Everything You Need to Know About Marine Fuels

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Contents

Liquid fuel…combustion…mechanical energy
…propulsion energy and electricity

I. Introduction

Through 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.

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 motor ship started to dominate. 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 World War I and World War II, the share of marine engine-driven ships increased to approximately 25 percent of the overall ocean-going fleet tonnage.

A series of innovations of 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 ships using residual fuel oil gained in popularity and in the second half of the 1960s, motor ships overtook steamships, both in terms of numbers, and in gross tonnage. By the start of the 21st century, motor ships accounted for 98 percent of the world fleet.

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

Chevron has been in the business
of finding, producing, trading,
and refining crude oil for
over 125 years.

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:

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

Most importantly, these four 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 has been acquired, it 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 are based on:

1. Hydrocarbons:
   - Paraffinic crudes
   - Naphthenic crudes
   - Asphaltenic (aromatic) crudes

   Each crude oil contains the three different types of hydrocarbons, but the relative percentage may vary widely. For example, there is paraffinic crude in Saudi Arabia, naphthenic crude in some Nigerian formations and asphaltenic crude in Venezuela.

2. American Petroleum Institute (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. Sulphur content: The ever-growing concern for the environment and the impact on refining cost calculations are the basis for this classification.
   - Sweet crude (low sulphur)
   - Sour crude (high sulphur)

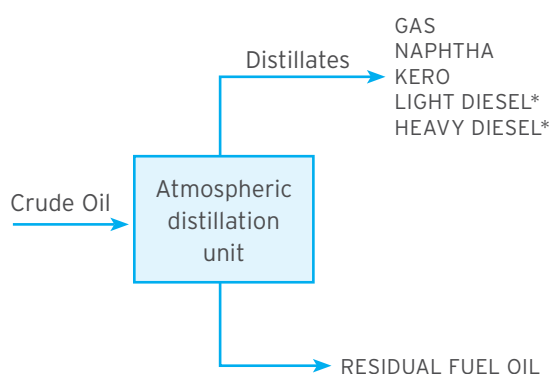## 3. Crude oil refining and stocks for marine fuel blending

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

Typical refining schemes and the influence on marine fuels

Straight run refinery
Atmospheric crude distillation and further refining of distillates:

```
                                              GAS
                          Distillates         NAPHTHA
                                              KERO
                                              LIGHT DIESEL*
                                              HEAVY DIESEL*

                        ┌──────────────┐
                        │ Atmospheric  │
  Crude Oil  ──────────▶│ distillation │
                        │     unit     │
                        └──────────────┘

                                    ──────▶   RESIDUAL FUEL OIL
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* Diesel refers here to specific atmospheric distillation cuts, and is not related to an engine application.

Straight run stocks for marine fuel blending
Light diesel, heavy diesel, and straight run residue

Straight run marine gasoil and distillate marine diesel (MDO)
Marine gasoil and distillate marine diesel oil (MDO) are manufactured from kero, light, and heavy gasoil fractions.

Straight run IFO 380 mm²/s (at 50°C)
This grade is obtained by blending the atmospheric residue fraction (typical viscosity of about 800 mm²/s at 50°C) with a gasoil fraction.

Straight run lower viscosity grade IFOs
Blending to lower grade IFOs is done from the IFO 380 mm²/s (at 50°C) using a gasoil cutter stock 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 marine fuels leads to relatively low densities for these products, ensuring easy and efficient onboard fuel purification.

The product slate of a straight run refinery, with its heavy fuel production of approximately 50% of the crude feed, does not correspond to the product demand in industrialized countries where the ever-growing demand for light products (jet fuel, gasoline, and gasoil) coincides 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 lighter, hence, more valuable, fractions and to the construction of complex refineries.

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 1980s and are intended to boost gasoline production. All further information herein is based on a complex refinery. The main marine fuel blending components from a fluidized bed catalytic cracking (FCC) 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.

* FCC: Fluidized Bed Catalytic Cracking
* LCO: Light Cycle Oil
* HCO: Heavy Cycle Oil
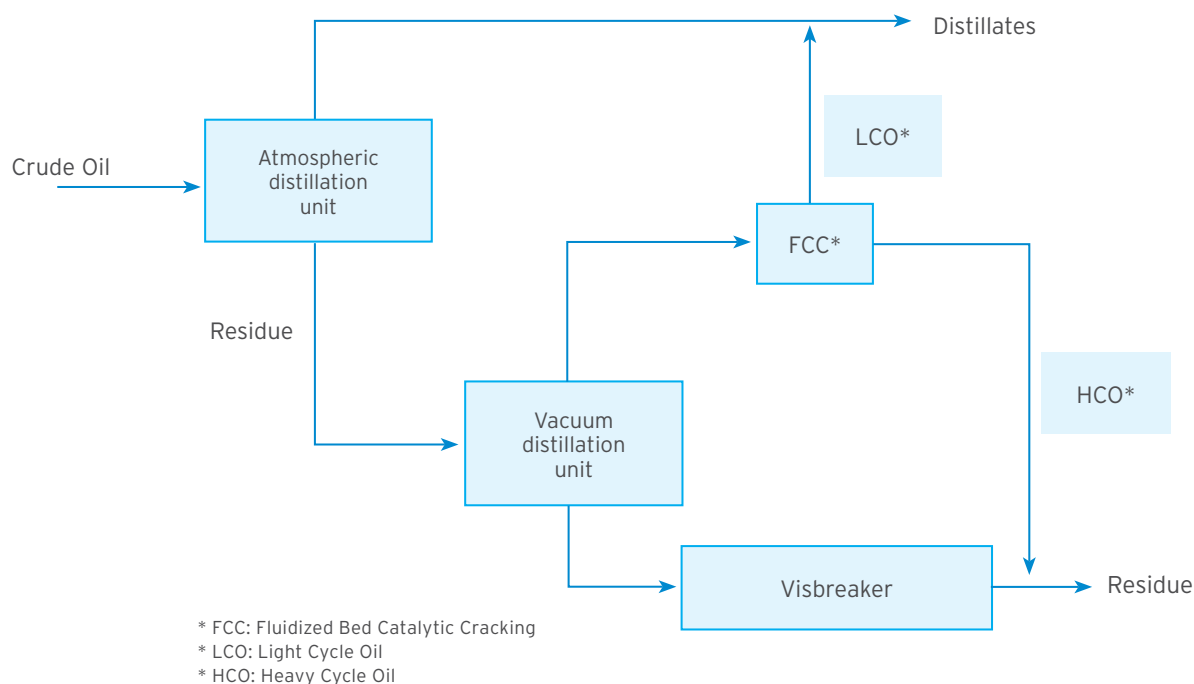
Atmospheric residue is used as feedstock for the vacuum unit and will seldom be available for fuel blending.

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

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

Marine gasoil (MGO/DMA/DMZ)[1]

A new blend component has appeared — light cycle (gas) oil — that 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 from an atmospheric distillation refinery. The density will typically be close to 860 kg/m³ (at 15°C). No performance or handling differences with atmospheric gasoil are to be expected. In 2010, the fourth edition of ISO 8217 standard

1. Marine products or grades are designated by a symbol consisting of a group of letters which together constitute a code. This code consists of:
a) the initials "ISO";
b) the letter "F" for the class of fuel;
c) the category of fuel, consisting of three letters:
    1) the family letter, "D" for distillate or "R" for residual,
    2) "M", designating the application "Marine",
    3) a letter, e.g. "A", "B"..."Z", which taken separately has no significance, but has meaning in relation to the particular properties in accordance with the product specification, ISO 8217:2010;
d) a number that corresponds to the maximum kinematic viscosity of the residual fuel, in square millimeters per second (mm²/s) at 50°C.

A product or grade may be designated in the complete form or in an abbreviated form, e.g. : ISO-F-RMG 380 or RMG 380.

introduced an additional grade of marine gasoil, DMZ, which has a higher minimum viscosity than DMA but is otherwise identical in its characteristics to DMA marine gasoil.

Note: Worldwide, marine gasoil has a sulphur content between approx. <0.10 and 1.50 m/m %. In some areas marine gasoil is, in fact, automotive diesel (not including biodiesel), with added marker and dye and without the excise duty applicable to automotive fuel. In the EU, the maximum S level of automotive diesel is currently 0.0010 m/m % or 10 ppm. The alkalinity (BN) of the lubricant may have to be adjusted accordingly. (See also Chapter III-2a on Sulphur.)

Distillate marine diesel (MDO/DMB)

Distillate marine diesel (commercial denomination) typically has a lower cetane index than marine gasoil, and has 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 m/m %. Due to EU legislation (Directive 2005/33/EC amending Directive 1999/32/EC), the sale of marine diesel oil with a sulphur content above 1.5 m/m % within the EU is prohibited since August 11, 2006 (see also Chapter III-2a on Sulphur).

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 asphaltenes[2], 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 mm²/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 catalyst 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. From there they end up in heavy fuel blended with HCO (see also Chapter III-2).

2. Asphaltenes: residual fuel components that are insoluble in heptane but soluble in toluene

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

LC(G)O (typical viscosity at 50°C: 2.5 mm²/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 mm²/s

In ISO 8217:2010, blended marine diesel known as DMC has been reclassified as a residual fuel oil, RMA10. With atmospheric refining, RMA10 can contain up to 10% IFO with either marine gasoil or distillate marine diesel. With complex refining, RMA10 no longer corresponds to a specific composition and extreme care must be used when blending this grade to prevent stability and/or combustion problems.

The other low viscosity residual fuel oil grades are generally blended starting from 380 mm²/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 constructed in such a way that the product stability is safeguarded, while at the same time direct or indirect density limits are fulfilled (see also Chapters III-2).

III. Fuel Oil

1. Fuel oil applications

All fuel oil applications create energy by burning fuel oil. Fuel oil combustion (oxidation reaction) releases a large amount of heat, which can be used for steam generation, for example, in steam boilers. The high volume (pressure) of the combustion gases can be used 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 to 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 led to the introduction of co-generation. In co-generation, some of the electrical energy lost is used to generate low-pressure steam, suitable for a wide range of heating applications.

2. Fuel specifications

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 sulphur dioxide (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. Through the late 1970s, 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).

An international ISO standard has existed since 1987: ISO 8217. The stated purpose of ISO 8217 is to define the requirements for petroleum fuels for use in marine diesel engines and boilers prior to appropriate treatment before use, and is provided for the guidance of interested parties such as marine equipment designers, suppliers and purchasers of marine fuels. These specifications are regularly revised to accommodate changes in marine diesel engine technology, crude oil refining processes and environmental developments. The ISO 8217:2010 specifications for marine fuels will be discussed in detail in Chapter III-2a (see pages 8 & 9, Tables 1 & 2). The specifications can also be applicable to fuels for stationary diesel engines of same or similar make as those used for marine purposes.

The most important specifications to ensure reliable engine operation with residual 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

Table 1: Requirements for distillate marine fuels

Characteristics	Unit	Limit	Category ISO-F-				Test method reference
			DMX	DMA	DMZ	DMB	
Kinematic viscosity at 40°C[a]	mm²/s	max.	5,500	6,000	6,000	11.00	ISO 3104
		min.	1,400	2,000	3,000	2,000	
Density at 15°C	kg/m³	max.	−	890.0	890.0	900.0	see 7.1 ISO 3675 or ISO 12185
Cetane index	−	min.	45	40	40	35	ISO 4264
Sulfur[b]	mass %	max.	1.00	1.50	1.50	2.00	see 7.2 ISO 8754 ISO 14596
Flash point	°C	min.	43.0	60.0	60.0	60.0	see 7.3 ISO 2719
Hydrogen sulfide[c]	mg/kg	max.	2.00	2.00	2.00	2.00	IP 570
Acid number	mg KOH/g	max.	0.5	0.5	0.5	0.5	ASTM D664
Total sediment by hot filtration	mass %	max.	−	−	−	0.10[e]	see 7.4 ISO 10307-1
Oxidation stability	g/m³	max.	25	25	25	25[f]	ISO 12205
Carbon residue: micro method on the 10% volume distillation residue	mass %	max.	0.30	0.30	0.30	−	ISO 10370
Carbon residue: micro method	mass %	max.	−	−	−	0.30	ISO 10370
Cloud point	°C	max.	−16	−	−	−	ISO 3015
Pour point (upper)[d] winter quality	°C	max.	−[j]	−6	−6	0	ISO 3016
Pour point (upper)[d] summer quality	°C	max.	−[j]	0	0	6	ISO 3016
Appearance	−	−	Clear and Bright[k]			[e,f,g]	see 7.6
Water	volume %	max.	−	−	−	0.30[e]	ISO 3733
Ash	mass %	max.	0.010	0.010	0.010	0.010	ISO 6245
Lubricity, corrected wear scar diameter (wsd 1.4) at 60°C[h]	µm	max.	520	520	520	520[g]	ISO 12156-1

a   1 mm²/s = 1 cSt.

b   Notwithstanding the limits given, the purchaser shall define the maximum sulfur content in accordance with relevant statutory limitations. See Annex C.

c   Due to reasons stated in Annex D, the implementation date for compliance with the limit shall be 1 July 2012. Until such time, the specified value is given for guidance. For distillate fuels the precision data are currently being developed.

d   Purchasers should ensure that this pour point is suitable for the equipment on board, especially if the ship operates in cold climates.

e   If the sample is not clear and bright, the total sediment by hot filtration and water tests shall be required, see 7.4 and 7.6.

f   If the sample is not clear and bright, the test cannot be undertaken and hence the oxidation stability limit shall not apply.

g   If the sample is not clear and bright, the test cannot be undertaken and hence the lubricity limit shall not apply.

h   This requirement is applicable to fuels with a sulfur content below 500 mg/kg (0.050 mass %).

j   Modified per approved correction to ISO 8217:2010.

k   If the sample is dyed and not transparent, then the water limit and test method as given in 7.6 shall apply.

Table 2: Requirements for marine residual fuels

Characteristics	Unit	Limit	RMA 10[a]	RMB 30	RMD 80	RME 180	RMG 180	RMG 380	RMG 500	RMG 700	RMK 380	RMK 500	RMK 700	Test method reference
Kinematic viscosity at 50°C[b]	mm²/s	max.	10.00	30.00	80.00	180.0	180.0	380.0	500.0	700.0	380.0	500.0	700.0	ISO 3104
Density at 15°C	kg/m³	max.	920.0	960.0	975.0	991.0	991.0				1010.0			see 7.1 ISO 3675 or ISO 12185
CCAI	–	max.	850	860	860	860	870				870			see 6.3 a)
Sulfur[c]	mass %	max.	Statutory requirements											see 7.2 ISO 8754 ISO 14596
Flash point	°C	min.	60.0	60.0	60.0	60.0	60.0				60.0			see 7.3 ISO 2719
Hydrogen sulfide[d]	mg/kg	max.	2.00	2.00	2.00	2.00	2.00				2.00			IP 570
Acid number[e]	mg KOH/g	max.	2.5	2.5	2.5	2.5	2.5				2.5			ASTM D664
Total sediment aged	mass %	max.	0.10	0.10	0.10	0.10	0.10				0.10			see 7.5 ISO 10307-2
Carbon residue: micro method	mass %	max.	2.50	10.00	14.00	15.00	18.00				20.00			ISO 10370
Pour point (upper)[f] — winter quality	°C	max.	0	0	30	30	30				30			ISO 3016
Pour point (upper)[f] — summer quality	°C	max.	6	6	30	30	30				30			ISO 3016
Water	volume %	max.	0.30	0.50	0.50	0.50	0.50				0.50			ISO 3733
Ash	mass %	max.	0.040	0.070	0.070	0.070	0.100				0.150			ISO 6245
Vanadium	mg/kg	max.	50	150	150	150	350				450			see 7.7 IP 501, IP 470 or ISO 14597
Sodium	mg/kg	max.	50	100	100	50	100				100			see 7.8 IP 501 IP 470
Aluminium plus silicon	mg/kg	max.	25	40	40	50	60				60			see 7.9 IP 501, IP 470 or ISO 10478
Used lubricating oils (ULO): calcium and zinc; or calcium and phosphorus	mg/kg	–	The fuel shall be free from ULO. A fuel shall be considered to contain ULO when either one of the following conditions is met: calcium > 30 and zinc > 15; or calcium > 30 and phosphorus > 15											see 7.10 IP 501 or IP 470 IP 500

a This category is based on a previously defined distillate DMC category that was described in ISO 8217:2005, Table 1. ISO 8217:2005 has been withdrawn.

b 1 mm²/s = 1 cSt.

c The purchaser shall define the maximum sulfur content in accordance with relevant statutory limitations. See 0.3 and Annex C.

d Due to reasons stated in Annex D, the implementation date for compliance with the limit shall be 1 July 2012. Until such time, the specified value is given for guidance.

e See Annex H.

f Purchasers shall ensure that this pour point is suitable for the equipment on board, especially if the ship operates in cold climates.

- Maximum Aluminum and Silicon (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 in mg/kg amounts 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 sediment aged 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 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 precleaning of the fuel.

The fuel treatment consists of the removal of the alkalimetals by fuel precleaning and inhibition of vanadium-induced corrosion by injecting magnesium-containing additives that 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 8217:2010

Acid Number:
All fuels have a naturally occurring acid number, however fuels with high acid numbers arising from acidic compounds can cause accelerated damage to large diesel engines, especially the fuel injection equipment. However, fuels manufactured from naphthenic crudes can have an acid number exceeding the maximum specified in ISO 8217:2010 but still be acceptable for use. Currently no identified correlation between the acid number of a fuel oil and its corrosivity exists.

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

Carbon residue:
Carbon residue is determined by a laboratory test performed under specified reduced air supply. It 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.

Catalytic fines:
Heavy cycle oil 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 catalytic fines. In order to avoid abrasive wear of fuel pumps, injectors and cylinder liners the maximum limit for Al+Si defined in ISO 8217:2010 is 60 mg/kg for RMG and RMK category fuels.

CCAI:
The Calculated Carbon Aromaticity Index (CCAI) is only applicable to residual fuel oils and provides an indication of the ignition delay of a fuel oil. The CCAI is calculated from the density and viscosity of a residual fuel oil. Some engine manufacturers specify CCAI limits for their engines, depending on engine type and application.

Cetane index:
Cetane index is 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 index. The cetane index is an approximate calculated value of the cetane number, based on the density and the distillation of the fuel. The cetane index is not applicable when cetane-improving additives have been used.

Density:
The official unit is kg/m³ at 15°C, while kg/l at 15°C is the most commonly used unit. Density is used to calculate the quantity of fuel delivered. 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).

Elements:
Vanadium and nickel are elements found in certain heavy fuel oil molecules (asphaltenes). Upon combustion, vanadium oxides are formed, and some 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.

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 Pensky–Martens closed-cup 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.

Hydrogen Sulfide (H₂S):

H_2S is a highly toxic gas and exposure to high vapor concentrations is hazardous and can be fatal in extreme cases. It is naturally present in crude oils and can be formed during the refining processes used to produce the fuel. H_2S can also evolve from the fuels in storage tanks, barges and customer tanks. Residual fuel oils can contain varying levels of H_2S in the liquid phase and in some circumstances higher levels of H_2S can be observed in marine distillate fuel oils. H_2S can be present in both liquid and vapor phase and the partitioning between the liquid and vapor phase depends on a number of factors (e.g., fuel temperature, viscosity, level of agitation, etc.).

ISO 8217:2010 states a liquid-phase H_2S limit of 2.00 mg/kg as measured by test method IP 570 as of July 2012. This limit intends to provide an improved margin of safety. The limit alone does not constitute a safe level or eliminate the risk of very high levels of H_2S vapor being evolved in enclosed spaces.

Kinematic viscosity:

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 must be within the limits prescribed by the engine manufacturer to obtain an optimal spray pattern. Viscosity outside manufacturers' specifications at the injectors will lead to poor combustion, deposit formation and energy loss. The viscosity of the fuel must be such that the required injection viscosity can be reached by the ship's preheating system.

Lubricity:

Lubricity is the ability to reduce friction between solid surfaces in relative motion. The fuel itself protects some moving parts of fuel pumps and injectors from wear. Higher viscosity fuels provide sufficient lubricity. To avoid excessive wear, the fuel must have some minimum level of lubricity.

Lubricity enhancing compounds are naturally present in diesel fuel derived from petroleum crude by distillation. They can be altered or changed by hydrotreating, the process used to reduce sulfur and aromatic contents. However, lowering sulfur or aromatics, per se, does not necessarily lower fuel lubricity.

The use of fuels with poor lubricity can increase fuel pump and injector wear. In order to avoid this, a lubricity limit of maximum 520 µm has been defined in ISO 8217:2010 for distillate marine fuels with S content less than 500 ppm. In some areas ultra low sulphur automotive diesel is supplied as a marine distillate fuel in order to comply with regulatory sulphur requirements.

Oxidation Stability:

Degradation of distillate fuels by oxidation can cause fuel stability problems. Unstable distillate fuels can form insoluble organic particles which may clog fuel

filters , cause wear and contribute to injector deposits. Current supply logistics make it almost inevitable that marine distillate fuels can contain bio-derived material, i.e., fatty acid methyl esters (FAME), that can impact the oxidation stability of the fuel (see also Chapter 8 on Biofuels).

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 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 because bunker fuel tanks are usually not completely heated – only before the fuel transfer pump. This can 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. Marine diesels with a high content of heavier n-paraffins require vigilance if wide temperature changes are expected. (Wax settling can occur, even when the pour point specification is met.)

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 liners 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 but may have environmental implications.

In 2008 the revised Annex VI to Marpol 73/78 was adopted and requires the sulphur content of any fuel used on board ships not to exceed :

- 4.50% m/m prior to 1 January 2012

- 3.50% m/m on and after 1 January 2012

- 0.50% m/m on and after 1 January 2020 or 2025, depending the outcome of a review to be completed by 2018 to determine availability of fuel oil to comply with the fuel oil standard.

Additionally, the revised Annex VI to Marpol 73/78 restricts the sulphur content of fuel oil used on board ships operating within an Emission Control Area (ECA) to :

- 1.00% m/m on and after 1 July 2010

- 0.10% m/m on and after 1 January 2015.

Annex VI to Marpol 73/78 allows for alternative technologies/methods which are at least as effective in terms of emissions reductions.

Currently adopted ECA areas are the Baltic Sea, North Sea and English Channel, the U.S. Caribbean ECA (including designated waters adjacent to Puerto Rico

and the US Virgin Islands) and the North American ECA (including waters adjacent to the Pacific Coast, the Atlantic/Gulf Coast and the eight main Hawaiian Islands, extending up to 200 nautical miles from coasts of the United States, Canada and the French territories).

In addition, the EU directive 2005/33/EC extended the 1.5 m/m % S limit to ferries operating to and from any EU port.

The EU directive also has set a maximum limit of 0.1 m/m % on the sulphur content of marine fuels used by ships when at berth for more than 2 hours.

The process to review the EU Directive 2005/33/EC started in 2011. Therefore, the limits and requirements stated above are subject to change.

In California, the Ocean-Going Vessels (OGV) Clean Fuel regulation applies to OGV main diesel engines, auxiliary diesel engines and auxiliary boilers, and requires:

1) the use of marine diesel DMB:
   − at or below 0.5 m/m % sulphur
   − at or below 0.1 m/m % sulphur as of January 1, 2014; or

2) the use of marine gasoil (DMA/DMZ):
   − at or below 1.5 m/m% sulphur prior August 1, 2012
   − at or below 1.0 m/m% sulphur on and after August 1, 2012
   − at or below 0.1 m/m% sulphur on and after January 1, 2014.

Total sediment aged:

Inorganic material naturally occurring in crude oil is removed in the refineries prior to the atmospheric distillation. Some minor contamination (for example, iron oxides) 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, only a relatively small fraction of the asphaltenes form 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 sediment aged is the total amount of sediment that can be formed under normal storage conditions, excluding external influences. If the total sediment aged of the heavy fuel oil markedly exceeds the specification value (0.10% m/m maximum) for all grades of IFOs and HFOs), problems with the fuel cleaning system can occur, fuel filters can get plugged and combustion can become erratic.

Used lubricating oil (ULO):

The use of used lubricants (predominantly used motor vehicle crankcase oils) in marine fuels first surfaced as a potential problem in the mid-1980s. Both CIMAC and ISO 8217 working groups have discussed the technical and commercial considerations at length. Calcium, zinc and phosphorous are considered "fingerprint" elements of ULOs, and limits for these elements were set in ISO 8217:2005. According to ISO 8217:2010, a fuel oil shall be considered to contain ULO when either calcium and zinc or calcium and phosphorus exceed these limits. This, however, does not necessarily imply that the fuel oil is not suitable for use. Generally, 10 mg/kg Zn corresponds to approximately 1% used oil in the fuel. This is only an approximation; the zinc dithiophosphate content of lubricants can vary considerably.

Water content:

Water in fuel is a contaminant 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 that remains standing in lines for a longer period can cause corrosion.

2b. Correspondence of specifications and test methods

ISO 8217:2010 lists test requirements and methods for testing. While these methods should be used worldwide for testing marine fuels, experience has shown that they are not. In some areas, 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.

Al+Si:

The ISO 8217 prescribed test methods are ISO 10478 or IP 501 or IP 470. Only these methods and fully equivalent methods from national standardization organizations should be used. A former industry-wide maximum limit for catalyst fines in heavy fuel was defined on Al alone (30 mg/kg). The ratio between Al and Si can, however, vary considerably between different types and manufacturers of aluminum silicate catalyst. This is why the test measures 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.

API gravity:

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

Density:
The mass (weight in vacuum) of the liquid per unit volume at 15°C. Official unit: kg/m³. Often used variant: kg/l. The density limits in ISO 8217 are expressed in kg/m³. 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.

Micro Carbon Residue (MCR):
MCR is the carbon residue test prescribed as of ISO 8217:2005. Formerly, the carbon residue test was Conradson Carbon Residue. MCR is quicker and more precise than CCR.

Total sediment by hot filtration & total sediment aged:
According to ISO 8217:2010 the total sediment by hot filtration (ISO 10307-1) shall be measured on all DMB category products that fail the visual inspection requirement to be bright and clear.

Organic type sediment can occur in DMB marine diesel and in intermediate fuel oils. The cause of the formation of organic sediment is due to the thermal cracking of the heaviest molecules of crude, generally in visbreaking operations. Asphaltenes, the heaviest molecules of crude, can be made 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 must be taken into account for fuel blending when using visbroken heavy fuel and gasoil (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 particular moment is given by the total sediment by hot filtration 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 sediment aged test shows 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). Either of the standard procedures for ageing in ISO 10307-2 can be used : accelerated total sediment (TSA) or potential total sediment test (TSP).

The test method originally used in the industry for determining the total sediment was 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 as mm²/s at a certain temperature (note: 1 mm²/s = 1 cSt). SSU, SSF and RW1 (Saybolt Seconds Universal, Saybolt Seconds Furol and Redwood No. 1) are obsolete units.

3. Test specifications and precision

ISO 8217:2010 not only specifies the requirements for marine distillate and residual fuels and the test method references, it also lists ISO 4259:2006, "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 acquiring the sample was 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. Chevron recognizes only the bunker fuel retain samples taken by its representative (for example, bunker barge attendant) at the moment of bunkering as valid.

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 be very time-consuming, and is very seldom done in practice. Both parties generally agree to the use of a third laboratory, the result of which will then be binding for both parties.

The testing margin, however, has an effect on a single result; for example, the analysis result of 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 a (single) test result, the product fails when the result exceeds the specification limit by more than 0.59R in case of an upper limit (where R is reproducibility of the test method), or is more than 0.59R lower than the specification limit in case of a lower limit.

The significance of reproducibility should not be underestimated. It is the basis for all quality control against specifications. Without reproducibility data, test results would lose 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 contains the methods for marine fuel testing listed in ISO 8217:2010, together with 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 1970s, the increasing market demand for distillate fuels (gasoline, diesel) and the resulting changes in refinery processes to cope with this demand, resulted in a deterioration of 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. Along with 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 need 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 gravity (g). The rate of separation by gravity, Vg, is defined by Stokes law:

$$V_g = [d^2 (D_2 - D_1) / 18 \, \eta] \, g$$

d: particle diameter
D_2: particle density
D_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:

$$V = Vg \times Z$$

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.

4a. Conventional cleaning with purifiers/clarifiers

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

In a purifier 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 a conventional purifier is 991 kg/m³ (at 15°C).

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 of the disc stack along its entire height. This is important since separation takes place in these channels.

For fuel oils with a viscosity above 180 mm²/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.
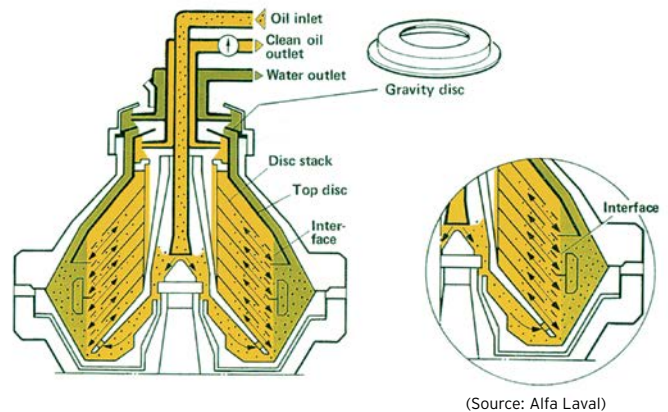

(Source: Alfa Laval)

Figure 1: Correct interface position – Oil distributed to all channels in the disc stack
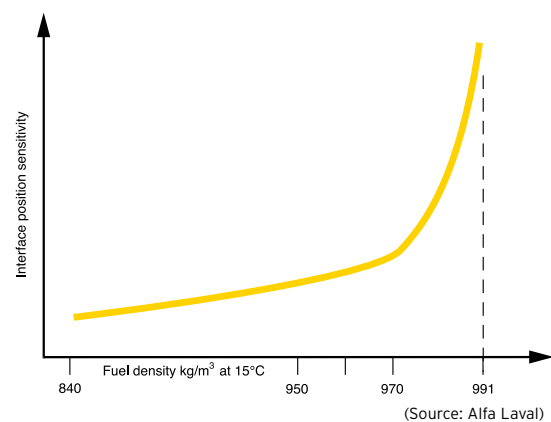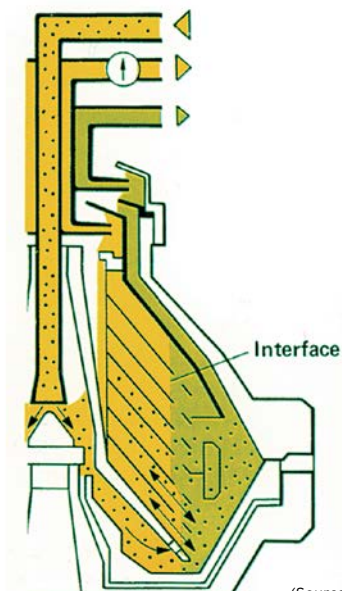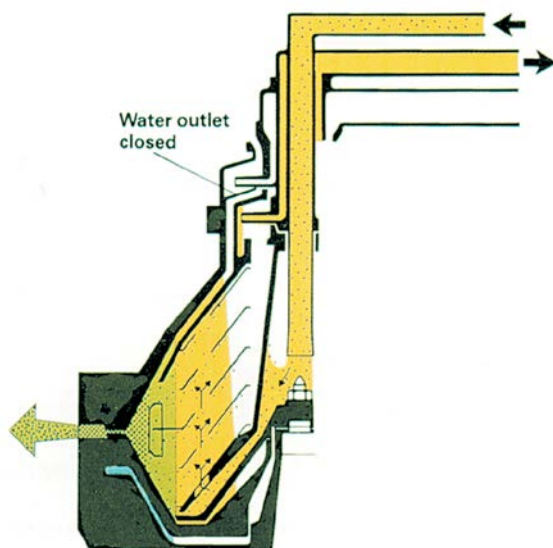

(Source: Alfa Laval)

Figure 2: Interface position sensitivity

If the interface is in an incorrect position (see Figure 3), the oil to be cleaned will pass through only 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

(Source: Alfa Laval)

Figure 4: Conventional clarifier

To ensure optimal cleaning of a fuel oil, a second separator can be used in series operation, for example, a purifier followed by a clarifier. The density limit of 991 kg/m³ 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/m³ 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. Efficient purification is not always possible when separators have been put in a parallel purifying function.

In a conventional clarifier (see Figure 4), 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/m³ at 15°C are available on the market and can be purified, for example, with the ALCAP system, which allows fuel oil densities up to 1010 kg/m³ 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. A signal from the water transducer is transmitted to a control unit and changes in water content are measured.

Increased water content in the cleaned oil is 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.
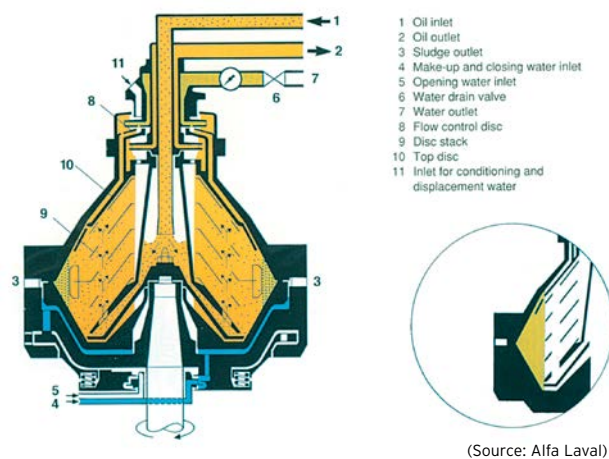

1 Oil inlet
2 Oil outlet
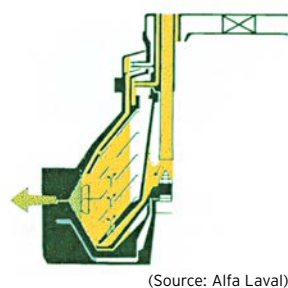3 Sludge outlet
4 Make-up and closing water inlet
5 Opening water inlet
6 Water drain valve
7 Water outlet
8 Flow control disc
9 Disc stack
10 Top disc
11 Inlet for conditioning and displacement water

(Source: Alfa Laval)

Figure 5: ALCAP separator

(Source: Alfa Laval)

(Source: Alfa Laval)

Figure 6a: Discharge of separated water through sludge outlet
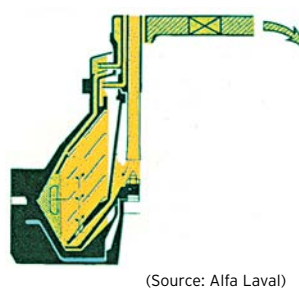
Figure 6b: Discharge of separated water through water drain valve

(Source: University Illinois-Chicago, TRL)
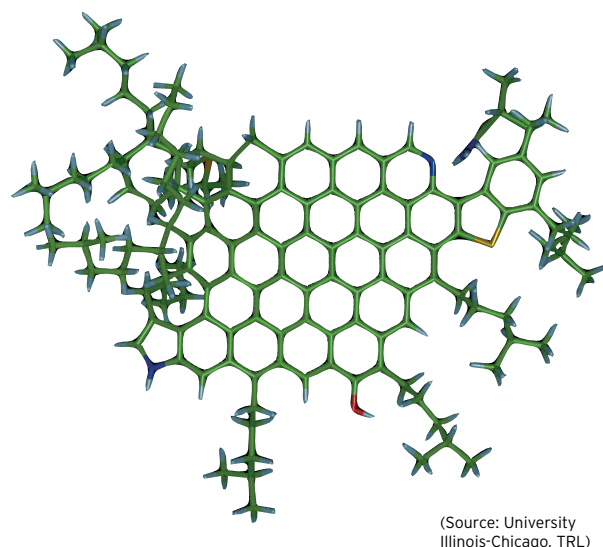
Figure 7: Asphaltene molecule

5. Fuel oil stability and compatibility

Total sediment aged is an important specification for heavy fuels. Currently, nearly all heavy fuel is marketed with the stability guarantee of maximum total sediment aged (ISO 10307-2) 0.10%. Stratification in heavy fuel oil tanks is minimal 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 also 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 in Figure 7.

Asphaltenes are polar molecules, kept in colloidal suspension[3] 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 that viscosity reduction of a visbroken fuel with a paraffinic-type cutterstock can make the fuel unstable. When this happens, the two fuels are said to be incompatible. When two fuels that 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 cutterstock with a high enough aromaticity to keep the asphaltenes dispersed (for example, by adding heavy and/or light cycle oil) and to provide an adequate stability reserve.

3 Colloidal suspension: a suspension in which gravitational forces are negligible

Two heavy fuels with diverse compositions (for example, one an atmospheric heavy fuel from paraffinic crude, and the other from a relatively severe visbreaker operation) can also be incompatible with each other. When storing fuel, the potential of compatibility problems between two different heavy fuels should be kept in mind.

6. Commingling of fuels

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 the responsibility of the individual who made the decision to commingle the fuels. 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 unavoidable, check the compatibility of the fuels in advance, and make a final decision based on the test result.

- If a compatibility check is not possible (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: Generally fuels of the same viscosity grade with similar densities will be compatible.

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 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

Microbiological contamination ideally occurs in tropical and sub-tropical regions due to high air humidity combined with a high ambient temperature.

To avoid contamination, VOS, the Dutch organization that supervises the quality of gasoil delivered in the Netherlands, offers these points:

- 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 are filthy fuel systems, plugged fuel filters and erratic engine operation.

- Bacterial contamination can be found in slime, sludge, possibly corrosion in filters, tanks, lines.

- What the end-user can do:

  - Make sure no water enters the gasoil

  - Check filters

  - Check bunker and day tank for water

  - Whenever necessary, drain tanks. Secure permanent connection devices at the fuel receiving site

  - Have de-aerating openings which can be closed (to prevent waves entering the bunker tank)

On-site macroscopic (visual) examination offers a first screening between the contaminated and non-contaminated tanks. Possible microbiological contamination indicators are:

- 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 occurs as co-contaminant). All are living cells, which multiply through cell division.

The prime contamination of fuel is almost 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. Besides being a very dangerous toxin, hydrogen sulphide can also cause severe corrosion.

Anaerobic microbiological contamination should be avoided at all costs. Keep close control on the presence of microbiological contaminants in the entire 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, water soluble biocides are generally the 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. Biofuels

Over the last several years, environmental concerns have resulted in both a voluntary and mandatory use of biodiesel in road diesel for passenger cars and heavy duty vehicles. Also in some sectors of the marine industry, blends of bio-derived fuels with petroleum products or bio-derived fuels are considered as potential alternative energy source as they are renewable and may result in reduction of Green House Gases (GHG) and SOx emissions.

Biodiesel refers to esters derived from vegetable oils (e.g., palm oil, soybean oil, rapeseed oil), animal fats (e.g., tallow oil) and waste material and is often referred to as Fatty Acid Methyl Esters (FAME). The variety of different FAME products has resulted in the development of FAME specifications EN 14214 and ASTM D6751.

Under current supply logistics, the practice of blending FAME in other distillate fuels makes it almost inevitable that some distillate fuels supplied in the marine market contain FAME. When FAME is detected in residual fuel oils, it is most likely the result of refinery processes or blending in a distillate cutterstock containing FAME. Adequate controls should be in place so that fuels as delivered are compliant with the requirements of Clause 5 of the International Standard ISO 8217:2010.

FAME has good ignition and lubricity properties, but there is currently little experience with respect to storage, handling, treatment in a marine environment where potentially complications can arise such as:

- Tendency to oxidation and long-term storage issues
- Affinity to water and thereto linked risk of microbial growth
- Degraded low-temperature flow properties
- Deposition of FAME related material on filter elements and other exposed surfaces.

Therefore, the ISO 8217:2010 standard has taken the precautionary approach and limits the FAME content in marine fuels to a *de minimis* level, which in the case of the distillate fuels (DMX, DMA, DMZ and DMB when bright and clear) is to be taken as not exceeding approximately 0.1 volume % (determined according EN 14078). For residual fuels there is currently no standardized test method that allows expressing the "de minimus" in a numerical term. It should then be considered as a contamination from the supply chain system.

9. Chemical fuel treatment

Residual fuel oils today are still an unprocessed product made from the heavy fraction of the crude oil remaining after the most valuable products have been extracted (see Chapter II). Blending this residue to a commercial residual fuel oil has become more complicated as the concentration of heavy aromatic molecules such as asphaltenes has increased and more aromatic cutterstocks are now required.

Residual fuel oils as bunkered are not fit for purpose without proper cleaning to remove or reduce contaminants that can be present in the fuel oil, such as water and catfines. Whereas in automotive applications, it is common practice to add fuel additives to distillate fuel oils to enhance performance aspects, and biocides are commonly used in marine distillate fuel oils to combat microbiological contaminations, the application of residual fuel additives in the marine and power generation sectors to improve combustion or provide other benefits is not yet widespread.

There is, however, no such single miracle product that can prevent or cure any fuel-related problem – the choice of additive really depends on the job to be done and can potentially be harmful if not carefully evaluated. Using residual fuel oil additives should not, however, be considered as a replacement for the onboard cleaning of the fuel oil.

The main types of residual fuel additives in the marine and power generation markets are:

- pre-combustion conditioning treatment additives (e.g., demulsifiers, dispersants)
- combustion improvers
- ash modifiers

The combustion phase is one of the areas where marine residual fuel oil additives can be used to advantage. A combustion improver can be organic or can include an organo-metallic compound, containing iron or other metals. The use of an iron-based component as an oxidation catalyst to accelerate the main combustion and enhance complete combustion of residual fuel oils is a proven technology.

10. Fuel contamination in lubricants

In the 1990s, the demands on marine lubricants changed considerably for medium-speed engines. Operating the engines at higher thermal and mechanical loads made it more difficult for the lubricant to cope with the issues of borderline lubrication. At the same time, engine design changes, such as the introduction of the anti-bore polishing ring, decreased oil consumption in medium-speed engines considerably from 1–1.5 g/kWh or more to 0.4–0.7 g/kWh or lower in modern engines.

Changes to engine construction and the deterioration of heavy fuel quality, which began in the late 1970s, spawned significant challenges to marine lubricants. Liner lacquering, undercrown deposits, increased oil consumption, base number depletion, hot corrosion of the piston crown, oil scraper ring clogging and increased piston deposits occurred. As a result, formulations needed to be adapted.

Medium-speed engine blackening due to HFO contamination of the lubricant, piston head corrosion and undercrown deposits were typical consequences of increased fuel pump pressure and the switch-over from atmospheric heavy fuel to visbroken heavy fuel.

It's possible for HFO to enter the lubricant directly as a result of leaking fuel pumps, or unburned HFO that remains on the cylinder walls can be washed down into the sump. HFO contamination can now be assessed by measuring the concentration of unburned asphaltenes in the lubricant. Chevron Belgium, in cooperation with MAN Diesel in Augsburg, developed a test method which accurately measures this concentration (in %wt) and also qualifies the origin of the asphaltene ingress. The test method to measure the concentration of unburned asphaltenes has been accepted into CEC and published as CEC L-94-10. The typical contamination level of medium-speed engine oil with asphaltenes, as measured by Chevron Belgium during the last ten years, has been between 0.25 and 0.30% m/m.

Common issues encountered with conventional lubricant due to HFO contamination:

1. Engine blackening
The increase of the fuel pump pressure up to 1600 bar in medium-speed diesel engines results in a higher fuel pump leakage, leading to increased fuel contamination. Most HFOs originate from visbreaking installations. The asphaltenes don't dissolve in the paraffinic lubricant, instead 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. This results in black deposits in the cambox and in the crankcase. These deposits 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, at times 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. These problems can be minimized by effectively removing the asphalt particles from the lubricant.

2. Undercrown deposits and piston head corrosion
The tendency to increase the piston undercrown temperature can result in 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 lubricants are used.

Undercrown deposits combined 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 melt with the piston crown material causing hot corrosion on the top of the piston.

To respond to the HFO challenges, Chevron Belgium developed a lubricant series with high asphaltene dispersancy, to optimize lubrication of medium-speed engines and to avoid the issues resulting from asphaltene contamination.

Taro® DP/XL (X) (available as a 20, 30, 40, 50 or 60 BN) were developed specifically to cope with increasing mechanical and thermal stresses and the changes in fuel quality. Since its introduction in the mid-1990s, the Taro DP/XL series has demonstrated excellent performance in a wide range of medium-speed engine types. Taro DP/XL (X) is currently recognized as a top-tier product technology for medium-speed engine lubrication.

Figure 12 illustrates the cambox cleanliness obtained with Taro DP (X) technology, compared with the blackening of the cambox using a conventional lubricant, as illustrated in Figure 9.
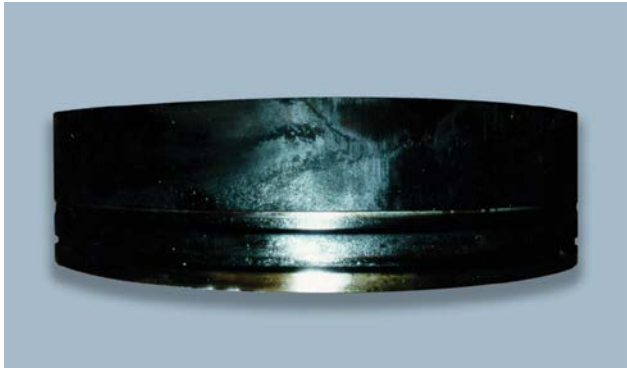

Figure 10: Conventional lubricant — typical piston deposits in a medium-speed engine with heavy fuel contamination
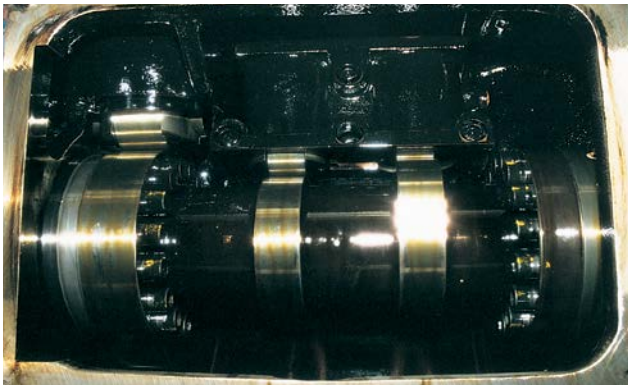

Figure 8: Conventional lubricant

Figure 9: Conventional lubricant — showing heavy fuel contamination
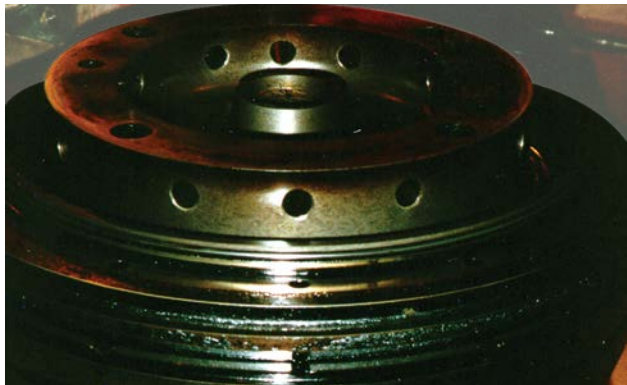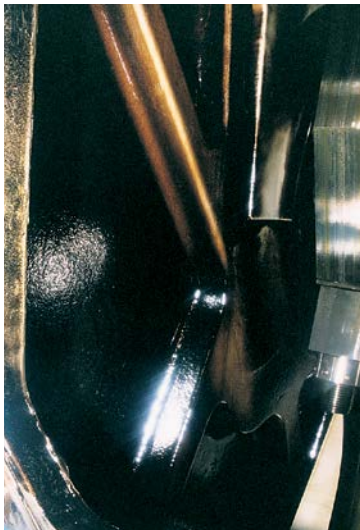

Figure 11: Conventional lubricant — typical oil scraper deposits in a medium-speed engine with heavy fuel contamination
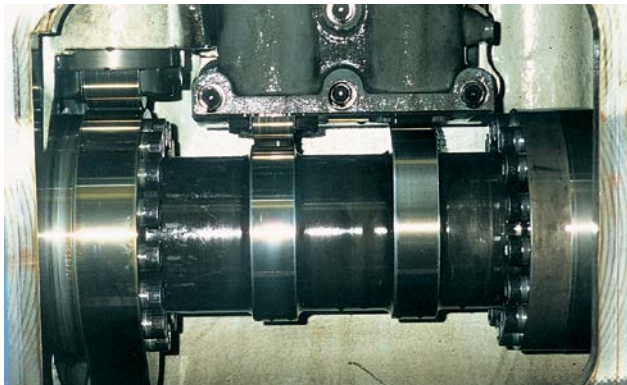

Figure 12: Taro DP (X) technology — cambox cleanliness despite 4% heavy fuel contamination

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, 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:

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, which 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.

4. Catalytic cracking (for example, 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 use catalytic hydrocracking as a supplementary operation to catalytic cracking. Catalytic hydrocracking is similar to catalytic cracking because it uses a catalyst, but the reactions take place under a high pressure of hydrogen. Hydrocracking further upgrades heavy aromatic stocks to gasoline, jet fuel and gasoil material. The heaviest aromatic fractions of a cat cracker and vacuum gasoil (VGO) are the normal feedstocks 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).

More processes are required before the end products leave a refinery. Most processes are designed 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 catalytic reforming, and are intended to upgrade low-octane naphtha 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 C4 olefins from the catalytic cracker unit and iso-butane.

10. Hydrotreating

The hydrotreating process uses hydrogen to remove impurities from product streams, replacing these impurities by hydrogen. When hydrotreating is used to remove sulphur to meet the very low sulphur limits in the specifications of gasoline and gasoil, it is called hydro-desulphurization. It is a catalytic process. The process is generally used on kerosene and gasoil fractions. Residual hydro-desulphurization is also a process, and is feasible, but not economical.

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 molecules (corrosive and obnoxious smelling) into disulphide type molecules.

12. Sulphur recovery

As a result of the removal of sulphur from the refinery streams by hydrotreating, and 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 highly toxic hydrogen sulphide 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, for example, 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 one SO_2 for two 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

Acid number, mg KOH/g

ASTM D664
> R (used oils buffer endpoint) = 0.44x
> Where x 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

Ca, Zn, P, mg/kg

1. Ca
> IP 501 (ICP) $R = 0.6440x^{0.65}$
> IP 470 (AAS) $R = 1.139x^{0.8}$

2. Zn
> IP 501 (ICP) $R = 0.5082x^{0.7}$
> IP 470 (AAS) $R = 0.580x^{0.75}$

3. P
> IP 501 (ICP) $R = 1.2765x^{0.55}$
> IP 500 (UV) $R = 1.2103x^{0.4}$
> Where x is the average of the results (mg/kg) being compared

Cat fines Al+Si, mg/kg

1. ISO 10478, IP 501
> ICP detection:
> Al: R = 0.337x
> Si: R = 0.332x
> Where x is the average of the results (mg/kg) being compared

2. IP 470
> AAS detection:
> Al: $R = 0.789x^{0.67}$
> Si: $R = 1.388x^{0.67}$
> Where x is the average of the results (mg/kg) being compared

CCAI (Calculated Carbon Aromaticity Index)

> Precision (R) depends on the precision (R) of the density and viscosity of the residual fuel oil that enter into the calculation

Cetane index (4 variable equation)
ISO 4264

Precision depends on the precision of the original density and distillation recovery temperature calculations.

Cloud Point, °C
ISO 3015

For distillate fractions: R = 4°C

Density at 15°C, kg/m³
1. ISO 3675

For transparent, non viscous products:
R = 1.2 kg/m³ or 0.0012 kg/l
For opaque products: R = 1.5 kg/m³ or 0.0015 kg/l

2. ISO 12185

For transparent middle distillates:
R = 0.5 kg/m³ or 0.0005 kg/l
For crude oils and other petroleum products:
R = 1.5 kg/m³ or 0.0015 kg/l

Flash point, P.M., closed tester
ISO 2719

Procedure A (distillate fuels): $0.071x$
Where x is the average of the results (°C) being compared
Procedure B (residual fuel oils): 6°C

H_2S, mg/kg
IP 570

Procedure A
Distillate and residual fuels: $R = 0.4459x^{0.55}$
Procedure B
Residual fuels: $R = 0.5232x^{0.6}$
Distillate fuels: $R = 0.2389x^{0.7}$
Where x is the average of the results being compared

Kinematic viscosity, mm²/s
ISO 3104

Heavy fuels: at 50°C: $R = 0.074x$
Distillate fuels : at 40°C: $R=0.0082(x+1)$
Where x is the average of the results being compared

Micro carbon residue, % (m/m)
ISO 10370

$R = X^{2/3} \times 0.2451$
Where X is the average of the results being compared

Oxidation stability, g/m³
ISO 12205

$R = 10.6\,(x/10)^{0.25}$
Where x is the average of the results being compared

Pour Point, °C
ISO 3016

R = 6.59°C

Sodium, mg/kg
1. IP 501 (ICP)

$R = 1.0667x^{0.55}$

2. IP 470 (AAS)

$R = 1.303x^{0.6}$
Where x is the average of the results being compared

Sulphur, % (m/m)
1. ISO 8754

For values > 0.05 m/m % and ≤ 5.00 m/m %:
$R = 0.0812(x + 0.15)$
for values ≥ 0.03 m/m % and ≤ 0.05 m/m %:
$R = 0.1781(x + 0.05)$
Where x is the mean sulphur content

2. ISO 14596

For sulphur content in the range 0.10–0.99 m/m %: R = 0.02
For sulphur content in the range 1.00–2.50 m/m %: R = 0.04

Total sediment aged, % (m/m)
ISO 10307-2

Heavy fuels: $R = 0.294 \sqrt{x}$
Distillate fuels containing heavy components:
$R = 0.174 \sqrt{x}$
Where x is the average of the test results in % (m/m)

Total sediment by hot filtration, % (m/m)
ISO 10307-1

Heavy fuels: $R = 0.294 \sqrt{x}$
Distillate fuels containing heavy components:
$R = 0.174 \sqrt{x}$
Where x is the average of the test results in % (m/m)

Vanadium, mg/kg
1. 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 5–30 mg/kg: R = 5 mg/kg
For V content between 31–100 mg/kg:
R = 10 mg/kg

2. IP 501

$R = 1.6799x^{0.6}$
Where x is the average of the results (mg/kg) being compared

3. IP 470

$R = 3.26x^{0.5}$
Where x is the average of the results (mg/kg) being compared

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

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. 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 (for example, heavy fuels), as a cost-effective option instead of gasoil for sites where natural gas will not be available in the foreseeable future.

The use of heavy fuels requires that 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 the mid-1980s. It is clear that the need to use magnesium-based additives 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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