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Everything you need to know about marine fuels

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This publication was prepared for Fuel and Marine Marketing LLC (FAMM) by Paula J. Spreutels and Monique B. Vermeire of Heavy Fuels Technology (HFT), located at the Texaco Technology Ghent Research Laboratory in Belgium. HFT does exclusive work for FAMM in the area of fuel technology, with related field support for matters concerning fuel quality issues. HFT is very active in supporting FAMM on various international fuel technical organizations and at industry seminars.

Table of Contents

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I. Introduction

Liquid fuel . . . Combustion . . . Mechanical Energy . . . Propulsion Energy and Electricity

Via thermal plants, marine engines and gas turbines, the energy obtained from fuel oil combustion is made available to fulfill our needs, be it for transport purposes, or for electrical power applications.

The contents of this brochure focus mainly on the use of liquid fuels (marine distillate fuels and marine residual fuels) in marine engines.

From the early 19th century until the third quarter of the 20th century, steamships crossed the Seven Seas, gradually eliminating sailing ships from commercial shipping.

In the second half of the 20th century, the motorship took the dominant position. The history of the diesel engine began in 1892 with Rudolf Diesel and twenty years later the first four-stroke marine diesel engine ships were operational.

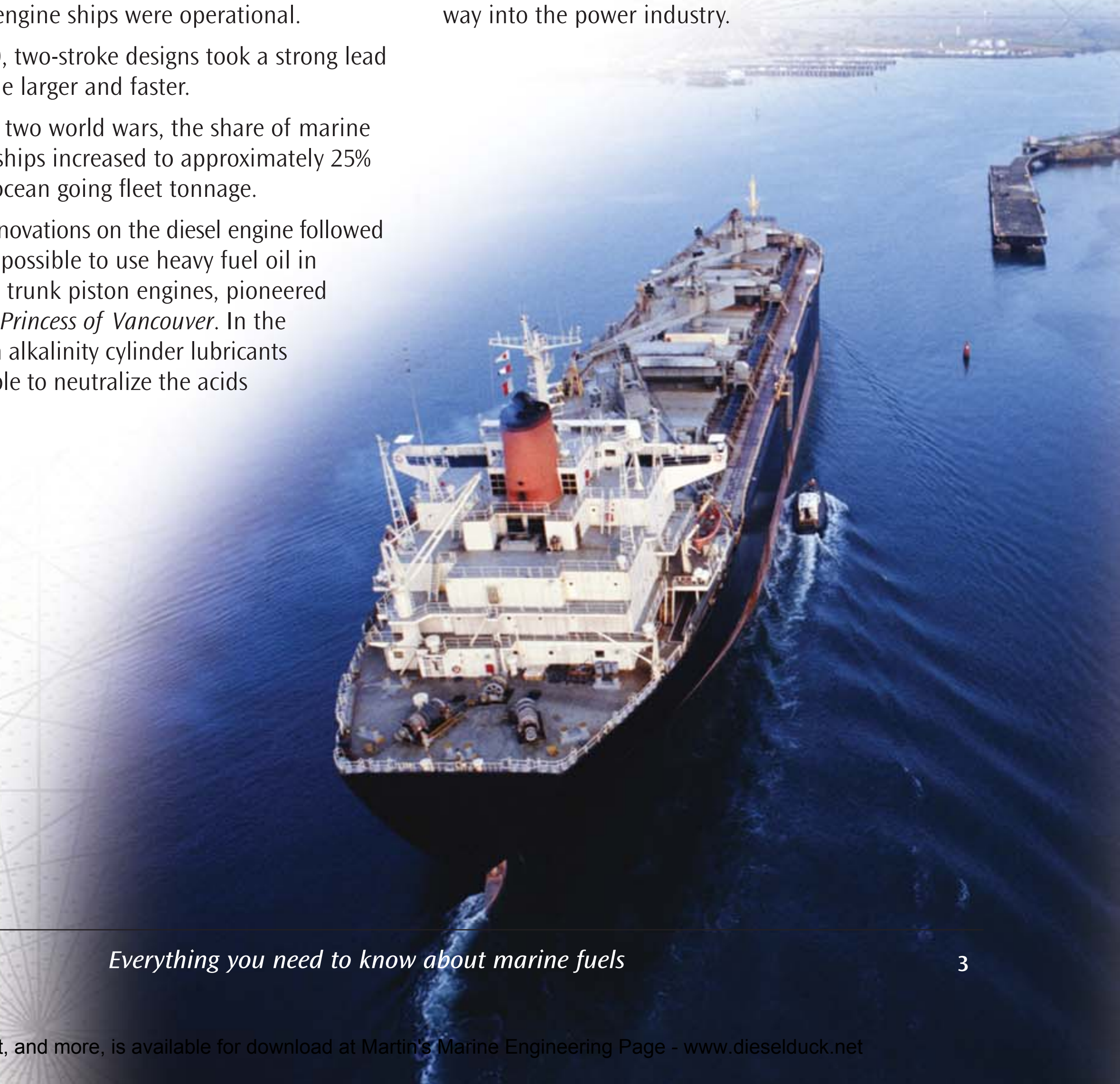
Around 1930, two-stroke designs took a strong lead as ships became larger and faster.

Between the two world wars, the share of marine engine driven ships increased to approximately 25% of the overall ocean going fleet tonnage.

A series of innovations on the diesel engine followed which made it possible to use heavy fuel oil in medium speed trunk piston engines, pioneered by the *MV The Princess of Vancouver*. In the mid-1950s high alkalinity cylinder lubricants became available to neutralize the acids generated by the combustion of high sulphur residual fuels, and wear rates became comparable to those found when using distillate diesel fuel.

Diesel engine powered ships capable of utilizing residual fuel oil gained in popularity because of excellent economics, and in the second half of the 1960s, motor ships took over the dominant position from steamships, both in terms of numbers, and in terms of gross tonnage. By the start of the 21st century, motor ships account for 98% of the world fleet.

Marine engines have also found their way into the power industry.



II. Crude Oil

1. How is a crude oil field formed?

The generally accepted theory is that crude oil was formed over millions of years from the remains of plants and animals that lived in the seas. As they died, they sank to the seabed, were buried with sand and mud and became an organic-rich layer. Steadily, these layers piled up, tens of meters thick. The sand and mud became sedimentary rock, and the organic remains became droplets of oil and gas. Oil and gas passed through the porous rock and were eventually trapped by an impervious layer of rock, collecting at the highest point.

The formation of an oil/gas field requires the presence of four geological features:

1) **Source rock:** contains suitable organic matter, which, under the conditions of heat and pressure, produces hydrocarbons.
2) **Reservoir rock:** a porous layer of rock in which the hydrocarbons are retained
3) **Cap rock:** a rock or clay, which prevents the hydrocarbons from escaping
4) **Trap:** a rock formation bent into a dome or broken by a fault which blocks the escape of the hydrocarbons either upwards or sideways.

Most importantly, the above factors have to occur at the right time, place and in the right order for oil and gas to be formed and trapped. Currently, successful petroleum exploration relies on modern techniques such as seismic surveying. The fundamental principle of seismic surveying is to initiate a seismic pulse at or near the earth's surface and to record the amplitudes and travel times of waves returning to the surface after being reflected or refracted from the interface(s) on one or more layers of rock. Once seismic data have been acquired they must be processed into a format suitable for geological interpretation and petroleum reservoir detection.

2. Composition and classification of crude oil

Crude oil is a mixture of many different hydrocarbons and small amounts of impurities. The composition of crude oil can vary significantly depending on its source. Crude oils from the same geographical area can be very different due to different petroleum formation strata.

Different classifications of crude oil exist:

1) Based on the type of hydrocarbons:
   - paraffinic type crudes
   - naphtenic type crudes
   - asphaltenic (aromatic) type crudes

   Each crude oil contains the three different types of hydrocarbons, but their relative percentage may vary widely. Examples of these type of crudes corresponding with a defined geographical area include paraffinic crude in Saudi Arabia, naphtenic crude in some Nigerian formations and asphaltenic crude in Venezuela.
2) Based on their API gravity: The lower the density of the crude oil, the higher its API gravity. A higher API gravity means that the crude contains more valuable lower boiling fractions.
3) Based on the sulphur content: The ever-growing concern for the environment and the impact on the refining cost calculations are the base for the third classification:
   - low sulphur crude
   - high sulphur crude

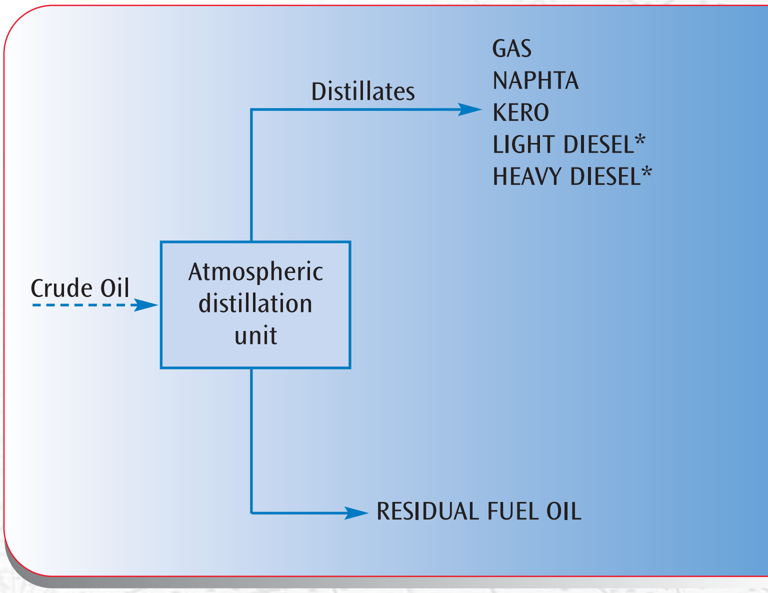
3. Crude oil refining and stocks for marine fuel blending

Petroleum refineries are a complex system of multiple operations and the processes used at a given refinery depend upon the desired product slate and characteristics of the design crude oil mix. The more complex refining of today has a definite impact on the characteristics of marine diesel and Intermediate Fuel Oil (IFO) bunker fuel.

Review of simplified/typical refining schemes and the influence on marine fuels

Straight run refinery

Atmospheric crude distillation and further refining of distillates



* "diesel" refers here to specific atmospheric distillation cuts, and is not related to an engine-type application.

Straight run stocks for marine fuel blending

Light diesel, heavy diesel, and straight run residue.

Straight run marine gasoil and distillate marine diesel

Marine gasoil and distillate type MDO are manufactured from kero, light, and heavy gasoil fractions. For DMC type gasoil, up to 10–15% residual fuel can be added.

Straight run IFO 380 mm^2/s (at 50°C)

This grade is made starting from the atmospheric residue fraction (typical viscosity of about 800 mm^2/s at 50°C) by blending with a gasoil fraction.

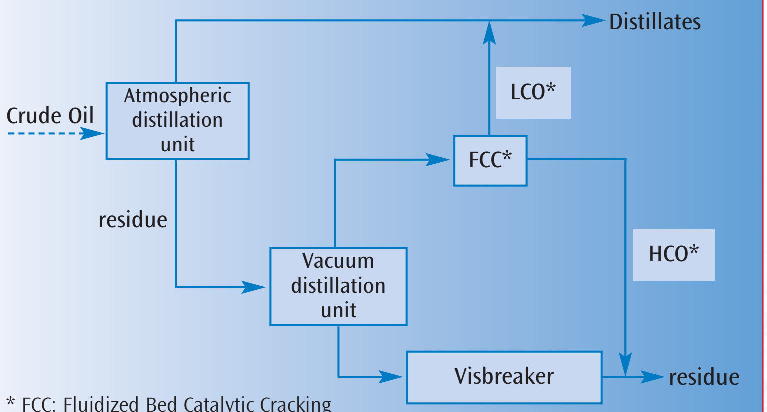
Straight run lower viscosity grade IFOs

Blending to lower grade IFOs is done from the IFO 380 mm^2/s (at 50°C) using a gasoil type cutterstock or with marine diesel.

All IFOs have good ignition characteristics, due to the high percentage of paraffinic material still present in the atmospheric residue, and the paraffinic nature of the cutterstocks used. The high amount of paraffinic hydrocarbons in the straight run type marine fuels leads to relatively low densities for these products, ensuring easy and efficient onboard fuel purification.

The product slate of a straight run type refinery, with its heavy fuel production of approximately 50% of the crude feed, does not correspond to the product demand in the industrialized countries where a high demand for light products (jet fuel, gasoline, and gasoil) goes together with a strong reduction in the demand for heavy fuel (10 to 15% of the crude oil). This results in the need to convert the residue fraction into light fractions, (also more valuable) and to the construction of complex refineries.

Example: Complex refinery with (fluid) catalytic cracking and visbreaking.



* FCC: Fluidized Bed Catalytic Cracking
* LCO: Light Cycle Oil
* HCO: Heavy Cycle Oil

Complex refinery

A complex refinery-processing scheme can be separated into two parts:

1) Crude oil distillation (atmospheric and vacuum distillation)
2) Streams from the vacuum distillation unit are converted through catalytic and thermal cracking processes.

Complex refineries have been favored since the early ’80s and are intended to boost gasoline production. All further information provided in this brochure is based on this type of complex refinery.

The main marine fuel blending components from a Fluidized Bed Catalytic Cracking (FCC) type refinery with visbreaker are the same distillates as those from a straight run refinery (light and heavy diesel) as well as light cycle (gas) oil (LC(G)O) and heavy cycle oil (HCO) from the catcracker and visbroken residue from the visbreaker.

Atmospheric residue is used as feedstock for the vacuum unit and will only seldom be available for fuel blending.

More detailed information on complex refining is provided in Attachment I.

Marine fuels resulting from a catalytic cracking/visbreaking refinery type have a composition that is markedly different from that of an atmospheric type refinery.

Marine gasoil (MGO/DMA)

A new blend component has appeared — LC(G)O (light cycle (gas) oil) — which contains about 60% aromatics. Due to the high aromatic nature of LC(G)O, the density of a marine gasoil blended with LC(G)O will be higher than when using gasoil of an atmospheric distillation type refinery. The density will typically be close to 860 kg/m^3 (at 15°C). No performance or handling differences with atmospheric type gasoil have to be expected.

Notes: – *Marine gasoil S max. legislation follows normally the one applicable to in-land use of gasoil. This is e.g. the case in the EU where the max. S level of marine gasoil for use in the territorial waters is 0.20 mass% max. as of July 1, 2000 (waiver for Greece). This has an effect on the acidity of the combustion gases, and it is possible that the alkalinity (BN) and dispersancy of the lubricant have to be adjusted accordingly.*

– *Due to logistics, it is possible that in some areas marine gasoil is in fact automotive diesel (with added marker and dye and without the excise duty applicable to automotive fuel), with in the EU at present a max. S level of 0.035 mass%, due to decrease to 0.005 mass% max. in 2005. Same remark on the effect on acidity of the combustion gases and on the lubricant as above.*

Distillate marine diesel (MDO/DMB)

Distillate marine diesel (commercial denomination) typically has a lower cetane number than marine gasoil, and a higher density. With the production slate of a catalytic cracking refinery, distillate marine diesel can therefore contain a higher percentage of LC(G)O than marine gasoil.

Note: Worldwide, marine diesel has a sulphur content between approx. 0.3 and 2.0 mass%. Due to recent EU legislation, this level is for the territorial waters belonging to the EU the same level as for gasoil, i.e. 0.20 mass% max. as of July 1, 2000 (waiver for Greece). This will have an effect on the acidity of the combustion gases, and it has to be taken into account for the lubrication of vessels using marine diesel, mainly when operating most of the time between EU ports.

Blended marine diesel (MDO/DMC)

With atmospheric type refining, blended marine diesel (MDO/DMC) can contain up to 10% IFO with either marine gasoil (MGO/DMA) or distillate marine diesel (MD)/DMB). With complex refining, blended marine diesel (MDO/DMC) no longer corresponds to a specific composition and extreme care must be used when blending this grade to prevent stability and/or combustion problems.

IFO-380

This grade is usually manufactured at the refinery and contains visbroken residue, HCO and LC(G)O. These three components influence the characteristics of the visbroken IF-380.

Vacuum distillation reduces the residue yield to about 20% of the crude feed, unavoidably leading to a concentration of the heaviest molecules in this fraction. Visbreaking converts about 25% of its vacuum residue feed into distillate fractions. This means that about 15% of the original crude remains as visbroken residue. The asphaltene[1], sulphur and metal content in visbroken residue are 3 to 3.5 times higher than in atmospheric residue. Visbreaking affects the molecular structure: molecules are broken thermally and this can deteriorate the stability of the asphaltenes.

HCO (typical viscosity at 50°C: 130 mm^2/s) contains approximately 60% aromatics, and is a high-density fraction: the density at 15°C is above 1 kg/l (typically 1.02). It is the bottom fraction of the FCC unit. The catalytic process of this unit is based on an aluminum silicate. Some mechanical deterioration of the catalyst occurs in the FCC process, and the resulting cat fines are removed from the HCO in the refinery. This removal however, is not 100% efficient, and a certain amount (ppm level) of cat fines remains in the HCO, and from there end up in heavy fuel blended with HCO (further discussed in Chapter III-2 on the significance of the marine fuel specifications).

The aromaticity of HCO assists in ensuring optimum stability for the visbroken fuel blend.

LC(G)O (typical viscosity at 50°C: 2.5 mm^2/s) has the same aromaticity as HCO, but is a distillate fraction of the FCC unit, with a distillation range comparable to that of gasoil. With a typical density of 0.94 kg/l at 15°C, it is used to fine-tune the marine heavy fuel oil blending where generally a density maximum limit of 0.9910 kg/l has to be observed.

IFOs < 380 mm^2/s

These grades are generally blended starting from 380 mm^2/s IFOs (at 50°C), by using a suitable cutterstock (marine diesel, gasoil, LC(G)O, or a mixture of these). The blend composition has to be construed in such a way that the product stability is safeguarded, while at the same time direct or indirect density limits are fulfilled (further discussed in Chapter III-2 on the significance of the marine fuel specifications).

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[1] *asphaltenes: residual fuel components which are insoluble in heptane but soluble in toluene.*

III. Fuel Oil

1. Fuel oil applications

Fuel oil applications are all based on energy becoming available through the burning of fuel oil. Fuel oil combustion (oxidation reaction) releases a large amount of heat, which can be used for steam generation, e.g. for steam turbines. The high volume (pressure) of the combustion gases can be used directly to drive an engine, or (less frequent for HFO, but widespread for gasoil) a gas turbine.

When fuel oil is burned, an amount of heat is released, which is defined by the specific energy (international unit MJ/kg) of the fuel.

Thermal plants use this heat to generate steam, which then drives steam turbines, thus providing mechanical energy that can be used for propulsion or be converted into electrical energy.

For marine engines and gas turbines, mechanical energy provided by the combustion gases is used either directly for propulsion, or converted into electrical energy for power plants. For larger installations, cost efficiency optimization and environmental constraints are leading to the introduction of co-generation. In co-generation, part of the energy lost in the generation of electrical energy is made available under the form of low-pressure steam, suitable for a wide range of heating applications.

2. Fuel specifications

The different types of fuel oil applications and environmental considerations have led to different types of fuel oil specifications. These are much more demanding than the original fuel oil n° 6 or Bunker C requirements when all heavy fuel was used for thermal plants and steam turbines. Emission standards for thermal plants can vary widely, depending on the geographical area. Since all emitted SO_2 originates from sulphur in the fuel, emission standards on SO_2 automatically limit the sulphur content of the fuel, except for large combustion plants, where the standard can be economically met by flue gas desulphurization.

In the late 1960s marine diesel engines were the primary means of ship propulsion. Initially, and through the late 1970s, the different marine engine heavy fuel oil grades remained identified solely by their maximum viscosity. This worked well with heavy fuel originating from atmospheric refineries. Fuel related operational problems arose with the generalized upgrading of refinery operations in the second half of the 1970s from straight run to complex refining.

1982 saw the publication of marine fuel specification requirements by the British Standard Organization (BS MA 100), and by CIMAC (Conseil International de Machines à Combustion).

Table 1: Requirements For Marine Distillate Fuels

Characteristic	Limit	Category ISO-F-				Test method reference
		DMX	DMA	DMB	DMC	
Appearance		Visual		–	–	See 6.2
Density at 15°C, kg/m^3	max.		890.0	900.0	920.0	ISO 3675 or ISO 12185 (see also 6.3)
Viscosity at 40 °C, mm^2/s 2)	min. max.	1.40 5.50	1.50 6.00	– 11.00	– 14.00	ISO 3104 ISO 3104
Flash point, °C	min.	43	60	60	60	ISO 2719 (see also 6.4)
Pourpoint (upper), °C 3)						
– winter quality	max.	–	−6	0	0	ISO 3016
– summer quality	max.	–	0	6	6	ISO 3016
Cloud point, °C	max.	–16 4)	–	–	–	ISO 3015 (see also 6.5)
Sulfur, % *(m/m)*	max.	1.0	1.5	2.0	2.0	ISO 8754 (see also 6.6)
Cetane number	min.	45	40	35	–	ISO 5165 (see also 6.7)
Carbon residue/micro method 10% (V/V) distillation bottoms). % *(m/m)*	max.	0.03	0.30	–	–	ISO 10370
Carbon residue (micro method), % *(m/m)*	max.	–	–	0.03	2.50	ISO 10370
Ash, % *(m/m)*	max.	0.01	0.01	0.01	0.05	ISO 6245
Sediment, % *(m/m)*	max.	–	–	0.07	–	ISO 3735
Total existent sediment, % *(m/m)*	max.	–	–	–	0.10	ISO 10307-1
Water, % (V/V)	max.	–	–	0.3	0.3	ISO 3733
Vanadium, mg/kg	max.	–	–	–	100	ISO 14597
Aluminum plus silicon, mg/kg	max.	–	–	–	25	ISO 10478 (see also 6.8)

1) In some geographical areas, there may be a maximum limit.
2) 1 mm^2/s = 1 cSt.
3) Purchasers should ensure that this pour point is suitable for the equipment on board, especially if the vessel operates in both the northern and southern hemispheres.
4) This fuel is suitable for use without heating at ambient temperatures down to –15°C.

An international ISO standard has existed since 1987: ISO 8217 (revised in 1996). The stated purpose of ISO 8217 is to define the requirements for petroleum fuels for use in marine diesel engines and boilers, for the guidance of interested parties such as marine equipment designers, suppliers and purchasers of marine fuels. The ISO 8217:1996 specifications for marine fuels (and by extension for fuels for stationary marine engines), Tables 1 and 2, will be discussed in detail in Chapter III-2a.

The most important specifications introduced to ensure reliable engine operation with fuel originating from complex refining are:

- Maximum density limit — Important for classical purifier operation, and to ensure satisfactory ignition quality for low viscosity fuel grades.
- Maximum Al+Si limit — In a complex refinery, HCO is used as a blending component. Mechanically damaged aluminum silicate catalyst particles of the catalytic cracker are not completely removed from the HCO stream, and are found back in mg/kg amount in heavy fuel blended with HCO. In order to avoid abrasive damage in the fuel system onboard the vessel, it is necessary to limit the amount of Al+Si to a level, which can be adequately removed by the ship's fuel cleaning system.
- Maximum total potential sediment limit – The stability of asphaltenes is deteriorated by the visbreaking process and instability problems can cause fuel purification and filter blocking problems, hence the need for a specification to ensure adequate fuel stability.

A much less widespread application of heavy fuel is found in heavy duty gas turbines: here the fuel specification requirements before the injection are very severe, and can only be obtained by an extremely thorough pre-cleaning of the fuel. The fuel treatment consists in the removal of the alkalimetals by fuel precleaning and inhibition of vanadium induced corrosion by injecting magnesium-containing additives, which react with the vanadium to form non-corrosive compounds. The heavy-duty gas-turbine application of heavy fuel is further discussed in Attachment II.

2A. SIGNIFICANCE OF THE MARINE FUEL PROPERTIES LISTED IN ISO 8217:1996

Kinematic viscosity:

Is a measure for the fluidity of the product at a certain temperature. The viscosity of a fuel decreases with increasing temperature. The viscosity at the moment the fuel leaves the injectors has to be within the limits prescribed by the engine manufacturers to obtain an optimal spray pattern. Viscosity outside manufactures specifications at the injectors will lead to poor combustion, deposit formation and energy loss. The viscosity of the fuel has to be such that the required injection viscosity can be reached by the ship's preheating system.

Table 2: Requirements For Marine Residual Fuels

Characteristic	Limit	Category ISO-F-															Test Method Reference
		RMA 10	RMB 10	RMC 10	RMD 15	RME 25	RMF 25	RMG 35	RMH 35	RMK 35	RMH 45	RMK 45	RML 45	RMH 55	RMK 55	RML 55	
Density at 15°C, kg/m^3	max.	975.0	981.0		985.0	991.0		991.0		1010.0	991.0	1010.0	–	991.0	1010.0	–	ISO 3675 or ISO 12185 (see also 6.3)
Kinematic viscosity at 100°C, mm^2/s 1)	max.	10.0			15.0	25.0		35.0			45.0			55.0			ISO 3104
Flash point, °C	min.	60			60	60		60			60			60			ISO 2719 (see also 6.4)
Pour point (upper) °C 2)																	
– winter quality	max.	0	24		30	30		30			30			30			ISO 3016
– summer quality	max.	6	24		30	30		30			30			30			ISO 3016
Carbon residue, % *(m/m)*	max.	10		14	14	15	20	18	22		22		–	22		–	ISO 10370
Ash, % *(m/m)*	max.	0.10			0.10	0.10	0.15	0.15	0.20		0.20			0.20			ISO 6245
Water, % (V/V)	max.	0.5			0.8	1.0		1.0			1.0			1.0			ISO 3733
Sulfur, % *(m/m)*	max.	3.5			4.0	5.0		5.0			5.0			5.0			ISO 8754 (see also 6.6)
Vanadium, mg/kg	max.	150		300	350	200	500	300	600		600			600			ISO 14597
Aluminum plus silicon, mg/kg	max.	80			80	80		80			80			80			ISO 10478 (see also 6.8)
Total sediment, potential, % *(m/m)*	max.	0.10			0.10	0.10		0.10			0.10			0.10			SO 10307-2 (see also 6.9)

1) Annex C gives a brief viscosity/temperature table for information purposes only. 1 mm^2/s = 1 cSt

2) Purchasers should ensure that this pour point is suitable for the equipment on board, especially if the vessel operates in both the northern and southern hemispheres.

Density:

The official unit is kg/m^3 at 15°C, while kg/l at 15°C is the most commonly used unit. Density is used in the calculation of the quantity of fuel delivered. From a technical point of view, the density gives an indication of the ignition quality of the fuel within a certain product class, this is particularly the case for the low viscosity IFOs. The product density is important for the onboard purification of the fuel; the higher the density the more critical it becomes (see Chapter III-4 on fuel oil treatment).

Cetane number, cetane index:

Only applicable for gasoil and distillate fuels. It is a measure for the ignition quality of the fuel in a diesel engine. The higher the rpm of the engine, the higher the required cetane number. The cetane number is determined on an engine. The cetane index — an approximate value of the cetane number based on the density and the distillation of the fuel — can be calculated and is usually used. The cetane index is not applicable when cetane-improving additives have been used.

Carbon residue:

A carbon residue determination is a typical laboratory test performed under specified reduced air supply and does not represent combustion conditions in an engine. It gives an indication of the amount of hydrocarbons in the fuel which have difficult combustion characteristics, but there is no conclusive correlation between carbon residue figures and actual field experience. The micro carbon residue method is specified by ISO 8217.

Ash:

The ash content is a measure of the metals present in the fuel, either as inherent to the fuel, or as contamination.

Flash point:

Flash point is the temperature at which the vapors of a fuel ignite (under specified test conditions), when a test flame is applied. The flash point for all fuels to be used in bulk onboard vessels is set at PM, CC, 60°C minimum (SOLAS agreement). DMX, a special low cloud point gasoil, may only be stored onboard in drums because of its <60°C flash point.

Sulphur:

The sulphur content of a marine fuel depends on the crude oil origin and the refining process. When a fuel burns, sulphur is converted into sulphur oxides. These oxides reach the lubricating oil via the blow-by gas. These oxides are corrosive to engine piston linings and must be neutralized by the cylinder lubricant. Marine engine lubricants are developed to cope with this acidity (high BN). If the correct lubricant is used, the sulphur content of a marine fuel is technically not important (although it has environmental implications in sensitive areas such as the Baltic Sea).

Water content:

Water in fuel is a contamination and does not yield any energy. The percentage of water in the fuel can be translated into a corresponding energy loss for the customer. Water is removed onboard the vessel by centrifugal purification. If after purification the water content remains too high, water vapor lock can occur and pumps can cut out. If water-contaminated fuel reaches the injectors, combustion can be erratic. Water in fuel which remains standing in lines for a longer period can cause corrosion.

Pour point:

Pour point is the lowest temperature at which a fuel will continue to flow when it is cooled under specified standard conditions. Contrary to straight run type heavy fuels (pour point typically in the +20°C range), bunker fuels from a complex refinery generally have pour points below 0°C (range –10 to –20°C). This is reflected in the fact that bunker fuel tanks are generally not completely heated any more, but only before the fuel transfer pump. This can then lead to problems, if a vessel receives high pour straight run bunker fuel. For distillate marine diesel, the cold temperature behavior is controlled in ISO 8217 by a pour point maximum. With marine diesels with a high content of heavier n-paraffins vigilance is required if strong temperature changes are expected (wax settling can occur, even when the pour point specification is met).

Elements:

Vanadium and nickel are elements found in certain heavy fuel oil molecules (asphaltenes). Upon combustion vanadiumoxides are formed and some of them have critical melting temperatures. The most critical are the double oxides/sulphates with sodium. Some countries have implemented maximum Ni concentrations for inland use of heavy fuel (emission regulations).

Total sediment, potential:

Inorganic material naturally occurring in crude oil is removed in the refineries prior to the atmospheric distillation. Some minor contamination (e.g. ironoxides) of a finished heavy fuel can not be excluded. The biggest risk for sediment formation in heavy fuel is due to potential coagulation of organic material inherent to the fuel itself: visbroken asphaltenes, if insufficiently stable, can form sediment (coagulation is influenced by time and temperature). A decrease in aromaticity of the fuel matrix by blending with paraffinic cutterstocks can also deteriorate the stability of the asphaltenes. In cases of heavy fuel instability, it is only a relative small fraction of the asphaltenes which forms sediment, but this organic sediment includes in its mass some of the fuel itself, and water (onboard purifying problems), and the amount of generated sludge can become quite high. The total potential sediment gives the total amount of sediment that can be formed under normal storage conditions, excluding external influences. If the total potential sediment of the heavy fuel oil markedly exceeds the specification value (0.10 % (m/m) max for all grades of IFOs and HFOs), problems with the fuel cleaning system can occur, fuel filters can get plugged and combustion become erratic.

Catalytic fines:

As described previously, HCO is used worldwide in complex refining as a blending component for heavy fuel. Mechanically damaged catalyst particles (aluminum silicate) cannot be removed completely in a cost-effective way, and are found in blended heavy fuel. Fuel precleaning onboard ships has a removal efficiency of approximately 80% for catalyst fines. In order to avoid abrasive wear of fuel pumps and injectors, a maximum limit of 80 mg/kg for Al+Si has been defined in ISO 8217.

Calculated carbon aromaticity index, CCAI:

CCAI is an indicator of the ignition delay of an IFO. CCAI is calculated from the density and the viscosity of the fuel oil. Although it is not an official specification, it has found its way in many users' bunker fuel specification requirements. Some manufacturers specify CCAI limits for their engines, depending on engine type and application.

2B. CORRESPONDENCE OF SPECIFICATIONS AND TEST METHODS

ISO 8217:1996 lists the test requirements and methods for the testing. While in theory these methods should be used worldwide for testing marine fuels, experience has shown that this is not always the case. In some areas other test methods, in some cases precursors of the presently defined ISO methods, are still being used. The correspondence (discrepancy) between such test methods/results and the test methods/data of ISO 8217 are described hereafter.

Density:

The mass (weight in vacuum) of the liquid per unit volume at 15°C. Official unit: kg/m^3. Often used variant: kg/l. The density limits in ISO 8217 are expressed in kg/m^3. Specific gravity 60/60°F: Specific gravity is the ratio of the mass of a given volume of liquid at 60°F to the mass of an equal volume of pure water at the same temperature. No unit.

API gravity:

Is a function of the specific gravity 60/60°F. API gravity is expressed as degrees API.

API gravity, deg = (141.5 / spec. gr. 60/60°F) –131.5

Micro Carbon Residue (MCR):

MCR is the carbon residue test prescribed by ISO 8217:1996. The formerly used carbon residue test was Conradson Carbon Residue. The test result obtained with MCR is the same as with CCR, but MCR is a relatively quick test method and has a better precision than CCR.

Al+Si:

The ISO 8217 prescribed test method is ISO 10478, and only this method and fully equivalent methods from National Standardization Organizations should be used. A former industry wide limit for catalyst fines in heavy fuel was defined on Al alone (30 mg/kg max.). The ratio between Al and Si can however vary considerably between different types and manufacturers of aluminum silicate catalyst. This is the reason for the test requirement change to the sum of Al and Si. In practice, the two ways of limiting the catalytic fines content in heavy fuel give the same degree of protection.

Sediment and Total Potential Sediment:

Differentiation has to be made between tests for inorganic sediment and organic sediment, existent sediment and potential sediment.

According to ISO 8217: 1996 inorganic sediment (rust, sand) determination (ISO 3735) is only applicable to DMB type marine diesel. The method (and equivalent methods) will not determine sediment from organic origin, due to the aromatic nature (toluene) of the extraction solvent.

Organic type sediment can occur in DMC type marine diesel and in intermediate fuel oils. The cause of the formation of organic type sediment resides in the thermal cracking of the heaviest molecules of crude, generally in visbreaking operations. Asphaltenes, the heaviest molecules of crude, can become unstable by thermal cracking, and must be carefully monitored by the refineries. Once visbroken, the asphaltenes are more or less sensitive to changes in the aromaticity of the total fuel matrix. This has to be taken into account for fuel blending when using visbroken type heavy fuel and gasoil type (paraffinic) blending stocks. The asphaltene sediment formation is a function of time and temperature (excluding external influences), and an unstable fuel will only reach its final sediment formation after a certain storage time. The sediment present in a sample of heavy fuel at a certain moment is given by the total existent sediment test, but there is no certainty that this figure corresponds to the condition of the bulk of the fuel at that same time. The total potential sediment test gives the total amount of sediment that can be formed under normal storage conditions, excluding external influences. The prescribed test method is ISO 10307-2 (IP 390+375 is equivalent).

The test method originally used in the industry for determination of total sediment is the Shell Hot Filtration Test; the test results can be existing sediment or potential sediment, depending on the ageing procedure. The results of this test are not equivalent to those of ISO 10307-2, due to a difference in the solvent used for the test. The Shell Hot Filtration test with ageing generally gives slightly higher results.

Viscosity:

Kinematic viscosity is the only accepted method, expressed in mm^2/s at a certain temperature, for bunker fuel deliveries usually 50°C. ISO 8217:1996 lists the maximum kinematic viscosities at 100°C (note: 1 mm^2/s = 1cSt). SSU, SSF and RW1 (Saybolt Seconds Universal, Saybolt Seconds Furol and Redwood No. 1) are obsolete units.

3. Test specifications and precision

ISO 8217:1996 not only specifies the Requirements for Marine Distillate and Residual fuels and the test method references, it also lists the method applicable for the use of precision data in relation to the methods of the test: ISO 4259:1992, “Petroleum products — determination and application of precision data in relation to methods of test”.

The application of precision data in relation to methods of test automatically assumes that the sample taking has been performed to the best industry standard possible, and that the sample is representative for the supply. Experience shows that the sample itself is often the weakest point in the chain. In cases of complaints and claims, FAMM only recognizes the bunker fuel retain samples taken by its representative (e.g. bunker barge attendant) at the moment of the bunkering as valid. The full details are described in the FAMM Terms of Sale.

Should a dispute arise due to a difference between test data obtained on valid retain samples by two different laboratories (one acting on behalf of the supplier, the other on behalf of the customer), ISO 4259 should be used to evaluate the validity of the results. If the reproducibility of the test method is met, both values are considered acceptable, and the average of the two is taken as the true value. If the reproducibility is not met, both results have to be rejected, and the guidelines set forth in ISO 4259 should be followed to solve the problem. This can however be very time-consuming, and is very seldom done in practice. Both parties generally agree to the use of a third laboratory, of which the result will then be binding for both parties.

It has to be noted that reproducibility limits are only applicable between two analysis figures on the same sample (or samples considered as being the same). The reproducibility of a test method may not be invoked to explain a deviation versus a specification limit.

The testing margin, however, has an effect on a single result, e.g. the analysis result on a certain specification test obtained by the end user. If the end user has no other information on the true value of the characteristic than his own (single) test result, it is accepted with 95% confidence that the product fails the specification limit when the result exceeds the spec limit by more than 0.59R (where R is the reproducibility of the test method) in case of an upper limit, and is more than 0.59R lower than the specification limit, in the case of a lower limit.

Although given less credit in real life situations than it really deserves, the significance of the reproducibility may not be underestimated. It is the basis for all quality control against specifications. Without reproducibility data, test results would loose a major part of their significance, since there would be no way to define how close a test result approaches the true value.

Attachment II lists the methods for marine fuel testing listed in ISO 8217:1996, together with their reproducibility. Whenever national standardization methods of testing are used, the full correspondence with the ISO prescribed method has to be checked. There can also be some differences in the precision data.

4. Onboard fuel oil treatment

In the late ’70s, the increasing market demand for distillate type fuels (gasoline, diesel) and the resulting changes in refinery processes to cope with this demand have resulted in a deterioration of the heavy fuel quality. Efficient cleaning of heavy fuel oil is mandatory to achieve reliable and economical operation of diesel engines burning heavy fuel.

Examples:

- Water is a common contaminant in fuel oil. Apart from water content in the fuel oil due to transport, there can be a further contamination in the storage tank due to water condensation as a result of temperature changes.
- Catalyst fines from aluminum silicate catalyst used in the catalytic cracking process may end up in the heavy fuel and have to be removed to avoid abrasive wear of various engine parts.

Fuel from the storage tank is pumped to the settling tank and contaminants (water, solids) sink to the bottom of the tank under influence of the gravity force (g). The rate of separation by gravity, V_g is defined by Stokes’ law:

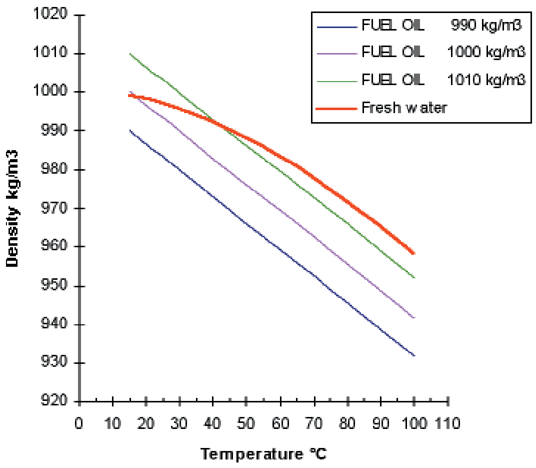
$$V_g = [d^2 (\rho_2 - \rho_1) / 18\, \eta]\ g$$

d : particle diameter
ρ_2: particle density
ρ_1: density of the fuel oil
η : viscosity of the fuel oil
g : gravitational acceleration.

Complete separation in a reasonable period of time can only be achieved by mechanically generated centrifugal force. Fuel from the settling tank is fed to a centrifugal system or purifier and water and solids are separated out of the fuel. The rate of separation in a centrifugal field (V) is defined as:

$$V = V_g \times Z$$

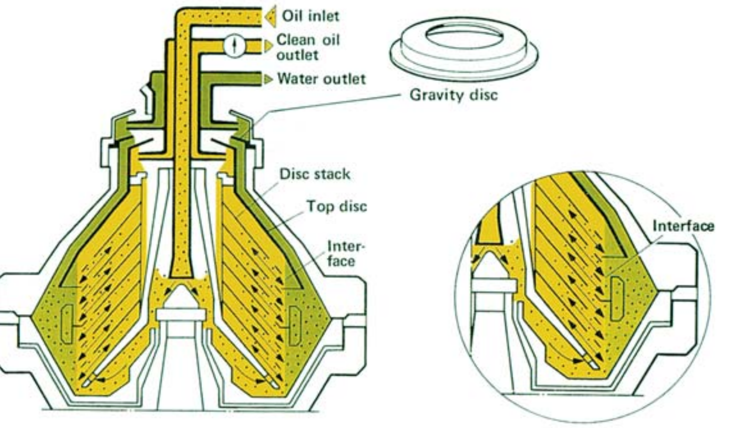
where Z equals $r\omega^2/g$ (r = distance of the particle from the axis of rotation, ω is the angular velocity). The factor Z specifies how much greater the sedimentation rate is in the centrifugal field compared to the gravitational field.



The increasing difference in density between water and fuel oil with increasing temperature is the base for centrifugal cleaning (purification).

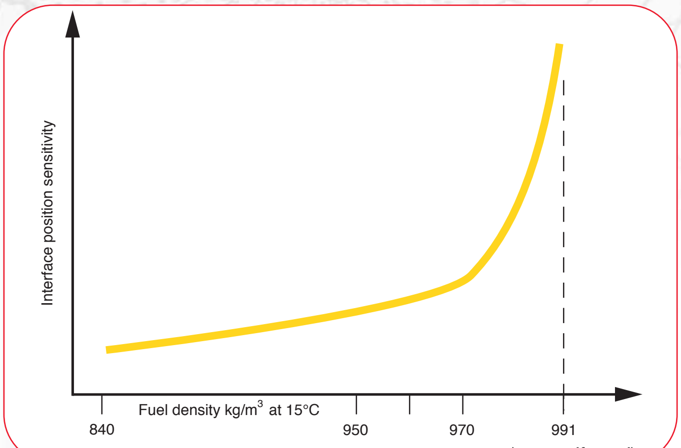
4a. Conventional cleaning with purifiers/clarifiers

In a purifier type separator, cleaned oil and separated water are continuously discharged during operation. An interface is formed in the bowl between the water and the oil (see Figure 1). This interface position is affected by several factors, such as density and viscosity of the fuel oil, temperature and flow rate. Figure 2 illustrates that the position of the interface becomes progressively more sensitive with increasing fuel density. The generally accepted maximum density limit for the conventional purifier is 991 kg/m^3 (at 15°C).



(Source: Alfa Laval)

Figure 1: Correct interface position: the oil is distributed to all channels in the disc stack

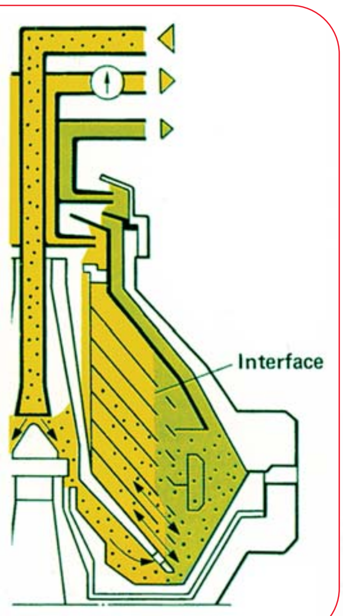


(Source: Alfa Laval)

Figure 2: Interface position sensitivity

In order to achieve optimum separation results with purifiers, the interface between oil and water in the bowl must be outside the disc stack but at the inside of the outer edge of the top disc (detailed view in Figure 1). The position of the interface is affected mainly by the density and the viscosity of the fuel oil. and is adjusted by means of gravity discs. The correct gravity disc is defined as the largest disc that does not cause a broken water seal. With the correct interface position, the oil feed can enter the narrow channels For fuel oils with a viscosity above 180 mm^2/s at 50°C, it is recommended that the highest possible temperature (98°C) be maintained. The fuel oil has to remain in the centrifuge bowl for as long as possible by adjusting the flow rates through the centrifuge so that it corresponds to the amount of fuel required by the engine.

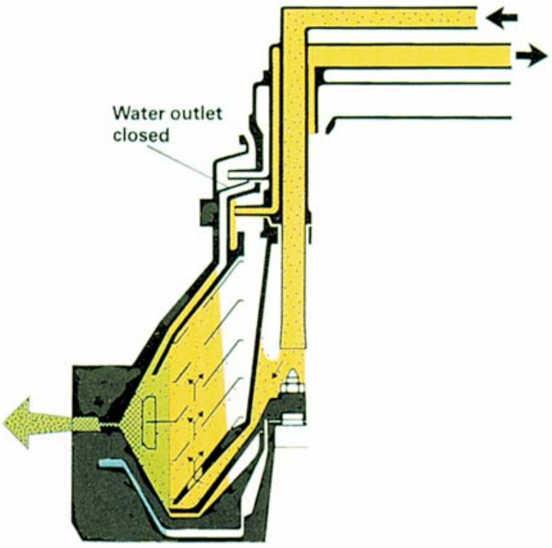
If the interface is in an incorrect position (see Figure 3), the oil to be cleaned will pass only through the lower part of the disc stack, since the upper part is blocked with water. Thus separation is inefficient because only part of the disc stack is being used.



(Source: Alfa Laval)

Figure 3: Incorrect interface position

To ensure optimal cleaning of a fuel oil, a second separator can be used in series operation, e.g. a purifier followed by a clarifier. The density limit of 991 kg/m^3 is not applicable to clarifier operation, but the combined system of purifier and clarifier in series remains restricted to a maximum density of 991 kg/m^3 at 15°C. Heavy movements of the vessel can stir up dirt, water and sludge that have accumulated over time on the bottom of the bunker and settling tanks. It is therefore potentially possible that efficient purification is not always obtained when separators have been put in a parallel purifying function.



(Source: Alfa Laval)

Figure 4: Conventional clarifier

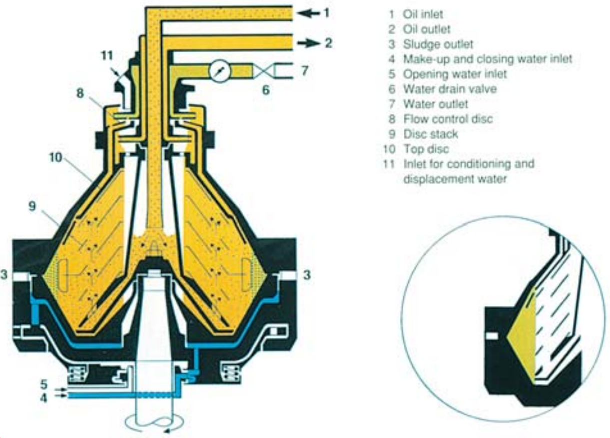
In a conventional clarifier the water outlet is closed off and the separated water can only be discharged with the sludge through the sludge ports at the bowl periphery. A sludge discharge causes turbulence in the bowl and leads to less efficient separation. Consequently, the water handling capability of a conventional clarifier is insufficient for the cleaning of fuel oil if the fuel oil has a significant amount of water (the prior use of a purifier with its continuous water removal is mandatory).

4B. ADVANCED COMPUTER DRIVEN FUEL CLEANING SYSTEMS

Example: ALCAP

Fuel oils with densities above 991 kg/m^3 at 15°C are available on the market and can be purified, e.g. with the ALCAP system, which allows fuel oil densities up to 1010 kg/m^3 at 15°C. Fuel oil is continuously fed to the separator. The oil flow is not interrupted when sludge is discharged.

The ALCAP basically operates as a clarifier. Clean oil is continuously discharged from the clean oil outlet. Separated sludge and water accumulate at the periphery of the bowl. Sludge (and water) is discharged after a pre-set time. If separated water approaches the disc stack (before the pre-set time interval between two sludge discharges is reached) some droplets of water start to escape with the cleaned oil. A water transducer, installed in the clean oil outlet immediately senses the small increase of the water content in the clean oil. The signal from the water transducer is transmitted to a control unit and changes in water content are measured.

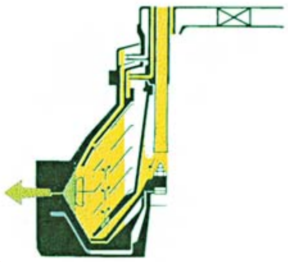


(Source: Alfa Laval)

Figure 5: ALCAP separator

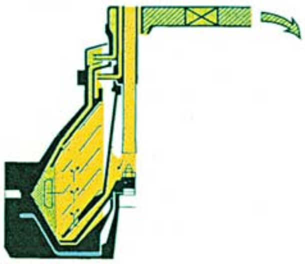
Increased water content in the cleaned oil is considered as the sign of reduced separation efficiency for not only water but for the removal of solid particles as well. When the water content in the cleaned oil reaches the pre-set trigger point, the control unit will initiate an automatic discharge of the water that has accumulated in the bowl through the water drain valve.

In summary: water is discharged either with the sludge at the periphery of the bowl (Figure 6a) (separated water does not reach the disc stack in the pre-set time between sludge discharges), or through the water drain valve (Figure 6b) (separated water reaches the disc stack before the pre-set time between sludge discharges).



(Source: Alfa Laval)

Figure 6a: Discharge of separated water through sludge outlet.



(Source: Alfa Laval)

Figure 6b: Discharge of separated water through water drain valve.

5. FUEL OIL STABILITY AND COMPATIBILITY

As discussed in the chapter on marine fuel specifications, total potential sediment is an important specification for heavy fuels. Currently, nearly all heavy fuel is marketed with the stability guarantee of total potential sediment (ISO 10307-2) 0.10% (m/m) max., and stratification in heavy fuel oil tanks due to stability problems of a heavy fuel delivery can be excluded when this specification is met.

The reason for the specification requirement is the presence of asphaltenes in the heavy fuel. Asphaltenes are present in crude oil, and are defined as the fraction insoluble in n-heptane, but soluble in toluene. Their concentration in the crude oil is dependent on the crude oil origin itself. Asphaltenes are the highest molecular weight molecules in the crude, and contain all of the organically bound vanadium and most of the nickel found in the crude. They further contain a relatively high percentage of sulphur and nitrogen. Their hydrogen content (and hence combustion characteristics) can be quite different from one crude to another. Asphaltenes have a predominantly aromatic structure and the C and H atoms are combined in ring structures as illustrated below.

Asphaltenes are polar molecules, kept in colloidal suspension[2] by their outer molecular structure. Thermally cracked asphaltene molecules have lost part of their outer structure (depending on the severity of the thermal cracking process) and even visbreaking, which is a relatively soft thermal cracking process, affects this outer molecular structure. If too much is removed, part of the asphaltenes can start clogging together, and will no longer be kept in suspension in the fuel matrix: sludge will be formed. Avoiding the formation of this sludge during the manufacturing of visbroken fuel is the responsibility of the refinery. A change in the fuel matrix composition by blending a stable visbroken fuel to a lower viscosity can also affect the stability of the asphaltenes. This means in practice that viscosity reduction of a visbroken fuel with a paraffinic type cutterstock can make the fuel unstable; when this would happen, the two fuels are said to be incompatible. When two fuels, which are mixed together, do not cause any asphaltene coagulation, they are compatible with each other. Test methods exist to predict the final stability of a fuel mixture, and hence the compatibility of the two components. In practice one chooses a cutter stock with a high enough aromaticity to keep the asphaltenes dispersed (e.g. by adding heavy and/or light cycle oil) and to provide an adequate stability reserve.

Two heavy fuels with diverse compositions (e.g. one an atmospheric type heavy fuel from paraffinic type crude, and the other from a relatively severe visbreaker operation) can also be incompatible with each other. The potential occurrence of compatibility problems between two different heavy fuels has to be kept in mind for fuel storage, also by the end user.

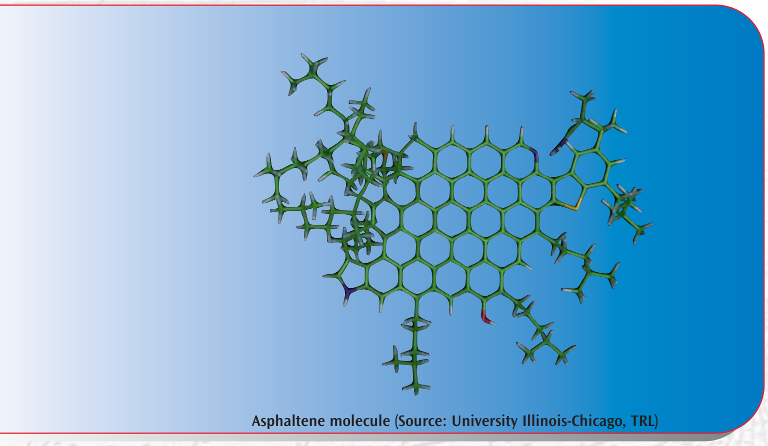
6. COMMINGLING OF FUELS

It is obvious from the discussion on fuel compatibility that indiscriminate commingling of fuels can lead to stability problems of the final fuel, due to incompatibility of the fuels used as blend components. Eventual problems/damages arising from the commingling of fuels are always the responsibility of whoever took the decision for the commingling. Fuel suppliers guarantee the stability of the fuel they deliver, but can not be held responsible for compatibility problems with another fuel.

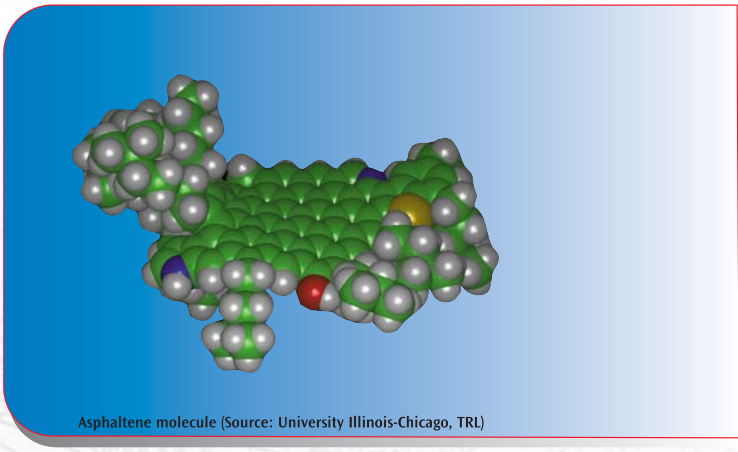
Rules, in descending order of safety:

- Do not commingle fuels.
- If commingling is considered unavoidable, check the compatibility of the fuels in advance, and make a final decision based on the test result.
- If a compatibility check is impossible (one component unavailable at the moment the decision has to be made), reduce the amount of one fuel to a minimum before adding the second fuel.

Note: There is generally not a big risk of incompatibility between fuels of the same viscosity grade when they have very similar densities.



Asphaltene molecule (Source: University Illinois-Chicago, TRL)



Asphaltene molecule (Source: University Illinois-Chicago, TRL)

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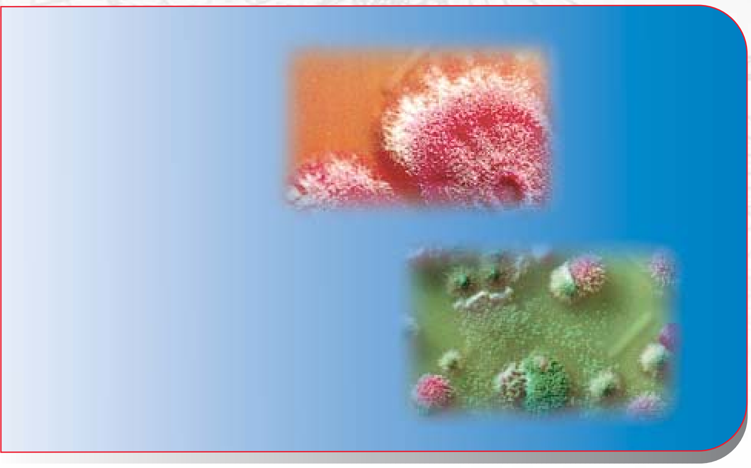
[2] *Colloidal suspension: a suspension in which gravitational forces are negligible.*



7. Microbiological contamination

Plugging of filters on gasoil and marine distillate fuel feed lines can be caused by microbiological contamination (bacteria, fungi and yeast).

Microbiological contamination can always occur, especially if the temperature conditions are favorable (between 15 and 40°C, for the most common types), and if non-dissolved water is present in the fuel.

NO WATER = NO MICROBIOLOGICAL CONTAMINATION.

The ideal conditions for the development of microbiological contamination occur in tropical and sub-tropical regions: high air humidity combined with a high ambient temperature.

A first screening for the possible site of the contamination can be made from the number of complaints: several simultaneous complaints make the supply chain suspect, a single complaint makes a contamination at the site of the customer more plausible.

Following is a summary of the topics quoted by VOS, the Dutch organization that supervises the quality aspects of gasoil delivered in the Netherlands to fishing and inland waterway vessels:

- Good water-housekeeping is essential.
- No water: no bacterial contamination.
- Fuel producing companies, dealers, and end-users have a common responsibility: bacterial contamination can occur in each link of the chain.
- Consequences of bacterial contamination: filthy fuel system, plugged fuel filters and erratic engine operation.
- How can it be recognized: slime, sludge, possibly corrosion in filters, tanks, lines.
- What can the end-user do:
  - Make sure no water enters the gasoil
  - Check filters
  - Check bunker and day tank for water
  - Whenever necessary drain tanks
  - Have permanent connection devices at the fuel receiving site
  - Have de-aerating openings which can be closed (to prevent waves entering the bunkertank)

On-site macroscopic (visual) examination can give a first screening between the contaminated and non-contaminated tanks. The following facts give an indication of a possible microbiological contamination:

- Gasoil is hazy and/or contains suspended fluffy material
- Emulsion or a slimy interface layer between water and gasoil
- A turbid, badly smelling water bottom, with sludge-like deposits

Bacteria and fungi are the most important agents of microbiological contamination (yeast normally only occur as co-contaminant). All are living cells, which multiply through cell division.

The prime contamination of fuel is nearly always by aerobic bacteria and/or by fungi. Both use the n.–paraffin fraction of the fuel as nutrient. Aerobic bacteria need oxygen for their metabolism and evolve at the interface between the water and the gasoil; fungi (aerobic) also attach themselves to the tank wall. When oxygen is no longer present, anaerobic bacteria start to develop. The anaerobic metabolism process generates hydrogen sulphide (smells like rotten eggs in low concentrations, is odorless in higher and potentially lethal concentrations). Besides being a very dangerous toxin, hydrogen sulphide can also cause severe corrosion.

It is obvious that anaerobic microbiological contamination has to be avoided at all cost, and this is only possible by keeping a close control on the presence of microbiological contaminants in the complete fuel system, from manufacturing to end use. In regions with moderate climatic conditions, efficient water draining is often sufficient to avoid exponential growth; in sub-tropical and tropical climates the continuous use of a biocide is often the only way to avoid problems. Biocides are also used worldwide to combat “imported” microbiological problems. Commercially available biocides have been developed to eliminate the total microbiological contamination (bacteria, fungi and yeast). There are two different types of biocides: water soluble and oil soluble. To eliminate microbiological contamination in fuel tanks, the water soluble biocides are generally most cost effective. The treat rate can differ according to the type and severity of the contamination (and the amount of non-removable water). Water drained from tanks after a biocide treatment cannot be sent directly to a biological water purification system, the biocide has to be deactivated first.

8. FUEL CONTAMINATION IN LUBRICANTS

During the last decade, the demands on marine lubricants have changed considerably for medium speed engines: the engines are run at higher pressures and temperatures. This makes it more difficult to cope with the problems of borderline lubrication.

The changes to engine construction and the deterioration of the heavy fuel quality in the late 1970s, early 1980s, have generated problems with conventional type marine lubricant formulations (high detergency, low dispersancy), such as liner lacquering, undercrown deposits, increased oil consumption, base number depletion, hot corrosion of the piston crown, oil scraper ring clogging, and increased piston deposits.

Medium speed engine blackening due to HFO contamination of the lubricant, piston head corrosion and undercrown deposits were the typical consequences of increased fuel pump pressure and the change over from atmospheric type heavy fuel to visbroken type heavy fuel when conventional type marine lubricant was being used.

FAMM has developed high dispersancy lubricants to cope with the trunk piston engine lubrication problems and the asphaltene contamination of the lubricant. This oil was developed specifically to cope with the increasing mechanical and thermal stresses and changes in fuel quality.

The following text and photos, taken from a FAMM lubrication brochure, further illustrate the problems encountered with the use of a conventional lubricant in medium speed engines, using visbroken heavy fuel. Figure 7 clearly illustrates the camshaft box cleanliness obtained with the Taro DP/XL technology, and contrasts dramatically with the blackening of the camshaft box using a conventional lubricant, as illustrated in Figure 8.

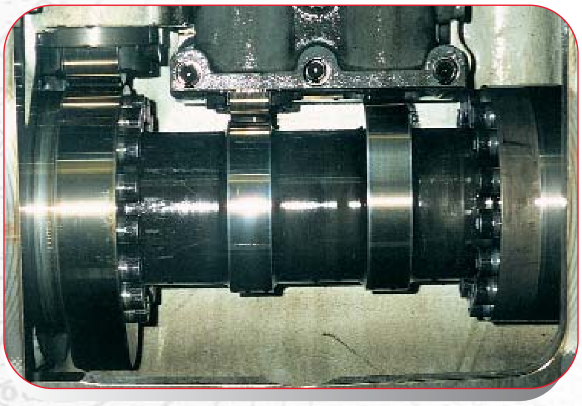


Figure 7: Camshaft box cleanliness obtained with Taro 40 XL 40 despite 4% heavy fuel contamination

MAIN PROBLEMS ENCOUNTERED WITH A CONVENTIONAL LUBRICANT:

1. Engine blackening due to HFO contamination

The increase of the fuel pump pressure up to 1600 bar in medium speed diesel engines results in a higher incidence of fuel pump leakage, which means an increased contamination of the fuel by the lubricant. Most of the HFOs originate from visbreaking installations and the asphaltenes don’t dissolve in the paraffinic lubricant. They coagulate and form floating asphalt particles of 2 to 5 microns in the lubricant. These particles are very sticky and form black deposits on all metal surfaces of the engine, resulting in black deposits in the camshaft box and in the crankcase. They cause oil scraper ring clogging, sometimes resulting in high oil consumption. They may form deposits in the hot areas of the piston grooves and on the piston lands and in the cooling spaces of the piston. If an oil barrier is used to seal the fuel pump, asphaltene coagulation can occur on the surface of the fuel pump plunger, sometimes resulting in fuel pump blockages. These deposits can obstruct the fuel pump drain.

This results in excessive fuel ingress into the lubricant, aggravating the deposit problems and causing serious viscosity increases due to fuel admixture. The problems can be minimized by effective purification removing the asphalt particles from the lubricant.

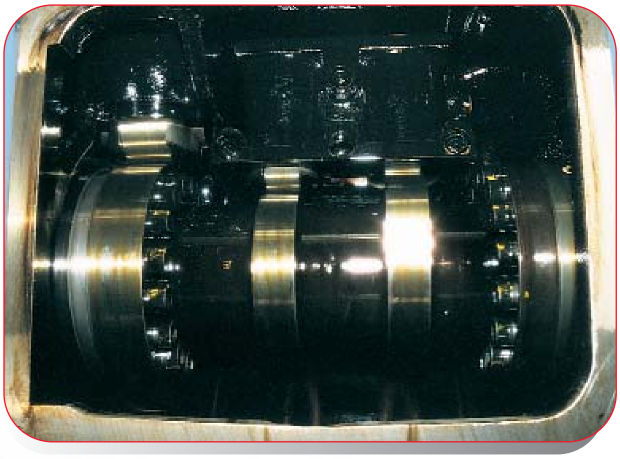


Figure 8: Typical blackening of camshaft box as a result of heavy fuel contamination of conventional type lubricant

Figure 9: Conventional type lubricant; typical crankcase blackening as a result of heavy fuel contamination of lubricant

2. Piston head corrosion and undercrown deposits

The tendency to increase the piston undercrown temperature can cause carbon deposits on the piston undercrown due to thermal carbonization of the lubricant. Also, asphalt particles originating from HFO can adhere to the piston undercrown when conventional type lubricants are being used. Undercrown deposits in combination with high load operations can lead to piston head corrosion. Undercrown deposits cause a reduction in the cooling effect, resulting in about 100°C increase in piston temperatures. Above 450°C, some Na/V oxides (when present) can form a melt with the piston crown material causing hot corrosion on the top of the piston.

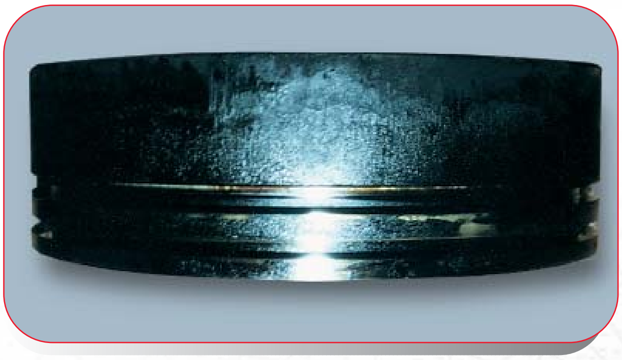


Figure 10: Conventional type lubricant; typical piston deposits in a medium speed engine suffering from heavy fuel contamination

Figure 11: Conventional type lubricant; typical oil scraper ring deposits in a medium speed engine suffering from heavy fuel contamination

9. USED OIL IN HEAVY FUEL

The use of used lubricants in marine fuels first surfaced as a potential problem in the mid 1980s. A “hard” sludge was sometimes produced when centrifuging the fuel, that was allegedly due to additives present in lubricating oils. Both CIMAC and ISO 8217 working groups consider that Ca, Zn and P, when found together in fuel in a significant concentration (still to be determined), are indicators for the presence of used oil.

A rule of thumb is that 10 mg/kg Zn corresponds to approximately 1% used oil in the fuel. This is only an approximation, because the zincdithiophosphate content of lubricants can be quite variable (some lubricants don’t contain any).

Attachments

Attachment I: Crude oil refining

The purpose of crude oil refining is to convert crude and other feedstocks into saleable products. The desired products are mainly gasoline, kerosene, jet fuel, gasoil and diesel.

In order to obtain these products, crude oil is first separated into fractions by distillation, and then the different fractions are further processed in order to obtain the desired characteristics and optimum yield.

The different processes used in a modern refinery are summarized below.

1. Crude oil desalting

Water and inorganic salts are removed in an electrostatic field. The main purpose of crude oil desalting is to protect the refining process units against corrosion.

2. Atmospheric distillation

Crude oil is a product with a very wide boiling range. In an atmospheric distillation column the fractions boiling below 360°C are distilled off under reflux, and, according to boiling range, recovered as naphtha, kero, and gasoil type stocks. Atmospheric distillation is limited to a maximum temperature of 360°C, because otherwise coking would start to occur, and this is not desirable at this stage of crude oil refining.

3. Vacuum distillation

In order to distill off a heavier cut, without exceeding the 360°C temperature limit, a second distillation is done under reduced pressure: the vacuum distillation. The distillate fraction of the vacuum distillation unit is the feedstock for a catalytic cracking unit (see item 4).

4. Catalytic cracking (e.g. fluidized bed catalytic cracking)

The main feedstock for a catalytic cracker is vacuum gasoil. The cracking operation breaks large molecules into smaller, lighter molecules. The process runs at high temperatures, and in the presence of the appropriate catalyst (crystalline aluminum silicate).

Atmospheric residue, with a low metal and MCR content, can also be used as catalytic cracker feed, necessitating an adjustment of the catalyst type.

The main purpose of a catalytic cracker is to produce light hydrocarbon fractions, which will increase the refinery gasoline yield.

Additional streams coming from the catalytic cracker are light cycle oil (increases the gasoil pool) and heavy cycle oil (base stock for carbon black manufacturing). Both streams are also used in heavy fuel oil blending.

5. Catalytic hydrocracking

Some refineries have catalytic hydrocracking as a supplementary operation to catalytic cracking. Catalytic hydrocracking further upgrades heavy aromatic stocks to gasoline, jet fuel and gasoil type material. The heaviest aromatic fractions of a cat cracker are the normal feedstock for a hydrocracker. Hydrocracking requires a very high investment , but makes the refinery yield pattern nearly independent from the crude oil feed.

6. Visbreaking

The feedstock of a visbreaker is the bottom product of the vacuum unit, which has an extremely high viscosity. In order to reduce that viscosity and to produce a marketable product, a relatively mild thermal cracking operation is performed. The amount of cracking is limited by the overruling requirement to safeguard the heavy fuel stability.

The light product yield of the visbreaker (around 20%) increases the blendstock pool for gasoil.

7. Coking (delayed coking, fluid coking, flexicoking)

Coking is a very severe thermal cracking process, and completely destroys the residual fuel fraction. The yield of a coker unit is lighter-range boiling material, which ultimately goes to the blending pool for the lighter products, and coke, which is essentially solid carbon with varying amounts of impurities. The heavier distillate fraction of a coker can be used as feedstock for a hydrocracker (see item 5).

The above listed processes give an idea of the different type of operations done in a refinery, but many more process units are required before the end products leave a refinery. Most processes improve the characteristics of the different refinery streams to meet the technical requirements of the end products, others are needed to meet environmental limits (mainly sulphur reduction, both in the end-products and in the refinery emissions).

8. Catalytic reforming and Isomerization

Both processes are in fact catalytic reforming, and are intended to upgrade low octane naphta fractions of the crude distillation unit into high octane components for gasoline production. The type of catalyst and the operating conditions determine if the reforming is mainly to iso-paraffins, or to aromatics. The terminology “reforming” is generally used for the change to aromatics, while the change to iso-paraffins is referred to as “isomerization”. Isomerization is normally done on a lighter fraction (C5/C6), while reforming is done on the heavy naphtha fraction (C7 and heavier, up to 150°C).

9. Alkylation

This is another process intended to increase the yield of valuable gasoline blend components. Alkylation is a catalyst steered combination reaction of low molecular weight olefins with an iso-paraffin to form higher molecular weight iso-paraffins. The feed to the alkylation unit is C3 and C4s from the catalytic cracker unit, and iso-butane.

10. Hydrotreating

A hydrotreating process is, as the name indicates, a process, which uses hydrogen to remove impurities from product streams, and replaces them with hydrogen. Hydrotreating is generally used to remove sulphur (re very low sulphur limits in the specifications of gasoline and gasoil) and is then called hydro-desulphurization. It is a catalytic process. The process is generally used on kerosene and gasoil fractions. Residual hydro-desulphurization is an existing process, and is in theory feasible, but the economics are not favorable.

11. Merox

A merox unit is used on naphtha and kerosene streams. It is a catalytic process which is not intended to remove the sulphur from the stream, but to convert mercaptan sulphur type molecules (corrosive, and with a very obnoxious smell) into disulphide type molecules.

12. Sulphur recovery

As a result of the removal of sulphur from the refinery streams by hydrotreating, the generation of hydrogen sulphide during cracking and coking, refinery gases contain a very high concentration of hydrogen sulphide. The simple solution to eliminate the hydrogen sulphide (extremely toxic) is to burn it, but this then generates SO_2, which contributes to acidification problems. In order to safeguard the environment, the hydrogen sulphide is converted in refineries to elemental sulphur. This is typically accomplished by extracting the hydrogen sulphide from the refinery gas by a chemical solvent, e.g. an aqueous amine solution. The rich solution is then preheated and stripped by steam. The Claus process consists of the partial combustion of the hydrogen sulphide rich gas stream (sufficient air is introduced to combust $^1/_3$ of the H_2S to SO_2). This SO_2 then reacts (under influence of a catalyst) with H_2S in the order of 1 SO_2 for 2 H_2S, and thus provides elemental sulphur. The tail gas of the Claus unit is still rich in SO_2, and environmental legislation can require the further clean-up of this tail gas.

Attachment II: Reproducibility (R) of marine fuel test methods

Density at 15°C, kg/m^3

ISO 3675

- For transparent, non viscous products:
  $R = 1.2\ kg/m^3$ or $0.0012\ kg/l$
- For opaque products:
  $R = 1.5\ kg/m^3$ or $0.0015\ kg/l$

ISO 12185

- For transparent middle distillates:
  $R = 0.5\ kg/m^3$ or $0.0005\ kg/l$
- For crude oils and other petroleum products:
  $R = 1.5\ kg/m^3$ or $0.0015\ kg/l$

Kinematic viscosity, mm^2/s

ISO 3104

Heavy fuels: at 50°C : $R = 0.074\chi$
at 100°C : $R = 0.04(\chi + 8)$

Where χ is the average of the results being compared

Flash point, P.M., closed tester

ISO 2719

For flash point < 104°C: $R = 3.5°C$

For flash point > 104°C: $R = 8.5°C$

Pour Point, °C

ISO 3016

$R = 6.59°C$

Cloud Point, °C

ISO 3015

For distillate fractions: $R = 4°C$

Sulphur, % (m/m)

ISO 8754

$R = 0.055(\chi + 0.8)$ where χ is the mean sulphur content

Cetane index (4 variable equation)

ISO 4264

Precision is dependent on the precision of the original density and distillation recovery temperature determinations that enter into the calculation.

Micro carbon residue, % (m/m)

ISO 10370

$R = \chi^{2/3} \times 0.2451$

Where χ is the average of the results being compared

Ash, % (m/m)

ISO 6245

For ash content between 0.001 and 0.079 wt %: $R = 0.005$

For ash content between 0.080 and 0.180 wt %: $R = 0.024$

Sediment by extraction, % (m/m)

ISO 3735

$R = 0.033 + 0.255\chi$

Where χ is the average result in percent

Total existent sediment, % (m/m)

ISO 10307-1

Heavy fuels: $R = 0.341\sqrt{\chi}$

Distillate fuels containing heavy components:
$R = 0.174\sqrt{\chi}$

Where χ is the average of the test results in % (m/m)

Total sediment, potential aging, % (m/m)

ISO 10307-2

Heavy fuels: $R = 0.341\sqrt{\chi}$

Distillate fuels containing heavy components:
$R = 0.174\sqrt{\chi}$

Where χ is the average of the test results in % (m/m)

Water, % (v/v)

ISO 3733

- Water collected between 0.0 and 1.0 ml:
  $R = 0.2$ ml
- Water collected between 1.1 and 25 ml:
  $R = 0.2$ ml or 10% of mean, whichever is greater

Vanadium, mg/kg

ISO 14597

- The method is applicable to products having V content in the range of 5 to 1000 mg/kg, although reproducibility data have only been determined up to 100 mg/kg for V

  For V content between 5 and 30 mg/kg:
  $R = 5$ mg/kg

  For V content between 31 and 100 mg/kg:
  $R = 10$ mg/kg

Cat fines Al+Si, mg/kg

ISO 10478

ICP detection: Al: $R = 0.337\chi$
Si: $R = 0.332\chi$

AAS detection: Al: $R = 0.7890\chi^{2/3}$
Si: $R = 1.388\chi^{2/3}$

Where χ is the average result in mg/kg

Attachment III: Gas turbine fuel requirements

Most heavy-duty gas turbines operate on natural gas and distillate fuels.

Gas turbines operating on natural gas require minimum fuel treatment. Distillate fuels, immediately after refining, have no, or extremely low contamination levels of water, solids and trace metals. Contamination (mainly by water) during transport can not be excluded, and centrifuging is the best method for the removal of water and solids (can contain sodium salts). Sodium salts are very detrimental for gas turbines, and seawater contamination must be completely removed.

Gas turbine manufacturers have also developed efficient technologies for gas turbine operation with ash forming fuels (e.g. heavy fuels), as a cost-effective option against gasoil for sites where natural gas will not be available in the foreseeable future.

The use of heavy fuels requires that utmost attention be paid to two types of potential hot path corrosion:

- Sulphidation corrosion, caused by alkaline sulphates (mainly Na_2SO_4).
- Vanadic corrosion, caused by low melting vanadium oxides (V_2O_5).

Sulphidation corrosion is avoided by removing the sodium and potassium from the fuel by stringent water washing up to the level Na+K < 1 mg/kg.

Vanadic corrosion is counteracted by the addition of magnesium additives to the fuel from the moment V > 0.5 mg/kg. The complex oxides between Mg and V which are then formed, are no longer corrosive (traditionally, a m/m ratio Mg/V of three is adhered to).

Heavy-duty gas turbines have been operating satisfactorily on ash forming fuels since mid-1980s. It is clear that the need for magnesium additivation to combat vanadic corrosion imposes a technical and economical upper limit on the vanadium content of the fuel.

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VOS, Publication Stichting VOS

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Notes

FAMM

FUEL AND MARINE MARKETING

The Company

Fuel and Marine Marketing LLC (FAMM), was formed November 1, 1998 by Texaco and Chevron, combining the global residual fuel and marine lubricants marketing businesses of both companies.

Marine Lubricants

FAMM is one of the largest suppliers of marine lubricants in the world. FAMM has a superior line of marine lubricants based upon proven experience of both parent companies, Texaco and Chevron. In addition to superior products, our seasoned marine professionals and technical support staff, including laboratories in Rotterdam and Ghent, offer you the best service and support available.

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FAMM is a premier supplier of marine fuels worldwide, offering consistently high quality products with timely delivery and service. Additionally, FAMM offers price risk management alternatives for your fuel needs. FAMM has a vast network of supply – including Texaco, Chevron and Caltex fuels – to meet your requirements. Make FAMM your first choice for marine fuels.

Industrial Products

FAMM's industrial customers include power plants throughout the United States, Latin America, Europe and Asia that have learned to rely on us to deliver their fuels and lubricants on time and on spec.

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