

DEVELOPMENTS IN DIESEL FUEL STABILITY FORECAST METHODS

Nahum Por and Dr. J. Ben Asher

The Israel Institute of Petroleum and Energy
P.O.B. 17081, Tel Aviv 69975, Israel

ABSTRACT

A rapid oven test was designed and used for estimation of diesel fuel stability forecasts as well as for establishing mechanisms of diesel fuel degradation processes. The 17 hours test at 110°C in specially designed bottles allows withdrawal of a vapour phase sample, enabling determination of the oxygen depletion rate, which, in conjunction with the gum formation rate, indicates whether the degradation process is of an oxidative or a polymerization type. In order to enable determination of gum formation rate in diesel fuels of a final boiling point above 300°C, a special procedure had to be devised. The gum content of any diesel fuel is of a large importance, since it indicates not only the rate of degradation products formation, but also allows its physical examination. The estimates for diesel fuel storage stability properties as used in the Rapid Oven Test (ROT) are existent gum (determined by the modified procedure), oxygen depletion in the vapour phase, acidity and colour, - all before and after exposure to the oven test. The rate of change of these properties indicates the resistivity of the diesel fuel to environmental influences during storage.

THE BACKGROUND

Difficulties have been experienced when diesel fuels had to be evaluated in respect of their behaviour in medium and in long term storage, especially in case of their operational stabilities. Operational stabilities, as referred to in this paper, are associated with the behaviour of diesel fuels in fuel tanks of vehicles or equipment, which have to be ready for immediate use, even when not operated constantly. Such vehicles or equipment are put into operation from time to time in order to ensure their proper functioning. The diesel fuel is thus circulated in the fuel system and exposed to high temperatures and contact with metals before it is returned to the fuel tank. Such conditions are extremely unfavourable to the diesel fuel properties, especially if their chemical composition makes them susceptible to changes in their original properties and to formation of degradation products.

The growing use of catalytic crackers and visbreakers, necessary for production of increased proportions of distillates in general and of motor gasolines in particular, yield correspondingly larger

amounts of cracked (unstable) middle distillates. These can be hydrotreated in order to saturate some of the unsaturated components, thus improving their stabilities, - or they can be used as diluents for back-blending heavy residues for obtaining specification grade residual fuel oils. Stability improving additives can be also used for obtaining satisfactorily stable products. Nevertheless, some of the cracked middle distillates find their way into the diesel fuels, impairing so their stability properties.

The situation described in the foregoing makes it necessary to:

- a. Employ efficient means for estimating stability properties of diesel fuels in short, medium and long term storage, as well as their operational stabilities;
- b. Have at disposal suitable testing procedures for evaluation of stability improving additives, in respect of types as well as of concentrations.

DIESEL FUEL STABILITY ESTIMATING PROCEDURES

Good diesel fuel stability estimates should fulfil the following requirements:

- a. They should be reliably indicative of the diesel fuel stability properties;
- b. The obtained results should be well reproducible;
- c. Testing procedures should be easily and fastly carried out and results should be obtainable after an as short a time as possible.

Most of the the presently used oven tests respond well to the first two conditions, but not to the third, which in itself is of a large importance in routine stability monitoring. An effort was therefore made to devise an accelerated oven test, which would respond to all the above mentioned requirements.

The oven test procedure suggested in this respect is the Rapid Oven Test (ROT), in which fuel samples are kept for 17 hours at a temperature of 110°C in half liter glass bottles, sealed with crimp type caps enabling puncture and withdrawal of vapour samples from the outage with a hypodermic syringe. The main parameters serving as stability estimates are total gums (composed of filterable sediment, adherent insolubles and existent gum), and oxygen depletion in the vapour phase above the tested fuel.

EXISTENT GUM OF WIDE BOILING POINT RANGE DIESEL FUELS

Values of existent gum are indicating the rate of degradation products formation and are therefore of a great importance. Moreover, the physical formation of gums allows the determination of their chemical composition, which in itself is also a valuable tool in the study of degradation products formation in diesel fuels.

The problem in this respect is that the current method for existent gum determination (ASTM D 381) is suitable only for diesel fuels the final boiling point of which does not exceed 320°C. A modified method allowing existent gum determinations of diesel fuels of a final boiling point of up to 400°C had to be therefore devised. The proposed procedure is based on evaporating a blend consisting of 25% volume of the full range diesel fuel and 75% volume of a kerosine, the existent gum of which had been previously determined and is used as a blank. 50 ml of the blend are evaporated under conditions prescribed by the ASTM D 381 procedure. The residue is weighed and the result is reported as mg gum per 100 ml of the diesel fuel, after the contribution of the kerosine gum (blank) had been deducted.

DETERMINATION OF BREAKDOWN MECHANISMS BY THE RAPID OVEN TEST

The oxygen depletion rates indicate not only the degradation products formation rate but also the nature of the particular degradation process: In case of gum formation without an appreciable drop in the oxygen content of the gaseous phase, the degradation process can be assumed to be of a polymerization nature:



In case the degradation process is accompanied by a significant drop in the oxygen content of the gaseous phase, it can be assumed to be of an oxidative nature. This can be also seen by the peroxides content of the tested fuel or the chemical composition of the gums:



Since these polymerization chain reaction mechanisms are well known, they are not discussed in detail in the framework of this paper.

DISCUSSION OF RESULTS

Table 1 summarizes properties of the four diesel fuel types used in the experimental sets described in this paper:

Type A is a straight run product of a relatively low final boiling point and is assumed to be relatively stable. Types B and C are diesel fuels of wider boiling point ranges, the final boiling point being

about 370°C. Type B is an aged product a sample of which had been drawn from an experimental long term field storage tank, while Type C is a corresponding freshly produced product.

Type D is a blend of the Type C commercial product and a cracked gas oil sample in a ratio of 2 to 1. This diesel fuel sample is assumed to be unstable. The analysis of the cracked gas oil component is given in the last column of Table 1.

Comparative results of long term storage stability tests of the four diesel fuel types, using several testing procedures, are given in Table 2 and Table 3:

Samples were drawn and analysed at the beginning of the storage period and after 14, 25 and 45 weeks of storage at ambient temperature in vented steel drums. Stability tests of each of the samples were carried out according to the particular procedure of each of the test methods and observations as to the following items were recorded:

- a. Comparison of results obtained by the various testing procedures, especially in respect of their correlation with results obtained by the Rapid Oven Test (Table 2);
- b. Effect of the long term storage period on the results obtained by the various testing procedures (Table 2);
- c. Effect of the diesel fuel characteristics on results obtained by the various testing procedures (Table 2);
- d. Evaluation of stability improving additives added to the various diesel fuel types, before, during and after long term storage, - using several stability test methods (Table 3).

a. Comparison of results obtained by the various testing procedures:

It is not always possible to compare absolute results obtained by the various stability tests: For example peroxide contents or gum formation rates in samples subjected to accelerated oxidations or to U.V. irradiations are higher than those obtained by the Rapid Oven Test, but peroxide contents and gums obtained by the Rapid Oven Test are higher than those obtained by other oven tests, in which contact with air is limited. Trends, rather than absolute results, should be therefore taken into consideration. Examination of these trends indicates a satisfactory correlation between the stability testing procedures used in this context.

It was observed that for diesel fuels containing stability improving additives, some of the obtained results were rather erratic. This is especially true in cases where unsuitable additives had been used or when their concentrations were either insufficient or excessive. This

phenomena can be explained by the susceptibility of some of the additives to the severity of some of the testing procedures, affecting the obtained results correspondingly. In this case oven storage tests, rather than accelerated oxidations or U.V. irradiations, should be used preferably. The Rapid Oven Test, being less time consuming, is especially suitable in this case.

b. Effect of long term storage:

Degradation formation rates are affected by exposure of diesel fuel samples to long term storage. It is interesting to note that Type B diesel fuel (taken from an experimental field storage tank, i.e. an aged sample) exhibits much higher degradation product formation rates than a corresponding fresh product (Type C); this is true before, as well as during the laboratory storage. All the stability testing procedures used show the same trend.

c. Effect of diesel fuel characteristics:

Fresh straight run diesel fuel samples (Type A and Type C) are less affected by long term storage as compared to the aged diesel fuel sample (Type B); the most affected sample during storage is the diesel fuel containing a cracked gas oil component (Type D). This trend can be seen by all the procedures used in this respect.

d. Evaluation of stability improving additives:

From the many data obtained in several experimental sets carried out in this respect, it can be seen that the type as well as the concentration of the stability improving additives has to be determined in each case. Some additives are suitable for one type of diesel fuels, while not improving the situation in case of another type. Concentrations of stability improving additives have also to be adjusted according to the diesel fuel type. Unsuitable additives, or insufficient or excessive concentrations, might affect the degradation product formation rate adversely.

It should be remarked that for brevity sake not all the results discussed in the foregoing are reported in this paper; however, the foregoing discussion is based on numerous data obtained in several experimental sets.

CONCLUSIONS

The proposed Rapid Oven Test has been described and compared to other diesel fuel stability testing procedures and satisfactory correlation has been established. The merits of this test have been discussed as follows: Results obtained by the ROT are usually well reproducible and indicative as to the stability properties of diesel fuels; as an oven test the ROT is not excessively time consuming and yields results in an acceptable period of time; the ROT enables drawing of conclusions as to breakdown mechanism for each particular case and finally, results obtained by the ROT are less erratic in case of diesel fuels containing less suitable additives especially if those are added at insufficient or excessive concentrations.

TABLE 1: Analyses of diesel fuel types used for evaluation of stability testing procedures

| Test Method | Unit | R e s u l t s | | | | |
|---|--------------------|------------------------------------|-------------------------------------|-----------------------------|-------------------------------------|-----------------|
| | | Light Atmospheric Gas Oil (TYPE A) | Gas Oil from Field Storage (TYPE B) | Commercial Gas Oil (TYPE C) | Comm. G. Oil - Blended 2:1 (TYPE D) | Cracked Gas Oil |
| Density, 15°C, ASTM D-1298 | gr/cm ³ | 0.8442 | 0.8544 | 0.8512 | 0.8696 | 0.9058 |
| Boiling Range, ASTM D-2887 | °C | 218-327 | 208-370 | 220-368 | 198-362 | 197-298 |
| Refractivity Index, ASTM D-1218 | | 1.40605 | 1.4730 | 1.47205 | 1.48605 | - |
| Pour Point, ASTM D-97 | °C | -15 | 0 | 0 | -6 | <-30 |
| Cloud Point, ASTM D-2500 | °C | -14 | +3 | +3 | -4 | <-30 |
| Cold Filter Plugging Point, IP-309 | °C | -15 | +2 | 0 | -5 | <-30 |
| ndM Analysis | | | | | | |
| Aromatic Rings | | 0.28 | 0.53 | 0.53 | 0.8 | - |
| Naphthenic Rings | | 0.93 | 0.56 | 0.56 | 0.31 | - |
| C in Aromatic Structure | % | 11.4 | 19 | 19 | 32.9 | - |
| C in Naphthenic Structure | % | 37.2 | 20 | 20 | 16.7 | - |
| C in Paraffinic Structure | % | 51.2 | 61 | 61 | 50.3 | - |
| Aniline Point, IP-2 | °C | 70.1 | 72.4 | 72.4 | 55.2 | <30 |
| Bromine Number, IP-129 | | 0.6 | 0.6 | 0.7 | 3.9 | 10 |
| Carbon Residue (Conradson), ASTM D-189 | % mass | 0.04 | 0.01 | 0.03 | 0.05 | 0.55 |
| Total Sulphur Content, ASTM D-129 | % mass | 0.42 | 0.52 | 0.53 | 1.05 | - |
| Basic Nitrogen Content, UOP-384 | ppm | 770 | 770 | 250 | 210 | - |
| Basic Nitrogen, UOP-269 | ppm | 67 | 120 | 59 | 69 | 95 |
| Pyrrroles, UOP-276 | ppm | 1.5 | 1 | 1.5 | 1 | - |
| Filterable Insolubles, ASTM D-2276 (mod.) | mg/liter | 0.4 | 1 | 2 | 2 | - |
| Existent Gum, ASTM D-381 (mod.) | mg/100 ml | <1 | <1 | <1 | 3 | 17 |
| Peroxides, ASTM D-5703 (mod.) | meq/liter | 0.7 | 1.8 | 0.4 | 0.9 | - |
| Acidity, ASTM D-974 | mg KOH/gr | 0.03 | 0.008 | 0.03 | 0.03 | 0.01 |
| Color, ASTM D-1500 | | 0.5 | 2 | 1 | 2.5 | 4 |

TABLE 2: Long term storage stabilities of diesel fuels without additives

| | TYPE A | | | TYPE B | | | TYPE C | | | TYPE D | |
|----------------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| | Oil all before storage | After 14 weeks storage | After 25 weeks storage | Oil all before storage | After 14 weeks storage | After 25 weeks storage | Oil all before storage | After 14 weeks storage | After 25 weeks storage | Oil all before storage | After 14 weeks storage |
| Carbon Residue, % mass | 0.05 | 0.06 | 0.04 | 0.01 | 0.05 | 0.02 | 0.09 | 0.03 | 0.05 | 0.03 | 0.06 |
| Filterable Insolubles, mg/100 ml | 0.04 | 0.26 | 0.5 | 0.1 | 0.4 | 0.2 | 22.3* | 0.2 | 0.2 | 0.3 | 4.2* |
| Existent Gum, mg/100 ml | 0 | 1.2 | 1.6 | 1 | 2.6 | 1.4 | 7.6 | <1 | 0.4 | 0 | 3.8 |
| Peroxides Content, mg/l | 0.75 | 0.12 | 0.14 | 1.4 | 0.8 | 1.4 | 3.9 | 0.43 | 0.16 | 0 | 0.23 |
| Acidity, mg KOH/gr | 0.03 | 0.03 | 0.03 | 0.01 | 0.1 | 0.006 | 0.13 | 0.033 | 0.04 | 0.03 | 0.29 |
| Colour Union | <0.5 | <0.5 | 1 | <1 | <3 | 4 | 4 | <1 | <1.5 | 1.5 | 1.5 |
| ACCELERATED OXIDATION | | | | | | | | | | | |
| ASTM D-2774 | | | | | | | | | | | |
| Peroxide Content, meq/l | 0.65 | 2.9 | 2.1 | - | 1.7 | 1.3 | 2.3 | - | 0.4 | 1.5 | 0.5 |
| Colour Union | - | - | 3 | - | - | - | 5 | - | - | - | 3 |
| Adherent Insolubles, mg/100 ml | 0.1 | 0.8 | 0.6 | 1.5 | 0.3 | 0.8 | 0.5 | 0.1 | 0.2 | 1 | 0.1 |
| Filterable Sediment, mg/100 ml | 0.3 | 1.1 | 0.7 | 0.4 | 0.6 | 0.7 | 0.2 | 0.2 | 0.4 | 0.3 | 0.6 |
| Total Sediment (ash), mg/100 ml | 0.4 | 3.9 | 3.3 | 1.9 | 0.9 | 1.0 | 0.5 | 0.3 | 0.6 | 1.3 | 0.7 |
| Existent Gum, mg/100 ml | - | 3.2 | 6.7 | 5.8 | - | 2.9 | 3.6 | 4 | - | 8.1 | 8.3 |
| UV IRRADIATION | | | | | | | | | | | |
| Peroxide Content, meq/l | 0.75 | 0.53 | 0.38 | 2 | 1.8 | 1.3 | 2.7 | 2.35 | 0.4 | 0.8 | 0.9 |
| Colour Union | <0.5 | <0.5 | 1 | 2 | <2 | <3 | 4.5 | 4.5 | <1 | <1.5 | 2.5 |
| Existent Gum, mg/100 ml | 1.4 | 1.2 | 4.4 | 4 | 2.8 | 6.6 | 5.4 | 14.8 | 4.4 | 1.2 | 3.6 |
| RAPID OVEN TEST | | | | | | | | | | | |
| Oxygen Consumption, % | - | 10 | 4.8 | 8.6 | 9 | 8 | 5 | 10.5 | 2 | - | 1 |
| Peroxides Content, meq/l | - | - | 1.4 | - | - | 2.6 | - | - | - | - | 1.5 |
| Colour Union | - | - | - | 3 | - | - | 5 | - | - | - | 2.5 |
| Filterable Sediment, mg/100 ml | 0.5 | 0.92 | 1 | 1.3 | 2.2 | 0.7 | 1.5 | 0.9 | 0.2 | 0.3 | 1.7 |
| Adherent Insolubles, mg/100 ml | 0.2 | 1.5 | 0.8 | 2.2 | 0.3 | 0.2 | 0.6 | 1.3 | 0.5 | 1.0 | 0.5 |
| Existent Gum, mg/100 ml | 2.7 | 2.1 | 5.2 | 3.9 | 2.8 | 6.2 | 6.3 | 11.3 | 2.9 | 1.9 | 6.5 |
| Total Gums (ash+c) | 3.4 | 4.5 | 7 | 7.4 | 5.3 | 7.1 | 3.4 | 13.5 | 3.6 | 3.7 | 6.7 |
| SHOULDER 150°C TEST | | | | | | | | | | | |
| Colour Union (before) | <0.5 | <0.5 | 1 | 1.5 | <2 | <3 | 4 | 4 | <1 | - | 1.5 |
| Colour Union (after) | 4.1 | <1 | 2 | 2.5 | <3 | <3.5 | 4.5 | 5.5 | <1.5 | - | 2 |
| Base of the Blotter | 3 | 4 | 3 | 3 | 5 | 7 | 3 | 8 | 2 | 2 | 4 |
| Filterable Sediment, mg/100 ml | - | - | 0 | - | - | - | 1.7 | - | - | - | 0.4 |
| Peroxides Content, meq/l | - | - | 0.3 | 1.2 | - | - | 2.1 | 1.6 | - | - | 0.3 |

*after

