

# AN INVESTIGATION OF THE THERMAL STABILITY OF ALTERNATIVE AVIATION FUELS

Young, N.<sup>1\*</sup>, Yuen, F.T.C.<sup>1</sup>, and Gülder, Ö.L.<sup>1</sup>

<sup>1</sup>Institute of Aerospace Studies, University of Toronto, Toronto, Canada

\* Corresponding author(neell.young@mail.utoronto.ca)

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## ABSTRACT

A new experimental testing apparatus has been used to assess the thermal stability characteristics of alternative aviation fuels when exposed to high temperatures. The apparatus was built to assess the coking behaviour of conventional jet fuels. The apparatus is a small-scale recreation of an aircraft fuel system consisting of a preheating and test section. The preheating region exposes the fuel to conditions it would experience as an on-board coolant for various aircraft systems such as avionics, electronics and the engines. The test section represents the geometry, temperature, pressure and fuel flowrate in the injection nozzles, exposing the fuel to temperatures higher than in the preheating section. The two sections are equipped with temperature controllers and both sections simulate the residence times that fuels experience in aircraft conditions. The accumulation of deposits is monitored by a pressure drop measurement across the test section, where larger pressure drops indicate a narrowing of the section diameter and increased coking. The pressure drop tests were also verified using a carbon burn-off apparatus after thermal stressing. This allows for controlled, parametric studies to examine the link between the chemical composition of fuels and the propensity for coking or thermal decomposition. Experimental results for both conventional and alternative fuels are presented for the purpose of comparison.

## 1 INTRODUCTION

The International Civil Aviation Organization has set the ambitious goal of limiting the contribution of commercial aviation to global greenhouse gas emissions to carbon neutral by 2020 [1]. To meet this goal, gas turbine engines can be improved by increasing peak combustor temperatures to enhance their thermal efficiencies. Unfortunately, this will eventually cause the turbine blades to melt with excess heat. One way to remedy this is to use jet fuel as a heat sink. If the jet fuel is heated for prolonged periods, it will begin to degrade and form insoluble deposits that accumulate in the fuel lines and clog the fuel spray nozzles, leading to a non-uniform fuel spray pattern. The end result is that the use of jet fuel as a heat sink adds to maintenance problems and reduces engine operating efficiency.

In order to prevent fuel decomposition, any type of fuel to be used in aviation gas turbines needs to be certified by numerous standards that govern their physical and chemical properties. One of these standards is the ASTM D3241 Standard Test Method for Thermal Oxidation Stability of Aviation Turbine Fuels. This standard uses a Jet Fuel Oxidation Tester (JFTOT) that heats the fuel in a single stage and assesses the fuel by a simple pass/fail test by comparing the color change of the thermally stressed fuel to a color chart. Unfortunately, this metric is a qualitative approach which may not be suitable for alternative aviation fuels, whose color change from thermal stressing may not be identical to that of conventional Jet A. The apparatus used in this study has been designed to allow for a more realistic and quantitative analysis of the thermal stability of fuels by using both pressure drop measurements and a carbon burnoff apparatus.

## 2 BACKGROUND

### 2.1 Formation of Deposits

To understand the coking mechanisms in aviation jet fuels, the chemical kinetics of how insoluble deposits form from the fuel needs to be studied. Unfortunately, the exact processes of the chemical kinetic mechanisms are very difficult to evaluate experimentally due to the large variety of compounds present in aviation jet fuels and the myriad reaction pathways that the coking process can take. Numerous studies have been conducted to describe the thermal stability of jet fuels. Balster et al. [3] showed that thermally stressed fuels degrade at a rate that depends strongly on temperature. The study also describes two temperature regimes, autoxidation and pyrolysis, where the type of fuel degradation markedly differs from one another. The autoxidation regime as examined by Hazlett [4] showed that the presence of dissolved O<sub>2</sub> in the liquid fuel causes the reaction pathway to produce hydroperoxide radicals, which act as precursors to deposit formation. The pyrolytic regime as investigated by Andresen et al. [5] showed that alkanes in fuels exposed to temperatures higher than the autoxidation regime or in the absence of dissolved oxygen tend to form cycloalkanes which proceed from small aromatic compounds. These smaller aromatics finally combine to larger polyaromatics leading to insoluble deposits.

Commodo et al. [6] used UV-visible absorption and fluorescence spectroscopy to examine the change in the chemical composition of fuels as they are heated. It was found that as the fuels are exposed to higher temperatures, more aromatic compounds form, and as the temperature increases, the number of aromatic rings per compound increases. Beaver et al. [7] determined that these large aromatics with molecular masses upwards of 600 g/mol are insoluble and deposit on the inner surface of the pipes. Liu [8] modeled the chemical and thermal rate kinetics of the formation of insoluble deposits in Jet A-1 using eighteen intermediate reactions and three terminating reactions for the formation of deposits. Two wall reactions were also considered as the autoxidation of fuel could be catalyzed by the metal wall.

### 2.2 Review of Existing Test Apparatuses

There are two main types of jet fuel thermal stability experiments: continuous flow dynamic tests and pressurized static tests. Dynamic tests range from bench-top single pipe heat exchangers to full-size gas turbines, fuel tanks, or nozzle simulators [4]. Dynamic tests have shorter fuel residence times, but a continuous supply of fresh fuel (which possibly carries dissolved oxygen) is needed. Dynamic tests also require a characterization of the fuel temperature profile through the heated test section to determine the actual fuel temperature inside the test section [9]. In contrast, pressurized static tests have much longer residence times, require less fuel and the fuel is heated at a fixed temperature. There have been a variety of dynamic flow apparatuses developed and each of them have differences from one another that can make data comparison between different research groups difficult, even if the experimental designs are similar. There are also standardized apparatuses for determining the thermal stability of a sample fuel, such as the Coordinating Research Council (CRC) coker (ASTM D-1660) and the subsequent JFTOT (ASTM D-3241). The CRC coker consists of a 330 mm long electrically heated aluminum pipe within a larger pipe, followed by an electrically heated housing containing a 25 μm filter [4]. The laminar fuel flow is along the outside of the aluminum pipe, and contained within a larger pipe. The fuel temperature at the end of the aluminum pipe is set to 149°C and the filter housing is kept at 205°C, simulating the passage size within fuel spray nozzles. The fuel volumetric flow rate is 60 mL/min for 5 hours at a system pressure of 1.0 MPa, causing the fuel residence along the aluminum pipe to be 10 s. The fuel is given a pass or fail based on the visual discoloration of the aluminum pipe by deposit buildup as long as the pressure drop across the filter did not exceed 10 kPa.

The JFTOT improved upon this and replaced the CRC coker in 1973 as ASTM D-3241 [2][4][10]. Instead of the 19 L of fuel required in ASTM D-1660, JFTOT uses only 0.6 L at a volumetric flow rate of 3 mL/min over 2.5 hours. Fuel still flows along the outside of an aluminum pipe, and heating was improved to achieve a 260°C pipe wall temperature 38.7 mm from the starting end of the pipe. Other changes included an increase of system gauge pressure to 3.45 MPa with a nitrogen gas blanket, a non-heated filter housing, and a reduction in filter pore size to 17 μm. The same visual discoloration criteria are still used, but the maximum allowable pressure

drop across the filter is reduced to 3.3 kPa. One of the main limitations of the JFTOT test is that it is only capable of testing a fuel up to 260°C, and today's research is interested in higher fuel temperatures since engines are burning ever hotter to improve thermal efficiency [9][11]. Another limitation is that much like the earlier ASTM D-1660, it judges the fuel by discoloration which is a highly subjective method of evaluation, and it is potentially problematic when different people see colors differently or in different lighting conditions. The most common apparatus used in universities or small laboratories consists of a single, heated pipe with fuel flowing through it to simulate a heat exchanger. There have been many examples such as in NASA Glenn Research Center's Heated Pipe Facility, the USAF's Phoenix Rig, the Australian Defence Science and Technology Organisation (DSTO) Thermal Stability Rig, and others by United Technologies Research Center (UTRC), Rocketdyne, and PSU Energy Institute's flow reactor [12][13][14]. Different methods have been used to heat the fuel pipe. Resistively heated isothermal copper blocks surrounded and conductively heat the fuel pipes in UTRC's rig and the Phoenix Rig [15][16][17][18]. Australia's Airframes and Engines Division of DSTO used a fluidized sand bath to conductively heat their submerged fuel pipe [13][14]. PSU's flow reactor used an electrically heated pipe furnace that provided radiative heating of the fuel pipe that was in the centre of the furnace [11][19].

### 2.3 Objectives

The objective of this study was to perform proof-of-principle experiments to verify whether the thermal stability of biojet fuels could be assessed using a new test rig developed recently at UTIAS. Four jet fuels, two from petroleum sources, and two produced from biomass, are evaluated and their thermal stability characteristics is discussed.

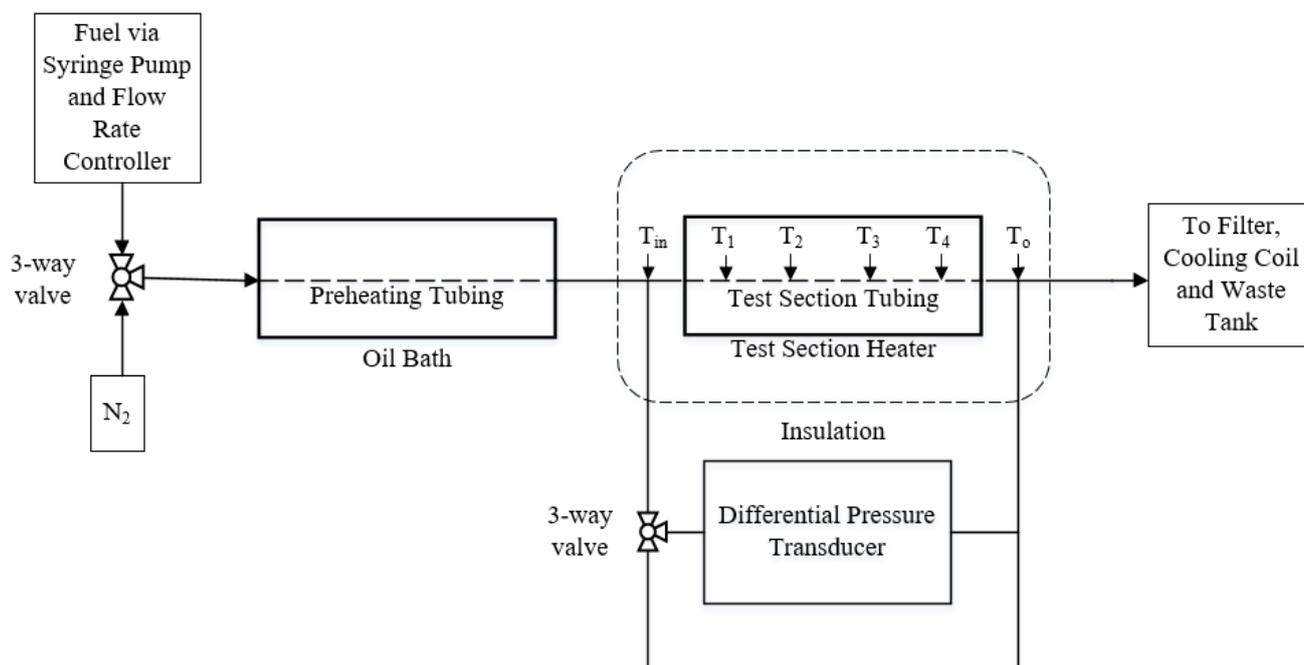


Figure 1. Layout of the testing rig showing all relevant components.

### 3 Methodology

The UTIAS jet fuel thermal stability rig has been described in detail by Yuen et al [20] and only a short description is given in Figure 1. The jet fuel is supplied by a syringe pump (Teledyne, ISCO model 500D) and the pipe material is made of type 316 Stainless Steel. The first portion of the pipe which has an inner diameter of 4.57 mm, outer diameter of 6.35 mm and length of 1 m is immersed in a heated oil bath to simulate the fuel acting as a coolant. The test section is 5.08 cm long, and currently can accommodate 1/8 inch nominal outer diameter stainless steel pipes with an inner diameter of desired size. For the current study, we used a test section with a nominal inner diameter of 0.7mm. This test section simulates fuel conditions in the fuel injection nozzle inside the engine combustor.

The fuel residence time in the oil bath is about 50s, on the same order as in the aircraft fuel systems [4] while the fuel passes through the test section in a much shorter time, on the order of 0.05s. The fuel from the supply tank is pumped at a constant rate of 20.4 mL/min. The test section is enclosed in a solid brass casing 38.1 mm in diameter and 50.8 mm long consisting of two halves. The brass block is heated by a 300 W band heater and insulating foam surrounds the brass blocks to reduce heat loss to the environment. The temperature on the outer wall of the pipe is monitored by six thermocouples labelled  $T_1$  through to  $T_4$ ,  $T_{in}$  and  $T_{out}$  in Figure 1 and are recorded by a thermocouple datalogger (Omega, OM-CP-OCTTEMP2000).  $T_{in}$  records the pipe outer wall temperature upstream of the test section and immediately after the oil bath section while  $T_o$  keeps track of the temperature downstream of the test section.  $T_1$  through to  $T_4$  are four thermocouples spaced 1.3 cm apart and monitor the outer wall temperature of the test section. In particular,  $T_1$  is the thermocouple that the temperature controller (Omega, CN7523) uses to control the band heater and set the test section temperature. It should be noted that the outer wall temperature of the test section is higher than the inner wall temperature. In-house simulation code was used to determine the required outer wall temperature to get the desired inner wall temperature. The back pressure regulator maintained the fuel flow pressure to about 68.9 kPa (100 psi) for all tests. Finally, a filter is used to collect any further coke deposit downstream of the test section and cold water at 10°C is pumped around a cooling coil around the piping after the test section to ensure that the fuel temperature is lower than the fuels' autoignition temperature prior to being emptied into the waste tank. The  $N_2$  is used for clearing and cleaning the pipes between tests.

To monitor and measure deposit formation within the test section, two static pressure taps were used, one upstream and another downstream of the heated test section to determine the pressure drop inside the test section. The pressure transducers (Omega, MMDWU001V5P3A0T1A1) have a range of 0-6.89 kPa (0-1 psi) and the differential pressures over time were recorded by a multifunction data acquisition device (National Instruments, USB-6210) and transmitted to a PC where it was recorded via MatLab.

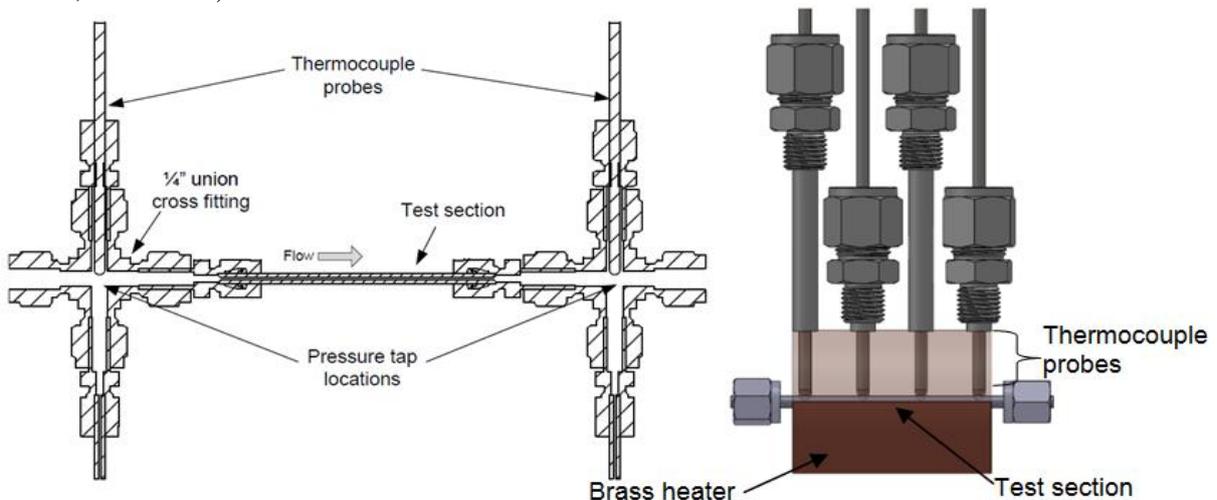


Figure 2. Schematic and close-up view of the pressure tap locations and thermocouple locations.

From the Hagen-Poiseuille Law in Equation (1), the pressure drop is inversely proportional to the fourth power of the pipe diameter. Thus, formation and collection of insoluble deposits inside the test section will result in progressively larger pressure drops.

$$\Delta P = \frac{8\mu QL}{\pi R^4} = \frac{128LQ\mu}{\pi D^4} = \frac{\text{constant}}{D^4} \quad (1)$$

$\Delta P$ , is the pressure difference between the inlet and outlet,  $\mu$  is the dynamic viscosity of the fuel,  $Q$  is the volumetric flow rate,  $L$  is the pipe length and  $D$  is the average diameter of the pipe. This equation is later used to calculate the diameter of the pipe from the pressure drop measurements under two key assumptions. The first is that the deposit collects uniformly around the pipe inner walls. The second is that the pressure drop comparisons are taken at the same temperature, since liquid viscosity decreases with increasing temperature.

Another method for calculating deposit accumulation used in this study is by using a carbon burnoff apparatus. The carbon burnoff apparatus (Eltra SC-800) heated specimens to 700 °C in a pure oxygen environment. This caused all of the thermal deposit to oxidize into CO<sub>2</sub>. The amount of CO<sub>2</sub> produced is measured by an infrared cell inside the apparatus and the amount of carbon deposit can be calculated from this measurement.

To determine the robustness of the design, trial experiments were undertaken and thermal stressing experiments were done in five hour increments. The oil bath was heated first, followed by initiation of the fuel flow. When the oil bath is heated, the fuel that passed through it will also be heated and cause the test section to heat up. Once the temperature in the test section reached a steady value, indicating that the rate of temperature increase has become negligible, pressure drop data taken for 15 minutes. Afterwards, the test section is heated to the desired test temperature and pressure drop data taken for a further 5 hours. As the syringe pump was set to a constant flowrate, the fuel pressure throughout the apparatus was maintained by a pressure regulator downstream, and cold water is passed through the cooling coil while pressure and temperature data were taken at 30 s intervals. Note that the test section temperature controller had to be set to a higher temperature than the desired inner wall temperature due to a temperature gradient. The effect of this gradient and the calculation of the outer wall temperature from the inner wall temperature was done by an in-house numerical simulation. After the 5 hour monitoring phase, the apparatus is shut down and left to cool. The procedure is repeated as necessary over several days to accumulate more thermal deposit. Upon conclusion of the thermal stressing phase, the test sections were cut, lightly rinsed with *n*-hexane to remove any remaining liquid fuel within while keeping the deposits intact and dried in a vacuum oven overnight. The test sections were then analyzed for the total carbon deposit accumulated via a carbon burnoff apparatus.

## 4 Results and Discussion

### 4.1 Initial Test Runs

Test runs were conducted to examine the functionality and behavior of the test apparatus. The temperature condition at the outer wall was set to 375 °C which corresponds to an inner wall temperature of 355 °C. The set temperature of the oil bath was 191.5 °C which corresponds to a temperature upstream of the test section  $T_{in}$  of 162.8 °C. The flow through pressure was set to 68.9 kPa by the back pressure regulator downstream of the test section. It was found that heating the test section above 375 °C at the outer wall caused the fuel in the test section to begin boiling, which caused large fluctuations in the apparatus of  $\pm 6.89$  kPa ( $\pm 10$  psi) as detected by the back pressure regulator.

A sample of the raw data is shown in Figure 3. It can be seen that over time, there is a detectable pressure drop across the test section due to progressive reduction of the pipe diameter. Tests were done in five-hour increments. Each five hour increment begins with a sharp slope indicating the warm up phase of the testing rig to match the steady-state temperature and flow pressure from the day before.

It is also important to ensure that the test section temperature is the same throughout, and Figure 4 shows that the temperatures monitored by four thermocouples labeled  $T_1$  through to  $T_4$  have a variation of less than 6 °C, which ensures that the test section temperature is roughly uniform.

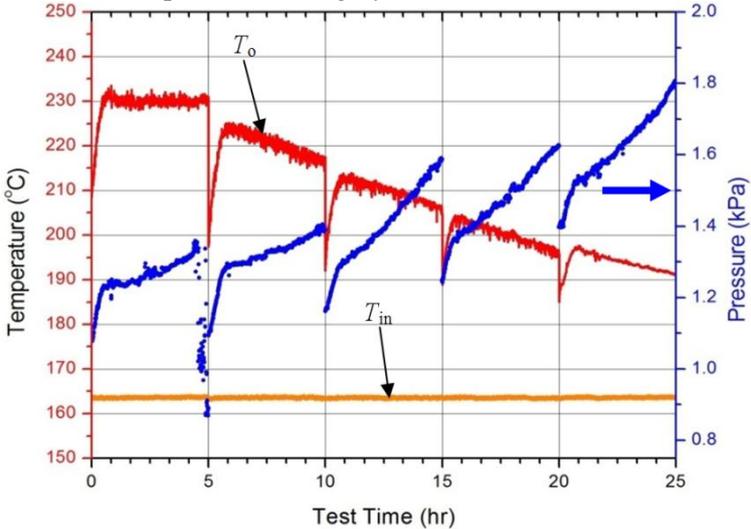


Figure 3. Sample test of pressure drop and temperature variations over a test period of 25 hours. Inner wall temperature of the test section is 355 °C and  $T_{in}$  is 162.8 °C.

**4.2 Initial Test Processed Results**

Processed results for a sample test section set to 355°C at the inner wall is shown in Figure 5. The data points were taken at the 15 minute pressure monitoring phase performed at the beginning of each five hour run. These correspond to the deposit collected up to that point in time. It can be seen that over time the average deposit thickness increased, which correspond to the graph in Figure 3 via Equation (1) with progressively larger pressure drops.

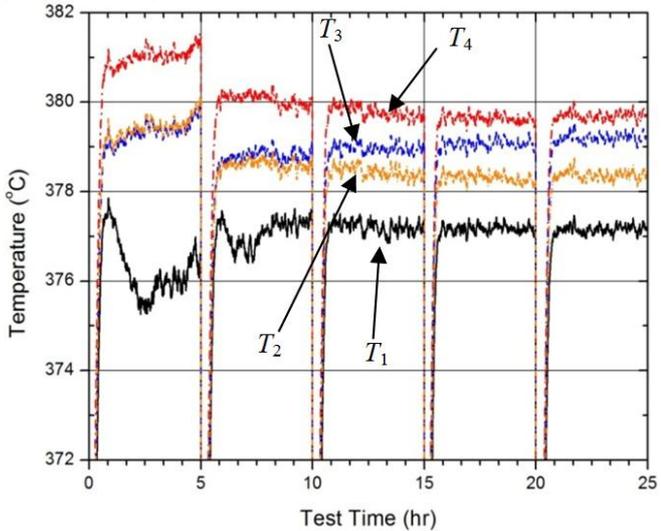


Figure 4. Sample test temperature variations as monitored by four thermocouples on the test section. Inner wall temperature of the test section is 355 °C, outer wall temperature is set to 375 °C and  $T_{in}$  is 162.8 °C.

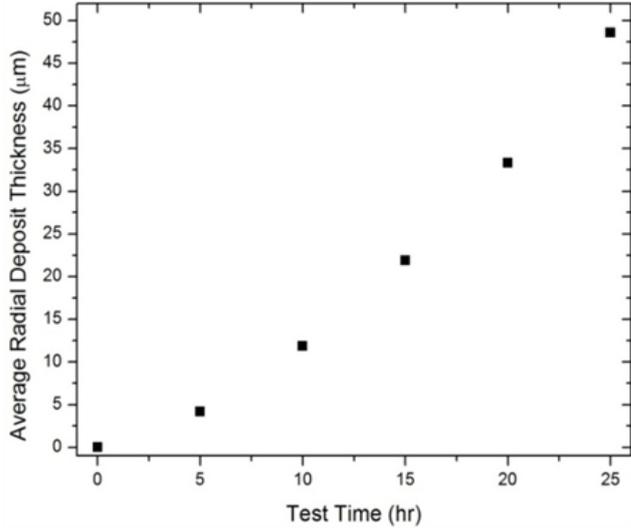


Figure 5. Sample test radial deposit thickness taken from the pressure drop data assuming uniform distribution of deposits in the test section. Inner wall temperature of the pipe is 355 °C and  $T_{in}$  is 162.8 °C.

### 4.3 Summary of Tests with Biojet Fuels

Due to the limited quantity of biojet fuels available for testing, thermal stressing for biojet tests were limited to five hours of test time, with the same test procedure outlined in Section 3, albeit at a slightly lower test section temperature of 346 °C because one of the biojet fuels had a slightly lower boiling point than the conventional fuels. Thermal stressing was performed on two conventional and two alternative aviation fuels and the coking propensities were compared using the pressure drop measurements and the carbon burnoff apparatus. Possibly due to the limited test time, two of the four fuels tested showed negligible deposit accumulation calculated from the Hagen-Poiseuille Equation. However, deposit accumulation as measured by the carbon burnoff apparatus found deposit accumulation for all four fuels.

Under the same temperature and flow Reynolds number, fuels with aromatic compounds produced more thermal deposit than fuels with no aromatic compounds. However, when comparing between fuels that have aromatic compounds in varying percentages, the amount of deposit produced from thermal stressing appeared to be identical, suggesting that once a fuel has some aromatic compounds, other factors such as the fuel temperature or residence time act as the rate-limiting factors to deposit formation.

Table 1. Summary of Accumulated Carbon Deposit via Carbon Burnoff after Thermal Stressing of Fuels

Fuel Composition (Fuel Code)	Percentage of Aromatic Compounds (by mass)	Total Carbon Deposit via Carbon Burnoff ( $\mu\text{g}$ of Carbon)
Jet A (JF1)	18.66	$159.7 \pm 37.7$
JP-5 (JF2)	20.59	$153.2 \pm 37.7$
Alcohol to jet (BJ1)	0	$82.2 \pm 37.7$
73% C-10 iso-paraffin 23% trimethyl benzene (BJ2)	30.68	$157.7 \pm 37.7$

The carbon deposit profiles from the burnoff apparatus are shown in Figures 6 and 7. The highest concentration of deposits accumulated near the inlet of the test section, likely a result of the steep temperature gradient when the fuel temperature jumps from 163 °C to 346 °C.

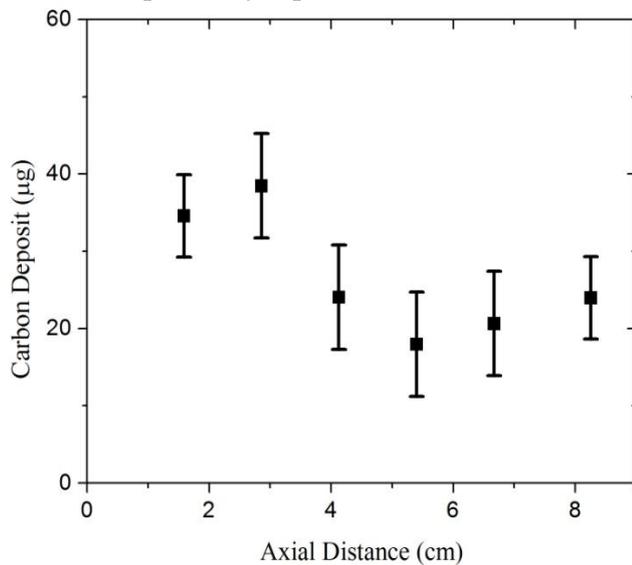


Figure 6: Graph of carbon deposit along the test section for JF1 with error bars at a fuel temperature of 346 °C and  $T_{in}$  of 163 °C.

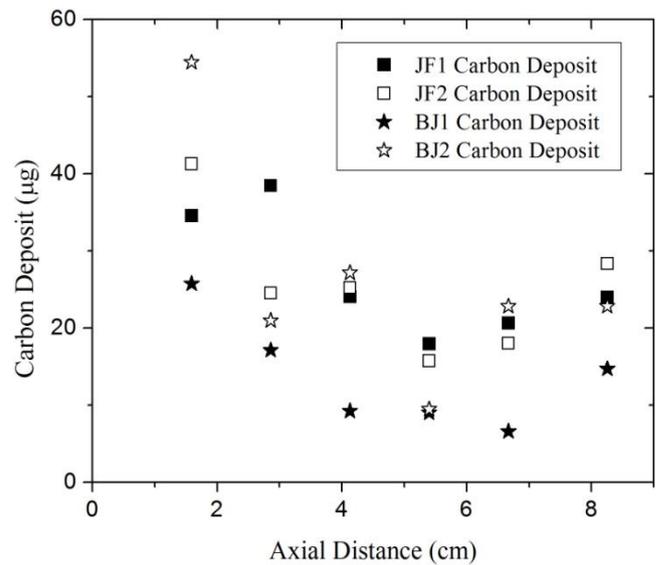


Figure 7: Graph of carbon deposit along the test section for the four fuels JF1, JF2, BJ1 and BJ2 at a fuel temperature of 346 °C and  $T_{in}$  of 163 °C.

## 5 Conclusions

A recently developed experimental rig was used to test the thermal stability of conventional jet fuels and biojets. The rig consists of a preheating section and a test section, each with different temperatures and residence times to mimic the fuel flow conditions on an aircraft. Fuel degradation was measured by the pressure difference across the test section, where larger pressure drops correspond to a narrower inner pipe diameter due to the accumulation of insoluble deposits and by a carbon burnoff apparatus that detected the carbon dioxide resulting from oxidation of the accumulated deposit within the test section. Fuels with aromatic compounds produced more thermal deposit when compared to fuels without aromatic compounds under the same temperature and flow rate conditions.

## 6 Acknowledgements

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