

Thermal Stability Testing of Fischer-Tropsch Fuel and Various Blends With Jet A, as well as Aromatic Blend Additives

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Abstract—

Fischer-Tropsch (F-T) jet fuel composition differs from petroleum-based, conventional commercial jet fuel because of differences in feedstock and production methodology. Fischer-Tropsch fuel typically has a lower aromatic and sulfur content and consists primarily of iso and normal paraffins. The ASTM D3241 specification for Jet Fuel Thermal Oxidation Test (JFTOT) break point testing method was used to test the breakpoint of a baseline conventional Jet A, a commercial grade F-T jet fuel, and various blends of this F-T fuel in Jet A. The testing completed in this report was supported by the NASA Fundamental Aeronautics Subsonics Fixed Wing Project.

Index Terms—Alternative Fuel, Break Point Testing, Fischer-Tropsch Fuel, Thermal Stability

I. INTRODUCTION

Fischer-Tropsch (F-T) fuel is a synthetic fuel derived from syn-gas. The syn-gas can come from various resources such as natural gas, coal, biomass, or even garbage. The use of Fischer-Tropsch fuel could have the added benefit of reducing the nation's energy reliance on foreign supply of petroleum based fuel. Fischer-Tropsch jet fuel composition differs from the petroleum based, conventional commercial jet fuel because of differences in feedstock and production methodology. F-T is generally composed of iso- and n-alkanes, with little aromatic content¹. These compositional differences provide some benefits and drawbacks for the use in jet engines.

In comparison to petroleum-derived fuels, F-T has shown increased thermal-oxidative stability and significantly lower particulate matter combustion emissions¹. F-T jet fuel is expected to be more stable than conventional jet fuel at elevated temperatures, thus offering a potentially cleaner burning fuel with better thermal stability characteristics. One method to quantify the fuel's oxidative thermal stability is to measure the fuel's breakpoint in accordance with ASTM D3241 specification test known as Jet Fuel Thermal Oxidation Test (JFTOT)².

JFTOT assesses fuel thermal degradation by two means: one by the heated tube's discoloration due to hydrocarbon coating, the other by determining a filter pressure drop (dp) due to particulate formation. Aerated fuel flows at 3 cc/min over an electrically heated tube at a preset temperature for 150 min. At the end of the test, the tube is removed from the test stand and visually examined. The tube is inserted into a Visual Tube Rater (VTR) which is an internally lit black box consisting of a standard ASTM color chart. The tube is optically compared to the color chart and is assigned a color number ranging from 1 to 4 (1 is metallic silver, 2 is slightly tan, 3-4 are brown). A tube color of 3 or less constitutes a pass. Fuel degradation forms particulates which are collected on a filter, and leads to a higher filter dp over the test period. 25 mmHg is the maximum pressure drop permitted over the full 150 min test for a fuel to pass the test. Both criteria, tube color (≤ 3) and dp (≤ 25 mmHg), must be met in order to pass the JFTOT. To determine the fuel's breakpoint, the fuel is tested at 5 °C increments from 260 °C. Breakpoint is defined as the highest temperature at which the fuel passes the JFTOT.

One of the drawbacks of Fischer-Tropsch fuel is that the lubricity and seal-swell may need to be improved before pure F-T jet fuel is approved¹. Aromatics are known to improve these seal-swell characteristics as well as increase engine particulate emissions¹. Previous studies have been completed by the Air Force Research Laboratory (AFRL) for the feasibility of adding aromatic solvents in order to meet these seal-swell requirements¹. AFRL studies showed that the particulate matter emissions increased as the aromatic molecular weight and concentration increased¹. They attributed these phenomena to the increased soot precursors in the aromatic blend additions to the fuel¹.

In another study, particle mass emissions were measured with the TEOM for various concentrations of aromatic blend added to synthetic fuel. This study showed that the particle mass concentration increased with increasing aromatic concentration³. This indicates that aromatic content may increase the particulate formation, thus affecting the thermal stability. It was previously found that aromatics have little effect on key gaseous emissions such as: CO, CO₂, and NO_x³.

It has also been shown that the seal-swell of nitrile rubber was increased mostly with addition of alkyl-naphthalenes as opposed to alkylbenzenes, which could have been because of increased polarity in larger aromatics¹.

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One way of increasing the aromatic content and the seal-swell characteristics is to blend the F-T fuel with conventional petroleum derived fuel. This study explores the use of blending F-T with conventional Jet-A and how these blends affect the thermal stability of this fuel. Furthermore, the addition of aromatic blends or feedstock may be required to achieve the seal-swell characteristics that are necessary. This paper further explores the thermal stability of Fischer-Tropsch fuel and how the increase in aromatic concentration affects its thermal stability.

II. TECHNICAL WORK PREPARATION

The thermal stability test laboratory located in the B109 Alternative Fuels Research Laboratory⁴ houses a Hot Liquid Process Simulator (HLPS), model HLPS-400 manufactured by Alcor⁵. The HLPS is designed to determine jet fuel breakpoint according to the test method outlined in ASTM D3241². The HLPS unit is located inside a fume hood (see Fig. 1) and requires water for cooling, gaseous nitrogen to pressurize the reservoir and Zero Air to aerate the fuel before conducting a test. The HLPS unit is connected to a PC which is used for data acquisition and control purposes.



Figure 1. Hot Liquid Process Simulator inside of fume hood in room 102.

The HLPS components are mainly constructed of stainless steel. The HLPS is capable of testing fuel thermal stability at temperatures up to 650 °C. Various types of heater tubes can be used in order to reach temperature requirements for each individual test. JFTOT tests require the use of an aluminum tube, which has a limit of 380 °C. Steel or stainless steel tubes are also available for tests needing to reach higher temperatures of up to 650 °C. The fuel flow rate can be varied from 0.25 to 5 mL/min for each test.

The HLPS was used to evaluate the breakpoint temperature for pure Jet A, pure F-T jet fuel, and various blends (by volume) of these two fuels (10, 30, 50, 70, and 90 percent F-T fuel). JFTOT breakpoint testing procedures were followed except at higher temperatures, where a steel tube was used. Figure 2 shows the diagram of the HLPS. A fuel sample was loaded into a stainless steel reservoir. The fuel reservoir was pressurized to 500 psig with gaseous nitrogen and set to a constant flow rate of 3 cc/min.

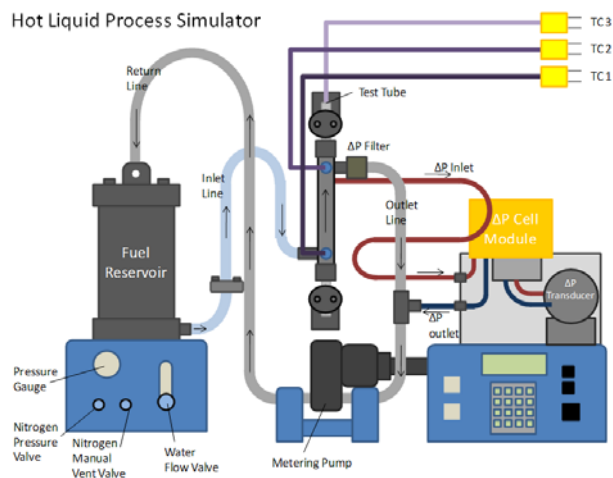


Figure 2. Hot Liquid Process Simulator Diagram

The HLPS pumped the fuel through a resistance heated tube-in-shell heat exchanger while monitoring flow, temperature, and pressure. At the outlet of the reservoir, the fuel flowed through a pre-filter and then over the heated tube. The heated tube was ramped up to a target temperature with minimal temperature variation (specified in test procedure) for each test, providing a stable “soak” temperature. At the outlet of the heated tube, a small disposable filter was in place to capture particulates which were formed during the heating process. The HLPS analyzer measured and recorded the pressure drop over this filter throughout the test duration. Figure 3 shows the diagram of the tube apparatus, which shows the fuel flow and outlet filter construction.

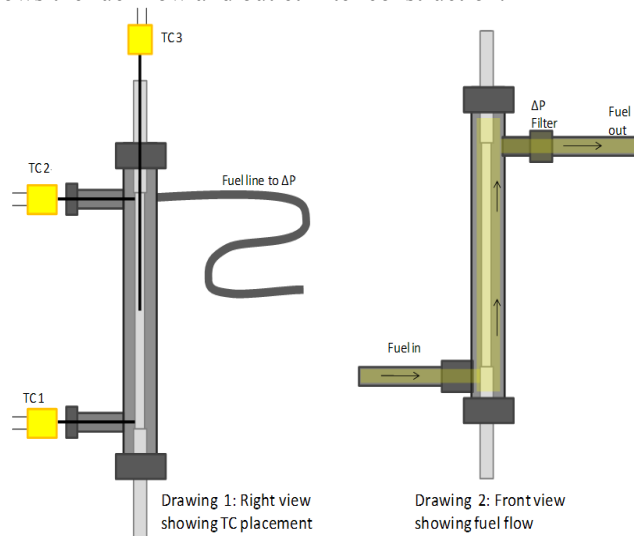


Figure 3. Hot Liquid Process Simulator Tube Graphic

Both criteria for the JFTOT can be evaluated using the HLPS. Each HLPS run result was ranked as pass/fail. Each test required approximately 500 mL of fuel; however multiple tests are required to determine the breakpoint temperature. If a test was completed with a “pass” rating on tube color and pressure drop, a new batch of the same fuel was retested at a higher temperature at intervals of 5 °C. This process was repeated until a failure occurred.

Results and Discussion

Fuel analysis results on F-T and Jet A fuel are shown in Table I.

TABLE I
FISCHER-TROPSCH AND JET A FUEL ANALYSIS RESULTS

Test	F-T	Jet A
Total Acid Number (mg KOH/g)	0.002	0.00
Aromatics (% vol)	0.0	19
Mercaptan Sulfur (% mass)	0.000	0.000
Total Sulfur (% mass)	0.00	0.0
Distillation		
Initial Boiling Point (°C)	149	
10% Recovered (°C)	162	180
20% Recovered (°C)	163	
50% Recovered (°C)	168	212
90% Recovered (°C)	184	251
End Point (°C)	196	
Residue (% vol)	0.9	1.3
Loss (% vol)	0.4	0.9
Flash Point (°C)	44	51
API Gravity at 60 °F	60.5	
Freezing Point (°C)	-55	-48
Viscosity at -20 °C (mm ² /s)	2.6	5.2
Net Heat of Combustion (MJ/kg)	44.2	
Hydrogen Content (% mass)	15.6	
Smoke Point (mm)	40.0	21
Copper Strip Corrosion (2 h at 100 °C)	1a	
Thermal Stability at 260 °C		
Change in Pressure (mmHg)	0	1
Tube Deposit Rating, Visual	1	0
Existent Gum (mg/100 mL)	<1	0.2
Particulate Matter (mg/L)	0.4	0.2
Filtration Time (min)	2	
Water Reaction Interface Rating	1	1
FSII (% vol)	0.00	0.00
Conductivity (pS/m)	217	10
Lubricity Test (BOCLE) Wear Scar (mm)	0.75	
Net Heat of Combustion (MJ/kg)	44.0	43.2
Workmanship	Pass	Pass

Figure 4 shows the breakpoint measurements for Jet A, F-T jet fuel, and blended mixtures of Jet A and F-T jet fuel. The different colored bars are repeat testing at the same blend of fuel. Results of blended fuels indicate that the fuel thermal stability break point is not linearly related to the fuel blending ratio. Results show that the thermal stability of a 50 percent Jet A/50 percent F-T fuel blend is consistent with that of less stable Jet A fuel. Even a sample of 30 percent Jet A/70 percent F-T blend does not result in a significantly higher breakpoint. A major difference in break point data is first noticed at a mixture of 90 percent F-T fuel. Fuel blends with less than 90 percent F-T fuel have fuel breakpoints consistent with that of less stable Jet A fuel. This indicates that the breakpoint depends on degradation of minor fuel components and is not a fuel bulk property. Three repeated tests on the same fuel/fuel blends confirmed that the results were reproducible with a maximum of 10 °C variation.

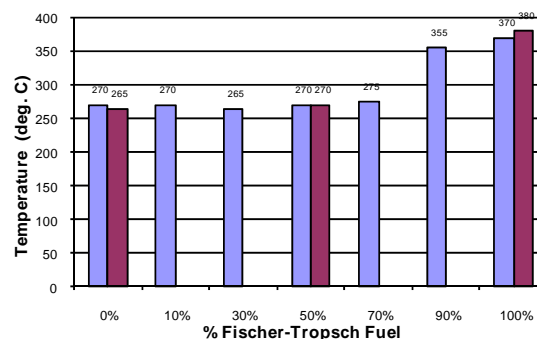


Figure 4.—Thermal stability breakpoint data for F-T Jet fuel and blended mixtures in Jet A fuel.

It is likely that Jet A produced a higher quantity of particles or the particles produced were larger. After testing, sample tubes for both Jet A and F-T Jet fuel were cut apart and examined with an optical microscope. Photographs of the heated tube surfaces are shown in Figure 5. It appears that larger particles are found on the heated tube surface with Jet A in comparison to F-T fuel, although further investigation is required to validate. The material properties of the tube surface may also make a difference. Figure 5 shows major differences in the aluminum tube surface versus the steel tube surface, both tested with F-T fuel. This may indicate that the fuel interacts with the tube surface differently, thus requiring a different “tube color” or tube coating rating when different tube types are used.

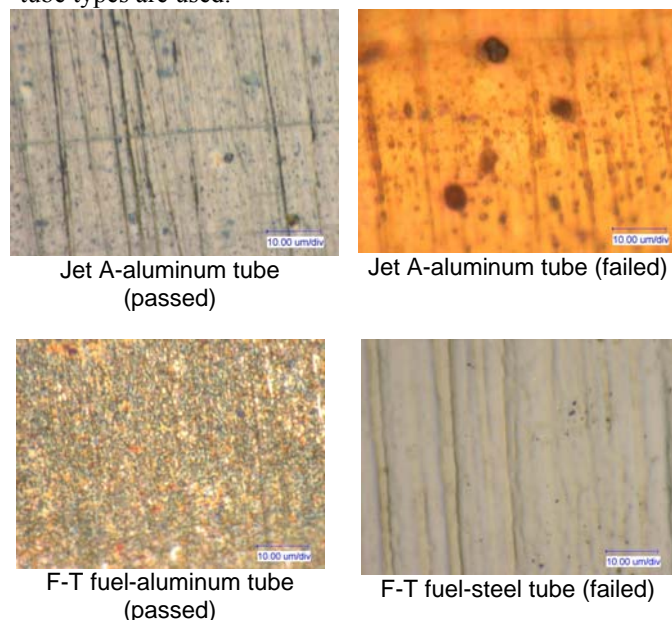


Figure 5.—Optical images of tubes after testing.

Optical images in Figure 5 indicate that there may be major differences between the tube surface composition and how the particulates form on the surface of the tube. These surface differences may affect the tube discoloration upon heating and its subsequent failure ranking; a different scale may be needed for measuring the tube color failure of a steel tube versus an aluminum tube. Since the VTR is designed to test for JFTOT

color schemes for aluminum tubes, it may or may not be a valid test for the steel tubes because of the difference in tube properties. Figure 6 shows the optical images of clean tube surfaces at magnifications of 1 and 5kx.

The clean tube optical images show the different surface characteristics. This observation leads us to believe that heated fuel may react differently on the steel tube versus the aluminum tube.

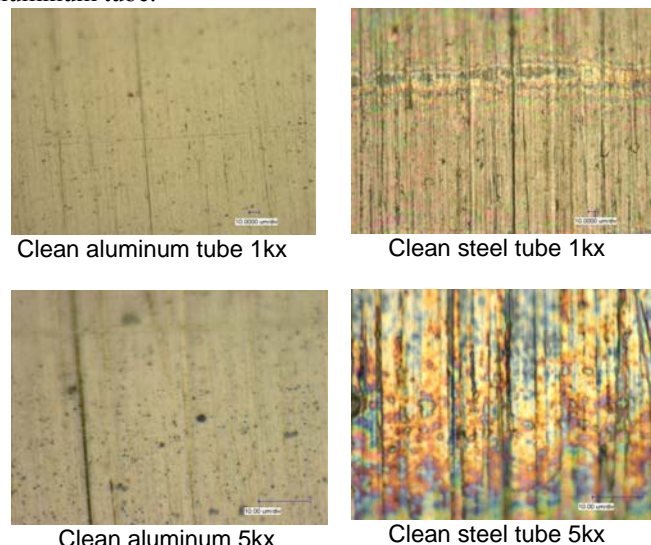


Figure 6.—Optical images of clean tube surfaces—comparison of aluminum to steel.

Figure 7 displays some previous data shown in Figure 4 but indicates the type of failure. It should be noted that petroleum based (100 %) Jet A breakpoints were reached because of high filter pressure drop after the heated tube. The 100 % F-T fuel breakpoints were not triggered by pressure drop, but by tube surface discoloration. F-T fuel seems to produce less particulate at elevated temperatures in comparison to the conventional Jet A. Typical JFTOT test only requires one of the criteria tests to fail for the complete test to be a failure. Since the validity of color rating on the steel tube is unknown, this may indicate that F-T fuel has a higher breakpoint temperature than observed per criteria stipulated in ASTM D 3241. Since JFTOT is a standardized test method developed and intended to be used with aluminum tubes, a new standardized method may be required for testing at temperatures above 380 °C.

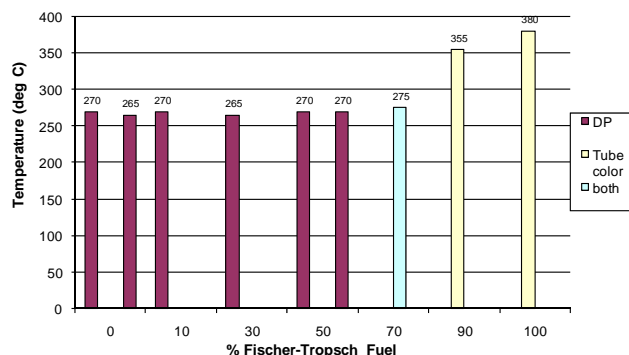


Figure 7.—F-T fuel thermal stability breakpoint based on type of failure.

The HLPS was also used to evaluate the effect of a heightened aromatic content on pure F-T jet fuel. This heightened aromatic content was achieved by mixing the pure F-T jet fuel with an aromatic blend, which was formed using a combination of different aromatic solvents. The two quantities were calculated depending on what the target aromatic content was, and mixed together to create a fuel sample. The aromatic blend information is included in Table II, which is the same additives used in the study completed by AFRL¹.

TABLE II
AROMATIC BLEND ADDITIVE INFORMATION

Aromatic 100 Fluid (Hydrocarbon)		
Properties	Test Methods	Sales Specifications
Appearance	Visual	Pass
Aromatics Content (vol. %)	ASTM D 1319	98.0 min
Color (Saybolt Units)	ASTM D 156	30 min
Distillation	ASTM D 86	
IBP (°C)		154 min
DP (°C)		174 max
Flash Point (°C)	ASTM D 56	42 min
Kauri-Butanol Value	ASTM D 1133	90 min
Specific Gravity @ 15.6/15.6°C	ASTM D 4052	0.868-0.878
Ultra Low Naphthalene Aromatic 150 Fluid (Hydrocarbon)		
Appearance	Visual	Pass
Aromatics Content (vol. %)	ASTM D 1319	95 min
Color (Saybolt Units)	ASTM D 156	27 min
Distillation	ASTM D 86	
IBP (°C)		175 min
DP (°C)		215 max
Flash Point (°C)	ASTM D 56	62 min
Naphthalene Content (wt.%)	GC	0.1 max
1,2,4 Trimethyl Benzene (wt.%)	GC	0.9 max
Aromatic 200 Fluid (Hydrocarbon)		
Properties	Test Methods	Sales Specifications
Aniline Point (°C)	ASTM D 611 (Mixed Aniline Point)	#7-18
Appearance	Visual	Pass
Aromatics Content (vol. %)	ASTM D 1319	98.0 min
Color (ASTM Units)	ASTM D 1500	1.0 max
Distillation	ASTM D 86	
IBP (°C)		220 min
DP (°C)		293 max
Flash Point (°C)	ASTM D 93	95 min
Specific Gravity @ 15.6/15.6°C	ASTM D 4052	0.99-1.01

In order to calculate the amount of aromatic blend to add to the current fuel, the current fuel aromatic content has to be integrated into the calculations. Since the HLPS requires a specified amount of fuel, the total fuel was held constant at 600mL for each run. The following equations were used in determining the volume of aromatic blend to add to the fuel sample. With the intention of limiting variables, the aromatic blend was added to fuel which came from the same fuel tank.

V_T : Total Volume

V_F : Volume of fuel

V_A : Volume of Aromatic Blend

$$V_T = V_F + V_A$$

x : target aromatic content

y : fuel aromatic content

$$x(V_T) = y(V_F) + 1(V_A)$$

For example, the total volume of fuel (V_T) was set to 600mL and the aromatic content (y) of the fuel was 1.6%. To find the quantity of the fuel needed (V_F), the target aromatic content (x) was multiplied by the target volume (V_T). Then the target volume (V_T) was subtracted. The answer was then divided by the current aromatic content (y) minus one. For instance, with the target volume at 600mL and the target aromatic content at 5%, the equation would be:

$$V_T = 600$$

V_F : Volume of fuel

$$V_A = V_T - V_F = 600 - V_F$$

$$x = 5\%$$

$$y = 1.6\%$$

$$5\%(600) = 1.6\%(V_F) + 1(600 - V_F)$$

Solve for V_F :

$$V_F = [(0.05 * 600) - 600] / (0.016 - 1) = \sim 589\text{mL}$$

Then, to find the volume of the aromatic blend (V_A) needed, the volume of fuel that has been found (V_F) was subtracted from the total volume (V_T). Once V_F and V_A were found, the two quantities were measured out, using a graduated cylinder. The aromatic blend (V_A) was poured into the fuel (V_F) and then stirred. From there, the blended fuel was filtered normally, and the rest of the experiment carried out.

$$V_A = V_T - V_F = 600 - 589 = \sim 11\text{mL}$$

JFTOT testing procedures were followed using the same procedures as previous experiments. Each test required approximately 500 mL of fuel, so 600 mL were used as a failsafe, in case of a leak. Once a test had been completed, if it passed, the aromatic content was increased for the next fuel sample. The testing began with a fuel that was 0.2% aromatic, and then increased to a fuel that was 1.6% aromatic. These fuels were F-T fuels alone, without any added aromatics. From that point, the aromatic content was increased to 5%, and each

passing test was increased in increments of 1% until a failure.

Upon reaching a sample that failed, a breakpoint test sequence was put into effect. This process included lowering the temperature at which a test of the same percent aromatic content fuel sample was conducted, until a pass occurred. Once a passing test was achieved, this was considered to be the breakpoint temperature.

Figure 8 shows preliminary data on a F-T fuel that was blended with aromatic additive. The preliminary data was all ran at 380°C and shows a pass dP rating via JFTOT procedures up to 10% aromatic content in F-T fuel.

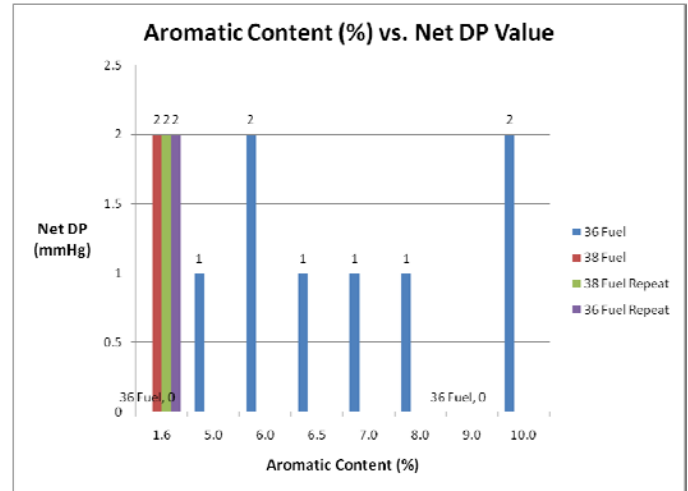


Figure 8: Aromatic Content compared to Net DP Value using the JFTOT method.

Figure 9 shows the tube color data collected via JFTOT on the same F-T fuel. This shows a failure based on tube color at 10% aromatic blend, although further investigation and repeat data is being collected at this time.

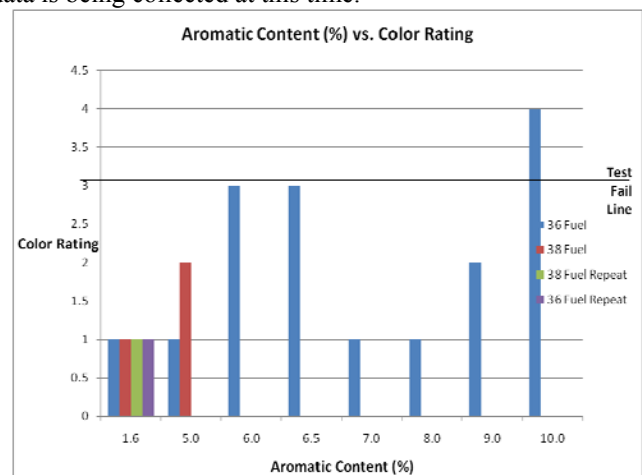


Figure 9: F-T fuel aromatic content in comparison to tube color rating.

Further investigation was carried out on the 10% aromatic content fuel to determine the breakpoint. Figure 10 shows the break point tube color data collected on a F-T fuel with 10% aromatics. It is interesting to note that the test failed at 335°C and passed at 300°C, so based on tube color rating only, the breakpoint would be 300°C. Figure 11 shows the break point

dP rating collected using JFTOT procedures. The fuel shows a pass at all temperatures. This outcome is consistent with previous data shown in Figure 8 and Figure 9 which showed a failure only based on tube color.

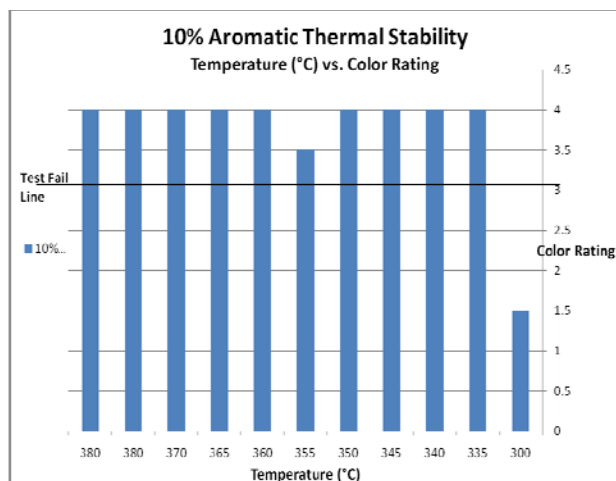


Figure 10: F-T fuel with 10% aromatic content JFTOT tube color rating in comparison to test temperature

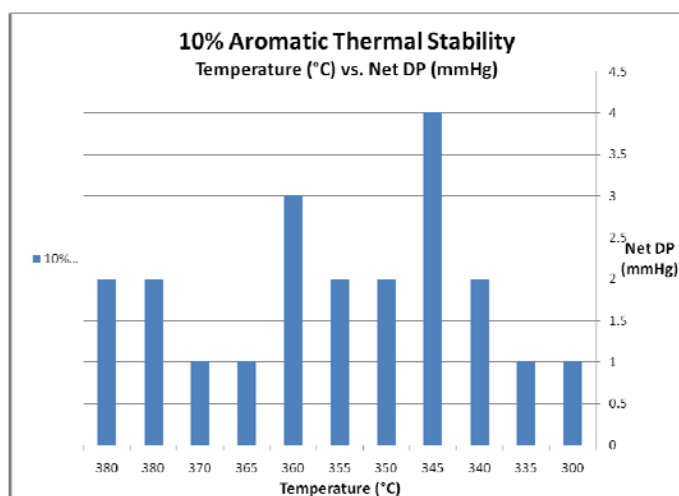


Figure 11: F-T fuel with 10% aromatic content JFTOT dP rating in comparison to test temperature

Summary and Conclusions

A conventional jet fuel, Jet A, was tested as a baseline fuel and its breakpoint was determined to be 270 °C. The breakpoint for F-T jet fuel was determined using a F-T fuel made by a natural gas feed stock (Gas to Liquid- GTL process) and was determined to be at least 370 °C. The F-T based jet fuel proves to be more thermally stable than the conventional Jet A with a breakpoint that is at least 100 °C higher than Jet A. Optical images have given insight to possible testing differences in Jet A and F-T breakpoint data. This may indicate that the fuel interacts with the tube surface differently, thus requiring a new tube color rating when using tube types other than aluminum. This would require the modification to the standardized test method or a new test method would need to be created for testing thermal stability at temperatures above 380 °C.

III. ACKNOWLEDGMENT

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