Stability of Fuel Oils

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Introduction

Prior to the implementation of the IMO Sulphur Cap in January 2020, it was anticipated that the characteristics of max. 0.50%-sulphur compliant fuels could vary considerably, given the wide range of residue streams and cutter stocks expected to be used as blend components. As such, fuel characteristics such as density and viscosity were expected to vary with location and supplier, and possibly even across different batches from the same supplier. Half a year on, many of these expectations have come to pass. As an example, compliant bunkers historically ordered as 'RMG 380' grade exhibit a rather wide range of viscosity, with typical values below 150 cSt.[1,2]

What is fuel stability?

Fuel oils are complex mixtures, with a wide range of different molecules, from simple hydrocarbons to large complex asphaltenes, stabilized in a homogenous colloidal suspension. Asphaltenes are operationally defined as the non-volatile and polar fraction of crude oil that is insoluble in *n*-pentane or *n*-heptane, but soluble in aromatic solvents such as benzene or toluene. In terms of chemical composition, asphaltenes mainly consist of condensed aromatic structures with associated heteroatoms, usually nitrogen, oxygen, and sulphur.

A fuel mixture can be considered as a three-phase system in which the asphaltene constituents, the aromatic fraction (including the resin constituents), and the saturate fraction are kept in a delicate balance (i.e. a stable fuel). Various factors can have an adverse effect on the system, such as changes in the polarity and bonding arrangements of the species in the mixture, leading to instability and ultimately resulting in flocculation and deposition of asphaltenes.[3,4,5]

[1] Joint Industry Guidance The supply and use of 0.50%-sulphur marine fuel
[2] MAN Energy Solutions – 0.50 % S Fuel Operation in 2020
[3] Speight. 2004. Oil & Gas Science and Technology 59(5):467-477
[4] Kondrasheva *et al*. 2019. Energy & Fuels 33(5):4671-4675
[5] Fakher *et al*. 2020. Journal of Petroleum Exploration and Production Technology 10:1183-1200

Asphaltenes are stabilised by aromatic components in the mixture, however the increasing use of paraffinic blend components to meet the more stringent sulphur requirement for compliant fuels has led to concerns regarding the stability of the resulting product. In the context of fuel oils, stability is defined as the resistance to breakdown and precipitation of asphaltenic sludge despite being subjected to forces, such as thermal and ageing stresses, while handled and stored under normal operating conditions.[6]

Bunkers are typically ordered to ISO 8217 specifications, a standard which specifies the requirements for use of fuels in marine diesel engines and boilers prior to conventional onboard treatment.[7] Since high levels of sludge can cause filtration and separator problems for on-board fuel systems, ISO 8217 includes a specification requirement for fuel stability.

How is fuel oil tested for stability?

There are actually three sediment tests covered within ISO 8217 all using the hot filtration test method. The primary difference between the methods is the treatment of the fuel sample prior to filtration. In the case of the Total Sediment Existent (TSE) procedure there is no specific sample preparation, and the sediment result indicates the dirt present in the sample. For the Total Sediment Accelerated (TSA) procedure the sample is mixed with 10% hexadecane (aka cetane) and heated at 100°C for 1h, prior to filtration. In the case of the Total Sediment Potential (TSP) test the sample is heated at 100°C for 24h to simulate thermal ageing of the fuel.[8,9]

As per ISO 8217, the reference method for fuel stability is TSP, which is the sum of the insoluble organic and inorganic material separated from the bulk of a fuel sample under thermal ageing, and if the value does not exceed 0.10% m/m, the specification limit is met and the fuel is considered stable, whilst significant precipitation would indicate that the fuel is unstable.

Two perfectly stable fuels can be incompatible

Stability is a characteristic that forms part of the specification of the fuel as supplied to ships, hence it is the responsibility of the fuel supplier to provide a stable fuel. On the other hand, compatibility is the term used when evaluating if two (or more) fuels can be mixed without asphaltenes coming out of suspension. As such compatibility is a handling issue and the responsibility of the operator. Given the variability in the composition of fuel oils, a stable fuel is not necessarily always compatible with

[6] ISO/PAS 23263 Considerations for fuel suppliers and users regarding marine fuel quality in view of the implementation of maximum 0,50 % sulfur in 2020
[7] ISO 8217:2017 Sixth Edition
[8] ISO 10307-1:2009 Petroleum products – Total sediment in residual fuel oils – Part 1: Determination by hot filtration
[9] ISO 10307-2:2009 Petroleum products – Total sediment in residual fuel oils – Part 2: Determination using standard procedures for ageing

another stable fuel stem, which means compatibility testing will always have to be carried out for instances when commingling cannot be avoided.

Are there other methods to assess stability and compatibility?

Outside of the scope of ISO 8217, the 'spot test' (ASTM D4740) is a quick test that can be carried out either on board or in a laboratory to evaluate the cleanliness of fuels, taken as an indication of stability. A drop of preheated sample is placed on a test paper, which is then placed in an oven at 100°C, for an hour. The resulting spot is examined for evidence of suspended solids and rated against reference spots.[10] ASTM D4740 can also be used to assess compatibility of different batches of fuels, by using a blend sample of the fuels (e.g. 90:10 or 50:50 blend proportion).

Sampling

Fuel quality disputes will invariably involve testing, and hence the provenance and integrity of the samples to be tested is of paramount importance. In general, the most representative samples would be the continuous manifold drip samples taken throughout the duration of bunkering. To ensure homogeneity of the replicate samples, the sampling cubitainer should be well shaken, then poured into the individual sample bottles in multiple passes (at least twice) to fill each bottle in turn. This becomes particularly important for potentially unstable fuels, as the sediments might settle to the bottom of the cubitainer during drip sampling. The sample bottles should be secured with uniquely numbered tamper proof seals, and countersealed where possible, the details for which should be well recorded in the respective sample labels and delivery notes.

Summary

Whilst it is expected that max 0.50% fuels would vary significantly in composition, compliant fuels remain covered by the specifications set out in ISO 8217. Blend components will need to be in conformance with the requirements of ISO 8217, and the resulting fuel has to be a homogenous blend, and able to withstand the expected forces through normal on-board use and storage. There are several methods available to assess fuel stability, however TSP is considered as the reference method. As in all fuel quality disputes, representative samples form a key part in supporting or defending a claim.

[10] ASTM D4740-04 Standard Test Method for Cleanliness and Compatibility of Residual Fuels by Spot Test