fuel flow rate, that is the longest fuel residence time. High levels of sulphur deposition require conditions of high fuel stressing temperature and long fuel stressing times, Figure 13.

**Sulphur Deposition Profile: Increasing Fuel Flow Rate**
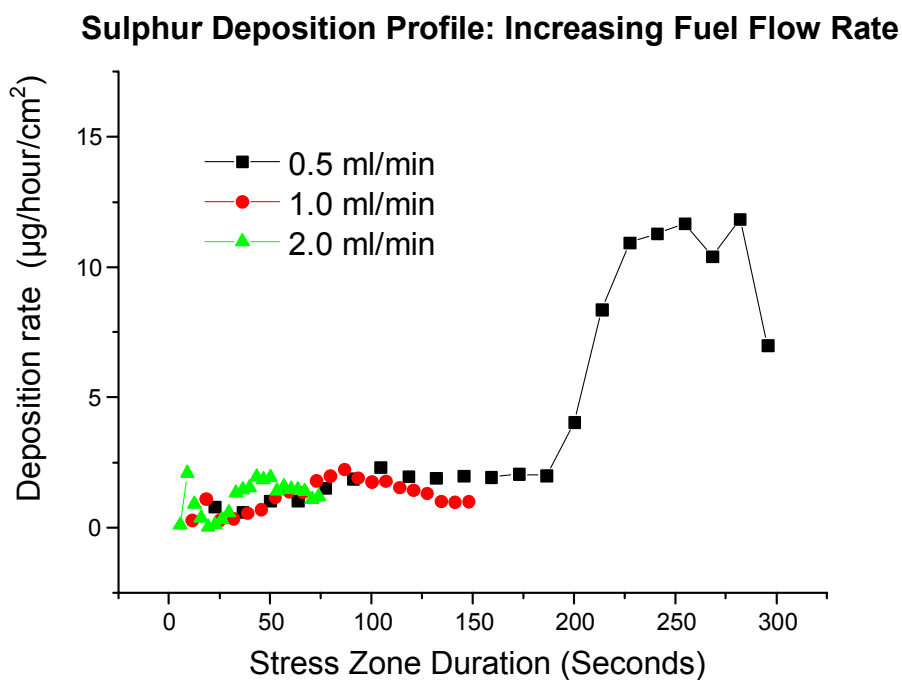


*Figure 11 Sulphur deposition profile with increasing fuel flow rate*

### 4.3.3 Total Carbon and Sulphur Compound Formation Increasing Fuel Flow Rate/Decreasing Fuel Stress Time.

Increasing fuel flow extends the time for the autoxidation reaction mechanism to dominate, that is the bulk fuel takes correspondingly longer to heat to test temperature. At lower flow rates the fuel is stressed for longer, allowing an increase in deposition rate due to pyrolysis of the fuel and thus a lower carbon deposition rate, Figure 14.

The sulphur deposit formation was reduced as the fuel flow rate was increased. The shorter stress duration was insufficient for complete reaction and deposition of the sulphur compounds, indicating the dependence of sulphur deposit formation on the fuel stress temperature, stress duration and a lesser dependence on the mass of fuel exposed to thermal stress. This effect is shown in Figure 14 where it can be seen that the highest sulphur deposit rate occurs with the conditions of longest stress duration and lowest fuel flow rates.

**Total Carbon and Sulphur Deposition: Variable Fuel Flow Rate**
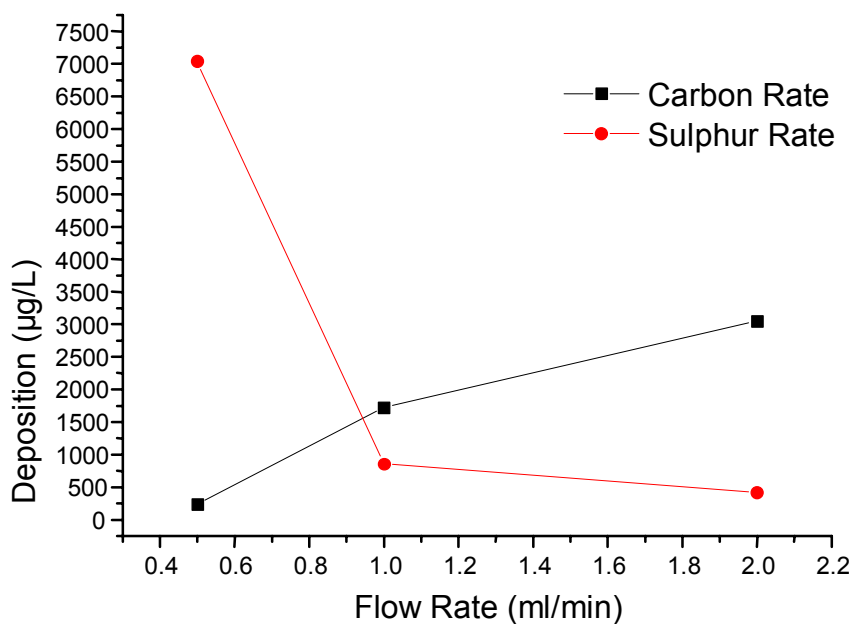


*Figure 12 Total carbon and sulphur deposition with increasing fuel flow rate*

## 4.4 Deposit Formation: Test Duration

The effect of test duration on fuel deposit formation was investigated through a series of tests conducted over 6, 12 and 18 hours. The 12 and 18 hour runs were done over two and three days, respectively, allowing investigation of rate of formation and total insoluble formation on separate days. The stress temperature and fuel flow rate were kept constant at 400ºC and 1.0 mL/min. respectively.

### 4.4.1 Carbon Deposit Formation: Test Duration

**Carbon Deposition Profile: Increasing Total Test Duration**
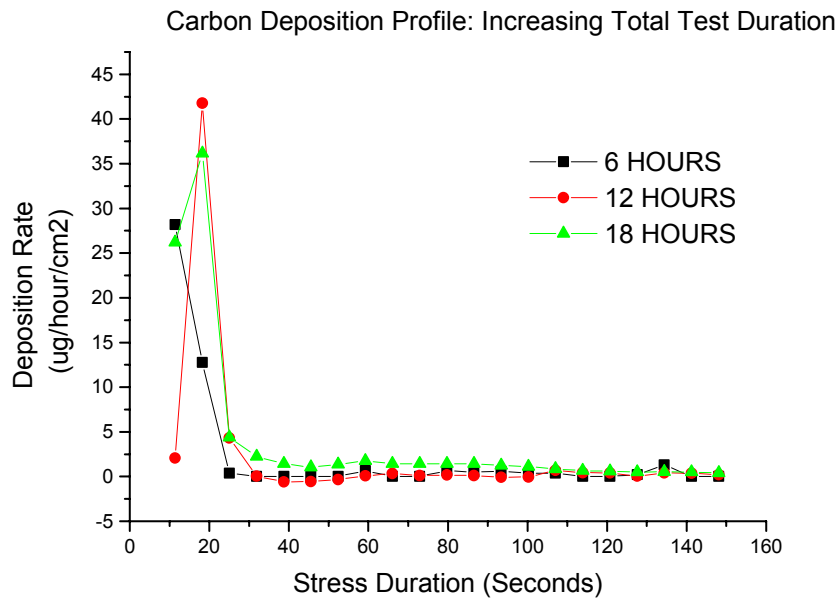


*Figure 13 Carbon deposition profile with increasing test duration (400ºC, 1 mLmin-1)*

### 4.4.2 Sulphur Deposit Formation: Test Duration

**Sulphur Deposition Profile: Increasing Total Test Duration**
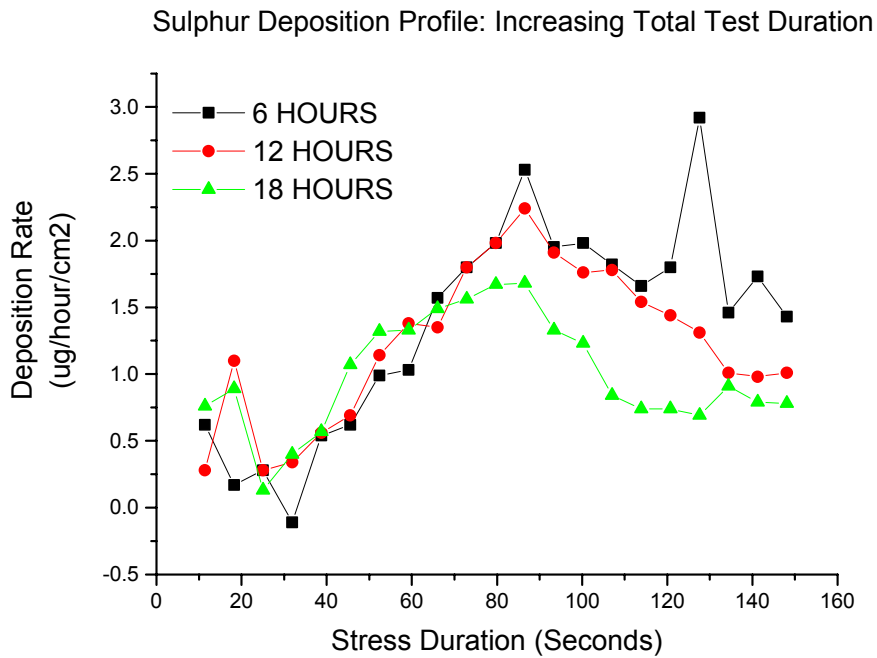


*Figure 14 Sulphur deposition profile with increasing test duration. (400ºC, 1 mLmin-1)*

The total carbon deposition rate increased with increasing test time. The carbon profile shows an increase for the 18 hour test, Figure 15.

The sulphur deposition profiles were similar, with the general trends the same for the three stress durations. The deposition rate dropped for the 18 hour test suggesting that the sulphur deposit formation mechanism was influenced by the deposition surface. That is, there was less exposed metal for reaction as the test time increased.

### 4.4.3 Total Carbon and Sulphur Compound Formation Rate: Test Duration
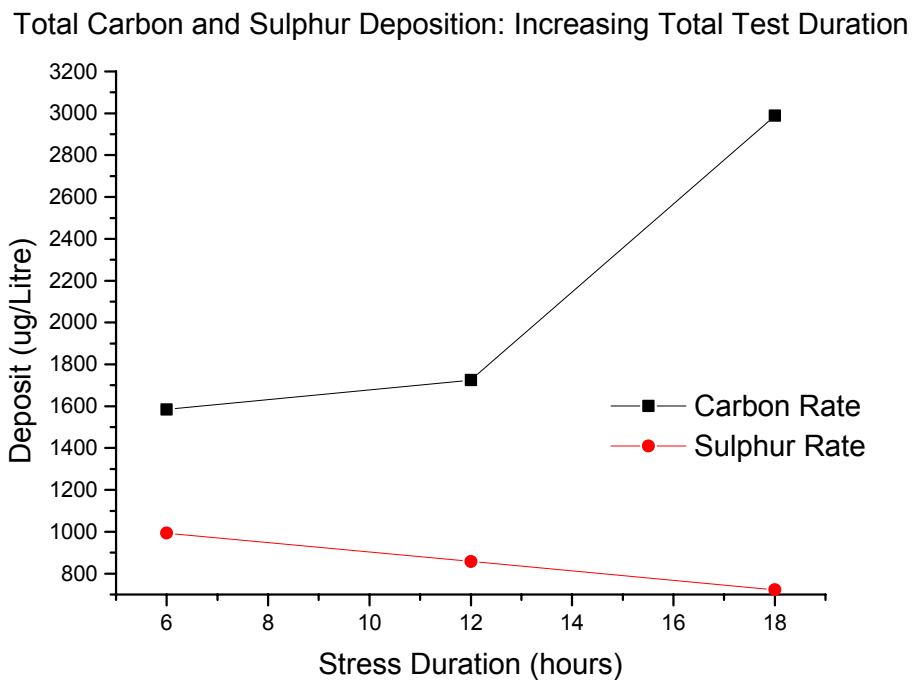


Figure 15 Total carbon and sulphur deposition with increasing total test duration (400°C, 1 mLmin⁻¹)

### 4.4.4 Carbon Deposition: Increasing Test Duration

Increasing the total test duration provided information on the effect of the test section material surface, including any dependence on stressing time and induction period associated with the thermal deposits coating the inner surface of the tube.

In a new test-tube the fuel interacts solely with a clean hot metal surface, in this case the interior of the stainless steel tube. As the amount of material deposited on to the inner surface increases, the fuel interacts with a metal surface coated with a layer of thermal deposits, until finally the fuel is interacting with fuel thermal deposit only.

The deposition rate for carbon deposits, Figure 15, was lowest when interacting with the fresh steel surface increasing to a maximum rate at 12 hours, then the rate dropping away for the 18 hour test. The layer of thermal deposit may have an insulating effect and cause a decrease in the heat transfer from the surface to the fuel. In the pyrolytic deposition region the rate increased to a maximum for the longest stress duration of 18 hours at 0.5-1.75 $\mu g/hour/cm^2$) with the rates for the 6 and 12 hours runs being comparable from 0- 0.5 $\mu g/hour/cm^2$. This small increase in the rate of deposition in this region of the tube will have a dramatic effect on the amount of carbon deposit formed in extended tests.

The amount of total carbon deposit increases significantly from 6-12-18 hours with the increase from 12-18 hours (1264 $\mu g$) being nine times the 6-12 hour increase (140 $\mu g$). Thus once a layer of thermal deposit has formed on a metallic surface the amount of deposition per litre of fuel in contact with the surface, will increase significantly.
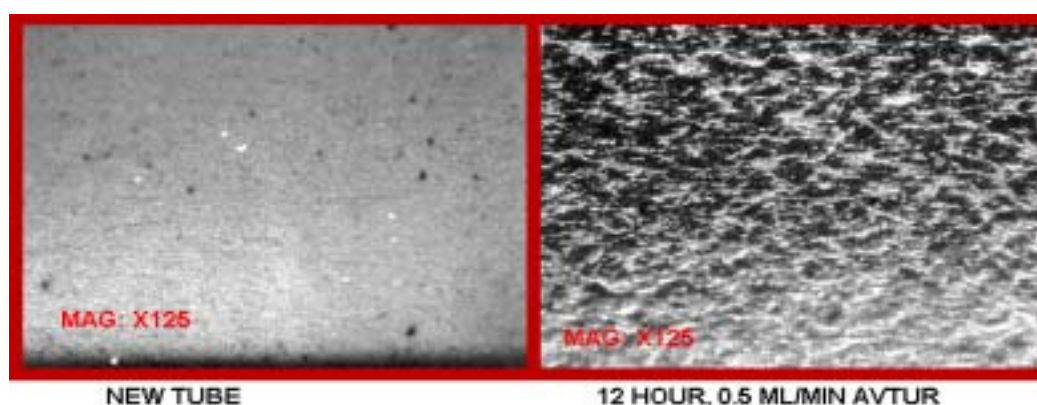


*Figure 16 Interior test section surfaces for a new tube vs. a tube after 12 hours exposure to fuel at 400ºC*

### 4.4.5 Sulphur Deposition: Increasing Test Duration

The rate of sulphur deposition was higher for the shortest run time and decreased with increasing test duration, Figure 16. The new steel surface promotes sulphur deposition. This effect was evident in the total amounts of sulphur deposit formed per litre of fuel as the test duration increased the amount of sulphur deposition per litre of fuel decreased linearly.

## 4.5  Filterable Insolubles: Rate of Formation

The rig includes a post filter assembly for the collection, quantification and rate of formation analysis for the filterable insolubles formed when jet fuel is heat-stressed. The fuel will generate both filterable insolubles in the bulk fuel and reaction products that form as the fuel cools in the cooler sections of the tube down-stream from the sand bath. These insoluble products are attributed to autoxidation reactions in the bulk fuel and are oxygen concentration dependant (10).
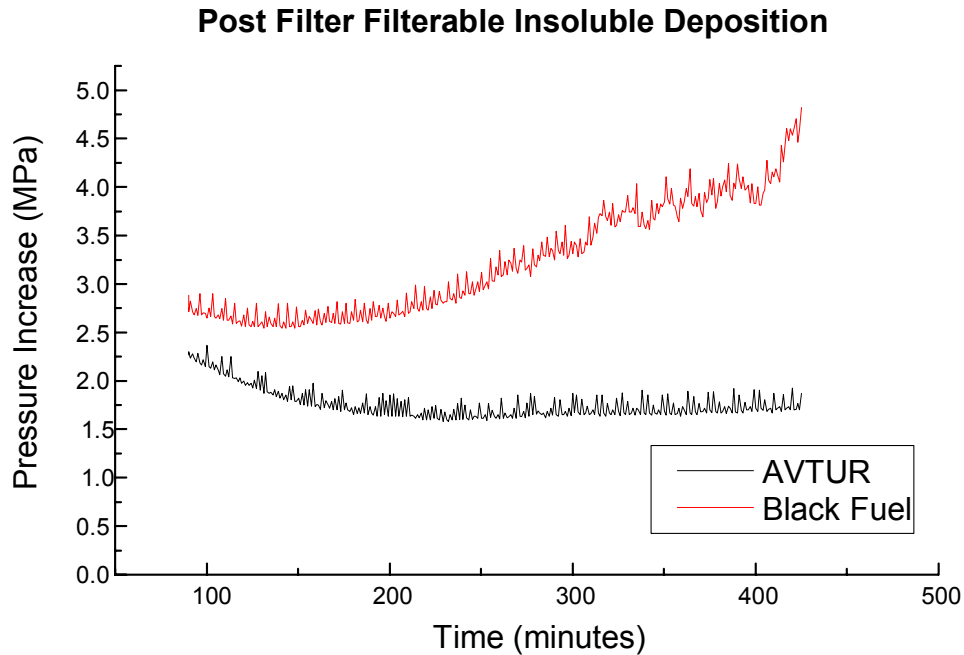
## Post Filter Filterable Insoluble Deposition



*Figure 17 Rate of filterable insoluble formation*

Figure 17 gives the rate of formation of filterable insolubles for two test fuels. The pressure increase corresponds to the backpressure developed by the post filter fuel pump caused by trying to maintain a fixed flow rate as the filter blocked. The 'Black Fuel' was filtered through a 2 µm filter and the AVTUR through a 0.5µm filter. The black fuel (known to be thermally unstable) totally blocked the 2µm filter in ~ 8hours.  The AVTUR showed only a very slight pressure increase in the same time and actually displaying an overall pressure decrease possibly due to lowering in the fuel viscosity as the test temperature is reached.

# 5. Conclusions

A single-pass flowing heat exchange rig has been commissioned with the capability to quantitatively rate fuel's thermal stability, quantify carbon and sulphur deposit formation and provide deposition profiles for all liquid fuels. Measurements of carbon and sulphur deposits from a fuel known the be both storage and thermally unstable, sourced from RAAF Townsville, demonstrated that the rig was capable of discriminating between differing carbon and sulphur deposit profiles experienced under differing test conditions, including altering fuel stressing temperatures, fuel stress duration and total test time.

Of significant interest for future high temperature fuels is the high degree of sulphur compound deposit formation displayed by the test fuel.

The concept of a gravimetric JFTOT, while sound, was found to give less information than the U-tube operation of the rig, and further development will be directed toward the U-Tube single pass heat exchanger.

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Current and planned gas turbine engines use fuel as their primary heat sink. When jet fuel is thermally stressed it will form gums and deposits. These deposits can block engine fuel nozzles, causing damage to the engine hot sections, especially the combustor region. The fuel's thermal stability is a critical fuel property with respect to optimum performance of modern military gas turbine engines. The current standard method to rate fuel thermal stability, the Jet Fuel Thermal Oxidation Tester (JFTOT), is a subjective, pass-fail type test and is not adequate as a tool to quantitatively investigate fuel thermal stability. This report describes a program to design, construct and commission a rig capable of quantifying fuel's thermal stability based on carbon and sulphur deposit formation in a heated metal test tube. A fuel known to be unstable both chemically and thermally, sourced from RAAF Townsville, was used as a test fuel for commissioning the rig. The rig was found capable of discriminating between differing test conditions and was successful in rating fuels' thermal stabilities based on quantification of the fuels' deposit-forming capacities. A significant finding of commissioning procedures was the high levels of sulphur deposit formed in the test fuel.