THERMAL STABILITY OF DIESEL FUELS BY QUANTITATIVE GRAVIMETRIC JFTOT

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INTRODUCTION

The current worldwide standard test method for assessing thermal stability of jet turbine aviation fuels is the ASTM D3241 method. This method generates a visual tube deposit rating which is not quantitative, but assumes that very dark colors equate to unstable fuels. The tube rating is coded against color standards and the darkest color is usually said to fail a fuel for use in jet turbine engines/fuel systems. The method also generates a semi-quantitataive filter pressure drop. The pressure drop is so semi-quantitative that it also is afforded a pass/fail criterion for fuel acceptance in jet aircraft.

In 1991, we described the construction of a test device which duplicated all of the experimentally important parameters of the D3241 method but which substituted a weighable 302 stainless steel (s/s) foil strip for the bulky tube, so that direct weighing of thermal surface deposits could be made.[1] In addition, the nominal 17 micron (dutch weave) s/s filter of the D3241 was substituted with a nylon membrane 0.8 micron filter which was also capable of direct weighing of the fuel entrained solids generated by the test.

In subsequent papers, the use of this device for generating a large data base of results based on aviation fuels from many different refinery processes and many different geographic/crude sources was described.[2-3] In addition this new device, dubbed the gravimetric jet fuel total oxidation tester (JFTOT) after the original ASTM D3241 device, was also used to assess quantitatively the effects of temperature, pressure, and fuel flow in addition to the effects of dissolved metals and various fuel additives.

Now that a reasonable data base for jet turbine fuels has been established regarding the deposit yields for s/s strip deposit weight and filterable deposit weight it was of interest to see how the gravimetric JFTOT would respond to mid distillate diesel type fuels. A suite of 7 fuels which were similar to number 2 diesel fuels and met all the additional criteria of NATO F-76 (US Navy) diesel fuel were selected for the test matrix.. These fuels had originally been selected for a separate study involving long term ambient storage stability and thus were chosen in an attempt to span as wide a range of fuel properties as possible and still meet the specification requirements for military use.

EXPERIMENTAL

The precision flow device consists of a reciprocating single piston HPLC pump which is connected to the fuel reservoir at atmospheric pressure on the suction side and to a high pressure filter holder containing a 0.8 micron Nylon 66 pre-filter on the high pressure side. The fuel then flows through a heated section which is maintained at the chosen test temperature by the thermostated block heater. This heated section contains the pre-weighed s/s strip (weighed to the nearest 0.001 mg on a microbalance) which is held in position by the strip holder which is assembled into the s/s tube. The fuel flows through this heated section which has a surface to volume ratio of 17 cm^{-1} at 3.0 ml/min and a residence time of 6 seconds. The fuel is cooled to room temperature and exits through a back pressure valve maintained at 3.4 MPa (500 psi) into a clean glass container.

The effluent fuel is immediately vacuum filtered through a pre-weighed 0.8 micron Nylon 66 filter (weighed to the nearest 0.01 mg for the 47mm filters and to the nearest 0.001mg for the 13mm filters). At the end of the timed test, the strip assembly is removed from the block heater and allowed to cool, while maintaining fuel flow, for about 10 minutes. The foil strip is then removed, rinsed with hexane and allowed to dry, along with the rinsed fuel filter, for approximately 1 hour at 70°C. After equilibration to room temperature the strip and filter are weighed. The increases in weights are reported in mg/L. Exact details of the weighing technique and examples are given in previously published papers.[1,2,3]

RESULTS

Seven recent production diesel fuels were tested with the Gravimetric JFTOT using the standard conditions of 260°C for 2.5 hours at a fuel flow of 3.0 mL/min at a pressure of 500 psi. The results are shown in Table I.

Figure 1 gives the ranking for the filterable deposit weights with a range from 0.9 mgs/L to 23.8 mg/L. For comparison the weight of filterable solids for n-tetradecane is indicated in this figure by a solid line and the maximum and minimum filterable solids weight for jet fuels tested to date is indicated by dashed lines.

The ranking of the s/s foil strip surface deposit weights are given in Figure 2. In this figure the solid line indicates the strip surface deposit weight for n-tetradecane and the dashed lines indicate the maximum and minimum strip surface weights for jet fuels tested to date.

DISCUSSION AND CONCLUSIONS

The dashed lines in Figures 1 and 2 show the maximum and minimum values of the jet turbine fuels used to generate the data base in the last 4 years. Jet fuel average strip weights (in Figure 2) range between 0.02 and 0.20 mg/L with a number average of about 0.08 mg/L and a worldwide volume weighted average of about 0.04 mg/L. These fuels represent a very high percentage of the huge volume of jet fuels currently used worldwide and thus form a significant set of values against which to compare any and all future jet fuel batches.

The jet fuel average filterable solids weights (dashed lines in Figure 1) range between 0.5 and 5.0 mg/L with a number average of about 1.5 mg/L and a worldwide volume weighted average of about 0.8 mg/L.

Table 1 shows the data generated by the gravimetric JFTOT device for 7 representative diesel fuels from the US. The yield of the two types of solid deposit mesured are given in mg/L of fuel for both the strip weight and the filterable solids weight. It is interesting to note that even with this very small number of fuels the gravimetric JFTOT is capable of easily distinguishing between fuels as to their tendency to form solids under the conditions of this particular test. Strip weights range between 0.00 and 0.32 mg/L with an average weight of about 0.12 mg/L. Filterable deposit weights range between 1.0 and 24.0 mg/L with an average weight of about 12 mg/L.

For the large jet fuel data base it has been pointed out already that the filterable deposit weight is always about 10 to 20 times the strip deposit weight for any given fuel. This effect appears to be even more pronounced with the diesel fuels where the filterable deposit weights appear to be about 100 times heavier than the strip deposit weights for any given fuel.

In order to compare the 7 diesel fuels with the jet fuel data base for thermal stability the data in Table 1 are arranged into strip weights in Figure 2 and filter deposit weights in Figure 1. In Figure 2 it can be readily seen that most of the diesel fuels exhibit very good thermal stability with respect to the strip deposit weights for the jet fuel data base. Only fuel B exceeds the heaviest jet deposit weights. If this part of the test can be interpreted as the tendency of a fuel to form insulating lacquer deposits on aircraft heat exchangers, then clearly many diesel fuels are as "stable" as jet fuels in this regard.

The filterable data are shown in Figure 1, where a somewhat different picture can be seen. In this case, two of the fuels (D and E) are very good with respect to the jet fuel data base. On the other hand, two of the diesels are very "thermally unstable" (B and C) when compared to the jet fuel data base, and 3 of the diesels are "marginal" (A, F and G) being somewhat higher than the highest weights obtained for jet fuel in the past 4 years.

If the filterable weight data (or strip plus filter weight data) are used to assess the overall thermal stability performance in any given fuel, then only about a third of the diesel fuels could be deemed thermally stable when compared to typical thermally stable jet fuels. It should be noted that although it is tempting to use the data in this way and call the filterable deposit the material when might cause filter blockage, flow control valve sticking and nozzle fouling/clogging, no attempt has yet been made to validate this kind of correlation.

One should also note in Figures 1 and 2 the solid line which is given for the pure component n-tetradecane in the gravimetric JFTOT. This data can be used in two ways. First, it can serve as a "solvent blank" for both filterable and strip deposit weights for jet fuels. If used in this way it is apparent that most production jet fuels worldwide are very thermally stable indeed to the JFTOT test conditions. Secondly, it can serve as a solvent blank for the diesel fuels, in which case some of the current production diesel fuels are also very thermally stable.

These results indicate that the gravimetric JFTOT is a useful concept for ranking diesel fuels for their thermal stability. The diesels ranged from quite low (better than jet) to quite high (an order of magnitude greater than jet fuel) in their overall deposit forming tendencies. This type of information can be used in two possible ways. First, if gravimetric JFTOT data can be correlated to such phenomena as diesel engine injector fouling, it could be used to assess any given diesel fuels thermal stability for the intended diesel engine application.

Second, and more provocative, this type of information on diesel fuels could be used by commercial or in some cases by military aircraft operators to assess the thermal stability application for aircraft use. This would be subject to a given diesel fuel's suitability in all other aspects in addition to thermal stability. Various additional areas where diesel fuel might be limited would be the higher viscosity and higher freeze point/cloud point of diesel fuel which would then preclude its use as aircraft fuel. The obvious advantage especially to long distance aircraft would be the extended range possible with the usually higher density diesel fuel in volume limited aircraft.

REFERENCES

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Table I. Insolubles Formed From Diesel Fuels After Gravimetric Testing. All weights in mg/L of fuel. Test conditions of 260°C, 3.0 mL/min for 2.5 hours

Fuel	s/s Strip Weight	Filter Weight	Total Weight
A	0.23	13.6	13.83
B	0.32	23.8	24.12
C	0.16	21.1	21.26
D	0.01	0.9	0.91
E	0.02	1.8	1.82
F	0.00	8.2	8.20
G	0.08	14.8	14.88

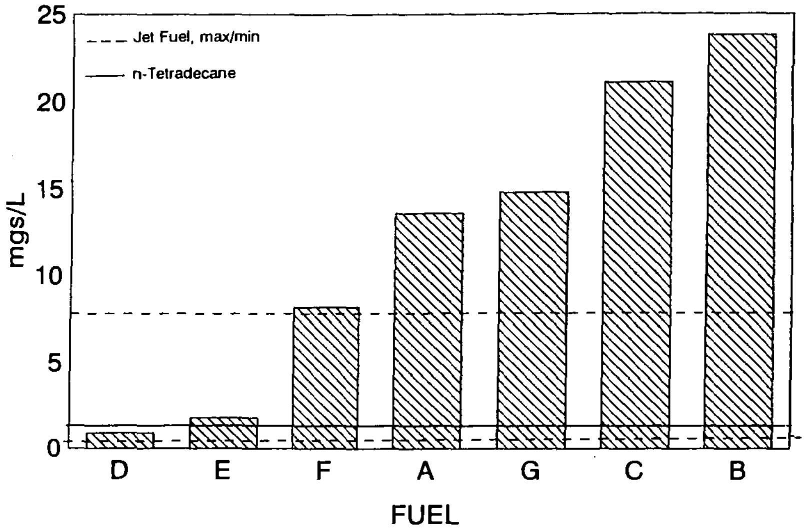

Figure 1 - Gravimetric JFTOT Filter Weights
Seven Diesel Fuels

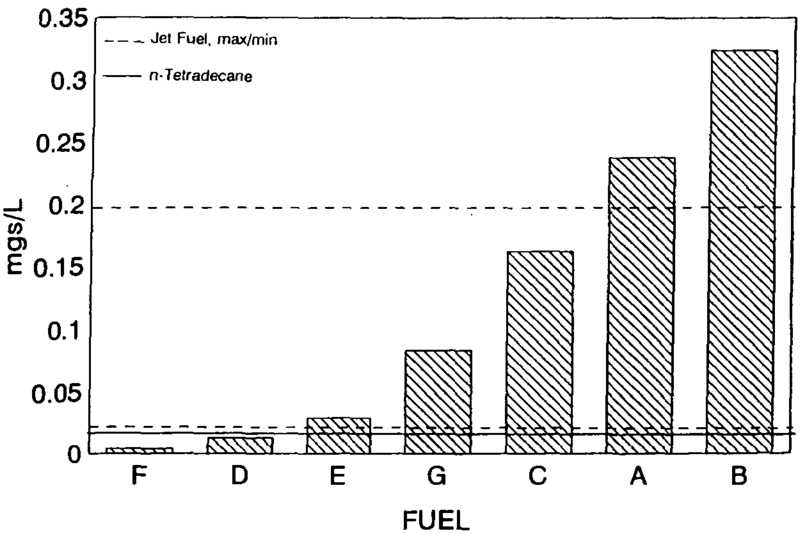

Figure 2 - Gravimetric JFTOT S/S Strip Weights
Seven Diesel Fuels