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Thermal Stability Results of a Fischer-Tropsch Fuel With Various Blends of Aromatic Solution

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December 2012

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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. F-T 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 commercial grade F-T jet fuel, and various blends of this F-T fuel with an aromatic solution. The goal of this research is to determine the effect of aromatic content on the thermal stability of F-T fuel. The testing completed in this report was supported by the NASA Fundamental Aeronautics Subsonic Fixed Wing Project.

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 F-T fuel has the added benefit of reducing the nation's energy reliance on foreign supply of petroleum based fuel. F-T jet fuel composition differs from the petroleum based, conventional commercial jet fuel because of differences in feedstock and production methodology. F-T fuel is generally composed of iso- and n-alkanes, with little aromatic content (Ref. 1). F-T fuel is also known to have a reduction in sulphur emissions and contrails formation. These compositional differences provide some benefits and drawbacks for the use in jet engines.

Fischer-Tropsch Synthetic Paraffinic Kerosene (FT-SPK) which has been derived from coal, biomass, or natural gas is currently approved for commercial use as a blend, up to 50% (by volume) with petroleum based jet fuel across the world. This approval was implemented in 2009 via ASTM D 7566 (Ref. 2). This specification requires that fuels containing synthesized hydrocarbons must contain a minimum of 8% by volume aromatics and hydroprocessed SPK must meet a minimum JFTOT breakpoint temperature of 325 °C (Ref. 2), which is significantly higher than the 260 °C required for conventional jet fuel.

In comparison to petroleum-derived fuels, F-T has shown increased thermal-oxidative stability and significantly lower particulate matter combustion emissions (Ref. 1). F-T jet fuel is expected to be more stable than conventional jet fuel at elevated temperatures, thus offering a potentially cleaner burning fuel. 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 Tester (JFTOT) (Ref. 2).

The JFTOT procedure's purpose is to measure fuel deposit and particulate formation of jet fuel when heated at a specific temperature, when oxygenated and flown over a metal surface. 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 (ΔP) due to particulate formation. Aerated fuel flows at 3 mL/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 and 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 ΔP (<=25 mmHg), must be met in order to pass the JFTOT. Breakpoint is defined as the highest temperature at which the fuel passes the JFTOT.

One of the drawbacks of F-T fuel is that the low lubricity and the lack of seal-swell properties may need to be improved before pure F-T jet fuel is approved (Ref. 1) for aviation. Aromatics are known to improve these seal-swell characteristics as well as increase engine particulate emissions (Ref. 1). Previous studies have been completed by the U.S. Air Force Research Laboratory (AFRL) for the feasibility of adding aromatic solvents in order to meet these seal-swell requirements (Ref. 1). AFRL studies showed that the particulate matter emissions increased as the aromatic molecular weight and concentration increased (Ref. 1). They attributed these phenomena to the increased soot precursors in the aromatic blend additions to the fuel (Ref. 1). 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 aromatics (Ref. 1).

In another study, particle mass emissions were measured with a tapered element oscillating microbalance (TEOM) for various concentrations of aromatic blend added to a synthetic

fuel. The synthetic fuel was aromatic-free jet fuel with similar hydrocarbon range and physical properties of Jet A, but the exact form of synthetic fuel is unknown. This study showed that the particle mass concentration increased with increasing aromatic concentration (Ref. 3). 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, CO_2, and NO_x (Ref. 3).

One way of increasing the aromatic content and the seal-swell characteristics is to blend the F-T fuel with conventional petroleum derived fuel. Previous research has been done on the blending of F-T with conventional Jet-A and how these blends affect the thermal stability of this fuel (Ref. 4). Preliminary results in this study showed a nonlinear relationship between blending ratios and thermal stability breakpoint temperatures. Approximately 75% F-T fuel was necessary in order to see an increase in fuel thermal stability breakpoint temperature. Given that the ASTM 7566 specification limits blend ratios of up to 50% F-T fuel, blending F-T with conventional jet fuel will not result in improved fuel thermal stability. Furthermore, the addition of aromatic solutions may be required to achieve the necessary seal-swell characteristics. This aromatic blend would serve as a partial surrogate fuel in blending the two. The use of surrogate fuels has been heavily researched in the past. Hazlett et al. (Ref. 5) proposed the chemical reactions in place for decomposition of jet fuel and they model the decomposition schemes with n-dodecane that was air saturated using JFTOT. Jet fuel composition varies greatly from batch to batches, however it is critical to understand the composition and fuel chemistry that controls fuel deposit formation when defining the thermal stability effects (Ref. 5).

Moses et al. showed that the addition of aromatics (approximately 21% by mass) to a Sasol iso-paraffinic kerosene (IPK) had no effect on the thermal stability breakpoint temperature of >340 °C (Ref. 6). The intent of this study is to determine if similar results are found by addition of aromatic solution provided by Air Force Research Laboratory to a Rentech F-T jet fuel. This paper further explores the thermal stability of F-T fuel and how the increase in aromatic concentration affects its thermal stability.

Experimental

The fuel used in this study was a gas to liquid F-T fuel, manufactured by Rentech in a Colorado pilot plant. The feedstock for this gas to liquid process was natural gas. This fuel was chosen because there were two different aromatic percentages by volume, which provided two baseline fuel samples for repeat thermal stability testing.

The thermal stability test laboratory, located in the NASA Glenn Research Center's Alternative Fuels Research Laboratory (Ref. 7), houses a Hot Liquid Process Simulator (HLPS), model HLPS-400 manufactured by Alcor. The HLPS is designed to determine jet fuel breakpoint according to the test method outlined in ASTM D3241(Ref. 8). The HLPS unit is located inside of a fume hood (see Figure 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.

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 effect of increasing the aromatic content on the thermal stability of pure F-T jet fuel. This increase of 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. Table 1 shows the sales specifications of the various aromatic additives. The additive used in this study was comprised of 30% Aromatic 100, 60% Aromatic 150, and 10% Aromatic 200. The blending ratios were determined as referenced in a previous publication by Monroig et al. (Ref. 3) and the mixture is believed to be more representative of the range of aromatic components within actual jet fuels. Figure 4, Figure 5, and Figure 6 show the gas chromatography of the individual aromatic solutions and Figure 7 shows the gas chromatograph of the aromatic solutions combined. The Air Force Research Laboratory premixed the aromatic solution and sent it to NASA Glenn Research Center prior to testing.

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

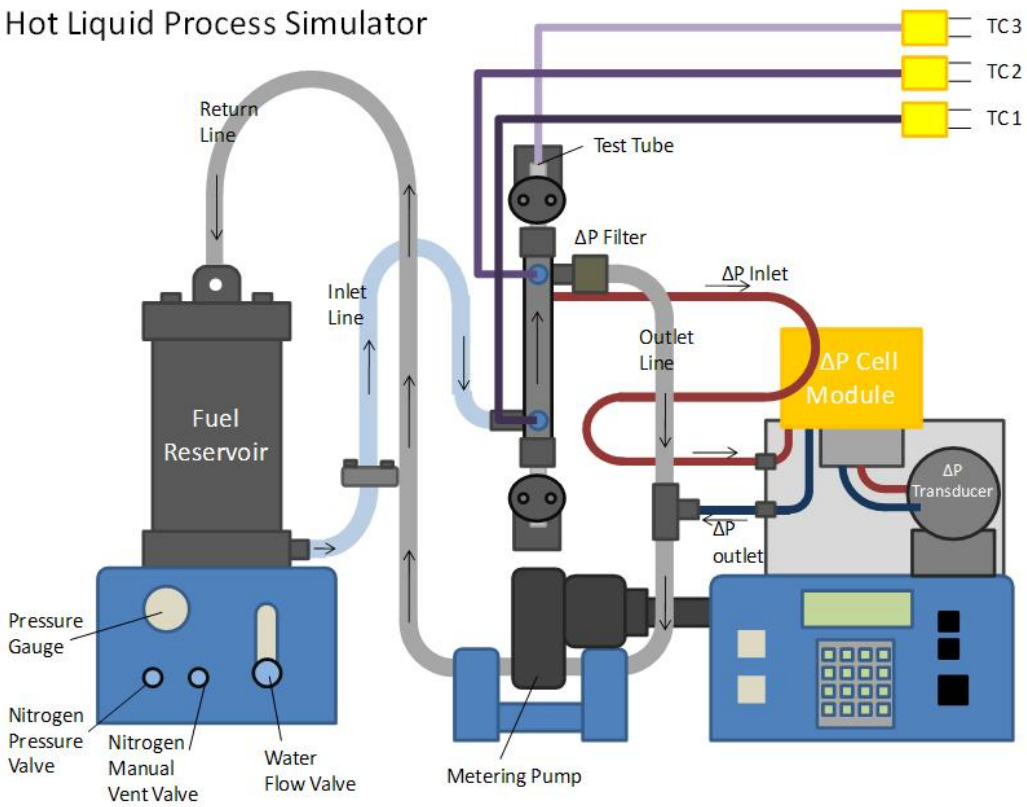

Figure 2.—Hot Liquid Process Simulator

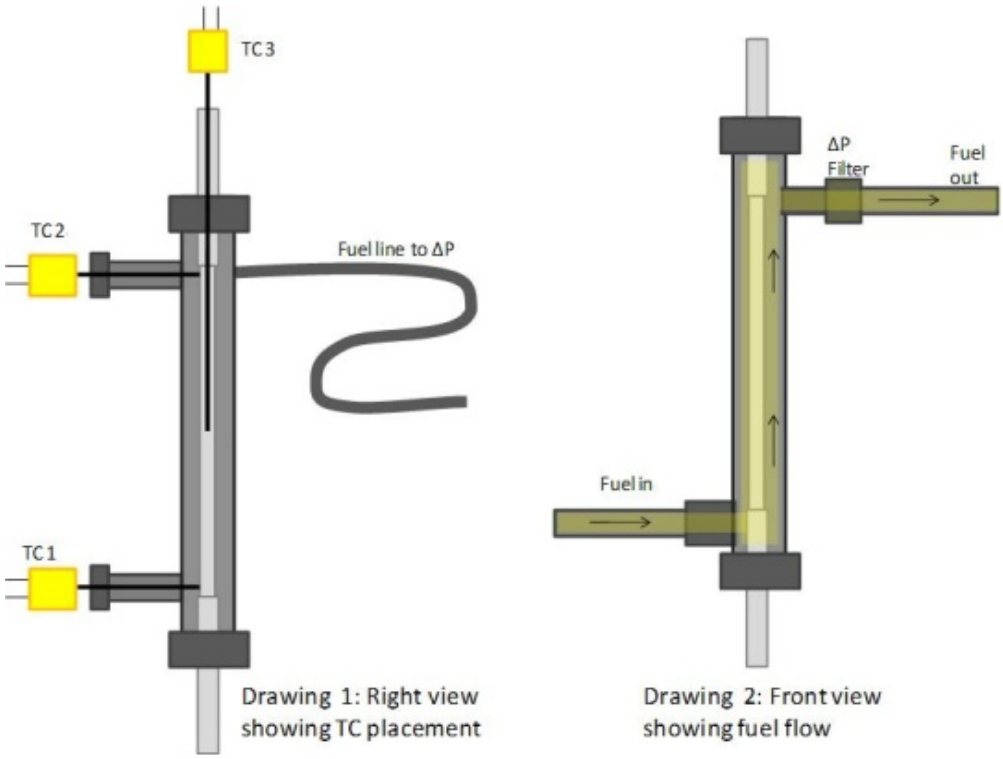

Figure 3.—Hot Liquid Process Simulator heated tube drawing

TABLE 1.—AROMATIC ADDITIVE SALES SPECIFICATIONS

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 at 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)		
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 at 15.6/15.6 °C	ASTM D 4052	0.99-1.01

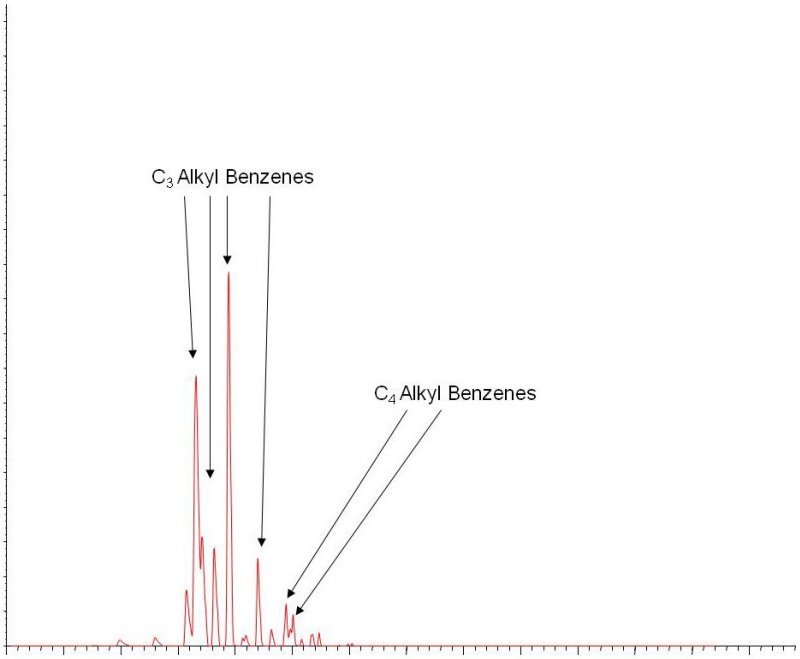

Figure 4.—Gas chromatograph of Aromatic 100.

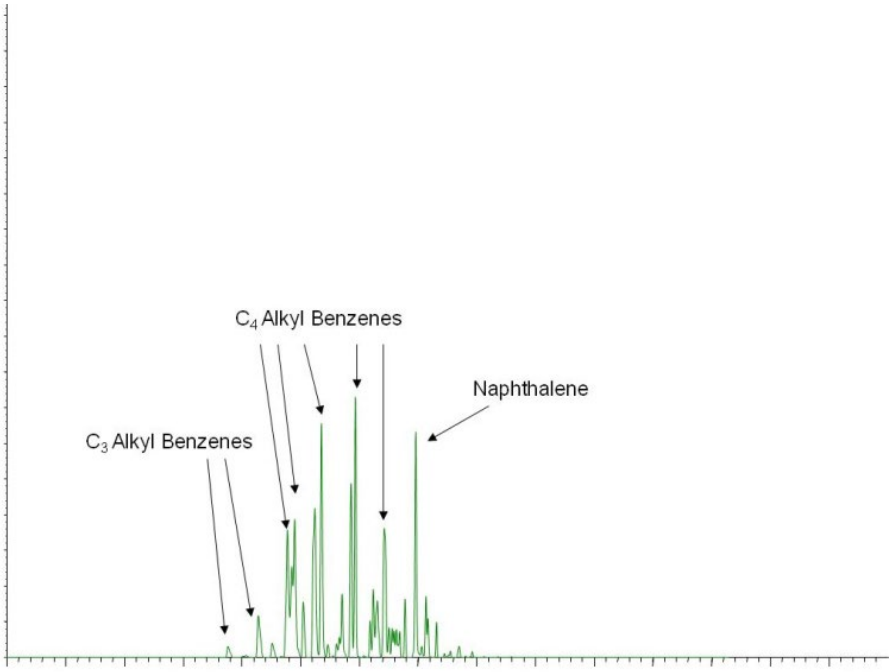

Figure 5.—Gas chromatograph of Aromatic 150.

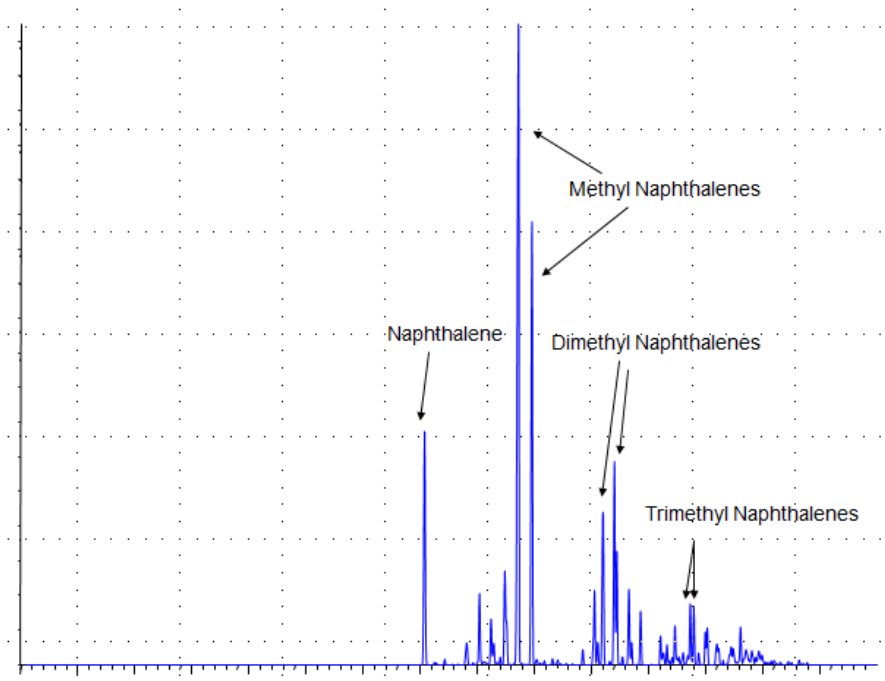

Figure 6.—Gas chromatograph of Aromatic 200.

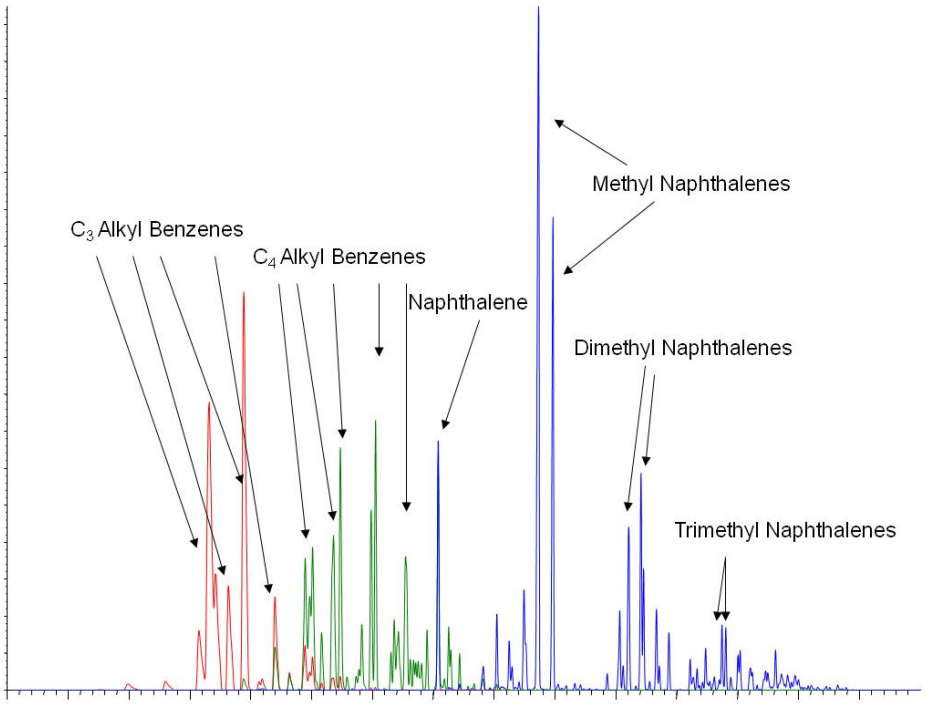

Figure 7.—Gas chromatograph of Aromatic 100, Aromatic 150, and Aromatic 200.

Fuel Blending

In order to calculate the amount of aromatic blend to add to the F-T fuel, the current fuel aromatic content was incorporated into the calculations. Since the HLPS requires a minimum fuel quantity for operation, the total fuel was held constant at 600 mL for each run. The following equations were used in determining the volume of aromatic blend to add to the fuel sample.

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

V_T : Total Volume

V_F : Volume of fuel

V_A : Volume of Aromatic Blend

$V_T = V_F + V_A$

x : aromatic content desired

y : fuel aromatic content

Table 2 shows the calculation results for various blends used in this study. Initially, the fuel was composed of 1.6% aromatics.

TABLE 2.—AROMATIC SOLUTION CALCULATION RESULTS

Target aromatic content, %	Fuel quantity, mL	Solution, mL
5.0	579.3	20.7
6.0	573.2	26.8
6.5	570.1	29.9
7.0	567.1	32.9
8.0	561.0	39.0
9.0	554.9	45.1
10.0	548.8	51.2
11.0	542.7	57.3
12.0	536.6	63.4
13.0	530.5	69.5
14.0	524.4	75.6
15.0	518.3	81.7

JFTOT testing procedures were followed using aluminum test tubes at 380 °C, using the HLPS. This temperature was chosen because it is the highest temperature achievable while maintaining JFTOT procedures. JFTOT requires the use of aluminum tubes and aluminum tubes are rated for temperatures up to 380 °C. The fuel sample was loaded into a stainless steel reservoir, pressurized to 500 psig with gaseous

nitrogen, and set to a constant flow rate of 3 mL/min. The fuel was pumped through a resistance heated tube-in-shell heat exchanger while monitoring flow, temperature, and pressure (see Figure 2 and Figure 3). 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 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.

As previously discussed, the JFTOT procedure uses two components to evaluate a test: tube color and maximum change in filter differential pressure, both of which HLPS can evaluate. Each HLPS run result was ranked as pass/fail. The testing began with a neat fuel (containing no aromatic blend) that was 0.2% aromatic, and then a fuel that contained 1.6% aromatic at 380 °C. Upon testing the two neat fuels, an increase in the aromatic content to 5% for testing, and then increased in increments of 1% until reaching a failure. After finding the lowest aromatic concentration that failed at 380 °C, testing continued to quantify that mixture's break point temperature.

Each test required approximately 600 mL of fuel; however multiple tests are required to determine the breakpoint temperature. If a test completed with a "pass" rating on tube color and pressure drop, a new batch of the same fuel was retested at an increased temperature increment of 5 °C. This process is repeated until a failure occurred. The breakpoint temperature for each fuel or fuel blend was the highest temperature with a "pass" rating.

Results

Figure 8 and Figure 9 show the JFTOT results for both dP and color rating of fuel containing 0.2% aromatic content by volume at 380 °C. The results indicate that all tests passed according to differential pressure and color rating criteria, since none of the results reached 25 mmHg.

Figure 10 and Figure 11 show the JFTOT results for both differential pressure and color rating of fuel containing 1.6% through 15% aromatic content by volume at 380 °C. The results indicate that all tests passed according to differential pressure criteria, since none of the results reached 25 mmHg. According to color rating, all tests above and including three of the four tests for 10% aromatic content failed JFTOT. It is interesting to point out one out of four tests passed according to the color rating at 10% aromatic content, thus bringing to question the repeatability of tube color rating.

Figure 12 and Figure 13 show the JFTOT results for 10% aromatic content F-T fuel. This data was collected in order to determine the break point of F-T fuel containing 10% aromatic solution. As previously mentioned, at 380°C, the JFTOT test failed due to tube color rating. This data is important in order to show the repeatability, as well as consistency of the results across fuel tanks. Figure 12 shows a slight increase in dP at 345 °C, though 1 to 2 mmHg increase would be acceptable within the range of noise in the system. At temperatures above 330 °C, the tube color isn't completely consistent. Color variation could be due to exact thermocouple placement within the heated tube. It is also interesting to point out that at 380 °C, the data for tube color and dP are not consistent. This brings to question whether the tube color data is a true failure, or not.

The breakpoint temperature of the F-T fuel with 10% aromatic content was determined to be 330 °C, by JFTOT's criteria. This breakpoint temperature was gotten based on the data previously shown in Figure 12 and Figure 13. Two passing JFTOT runs were completed at 330 °C and two failing JFTOT runs were completed at 335 °C, resulting in a breakpoint temperature of 330 °C.

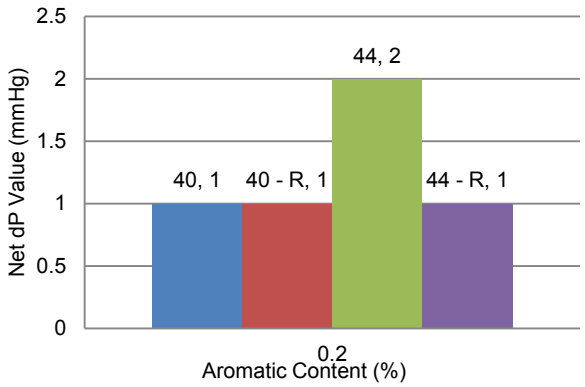

Figure 8.—JFTOT differential pressure results neat F-T fuel tested at 380 °C, taken from tank numbers P000025740 and P000025744. The numbers 40 and 44 refer to the tank numbers and the "-R" indicates a repeat run.

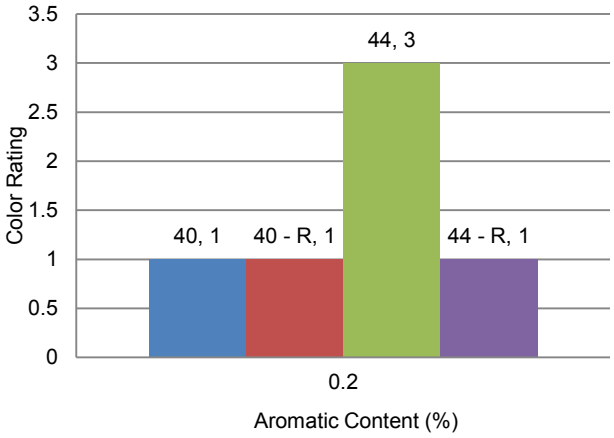

Figure 9.—JFTOT color rating results of neat F-T fuel tested at 380 °C, taken from tank numbers P000025740 and P000025744. The numbers 40 and 44 refer to the tank numbers and the "-R" indicates a repeat run.

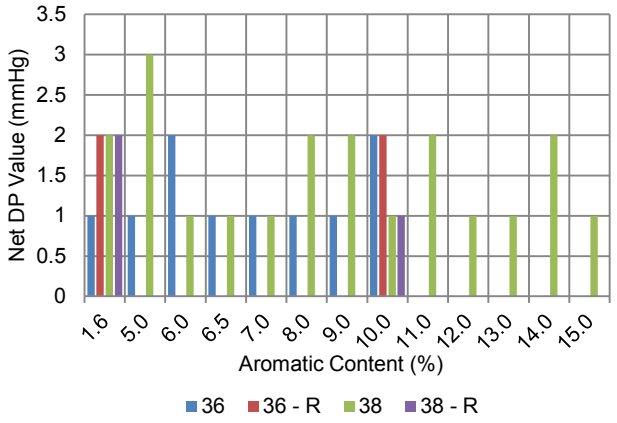

Figure 10.—JFTOT differential pressure results of neat F-T fuel (1.6% aromatics) and blended F-T fuel at 380 °C, taken from tank numbers P000025736 & P000025738.

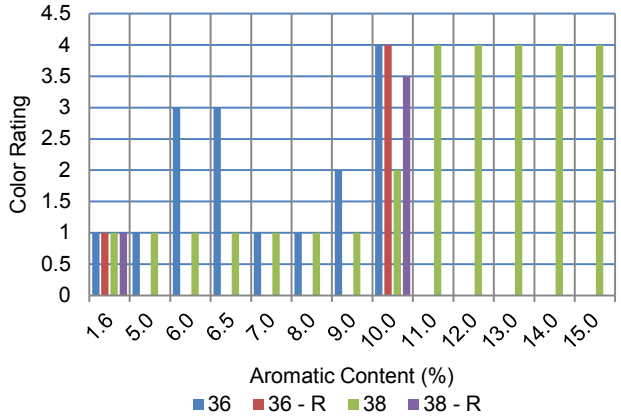

Figure 11.—JFTOT color rating results of neat F-T fuel (1.6% aromatics) and blended F-T fuel at 380 °C, taken from tank numbers P000025736 & P000025738.

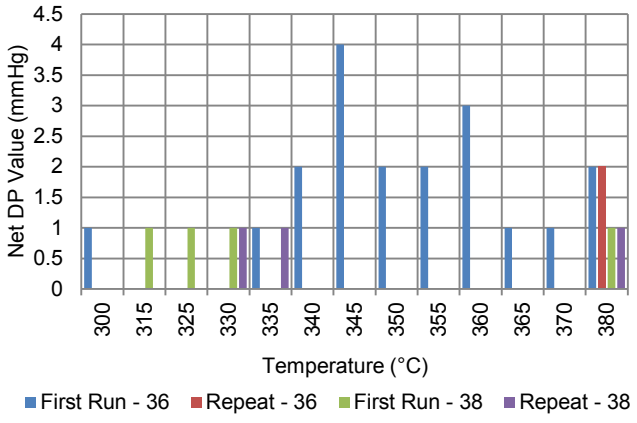

Figure 12.—JFTOT differential pressure results at various temperatures with 10% aromatic content, from fuel tanks P000025736 & P000025738.

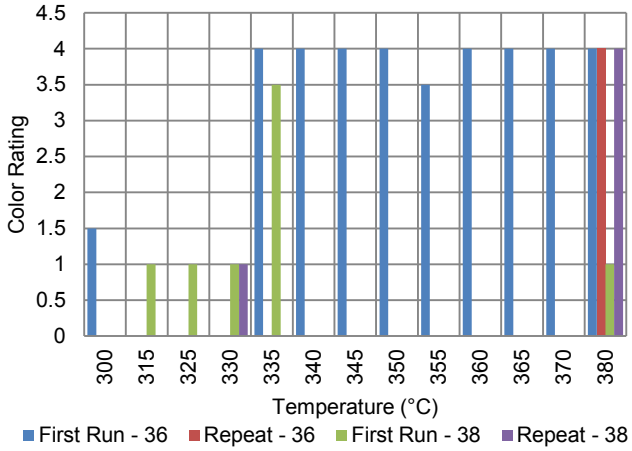

Figure 13.—JFTOT color rating results at various temperatures with 10% aromatic content, from fuel tanks P000025736 & P000025738.

TABLE 3.—FUEL SPECIFICATION DATA

Test	Shell F-T	Jet A	Rentech F-T
Total acid number, mg KOH/g	0.00	0.00	0.00
Aromatics, % vol	0.00	19.00	1.70
Mercaptan sulfur, % mass	0.00	0.00	0.00
Total sulfur, % mass	0.00	0.00	< 3
Distillation			
Initial boiling point, °C	149.00		152.00
10% recovered, °C	162.00	180.00	168.00
20% recovered, °C	163.00		179.00
50% recovered, °C	168.00	212.00	216.00
90% recovered, °C	184.00	251.00	263.00
End point, °C	196.00		275.00
Residue, % vol	0.90	1.30	1.00
Loss, % vol	0.40	0.90	0.80
Flash point, °C	44.00	51.00	44.00
API gravity at 60 °F	60.50		54.00
Freezing point, °C	–55	–48	–50.00
Viscosity at –20 °C, mm²/s	2.60	5.20	5.10
Net heat of combustion, MJ/kg	44.20	43.20	44.10
Hydrogen content, % mass	15.60		15.20
Smoke point (mm)	40.00	21.00	> 40
Copper strip corrosion, 2 h at 100 °C	1a		1a
Thermal stability at 260 °C			
Change in pressure, mmHg	0.00	1.00	0.00
Tube deposit rating, visual	1	0	1
Existent gum, mg/100 mL	<1	0.20	< 1
Particulate matter, mg/L	0.40	0.20	0.50
Filtration time, min	2.00		4.00
Water reaction interface rating	1.00	1.00	1.00
FSII, % vol	0.00	0.00	0.00
Conductivity, pS/m	217.00	10.00	897.00
Lubricity test (BOCLE) Wear Scar, mm	0.75		0.82
Workmanship	Pass	Pass	Pass

Conclusions

Two different aromatic content fuels from Rentech, as well as these fuels with added aromatic blend were analyzed for thermal stability using the JFTOT method. Preliminary results indicate a reduction in thermal stability occurs upon increasing the aromatic content to 10% by adding an aromatic blend to the neat fuel. These results do not specify a failure based on pressure drop, but only on tube color. It is unclear whether tube color correlates to more deposition on the tube surface or not. Further research is necessary in order to determine if these failures are true failures based on tube color. Research using ellipsometry to determine tube deposit thickness rather than color will be continued in follow-up of this study.

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