

THERMAL STABILITY MEASUREMENT DEVICES REVISITED: GRAVIMETRIC JFTOT VERSUS SIMULATED TEST RIG

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INTRODUCTION

Fuel thermal stability is one of the most critical fuel properties,¹ consequently, a reliable method for its measurement is desirable. The Jet Fuel Thermal Oxidation Tester (JFTOT: ASTM D3241) has been designated as the specification test method for measuring the aviation turbine thermal stabilities of commercial fuels (ASTM D1655), and military fuels (MIL-T-5624). However, JFTOT data have been reported to correlate poorly^{2,5} with the thermal deposit results from test rigs that were designed to simulate the aircraft engine fuel system. Two examples of many such simulated test rigs include: (a) the injector feed arm rig (IFAR),² which measures burner stem fouling; and (b), the single tube heat transfer rig (STHTR),^{3,4} which measures fuel degradation within an oil cooler. Reported disparities between the JFTOT and the IFAR/STHTR have been ascribed to:

(1) The short test duration of the JFTOT (2.5 hr).^{2,4} This was the explanation given to account for the beneficial effect of MDA (the commonly used metal deactivator, N,N'-disalicylidene-1,2-propane diamine), observed in the JFTOT, and the innocuous effect of MDA on extended testing in the IFAR.²

(2) The differences in flow velocities. For example, in the JFTOT, the fuel flow is laminar (3 mL/min) whereas in aircraft operating systems, the flow is turbulent.^{3,5}

To explore these differences, we used the gravimetric JFTOT (grav-JFTOT) since its operating conditions are not only similar to the JFTOT, but it has the added advantage of quantifying both the surface and bulk fuel deposits, based on weight.⁶ Furthermore, the grav-JFTOT offers a more sensitive measure of the bulk fuel deposits than the JFTOT because the pore size of its effluent filter is considerably smaller, viz., 0.8 micron versus 17 microns for the JFTOT.

The effect of test duration was examined in a recent study, the results of which do not support the explanation that test duration is a factor. Specifically, we found⁷ MDA to be beneficial in a non-copper doped Jet A and JP-5 type (Jet A + antioxidant) fuel, on extended duration testings which were conducted in the grav-JFTOT for approximately 150 hours.

Regarding the effect of fuel velocity on fuel thermal deposition, compared to laminar flow, turbulent flow has been suggested to increase thermal deposition by increasing both the mass transfer of oxygen to the heated surface and the quantity of reactants.^{3,8} Nevertheless, on increasing test duration in the IFAR,² an underlying variable appears to be a temperature effect. In this paper we report the results of a grav-JFTOT study that was designed to investigate the effects of increasing temperature on thermal deposits, with and without the presence of MDA.

EXPERIMENTAL

Materials. All materials were used as received. The test fuel was a typical, though aged, JP-5. The metal deactivator, N,N'-disalicylidene-1,2-propane diamine, commonly known as MDA, was obtained from Pfaltz and Bauer and used at 5.8 mg/L concentration.

Procedure. Thermal stability was determined using the grav-JFTOT. This laminar flow, bench test method gives the weight of total thermal deposits formed when the filtered fuel flowing at 3mL/min, under a back pressure of 500 psi, passes over a stainless strip (grade 302 and approximately 7 cm long, 0.5 cm wide, and 0.025 mm thick), contained in a strip

holder that is heated to 260°C, for 2.5 hours. These are the standard operating conditions of the grav-JFTOT.

However, for the studies conducted, the test temperatures ranged from 165° to 350°C for the neat fuel, and 220 to 350°C for the MDA additized fuel. The overall temperature range of 165° to 350°C was selected to mimic temperature increases in the IFAR, which include: the 165°C inlet fuel temperature and subsequent increases in the inner wall temperature. Specifically, in the IFAR, over a 70-h test duration and at a flow rate of 72 kg/h (approximately 1500 mL/min), the inner wall temperature increased from an initial 300°C to approximately 440°C.

The test duration per test temperature in the grav-JFTOT was 5 hours, and to simulate continuity, the same strip was used in the series of temperature-testings conducted per test fuel. The total deposit is the sum of the deposits formed on the stainless steel strip and the filterables contained in the effluent. The effluent was filtered using two Magna nylon membranes of 0.8 micron pore size. Further details of the method are described elsewhere.^{8,9}

RESULTS AND DISCUSSION

Neat Fuel. The effects of increasing wall temperature on thermal deposition in the grav-JFTOT, for the strip and filterable deposits are depicted in Figures 1 and 2, respectively. The overall results indicate a typical deposit distribution pattern for the grav-JFTOT, viz., higher deposition in the filterables than on the strip. Nevertheless, for both types of deposit, similar deposition profiles were observed with an increase in temperature. For example, in the case of the filterables, at 165° to 200°C, thermal deposition is apparently constant and likely simulates the "induction period" observed in the IFAR;² as the temperature is increased from approximately 200° to 300°C, deposition increases, but on further increase in temperature, i.e., from approximately 320°-350°C, deposition decreases.

For the temperature range, 200°-300°C, the rate of increase of the total thermal deposit with temperature is in accordance ($R^2 = 0.99$) with the well known Arrhenius rate equation (rate = constant $\times e^{-E/RT}$), where E is the activation energy, R , the gas constant, and T , the temperature in kelvin (see Figure 3). Moreover, calculation of the activation energy gives a value of approximately 83 kJ/mol. The corresponding value (65 kJ/mol) for the same fuel, obtained using a turbulent flow test rig, viz., the Naval Aviation Fuel Thermal Stability device (NAFTS), may be regarded as somewhat similar.

Comparison with the IFAR. The thermal deposition profile described above for the grav-JFTOT - wherein thermal deposition was plotted versus temperature - is similar to the IFAR's thermal deposition profile, wherein thermal deposition was plotted versus test duration. Specifically, in the case of the IFAR, with increasing test duration, an initial low rate of deposition, which was interpreted² to be an "induction period" is followed by an increase, then a decrease in thermal deposition.²

Furthermore, in the IFAR, the increase in deposition with test duration is concomitant with an increase in the inner wall temperature (ΔTIW), since ΔTIW was the parameter used to measure thermal deposition. Use of the ΔTIW parameter is based on the relationship² that the weight of carbon $\propto [\Delta TIW]^2$. Consequently, based on the above analyses, the operative variable between the two test devices is likely related to a temperature effect and not to a difference in flow velocity. In addition, the "induction period" that is reported to occur² can also be ascribed to a temperature effect as demonstrated in the profiles of the plots in Figures 1 and 2.

MDA Additized Fuel. For the MDA additized fuel, the strip and filterable thermal deposition profiles versus temperature show similar trends to that of the neat fuel, but the rate of deposition differed significantly with the type of deposit measured (Figures 1 and 2). For example, relative to the neat fuel, the rate of increase of the *strip* deposit was significantly lower in the MDA additized fuel. In contrast, the rate of increase of the *filterable* deposits of the MDA additized fuel was fairly similar to that of the neat fuel. These differences may well explain the beneficial effect of MDA observed in the JFTOT, where mainly the surface tube deposits are measured, versus the innocuous effect observed in the IFAR, on increasing test duration.² The diminished performance of MDA on increasing test duration in the IFAR,² may

will be due to a temperature effect, specifically, to the relative stability of MDA as the IFAR's initial inner wall temperature increases (see below). Possible breakdown of the MDA molecule at high temperatures (no numerical values given) has been suggested by Clark *et al.*¹⁰

Realistic operating conditions/temperature effect. Temperature is considered to be the most important physical factor in fuel thermal deposition.¹¹ The initial operating conditions in the IFAR (e.g., inner wall temperature of 300°C) were selected to represent a severe condition.² However, this severity is further exacerbated by subsequent temperature increases with increasing test duration. Such temperature increases likely exceed realistic operating conditions. Consequently, at inner wall temperatures above 300°C, the results obtained in the IFAR are flawed. Thus, the innocuous effect observed with MDA, on increasing test duration, is also likely flawed.

CONCLUSIONS

The overall results suggest that the underlying variable between laminar and turbulent flow test devices for measuring thermal stabilities is a temperature effect and not their differences in flow velocities. Thus, the initial low rate of deposition observed in the turbulent flow test rigs, which was interpreted as an "induction period" is likewise a function of temperature.

At increasing test temperatures, the beneficial effect of MDA observed in the JFTOT (ASTM D3241) may well be related to the type of deposit measured, viz., surface deposit. In contrast, thermal deposition based on the corresponding filterable deposits, which comprise the bulk of the total deposits in the grav-JFTOT, is in agreement with the findings observed in turbulent test rigs for neat and MDA-doped jet fuels.

Consequently, the diminished performance of MDA/innocuous effect observed on increasing test duration in the IFAR, may be related to an increase in temperature effect. However, in the IFAR, the MDA results are likely flawed since its operating conditions, on increasing test duration, are not only severe but unrealistic. In conclusion, on the basis of test conditions, particularly, the very important parameter, temperature, the gravimetric JFTOT offers a more realistic measurement of fuel thermal stability than the IFAR.

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LITERATURE CITED

- (1) Lyon, T.F., Fuel Thermal Stability Outlook for GE Aircraft Engines in 1991; In *Aviation Fuel Thermal Stability Requirements*, ed Kirklin, P.W. and David, P., ASTM STP 1138, American Society for Testing and Materials: Philadelphia, PA., May 1992, p. 73.
- (2) Kendall, D.R.; Houlbrook, G.; Clark, R.H.; Bullock, S.P.; Lewis, C. The Thermal Degradation of Aviation Fuels in Jet Engine Injector Feed Arms. Part I. - Results from a Full Scale Rig. Presented at the Tokyo International Gas Turbine Congress, October, 26-31, Tokyo, Japan, 1987, Paper 87-IGTC-49.
- (3) Kendall, D.R. and Mills, J.S., SAE Technical Paper Series, 851871, Society of Automotive Engineers: Warrendale, PA, 1985.
- (4) Clark, R.H. The Role of a Metal Deactivator in Improving the Thermal Stability of Aviation Kerosines. Presented at the *3rd International Conference on the Stability and Handling of Liquid Fuels*: London, September 1988, Paper No. 47, p.283, Institute of Petroleum, 1989.
- (5) Clark, R.H.; Stevenson, P.A. *Prepr.-Am. Chem. Soc., Div. of Fuel Chem.* **1990**, 35, 1302.
- (6) Beal, E.J.; Hardy, D.R.; Burnett, J.C. In (a) *Proceedings of the 4th International Conference on Stability and Handling of Liquid Fuels*: Orlando, FL, Nov. 1991, pp. 245-259. (b) *Aviation Fuels Thermal Stability Requirements*, ASTM STP 1138; Kirklin, P.W.; David, P., Eds; American Society for Testing and Materials: Philadelphia, PA, 1992, pp. 138-150.

(7) Pande, S.G. and Hardy, D.R. accepted for publication in *Energy and Fuels*, **1998**.

(8) Clark, R.H. and Thomas, L. SAE Technical Paper Series, 881533, Society of Automotive Engineers: Warrendale, PA, 1988.

(9) Pande, S.G.; Hardy, D.R. *Energy and Fuels* **1995**, *9*, 177-182.

(10) Clark, R.H.; Delargy, K.M.; Heins, R.J. *Prepr.-Am.Chem. Soc., Div. Fuel Chem.* **1990**, *35*, (4), 1223.

(11) Hazlett, R.N. *Thermal Oxidation Stability of Aviation Turbine Fuels*; ASTM Mongraph 1, American Society of Testing and Materials: Philadelphia, 1991, page 51.

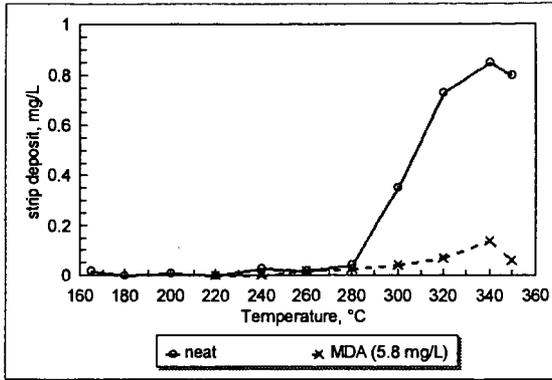


Figure 1. Effect of temperature on strip thermal deposit for a JP-5 fuel: with and without MDA.

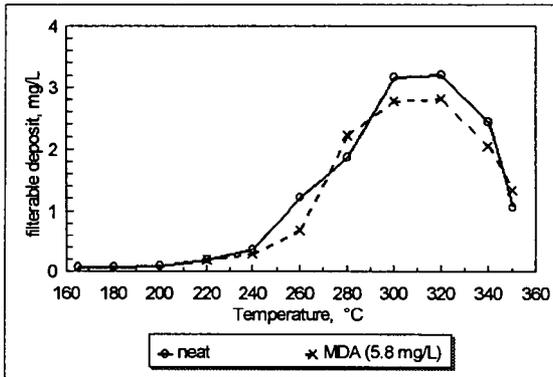


Figure 2. Effect of temperature on filterable thermal deposits for a JP-5 fuel: with and without MDA.

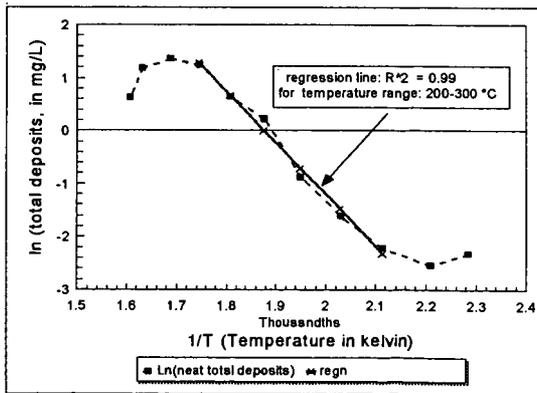


Figure 3. Arrhenius plot of total gravimetric JFTOT deposits formed at test temperatures, 165-350°C for a JP-5 fuel.